NUCLEATION AND GROWTH
OF A
SINGLE MARTENSITIC PARTICLE

by
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ABSTRACT

The energetics of homogeneous and heterogeneous martensitic nucleation were evaluated numerically utilizing a unified diffuse-interface description of the nucleus structure, represented by a one-dimensional strain variation. A free-energy functional employing a fourth-order Landau expansion modified by a gradient-energy term was used to describe the free-energy change for the inhomogeneous deformation attending the formation of a critical nucleus. The critical-nucleus free energy was minimized with respect to nucleus structure in order to assess the potential advantage of nonclassical nucleation paths. The occurrence of homogeneous martensitic nucleation requires the suppression of heterogeneous nucleation at lattice imperfections; small metastable particles or precipitates offer the greatest opportunity for obtaining defect-free crystals in which homogeneous nucleation will be possible very near a mechanical instability. Under these conditions, martensitic nucleation favors nonclassical paths involving changes in both nucleus structure and size.

Heterogeneous martensitic nucleation at low driving forces and potent defects favors classical paths because of the influence of the defect/nucleus interaction. Barrierless nucleation is preceded by the formation of classical embryos which become critical at a sufficient driving force leading to operational nucleation. Nonclassical paths are favored only at sufficiently weak defects which require driving forces near the critical driving force for lattice instability.

Both homogeneous martensitic nucleation and heterogeneous nucleation at weak defects must compete with an alternative transformation mechanism—quasimartensitic continuous strain modulations. The structure and energetics of quasimartensite formation was modeled using the same strain-variational approach that was applied to martensitic nucleation. Very near a mechanical instability, thermal fluctuations may promote a thermally assisted quasimartensitic instability, which can be regarded as the displacive analogue of spinodal decomposition.
A continuum model for the growth of a single martensitic particle was developed, incorporating the interrelations between thermodynamic driving force, interfacial mobility, heat transfer, elastic strain energy, and size- and rate-dependent plastic accommodation. The highly stressed region near the particle tip acts as an effective source for nucleating lattice dislocations. However, elastic radial growth at microscopic particle sizes is stabilized until the process of dislocation generation at the particle tip is energetically favored. In addition, dislocation-mobility factors, related to high-strain-rate plastic deformation ahead of the particle tip, play an important role in determining the onset of plastic accommodation.

Growth simulations were conducted for lath-forming Fe-24Ni and plate-forming Fe-32Ni, using a time-incremental method of numerical analysis. These two alloys show large differences in transformation temperature and dynamic plastic-flow behavior. Conditions leading to the cessation of radial growth via interface/plastic-zone interactions were examined and contrasted between the two alloys. It is proposed that the lath-to-plate morphological transition in ferrous alloys is related to premature radial-growth arrest due to the onset of radial plasticity. The results suggest that elastic radial growth is promoted by a high radial growth rate and high mechanical threshold stress for plastic flow in the austenite. Extended elastic radial growth favors a plate morphology, whereas the lath morphology is associated with a highly plastic mode of growth. Therefore, a high radial growth rate and a high threshold stress will promote a plate morphology. This conclusion is consistent with experimental observations on the effect of a high magnetic field and the influence of austenite yield strength on martensite morphology in ferrous alloys.

Local interfacial heating cannot account for the observed transition in the operative lattice-invariant-deformation mode from slip to twinning during thickening of plate martensite. Instead, this transition may be triggered by the onset of plastic accommodation ahead of the advancing martensitic interface causing the thickening rate to decrease favoring slip over twinning due to interface-mobility factors. Following this transition, plastic accommodation takes place in both the martensite and the austenite. The final plate aspect ratio is determined by the total amount of plastic relaxation, which depends on the flow properties of both phases. The observed dependence of the plate aspect ratio on transformation temperature can be rationalized, qualitatively, based on the negative temperature dependence of the flow stress of both the austenite and martensite.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>2</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>8</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>14</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>15</td>
</tr>
<tr>
<td>1)  INTRODUCTION AND SCOPE OF THE RESEARCH</td>
<td>16</td>
</tr>
<tr>
<td><strong>PART I: ENERGETICS OF MARTENSITIC NUCLEATION:</strong></td>
<td></td>
</tr>
<tr>
<td>CLASSICAL VS. NONCLASSICAL PATHS.</td>
<td>20</td>
</tr>
<tr>
<td>2)  INTRODUCTION TO MARTENSITIC NUCLEATION</td>
<td>20</td>
</tr>
<tr>
<td>2.1) General Characteristics of Martensitic Nucleation</td>
<td>22</td>
</tr>
<tr>
<td>2.2) Classical Heterogeneous Martensitic Nucleation</td>
<td>25</td>
</tr>
<tr>
<td>2.2.1) Martensitic Embryo Models</td>
<td>25</td>
</tr>
<tr>
<td>2.2.2) The Olson-Cohen Defect Dissociation Model</td>
<td>28</td>
</tr>
<tr>
<td>2.3) Nonclassical Martensitic Nucleation</td>
<td>35</td>
</tr>
<tr>
<td>2.3.1) The Reaction-Path Model</td>
<td>35</td>
</tr>
<tr>
<td>2.3.2) Localized Soft-Mode Models</td>
<td>37</td>
</tr>
<tr>
<td>2.3.3) The Olson-Cohen Nonclassical Nucleation Model</td>
<td>40</td>
</tr>
<tr>
<td>3)  HOMOGENEOUS MARTENSITIC NUCLEATION</td>
<td>42</td>
</tr>
<tr>
<td>3.1) Energetics of Homogeneous Lattice Deformation</td>
<td>43</td>
</tr>
<tr>
<td>3.2) One-Dimensional Inhomogeneous Lattice Deformation</td>
<td>49</td>
</tr>
<tr>
<td>3.3) Nonclassical Homogeneous Nucleation Model</td>
<td>55</td>
</tr>
<tr>
<td>CHAPTER</td>
<td>TITLE</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>3.4)</td>
<td>Results and Discussion</td>
</tr>
<tr>
<td>3.4.1)</td>
<td>Results of the Model Calculations</td>
</tr>
<tr>
<td>3.4.2)</td>
<td>Comparison with the Cahn-Hilliard Model</td>
</tr>
<tr>
<td>3.4.3)</td>
<td>Possibility of Homogeneous Martensitic Nucleation</td>
</tr>
<tr>
<td>4)</td>
<td>HETEROGENEOUS MARTENSITIC NUCLEATION</td>
</tr>
<tr>
<td>4.1)</td>
<td>Continuum Description of Classical Heterogeneous Nucleation</td>
</tr>
<tr>
<td>4.2)</td>
<td>Classical Heterogeneous Nucleation Model</td>
</tr>
<tr>
<td>4.3)</td>
<td>Nonclassical Heterogeneous Nucleation Model</td>
</tr>
<tr>
<td>4.4)</td>
<td>Results and Discussion</td>
</tr>
<tr>
<td>4.4.1)</td>
<td>Classical Martensitic Nucleation</td>
</tr>
<tr>
<td>4.4.2)</td>
<td>Nonclassical Martensitic Nucleation</td>
</tr>
<tr>
<td>5)</td>
<td>QUASIMARTENSITIC TRANSFORMATIONS</td>
</tr>
<tr>
<td>5.1)</td>
<td>Quasimartensitic Continuous-Modulations Model</td>
</tr>
<tr>
<td>5.2)</td>
<td>Results and Discussion</td>
</tr>
<tr>
<td>6)</td>
<td>SUMMARY OF PART I</td>
</tr>
<tr>
<td>7)</td>
<td>INTRODUCTION TO MARTENSITIC GROWTH</td>
</tr>
<tr>
<td>7.1)</td>
<td>General Experimental Observations</td>
</tr>
<tr>
<td>7.2)</td>
<td>Martensite Morphology</td>
</tr>
<tr>
<td>7.2.1)</td>
<td>Morphology of Fe-Ni Martensites</td>
</tr>
<tr>
<td>7.2.2)</td>
<td>Theories for the Morphological Transition in Steel</td>
</tr>
<tr>
<td>7.3)</td>
<td>Models for the Growth of Martensite</td>
</tr>
</tbody>
</table>

**PART II: GROWTH OF A SINGLE MARTENSITIC PARTICLE** | 117
CHAPTER | PAGE
--- | ---
8) THERMOELASTIC GROWTH | 135
8.1) Overview of the Thermoelastic Growth Model | 135
8.2) Particle Geometry and General Assumptions | 138
8.3) Temperature of the Austenite/Martensite Interface | 139
8.3.1) Interface Temperature Near the Plate Tip | 139
8.3.2) Interface Temperature of the Plate Faces | 142
8.4) Free Energy of the Particle/Matrix System | 143
8.5) Interfacial Forces | 144
8.6) Interfacial Mobility Relations | 146
8.6.1) Thermally Activated Interfacial Motion | 147
8.6.2) Drag-Controlled Interfacial Motion | 150
8.6.3) Superposition of Mechanisms | 152
8.7) Numerical Methods | 153
8.8) Estimation of Parameters | 153
8.9) Initial Conditions—Growth Start-up | 159
8.10) Growth-Simulation Results and Discussion | 160

9) NONTHERMOELASTIC GROWTH | 168
9.1) Overview of the Nonthermoelastic Growth Model | 169
9.2) Plastic-Accommodation Model | 172
9.2.1) Energetic Criterion for the Initiation of Plastic Accommodation | 173
9.2.2) Radial Plastic Zone | 177
9.2.3) Perpendicular Plastic Zone | 183
9.2.4) Interfacial Forces | 186
9.2.4.1) Plastic-Accommodation Work | 186
9.2.4.2) Interface-Frictional Work | 188
9.2.4.3) Elastic Strain Energy | 189
9.2.5) Kinetic Criterion for the Initiation of Plastic Accommodation | 192
9.3) Estimation of Parameters | 194
<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.4) Growth Simulation Results and Discussion</td>
<td>197</td>
</tr>
<tr>
<td>9.4.1) Computed Nonthermoelastic Growth Behavior</td>
<td>198</td>
</tr>
<tr>
<td>9.4.2) Radial-Growth Arrest and the Morphological Transition</td>
<td>208</td>
</tr>
<tr>
<td>9.4.3) The Internal Structure of Plate Martensite</td>
<td>212</td>
</tr>
<tr>
<td>10) SUMMARY OF PART II</td>
<td>216</td>
</tr>
<tr>
<td>CONCLUSIONS</td>
<td>220</td>
</tr>
<tr>
<td>SUGGESTIONS FOR FUTURE WORK</td>
<td>221</td>
</tr>
<tr>
<td>APPENDICES</td>
<td>224</td>
</tr>
<tr>
<td>A1) SOLUTIONS TO THE ONE-DIMENSIONAL VARIATIONAL PROBLEM</td>
<td>224</td>
</tr>
<tr>
<td>A1.1) Martensitic Nucleation</td>
<td>224</td>
</tr>
<tr>
<td>A1.2) Quasimartensitic Strain Modulations</td>
<td>227</td>
</tr>
<tr>
<td>A2) COMPUTER ALGORITHM FOR THE GROWTH CALCULATIONS</td>
<td>230</td>
</tr>
<tr>
<td>A3) DISLOCATION-SLIP KINETICS FOR THE MODEL ALLOYS</td>
<td>235</td>
</tr>
<tr>
<td>A3.1) Fe-32Ni</td>
<td>236</td>
</tr>
<tr>
<td>A3.2) Fe-24Ni</td>
<td>239</td>
</tr>
<tr>
<td>A3.3) Predicted Flow Curves</td>
<td>240</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>243</td>
</tr>
<tr>
<td>BIOGRAPHICAL NOTE</td>
<td>251</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Schematic diagram depicting three different paths leading to the operational nucleus. (After Olson and Cohen [9])</td>
<td>21</td>
</tr>
<tr>
<td>2.2</td>
<td>Knapp-Dehlinger martensitic embryo model showing the dislocation loops which accomplish the lattice-invariant deformation. (After Kaufman and Cohen [14])</td>
<td>26</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic illustration of defect dissociation. (a) Initial nucleating defect consisting of a finite dislocation tilt boundary. (b) Component of nucleus interfacial structure derived directly from the defect. (After Olson and Cohen [28])</td>
<td>29</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic of the interfacial-dislocation structure of a martensitic nucleus in the fcc-bcc transformation. (Olson and Cohen [28])</td>
<td>31</td>
</tr>
<tr>
<td>2.5</td>
<td>Defect dissociation and fault formation at a nucleating defect having a finite extent. (a) The nucleating defect. (b) Dissociation of the defect to produce a faulted region bounded by partial dislocations. (c) Simultaneous generation of lattice-dislocation loops. (Olson and Cohen [40])</td>
<td>32</td>
</tr>
<tr>
<td>2.6</td>
<td>Total defect-plus-nucleus energy as a function of separation of the partial dislocation walls bounding the nucleus, drawn schematically for the conditions: ( \gamma_f &gt; 0, \gamma_e = 0, ) and ( \gamma_f &lt; 0. ) (Olson and Cohen [2])</td>
<td>34</td>
</tr>
<tr>
<td>3.1</td>
<td>Calculated free-energy change at 0°K (enthalpy) for the bcc-fcc homogeneous lattice deformation in sodium along the proportional-strain path. Pressure was used to vary the relative stability of the two structures. (Krasko et al. [59])</td>
<td>45</td>
</tr>
<tr>
<td>3.2</td>
<td>Compilation of second-order elastic-constant data for alloys in the second and third classes of materials which transform martensitically. Delaey et al. [46] proposed three classes based on elastic softening behavior. (Compiled by Delaey et al. [46])</td>
<td>48</td>
</tr>
</tbody>
</table>
3.3 Infinite slab of material centered in the z=0 plane, undergoing an invariant-plane-strain transformation. The displacement along the z-axis is depicted by the solid and dotted lines for a sharp and diffuse interface respectively. The displacement function, $u$, is defined such that the total displacement equals $u + \gamma_r$.

(Olson and Cohen [9])

3.4 Schematic strain profile across a martensitic interface illustrating the definition of the effective interfacial thickness.

3.5 Assumed nucleus geometry for the homogeneous nucleation calculations. The transformation shape-strain is assumed to be a simple shear IPS with the invariant plane normal to the c-direction.

3.6 Saddle-point free-energy barriers as a function of nucleus-structure parameter, $\eta_0$. The minimum at each driving force represents the predicted critical energy barrier for nonclassical homogeneous martensitic nucleation.

3.7 Critical-nucleus-structure parameter as a function of thermodynamic driving force.

3.8 Critical free-energy barrier as a function of thermodynamic driving force. The dashed lines in the inset indicate the range of the critical barrier which would lead to observable nucleation rates at room temperature assuming $\delta_0=0.75$ nm and $\varphi_0=100$ to 1000 J/m$^3$.

3.9 Critical-nucleus semithickness, calculated as a function of driving force for nonclassical homogeneous martensitic nucleation.

3.10 Effective interfacial thickness of a critical nucleus undergoing homogeneous martensitic nucleation, computed as a function of driving force.

3.11 Driving-force dependence of the effective interfacial energy for a critical nucleus, according to the nonclassical homogeneous martensitic nucleation model.

4.1 Schematic diagram illustrating the defect-dissociation mechanism of martensitic nucleation in the discrete dislocation and continuum limits. (a) Discrete-dislocation model. (b) Superposition of the discrete defect with the nucleus producing the nucleus–interfacial structure in (a). (c) Same as (b) except that the nucleus is treated as a continuum particle undergoing a transformation strain.
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>Schematic diagram depicting the defect/nucleus geometry assumed in the classical heterogeneous martensitic nucleation model.</td>
<td>82</td>
</tr>
<tr>
<td>4.3</td>
<td>Normalized free-energy change as a function of nucleus width for classical martensitic nucleation. ( \theta_1=\theta_2=0 ) (edge/edge), ( n_0=15 ), ( n_d=5 ), ( m=3 ), ( r_o=d ), ( 4\sigma/\gamma_r d^2=1 ). (a) Variable (minimum-energy) thickness case. (b) Constant thickness case.</td>
<td>86</td>
</tr>
<tr>
<td>4.4</td>
<td>Normalized free-energy change as a function of nucleus width for classical martensitic nucleation at constant-nucleus thickness. ( \theta_1=44.46^\circ ), ( \theta_2=69.46^\circ ), ( n_0=27 ), ( n_d=5 ), ( m=3 ), ( r_o=d ), ( 4\sigma/\gamma_r d^2=1 ). (a) ( f=1.0 ). (b) ( f=1.6 ).</td>
<td>91</td>
</tr>
<tr>
<td>4.5</td>
<td>Dependence of the short-range free-energy barrier on driving force, for the calculations represented in Fig. 4.4b. The barrier vanishes at the critical driving force for barrierless nucleation.</td>
<td>93</td>
</tr>
<tr>
<td>4.6</td>
<td>Normalized free-energy change as a function of nucleus width, plotted for several values of the normalized driving-force parameter, ( \alpha ). These results were obtained using the nonclassical heterogeneous nucleation model assuming a defect potency characterized by ( n_0=15 ). The minimum-energy path follows the classical path with ( n_0=1 ).</td>
<td>96</td>
</tr>
<tr>
<td>4.7</td>
<td>Free-energy curves versus nucleus width for heterogeneous martensitic nucleation at a less-potent defect than in Fig. 4.6 with ( n_0=9 ).</td>
<td>97</td>
</tr>
<tr>
<td>4.8</td>
<td>Same as Fig. 4.7 except that the defect potency was further reduced to ( n_0=3 ).</td>
<td>99</td>
</tr>
<tr>
<td>4.9</td>
<td>Constant free-energy contours for nonclassical heterogeneous nucleation at a weak defect (( n_0=3 )), plotted as a function of nucleus structure, ( n_0 ), and width, ( a ), at a driving force of ( \alpha=0.7 ). The free-energy saddle point lies appreciably off the ( n_0=1 ) axis indicating an energetic advantage of nonclassical nucleation paths.</td>
<td>101</td>
</tr>
<tr>
<td>5.1</td>
<td>Schematic illustration of a section of the model-quasi-martensitic region, consisting of a stack of transforming plates whose transformation shears alternate in sign, between ( +n_0 ) and ( -n_0 ).</td>
<td>106</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>5.2</td>
<td>Normalized energy-density contours for minimum-energy strain modulations as a function of strain amplitude, $\eta_0$, and reciprocal wavelength, $1/\lambda$, at a driving force of $\alpha=0.9$.</td>
<td>110</td>
</tr>
<tr>
<td>5.3</td>
<td>Strain profiles, $\eta(z)$, for critical strain modulations for two wavelengths at a driving force of $\alpha=0.9$. (a) $\lambda=5\delta_0$, and (b) $\lambda=30\delta_0$.</td>
<td>111</td>
</tr>
<tr>
<td>7.1</td>
<td>Optical micrograph showing a fully-twinned martensitic plate formed in Fe-33.7Ni. (Datta and Raghavan [104])</td>
<td>123</td>
</tr>
<tr>
<td>7.2</td>
<td>Optical micrograph showing a portion of a partially twinned martensitic plate formed in Fe-32.0Ni. (Patterson and Wayman [107])</td>
<td>124</td>
</tr>
<tr>
<td>7.3</td>
<td>Transmission electron micrographs showing the structure of groups of laths formed in Fe-12.0Ni (a), and Fe-20.4Ni (b). (Speich and Swann [109])</td>
<td>126</td>
</tr>
<tr>
<td>8.1</td>
<td>Flow chart showing the basic components of the thermoelastic martensitic growth model. The arrows indicate interactions between the components.</td>
<td>136</td>
</tr>
<tr>
<td>8.2</td>
<td>Schematic temperature profile across a martensitic interface during growth.</td>
<td>140</td>
</tr>
<tr>
<td>8.3</td>
<td>Schematic dependence of plastic strain-rate on applied stress, for crystal plasticity via slip, depicting the entire range of kinetic behavior. (Kocks, Argon, and Ashby [123])</td>
<td>148</td>
</tr>
<tr>
<td>8.4</td>
<td>Predicted dependence of interfacial velocity on the effective interfacial force. The low-velocity regime was modeled after thermally activated dislocation slip, whereas, phonon-drag mechanisms controls the high-velocity growth rate.</td>
<td>158</td>
</tr>
<tr>
<td>8.5</td>
<td>Computed growth path (r and c vs. time) for an elastically accommodated martensitic plate in Fe-32Ni.</td>
<td>161</td>
</tr>
<tr>
<td>8.6</td>
<td>Radial growth rate and interfacial temperature near the plate tip ($v_r$ and $T_r$) as a function of plate radius for the thermoelastic growth simulation in Fe-32Ni.</td>
<td>164</td>
</tr>
<tr>
<td>8.7</td>
<td>Thickening rate and temperaure interfacial temperature along the plate faces ($v_c$ and $T_c$) as a function of plate semithickness for the thermoelastic growth simulation.</td>
<td>166</td>
</tr>
</tbody>
</table>
9.1 Flow chart showing the basic components of the nonthermoelastic martensitic growth model. Components (g)-(j) extend the thermoelastic growth model in order to include plastic-accommodation effects.

9.2 Schematic illustration depicting nucleation of a lattice-dislocation loop, in the stress field at the tip of a martensitic particle

9.3 Critical combinations of particle radius and aspect ratio necessary to nucleate dislocation loops, athermally, in the stress field at the tip of the model-martensitic particle.

9.4 Schematic diagram illustrating the connection between the in-plane stress fields of an enclosed, shearing, elliptically-shaped inclusion particle, with that of a blunt, mode III shear crack.

9.5 Schematic illustration of a cross section through the model-martensitic particle showing the assumed radial plastic-zone shape.

9.6 Schematic illustration of a cross section through the model-martensitic particle showing the assumed perpendicular plastic-zone shape.

9.7 Flow curves (solid) for Fe-32Ni at 200 K and Fe-24Ni at 400 K, predicted by the slip-kinetics model, presented in Appendix 3. Also included are solutions to the radial-plastic-zone model (dashed), corresponding to two ratios of \( v/r \), where \( v \) is the radial growth rate. \((v/r)_1 \) \( > (v/r)_2 \).

9.8 Predicted radial-growth behavior of a single martensitic particle in Fe-24Ni transformed at 400 K, and Fe-32Ni transformed at 200 K. \( \Theta = 1.0 \) GPa; \( \beta = 0.001 \).
   a) Radial growth velocity versus particle radius.
   b) Interfacial temperature at the particle tip.

9.9 Predicted thickening behavior of a single martensitic particle in Fe-32Ni transformed at 200 K. The thickening rate is plotted as a function of particle semithickness. \( \Theta = 1.0 \) GPa; \( \beta = 0.025 \).
9.10 Plastic-accommodation factor as a function of transformation temperature for Fe-Ni alloys and one Fe-Ni-Mn alloy. The plastic-accommodation factor is defined as the fraction of stored elastic energy released by plastic accommodation of the transformation strain during martensitic transformation.

(Datta, Ghosh and Raghavan [164])

212

9.11 The mean value of the relative fraction of untwinned versus twinned region within martensitic plates as a function of the plastic-accommodation factor in Fe-Ni alloys.

(Datta, Ghosh and Raghavan [164])

214

A1.1 Schematic diagram illustrating the three types of solutions to the strain-variational problem as applied to martensitic nucleation.

(a) The strain gradient is non-zero at the origin.
(b) \( \eta' \) is zero at the origin; piecewise solutions are allowed.
(c) \( \eta' \) is non-zero at the origin and the strain tends to concentrate near \( \eta_t \).

226

A1.2 Free energy of homogeneous lattice deformation, plotted schematically as a function of \( \eta \), at a driving force potentially favorable for the transformation of the parent structure (\( \eta=0 \)) to the product structure (\( \eta=1 \)). The integration constant, arising from the solution of the Euler equation under the prescribed boundary conditions for the quasi-martensitic strain-modulation model, is indicated on the diagram.

228

A3.1 Compilation of critical-resolved shear-stress data for four ferromagnetic Fe-Ni invar alloys, with Ni contents in the range: 30-36.1 wt.-percent Ni, and paramagnetic (non-invar) Fe-25Ni-16Cr. Invar strengthening strongly affects plastic-flow behavior below the Curie temperature for Fe-Ni austenites in this composition range.

238

A3.2 Predicted slip kinetics for the austenites: Fe-32Ni at 200 K, and Fe-24Ni at 400 K. These curves describe the response of a crystal to an applied stress; inversion of the governing equations gives the flow stress as a function of imposed strain rate.

241
LIST OF TABLES

Table                                                                 Page
  8.1  Parameter List for the Thermoelastic Growth Model                154
  A2.1 List of Symbols Used in the Growth-Algorithm Outline            232
  A3.1 Estimated Parameters for the Kinetic Equations of Plastic Flow  242
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CHAPTER 1

INTRODUCTION AND SCOPE OF THE RESEARCH

Perhaps the most prominent feature distinguishing martensitic transformations from other structural solid-state phase transitions is the diffusionless nature of the transformation. It has long been recognized that martensitic transformations are accomplished by the coordinated displacements of atoms over distances less than the unit-cell dimensions of the transforming crystal lattice. However these two characteristics alone—diffusionless and displacive—define a rather broad class of phase transitions, which encompasses a wide variety of transformation behavior. In order to establish the important phenomenological similarities and differences within the universe of displacive/diffusionless phase transformations, Olson, Cohen, and Clapp [1] proposed a classification based on observable transformation characteristics, manifested by transformation kinetics and morphology.

Accordingly, martensitic transformations are defined as a subset of displacive/diffusionless phase transformations in which lattice-distortive displacements dominate over shuffle displacements, and the lattice distortion is sufficiently deviatoric to preserve an undistorted line. These two requirements are necessary but not sufficient to classify a displacive/diffusionless transformation as being martensitic. In addition, the transformation kinetics and morphology must be dominated by strain energy. Transformations which fail this final test include those for which the displacements are so small that the transformation can occur continuously instead of requiring nucleation and growth. The term quasimartensitic has been adopted to define those transformations which
are diffusionless, displacive, and deviatorically lattice-distortive, but
for which the kinetics and morphology are not dominated by strain energy.

This thesis presents the results of quantitative modeling of the
nucleation and growth of a single martensitic particle. Treatment of the
martensitic transformation as a two-stage nucleation-and-growth process
follows the approach traditionally applied to first-order phase
transitions. Martensitic transformations are unusual, however, in the
sense that the progression of the transformation usually requires the
generation and/or triggering of nucleation sites, by previously-formed
martensitic units. This autocatalytic nucleation reflects a strong
interaction between nucleation and growth, which greatly influences the
course of the transformation. The present focus on the transformation
behavior of non-interacting, individual units, therefore, best applies to
the initiation of the transformation. However, many of the essential
features of martensitic nucleation and growth, characteristic to the
formation of isolated transforming units, are believed to be preserved,
even in the later stages of the transformation.

Martensitic transformations have been the subject of considerable
experimental research; the kinetics of martensitic nucleation and the
morphology of the transformation product are fairly well understood.
However, many important details of the transformation escape observation
by present-day experimental techniques. Modeling provides an alternate
means by which to study the martensitic transformation, complementing the
experimental approach, and possibly suggesting additional areas of
experimentation. The development of detailed models requires a reasonable
understanding of the underlying microscopic mechanisms. Recent
theoretical advances, based on experimental observations, provided a basis
for all of the models described in this thesis.

Part I is concerned with the modeling of martensitic nucleation for
the purpose of advancing our understanding of the general phenomenon. A
physically appealing mechanistic model for classical heterogeneous
martensitic nucleation was proposed by Olson and Cohen [2-3], which
successfully accounts for experimentally observed kinetic behavior. These investigators also proposed a model for nonclassical nucleation, allowing the structure of the nucleus to vary along the nucleation path. The distinction between classical and nonclassical nucleation paths will be discussed in Chapter 2. In the present study, the potential for nonclassical martensitic nucleation was evaluated through numerical analysis of the Olson-Cohen model for homogeneous martensitic nucleation. The results of this investigation will be presented in Chapter 3, together with a discussion of the special circumstances required for the occurrence of homogeneous martensitic nucleation. In Chapter 4 the nonclassical nucleation model is generalized to include a defect/nucleus interaction resulting in a model for nonclassical heterogeneous martensitic nucleation. In certain cases, the closely related quasimartensitic transformation may compete with the martensitic transformation. Chapter 5 presents a model for the formation of a quasimartensitic structure consisting of a continuous strain modulation, in which interfacial (gradient) energy dominates the morphology and kinetics of the transformation.

Martensitic growth will represent the main topic of Part II of this thesis. The details of the growth process are thought to play a vital role in determining the final morphology of the product phase. The martensitic-growth process involves complex interactions between various kinetic phenomena including heat transfer, interfacial mobility, and plastic flow processes. A detailed model, accounting for these interactions, was constructed based on experimental kinetic and morphological observations, reported by previous investigators. In Chapter 8, a model for the growth of an elastically accommodated, isolated martensitic particle will be presented. Plastic accommodation of the transformation shape-strain is an important feature of martensitic transformations in ferrous alloys, and may account for the observed morphological transition in steels. Chapter 9 addresses the plastic-accommodation problem by extending the thermoelastic growth model to include plastic accommodation effects.
Numerous review articles have been written addressing various aspects of the martensitic transformation; reference will be made to these papers throughout the following text. Two recent and particularly comprehensive publications should serve as useful background material: 1) Cohen and Wayman [5] present an overview of the many facets of martensitic transformation phenomena, and 2) Olson and Cohen [6] summarize contemporary theories of martensitic nucleation and growth.
PART I: ENERGETICS OF MARTENSITIC NUCLEATION:

CLASSICAL VS. NONCLASSICAL PATHS

CHAPTER 2

INTRODUCTION TO MARTENSITIC NUCLEATION

In classical nucleation theory [7] a distribution of nuclei of constant composition and/or structure, but varying size, is assumed to form by statistical heterophase fluctuations. These nuclei have an energy greater than the bulk phase in which they form; however, those which achieve a critical size may grow with a concomitant decrease in energy. But the critical nuclei have an equal probability of growth or reversion, and therefore, the steady-state nucleation rate is controlled by the rate of formation of supercritical nuclei of operational size. In diffusional transformations, the operational nucleus size is defined such that the probability of reversion is negligible. On the other hand, the operational nucleus size for martensitic transformations has been defined as that required for rapid growth [8]. This choice is consistent with both contemporary viewpoints concerning the mechanism of martensitic nucleation and the detectable events in martensitic nucleation kinetic experiments.

When considering the various possible ways in which a nucleus may form in the parent phase, a distinction can be made between classical and nonclassical nucleation paths. Following Olson and Cohen [9], a classical nucleation path involves a nucleus of the same structure as the fully developed product, increasing in size by the motion of its interface. Nonclassical nucleation paths include all other possibilities whereby the nucleus size and structure may vary simultaneously, during the formation of an operational nucleus. This distinction is illustrated schematically in Fig. 2.1 where the classical nucleation path (a) and two nonclassical
Fig. 2.1: Schematic diagram depicting three different paths leading to the operational nucleus.  (After Olson and Cohen [9])
paths (b and c) are indicated by dashed lines. The structure parameter, \( \eta \), (to be defined later) varies from zero for the parent phase to one for the product phase. The size parameter, \( n \), represents the number of atoms in the nucleus, with \( \hat{n} \) being the operational nucleus size.

Several interesting models for martensitic nucleation have evolved over the past four decades; some of the earliest ideas have survived the years while others have been recently revived. The martensitic embryo concept represents one of the important "survivors", whereas nonclassical nucleation paths, once regarded as unimportant, has recently attracted renewed attention.

The following section introduces some general observable characteristics of martensitic nucleation and serves as general background information for later discussions.

2.1) General Characteristics of Martensitic Nucleation

Martensitic nucleation in ferrous alloys typically exhibits athermal kinetic behavior with the amount of product phase being substantially independent of time at a given temperature below \( M_s \). In fact, this athermal behavior was once considered to be one of the general defining characteristics of the martensitic transformation [10]. Isothermal kinetics were first reported in Fe-Mn-C and Fe-Ni-Mn alloys by Kurdjumov and Maksimova [11,12], who observed a time-dependent martensitic transformation which could be suppressed by rapid cooling. These authors proposed that isothermal martensite forms via nucleation and growth, although nucleation controls the overall transformation rate. The occurrence of isothermal nucleation proved that the nucleation process is, at least sometimes, thermally activated, although the possibility remained that athermal kinetics may be a manifestation of very rapid isothermal nucleation. Nevertheless, the term, athermal nucleation was used when referring to martensitic nucleation under conditions for which the observed transformation behavior is time-independent.
A simple model for a martensitic nucleus consists of a thin, oblate spheroidal or lens-shaped inclusion, undergoing an invariant-plane strain, for which the Gibbs free energy is written as the sum of the chemical, elastic-strain, and interfacial energies. Below the austenite/martensite equilibrium temperature, the free energy as a function of particle radius, \( r \), and semithickness, \( c \), contains a saddle point which defines the most probable energy barrier for homogeneous nucleation. If one assumes that the particle grows along the path which minimizes nonchemical free-energy contributions, then \( c \) is determined, and the free energy exhibits a maximum at \( r = r^* \), the critical particle radius for homogeneous martensitic nucleation.

Classical homogeneous nucleation theory fails to account for the magnitude and temperature dependence of the experimental activation energy, as determined by isothermal martensitic nucleation kinetic measurements [13,14]. Attempts to apply homogeneous nucleation theory assumed a nucleus-interfacial energy appropriate to the fully-coherent state [15-17], but this vital assumption was rejected in favor of predictions that the martensitic interface is semicoherent with considerably higher energy [18,19]. The homogeneous nucleation barrier for a semicoherent nucleus was estimated to be about \( 10^4 \) eV in steels [14]: a prohibitively high value which could not be reconciled by experiment. Critical experiments performed by Kaufman and Cohen [20] and Cech and Turnbull [21] provided indisputable evidence that martensite nucleates heterogeneously under normal circumstances\(^1\) in steels.

An externally applied elastic stress raises the \( M_s \) temperature for athermal martensitic transformation [22] and has a stimulating effect on isothermal transformation kinetics [23]. These observations are readily understood in terms of a driving-force enhancement due to a favorable interaction between the applied stress and the transformation

\(^1\)Special conditions under which martensitic nucleation may occur homogeneously will be discussed in Chapter 3.
shape-strain [24]. High magnetic fields have similar effects on the transformation behavior of paramagnetic austenites which transform to a ferromagnetic martensite [25].

Except for the very first martensitic units to form, autocatalytic nucleation plays a predominant role in determining the overall nucleation kinetics. This cooperative nature of martensitic nucleation is most conspicuous in alloys which show "bursting" behavior, characterized by a zig-zag arrangement of plates suggesting a chain reaction [26,27]. Two major mechanisms of autocatalysis have been proposed: stress-assisted and strain-induced [28]. Stress-assisted autocatalytic nucleation involves the triggering of pre-existing nucleation sites by the internal stresses generated by previously formed martensite. These nucleation sites are of insufficient potency to produce martensite spontaneously, without the aid of stress, at the given temperature. On the other hand, strain-induced autocatalysis relies on the production of new nucleation sites, by plastic accommodation processes involving defect generation and rearrangement. In principle, it is also possible to produce additional martensitic variants by dissociation processes in the martensitic interface [3].

Knorovsky [29] studied autocatalysis in Fe-Ni single crystal austenite transformed to martensite in a temperature gradient, and concluded that stress-assisted nucleation of strain-induced nuclei is the predominant mechanism of autocatalytic nucleation. However, this conclusion may not universally apply to all martensitic transformation or under all conditions of transformation.

A brief review of current martensitic nucleation theory follows which covers classical heterogeneous and nonclassical nucleation. Due to limits on space, a complete historical review cannot be presented; consequently, only the important highlights relevant to later discussions will be outlined.
2.2) Classical Heterogeneous Nucleation

2.2.1) Martensitic Embryo Models

Following the dismissal of homogeneous nucleation as a plausible mechanism of martensitic nucleation, Kaufman and Cohen [14] proposed that local heterogeneities called "embryos" trigger the martensitic transformation. These embryos were described as nonequilibrium lattice imperfections which survive the austenitizing treatment, and represent centers of high energy, available for heterogeneous nucleation of martensite. In other words, the embryos represent finite regions in the crystal where the local free energy partially surmounts the free-energy barrier for martensite formation.

Athermal nucleation was explained by assuming that real crystals contain a spectrum of embryos of various potencies. An embryo of a given potency nucleates martensite athermally, when the chemical driving force reaches a level such that the nucleation free-energy barrier drops below the energy of the embryo. The most potent embryos are triggered at $M_s$; less potent embryos are triggered at lower temperatures, under the action of a higher chemical driving force. Isothermal nucleation was envisioned to occur via thermal activation of embryos over the free-energy barrier. This barrier was expected to be reduced locally, by an amount equal to the embryo free energy. However, in a calculation assuming a classical nucleation path, Kaufman and Cohen found that the predicted driving-force dependence of activation energy was far greater than experimentally observed.

Kaufman and Cohen [14] then considered other potential barriers to martensitic nucleation, reasoning that these barriers may hinder the growth of a supercritical embryo, i.e., one whose size and shape place it beyond the homogeneous nucleation barrier. At around the same time, Knapp and Dehlinger [19] proposed a geometric model of a martensitic embryo based on Frank's interface-structural model [18]. Fig. 2.2 shows schematically, the embryo model, which consisted of a thin, oblate
Fig. 2.2: Knapp-Dehlinger martensitic embryo model showing the dislocation loops which accomplish the lattice-invariant deformation. (After Kaufman and Cohen [14])
spheroidal particle, with an invariant-plane habit, undergoing an
invariant-plane strain. Knapp and Dehlinger suggested that athermal
martensitic nucleation occurs at a driving force which allows spontaneous
generation of the interfacial dislocation loops encompassing the embryo
(see Fig. 2.2). These dislocation loops accomplish the lattice-invariant
shear necessary to achieve an invariant-plane habit.

Recognizing the complexity of the dislocation-loop-nucleation
problem, Kaufman and Cohen [14], instead, modeled the thin embryo as a
giant dislocation loop, lying in the habit plane. The calculated energy
change accompanying expansion of the loop exhibited a maximum, or barrier,
at a radius, \( r_c \), which was more than twice the critical radius for
homogeneous nucleation. According to these investigators, \( r_c \) represents
the critical radius for cataclysmic growth; embryos with \( r = r_c \) trigger
athermally at a given temperature, while larger (more potent) embryos
would have already produced martensite at a higher temperature.
Furthermore, smaller (less potent) embryos can be thermally activated over
the energy barrier, thus accounting for isothermal nucleation. By
assuming reasonable values for the interfacial energy and embryo size,
good agreement was obtained between the predictions of the model and
experiment.

Raghavan and Cohen [31] refined the Knapp-Dehlinger embryo model by
considering, in more detail, the dislocation-loop formation process. The
energetics of dislocation-loop nucleation at the coherent embryo tip were
modeled, utilizing the concept of transformational stresses due to the net
free-energy change accompanying a unit growth step. The results were in
general agreement with the Kaufman-Cohen model; that is, the magnitude and
driving-force dependence of the predicted activation energy for embryo
growth agreed with experiment.

The embryo model succeeds in rationalizing martensitic nucleation
kinetic measurements by supposing that stable embryos form in the vicinity
of defects at a temperature above \( M_s \). It is essential that the embryos
achieve a configuration such that, with the exception of interfacial
processes such as dislocation-loop formation, nucleation is barrierless. The exact origin and structure of the martensitic embryos, however, was left to be determined.

2.2.2) The Olson–Cohen Defect Dissociation Model

The mechanism of martensite formation has long been associated with the action of one or more shears, effecting the change in structure from parent to product phase [32–34]. The simplest case involves the fcc-hcp transformation which can be accomplished by the motion of a/6<112> Shockley partials on alternate parallel {111} planes of the fcc lattice [35]. Jaswon [36] proposed that a half-twinning shear on {111} planes in the fcc structure could produce a fault, which is structurally close to bcc. Bogers and Burgers [37] suggested that the bcc structure may result from the combination of two shears on adjacent {111} fcc planes. These authors further proposed that these shears are brought about by dislocation processes, involving simple lattice dislocations of the fcc structure.

Olson and Cohen [2–4] synthesized the shear concept into a general model for martensitic nucleation, based on defect dissociation on close-packed planes of the parent phase. This model accounts for the energetics and kinetics of nucleation and predicts the nucleus interfacial structure. The nucleation process begins by the spontaneous formation of a fault in the austenite, bounded by finite partial dislocation walls, producing a volume of material resembling the martensitic structure. The displacements in the faulted region are, in part, derived directly from the nucleating defect via dissociation of lattice dislocations.

As an illustrative example, nucleation of the fcc-bcc transformation, at a specific nucleating defect will be consider here (for further details see Olson and Cohen [28]). Fig. 2.3 shows schematically the dissociation of a set of three infinite, parallel a/2[011] edge dislocations, lying in and separated by three close-packed (111) fcc planes (Fig. 2.3a).
Fig. 2.3: Schematic illustration of defect dissociation.
(a) Initial nucleating defect consisting of a finite dislocation tilt boundary.
(b) Component of nucleus interfacial structure derived directly from the defect. (After Olson and Cohen [28])
Fig. 2.3b represents the faulted region which results from the
dissociation and spreading of the cores of the original lattice
dislocations to produce a/18[\overline{1}21] dislocations on every (111) fcc plane.
This fault does not represent the complete nucleus structure, but only the
part derived directly from the nucleating defect. Further relaxations in
the form of shears on adjacent (11\overline{1})_f planes in the [\overline{1}21]_f direction,
accompanied by additional minor distortions, result in a fully-coherent
bcc nucleus. Addition shears on (011)_b planes in [\overline{1}10]_f and [011]_f
directions reduce the nucleus-strain energy such that nucleation is
possible, at the level of driving force typical of steels. The shears
responsible for the change in structure are accomplished by the passage of
coherency dislocations [38], some of which are derived from the
dissociation process. Likewise, dislocations produce the shears
responsible for the reduction in coherency; these dislocations have been
termed anticoherency dislocations [38].

The proposed nucleus-interfacial structure, consisting of discrete
dislocation arrays, is depicted schematically in Fig. 2.4. For the
purpose of modeling the energetics of defect dissociation, the nucleus is
treated as a thin ribbon, or lath, with infinite length or extent along
the nucleating defect, but having finite height and width. Of course, in
real crystals the defect will have a finite extent, and one can envision
the bowing out of partial dislocations into the parent lattice. This
process is depicted schematically in Fig. 2.5 which also shows the
anticoherency dislocation loops bounding the nucleus. In the energetic
analysis it is assumed that the bow-out is small relative to the extent of
the defect so that line tension effects can be neglected.

For a nucleus of width, "a", lying along the nucleating defect, the
total energy per unit length, G(a), is conveniently divided into a
"dislocation energy", E_{\text{d}}(a), and "fault energy", \gamma_f, leading to the
Fig. 2.4: Schematic of the interfacial-dislocation structure of a martensitic nucleus in the fcc-bcc transformation.

(Olson and Cohen [28])
Fig. 2.5: Defect dissociation and fault formation at a nucleating defect having a finite extent.
(a) The nucleating defect.
(b) Dissociation of the defect to produce a faulted region bounded by partial dislocations.
(c) Simultaneous generation of lattice-dislocation loops.
(0lson and Cohen [40])
following expression:

\[ G(a) = E_\perp(a) + \gamma_f \cdot a \, , \]  

(2.1)

with

\[ \gamma_f = n \rho_A (\Delta G^{ch} + E^{str}) + 2\sigma(n) \, . \]  

(2.2)

where \( \rho_A \) is the density of atoms in the close-packed plane in moles per unit area, \( \Delta G^{ch} \) is the molar chemical free-energy difference between phases, \( E^{str} \) is the molar strain energy, \( \sigma \) is the surface energy, and \( n \) is the number of close-packed planes comprising the fault [2]. For dissociation of a finite dislocation wall, \( E_\perp(a) \) is a monotonically decreasing function of separation such that stability of a nucleus is controlled by the long-range restoring force associated with the fault energy, \( \gamma_f \). This situation is illustrated in Fig. 2.6 where total energy is plotted schematically as a function of nucleus width. At sufficient driving force, \( \gamma_f \) becomes negative, producing a barrierless condition in which the nucleus can grow spontaneously, at a rate controlled by the kinetics of interfacial motion. When \( \gamma_f \) is positive, however, the energy of the system can be minimized by the formation of a stable nucleus or embryo (see the arrow in Fig. 2.6), thus confirming early predictions of the existence of stable embryos above \( M_s \).

Calculations using parameters appropriate to Fe-30Ni at \( M_s \) were made by setting \( \gamma_f = 0 \) in eqn. 2.2, and solving for the critical value of \( n \) which would lead to barrierless nucleation. The fault thickness, in number of close-packed planes, \( n \), is a direct measure of the potency of the nucleating defect. This led to the prediction that four or five properly spaced lattice dislocations can account for martensitic nucleation at \( M_s \). Such dislocation arrangements are likely to exist as extrinsic defects in various internal interfaces such as grain boundaries, subboundaries, and interphase boundaries. Olson and Cohen consider defects of this type to be consistent with the known sparseness of initial martensitic nucleation sites [2]. Moreover, they cite thin-foil TEM studies of the early stages of martensitic transformation at internal interfaces as evidence in support of the faulting mechanism [2,28].
Fig. 2.6: Total defect-plus-nucleus energy as a function of separation of the partial-dislocation walls bounding the nucleus, drawn schematically for the conditions $\gamma_f > 0$, $\gamma_f = 0$, and $\gamma_f < 0$. (Olson and Cohen [2])
Since the Olson-Cohen model predicts the formation of stable martensitic embryos above $M_s$, athermal nucleation is explainable in terms of a distribution of nucleating-defect potencies, as discussed in the previous section. Isothermal nucleation can be rationalized by considering short-range barriers to interfacial motion which may be overcome by thermal energy. The formation of anticoherency dislocation loops represents one possible rate-limiting process, originally addressed by the Kaufman-Cohen model. Another possibility is the motion of the interfacial dislocations, through obstacles in the lattice, as suggested by Magee [39]. Olson and Cohen have recently shown that the latter process is more likely to be rate-limiting and probably involves the coherency dislocation component of the nucleus interface [40]. By considering thermally-activated nucleation in terms of plastic-deformation theory, Olson and Cohen demonstrated that the proposed nucleation model predicts an approximate linear dependence of activation energy on chemical driving force, in agreement with experimental observations [4].

2.3) **Nonclassical Martensitic Nucleation**

2.2.1) **The Reaction-Path Model**

Cohen, Machlin and Paranjpe [30], recognizing that the martensitic transformation occurs nonrandomly within austenite grains, proposed that strain embryos exist in the austenite, which heterogeneously nucleate the reaction when conditions become favorable. These strain embryos were described as regions of localized strain where the lattice is partially displaced along the reaction path that leads to the martensitic state. It was further anticipated that the strain embryos might form in association with one or more lattice-screw dislocations. The above ideas

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2 The strain embryo should not be confused with the embryos proposed by Kaufman and Cohen. The latter entities were considered to be tiny regions of fully-developed product phase, and therefore, represent an application of classical heterogeneous nucleation. The nonclassical strain-embryo model actually preceded the Kaufman-Cohen embryo model.
were presented a number of years before homogeneous nucleation theory was abandoned as a viable martensitic nucleation mechanism.

The martensitic transformation was thought to take each volume of material through a continuous succession of free-energy states, from a local minimum in the austenitic state, to a lower-energy minimum in the martensitic state. This reaction path was expected to contain a free-energy barrier whose height is a function of both temperature (driving force) and coherency state. The nucleation model based on these concepts became known as the reaction-path model. According to this model, a strain embryo becomes critical when the strain at its center corresponds to a local reduction in free energy. Once this condition is achieved, for example at a critical driving force, the strain embryo can grow via the propagation of the strain, resulting in a reduction in the total free energy of the system [30].

Machlin and Cohen [41] extended the reaction-path model to include thermal activation and a distribution of embryo potencies. These refinements were used to explain the observance of both athermal and isothermal martensitic nucleation in the same alloy. The nonclassical nature of the reaction-path model is readily apparent since the critical nucleus has a structure intermediate between austenite and martensite. Furthermore, the model predicts a diffuse embryo interface in the sense that strain varies continuously from the center of the strain embryo to the surrounding austenite.

Fisher and Turnbull [42] attempted to evaluate the validity of the reaction-path model by applying homogeneous nucleation theory with a variable transformation shape-strain. Since the reaction-path model assumes the presence of a defect, the Fisher-Turnbull analysis implicitly assumes that the free-energy barrier and critical embryo configuration is not changed by the presence of the defect. The calculation was similar to those previously made in connection with classical homogeneous nucleation [15], except that the nucleus interfacial energy, \( \sigma \), was
assumed to take the following form:

$$\sigma = \sigma_0 (\theta/\theta_0)^p$$  \hspace{1cm} (2.3)$$

where $\theta$ is the shear angle for the transformation shape-strain, which varies between zero for the austenite, and $\theta_0$ for the fully developed martensitic structure. The exponent $p$ was assumed to lie in the range $0 \leq n \leq 2$.

The critical shear angle was found to be within 10% of the classical value ($\theta=\theta_0$), although the free-energy barrier was reduced by as much as 37%. However, Fisher and Turnbull concluded that the results are sufficiently close to the classical case that the incorporation of nonclassical reaction path theory represents an unnecessary refinement to martensitic nucleation theory. The Fisher-Turnbull approach implicitly assumes a sharp nucleus interface and a constant strain within the nucleus, in contrast to the more general embryo strain profile admitted by the reaction-path model. Nevertheless, Olson and Cohen [43] agree that this conclusion is probably true in the case of steels, but may not hold for those systems which exhibit elastic anomalies indicative of incipient mechanical instability.

2.3.2) Localized Soft-Mode Models

A number of attempts have been made to correlate martensitic nucleation with anharmonic elastic effects associated with third and higher-order elastic constants. Such studies have been motivated by the prediction that anharmonic terms in the elastic energy of a lattice may lead to a lattice instability or strain spinodal, beyond which further straining could cause the lattice to collapse into a different structure [44]. In addition, anomalous elastic softening and phonon-dispersion behavior is observed above $M_s$ in many alloy systems, including $\beta$-phase, In-Tl, Fe-Pt, Au-Cd, and others, indicating a reduction in lattice stability as temperature is decreased toward $M_s$ [45,46].
Clapp [44] suggested that local strains near lattice defects may be close to a strain spinodal, resulting in local "soft-mode centers", where certain elastic constants experience appreciable softening. Accordingly, lattice vibrations in these regions are expected to have abnormally high amplitudes and low frequencies. Clapp proposed that martensitic nucleation occurs if the dynamic strain fields associated with these vibrations bring the local region even closer to the strain spinodal. By analyzing the lattice stability of bcc phases, Clapp concluded that strains near free surfaces can act as primary nucleation sites. However, Clapp's analysis is based upon homogeneous lattice deformation, whereas a local instability involves an inhomogeneous deformation and must include a surface or gradient energy. The Clapp analysis really addresses the dynamics of homophase fluctuations in the strain field of lattice defects, and has little applicability to the problem of martensitic nucleation. Furthermore, while the strain spinodal is important in connection with lattice stability during homogeneous deformation, it is not directly relevant to local deformation processes such as martensitic nucleation at defects.

Suzuki [47,48] investigated the behavior of transverse lattice waves, thought to be connected with martensitic nucleation, in a one-dimensional anharmonic crystal. The free energy of homogeneous deformation was modified to include a gradient-energy contribution, resulting in a total free-energy functional similar to that used in connection with the theory of spinodal decomposition. Numerical analyses identified a critical amplitude which must be achieved in order to produce martensitic nuclei. However, since the amplitude of normal-mode vibrations is far less than the critical amplitude, nucleation cannot take place homogeneously in a perfect crystal. Instead, Suzuki suggested that the presence of defects greatly reduces the number of atoms involved in the normal modes, which in turn, enhances vibrational amplitudes. Hence, nucleation was predicted to occur inhomogeneously [48], presumably near lattice defects. However, the analysis ignored additional strain-energy contributions due to the inhomogeneous nature of the deformation; consequently, the significant role of lattice vibrations remains unclear.
Guenin and Gobin [49,50] extended the localized soft-mode concept and treated the specific case of the \( \beta \rightarrow \theta \) transformation in Cu-Zn-Al. The major portion of the shape-deformation was assumed to be a simple shear on the \( \{011\} \langle 0\bar{1}1 \rangle \) system of the \( \beta \) phase, while other distortions were neglected. Shear resistance on this system is characterized by the anomalously low C' elastic constant (\( C'=(C_{11}-C_{12})/2 \)). Using experimentally determined, third-order elastic constants to account for lattice anharmonicity, Guenin and Gobin predicted the instability strain along the homogeneous lattice deformation path. Strain fields of lattice defects were identified as local regions of instability where martensite is likely to nucleate.

It was assumed that the effective strain energy of a nucleus forming completely within the unstable region approaches zero so that martensitic nucleation is resisted only by interfacial energy. Furthermore, the nucleus interface was assumed to be fully coherent with a correspondingly low interfacial energy. The estimated critical nucleus size of 10 nm was consistent with the size of the predicted unstable zone near a pair of parallel lattice dislocations. According to Guenin and Gobin, nucleation attempts are made by large-amplitude lattice vibrations which produce an increase in strain over the entire soft region; those regions larger than the critical nucleus size develop into martensite.

Distortions in addition to the lattice deformation, neglected by Guenin and Gobin, will certainly contribute to the nucleus free energy. Moreover, the assumption of a fully-coherent nucleus was not justified and probably leads to an underestimate of the interfacial energy. Nevertheless, it is reasonable to assume that lattice softening, indicative of incipient mechanical instability, can assist in the heterogeneous nucleation of martensite. This assistance would account, in part, for the typically low chemical driving force at \( M_s \) in those alloys which show anomalous elastic behavior.

Proper evaluation of the influence of local mechanical instability at defects on martensitic nucleation must address the complex inhomogeneous
deformations which will contribute to the energetics of the nucleation process. Strain and gradient energies will tend to inhibit the formation of locally unstable zones; consequently, the existence of such zones under the conditions in which martensitic transformations occur has not been established.

The Olson-Cohen defect dissociation model predicts the formation of stable embryos at lattice defects, but the critical step in martensitic nucleation is the barrierless growth of supercritical embryos, which does not appear to require the presence of soft-phonon modes. Indeed, lattice vibrations are likely to play a role in the formation and growth of these embryos since these processes involve the cooperative motion of atoms. However, in addition to an enhanced amplitude, soft-phonon modes are predicted to show a reduced vibrational frequency. Hence, the attempt frequency for the above processes via soft-phonon modes would be reduced, so that the relevance of soft modes is somewhat suspect.

Apart from the proposed soft-phonon dynamics of embryo formation, the localized soft-mode model amounts to little more than a revival of the reaction-path model. The reaction-path model, however, goes further in anticipating the energetic requirements for martensitic nucleation at a defect, taking into account the constraints imposed by the surrounding matrix. Nevertheless, the more quantitative treatment of the energetics of homogeneous lattice deformation represents a significant contribution to the theory of nonclassical martensitic nucleation.

2.3.3) The Olson-Cohen Nonclassical Nucleation Model

Recently, Olson and Cohen [9] proposed a general approach to modeling the energetics of martensitic nucleation, in which the transformation strain is allowed to vary arbitrarily, in the region of a crystal containing a nucleus. The total free-energy change for the formation of a coherent martensitic nucleus was decomposed into the following
contributions:

a) The free-energy of homogeneous deformation of the parent phase along the nucleation path.

b) A gradient-energy term due to the change in structure across the potentially diffuse interface.

c) A strain-energy term, and.

d) A nucleus-defect interaction energy.

In contrast to sharp-interface models which employ surface energy, normally taken as constant and scaling with interfacial area, this approach admits a general variation of nucleus structure across the interface, with gradient-energy replacing surface energy. This formal description of nucleation energetics, which introduced the concept of gradient-energy, was first proposed by Cahn and Hilliard [51], and applied to diffusional precipitation near a chemical free-energy spinodal. The use of a strain-gradient-energy term in total free-energy of an inhomogeneous system was later proposed by Roitburd [52], in connection with the mobility of diffuse coherent martensitic interfaces.

Olson and Cohen set up the problem for the model case of homogeneous nucleation of a coherent plate-shaped nucleus, with a one-dimensional variation in structure, normal to the plate. By inspection of the resulting equations, they concluded that at low driving forces, nucleation should be essentially classical and the nucleus interface sharp. However, near a mechanical instability, thermal activation may assist homogeneous nucleation along a nonclassical path, with the nucleus interface becoming diffuse. Furthermore, these authors anticipated that nucleus-defect interaction will favor the classical nucleation path so that heterogeneous nucleation is expected to be closely classical.

A quantitative analysis of homogeneous martensitic nucleation, using the above approach to the energetics of nucleation, and the extension to of this model to include defect interactions, will be presented in the following two chapters. The results will be compared with the predictions made by Olson and Cohen, as well as the analogous diffusional case treated by Cahn and Hilliard.
CHAPTER 3

HOMOGENEOUS MARTENSITIC NUCLEATION

The heterogeneous nature of martensitic nucleation in ferrous alloys was clearly demonstrated by small-particle experiments which showed that the martensitic nucleation temperature is particle-size dependent [21]. The only reasonable explanation for this effect assumes that defects, of variable potency, assist in the nucleation process. Nevertheless, homogeneous martensitic nucleation may occur, at sufficiently high driving forces, in defect-free crystals, if heterogeneous nucleation is suppressed.

Although Fisher and Turnbull's [42] estimates indicate that martensitic nucleation, in the bulk at $M_s$, is essentially classical, nonclassical paths may be favored near a mechanical instability. As the parent phase approaches general mechanical instability, anharmonic effects will contribute to a reduction in the energy of intermediate states, possibly leading to the formation of martensitic nuclei with nonclassical structures and diffuse interfaces. Examples of the circumstances which are expected to promote nonclassical behavior will be discussed.

This chapter is concerned with exploring the potential for nonclassical homogeneous martensitic nucleation, in a simple model system.

1According to the present definition of nonclassical-nucleation paths, the structure of a nucleus containing a diffuse interface is not necessarily nonclassical. The admittance of diffuse interfaces is considered to be a generalization of the sharp-interface approximation and may be applied in both classical and nonclassical nucleation models.
by adopting the nonclassical nucleus model proposed by Olson and Cohen [9]. The total free energy of a martensitic nucleus was computed as a function of size, shape, structure, and thermodynamic driving force, in order to determine the critical nucleus configuration. The Olson–Cohen model provides the equations necessary to describe the nucleus structure and free energy; therefore, the present study contributes through a numerical analysis of this model and interpretation of the results. The following presentation of the Olson–Cohen nonclassical martensitic nucleation model closely parallels the original development given in ref. [9].

3.1) Energetics of Homogeneous Lattice Deformation

In the general treatment of nonclassical martensitic nucleation, the nucleus formation process is envisioned to take place via continuous distortion of the parent phase into a critical configuration, which may not necessarily resemble the product phase. These distortions represent homophase fluctuations on the parent lattice whose distribution can, in principle, be predicted by statistical dynamics. The rate of nucleation was assumed to be controlled by the density of critical nuclei, having an energy equal to the maximum free energy along the minimum-energy nucleation path. In other words, the critical nucleus corresponds to a saddle point on the free-energy surface, describing the free-energy as a function of nucleus size, shape, and structure.

Since nonclassical nucleation paths involve the simultaneous development of both nucleus structure and size, the energetic analysis must address the energies of intermediate structures, along paths leading to the formation of a critical nucleus. In this simplified treatment, the lattice energy was assumed to be a continuous, smooth, function of distortion or strain, and this strain was taken to be described by a single order parameter.

The quantitative prediction of lattice-deformation energetics represents an important problem in the field of displacive phase
transitions. Recent progress has been made, based on higher-order elastic constants [44,50,53], interatomic potentials [54-56], and electronic calculations [57-59]. Fig. 3.1 summarizes the results of electronic pseudopotential calculations, for the bcc-fcc lattice deformation in sodium, along the minimum-energy path\textsuperscript{2}, at 0 K [59,6]. The free-energy change per-unit-volume, $A_g$, relative to the parent (bcc) phase is plotted as a function of lattice strain. The strain parameter, $\eta$, is defined such that it varies from zero in the parent structure, to unity in the product structure. The free energy passes through a maximum between the two structures, producing an energy barrier of magnitude, $\varphi$. The equilibrium state is defined such that the two structures have equal free energies; the corresponding barrier height is denoted by $\varphi_0$. The difference in chemical free energy between the phases, $A_g^{ch}$, distorts the curves, introducing a dependence on intrinsic thermodynamic variables. In the calculations represented in Fig. 3.1, pressure was used to vary the thermodynamic stability of the fcc structure relative to bcc, thus determining the driving force for the fcc-bcc transformation, in sodium at 0 K. Although only a limited range of pressures could be explored in these calculations, extrapolation of the observed behavior predicts that the metastable structure eventually become mechanically unstable at a critical instability pressure.

It is convenient to characterize the thermodynamic conditions by a normalized driving-force parameter, $\alpha$, defined such that $\alpha=0$ at equilibrium, and $\alpha=1$ at the instability. More specifically, $\alpha$ is defined by: $\alpha=\frac{A_g^{ch}}{A_g^{ch}_1}$, where $A_g^{ch}_1$ is the chemical free-energy difference at instability. In Fig. 3.1, the $\alpha$-value for each curve is indicated, instead of pressure, emphasizing the more general dependence on thermodynamic driving force. Similar behavior is expected if driving force is varied by varying temperature. While not all transforming materials exhibit the type of behavior indicative of a finite instability temperature, any metastable lattice can become unstable if the

\textsuperscript{2}The minimum-energy path was determined to be the proportional-strain path, also known as the Bain path.
Fig. 3.1: Calculated free-energy change at $0^\circ$K (enthalpy) for the bcc-fcc homogeneous-lattice deformation in sodium along the proportional-strain path. Pressure was used to vary the relative stability of the two structures. (Krasko et al. [59])
thermodynamic driving force is made large enough, for example by the application of stress [9].

A fourth-order polynomial is the simplest functional form, capable of capturing the major features of the free energy of homogeneous lattice deformation. Such a form is frequently used in the study of structural phase transitions, and models based on a polynomial expansion of free energy are known as "Landau theories". Adopting the notation of Olson and Cohen [9], the free energy per-unit-volume, $A_g(\eta)$, was approximated by the following function:

$$A_g = A\eta^2 - B\eta^3 + C\eta^4 ,$$  \hspace{1cm} (3.1)

where the coefficients, A, B, and C are related to the second, third and fourth order elastic constants of the parent phase. The dependence of $A_g$ on thermodynamic conditions can be approximated by expressing the coefficients in terms of $A_{g^{ch}}$ . The following relationships result when $A_g$ is constrained to exhibit local minima at $\eta=0$ and $\eta=1$, and $A_g=A_{g^{ch}}$ at $\eta=1$:

$$B = 2(A - 2A_{g^{ch}})$$  \hspace{1cm} (3.2a)

$$C = A - 3A_{g^{ch}}$$  \hspace{1cm} (3.2b)

For this simplified model, the mechanical stability of the parent phase requires that:

$$\frac{\partial^2 A_g}{\partial^2 \eta} = 2A > 0 .$$  \hspace{1cm} (3.3)

therefore, the coefficient, A, and its dependence on thermodynamic conditions controls the stability of the lattice. Since A is directly proportional to the second-order elastic constant associated with the lattice deformation in the model, it is appropriate to examine the behavior of the linear elastic constant associated with lattice deformations in real alloys.
As discussed above, an increase in the chemical stability of the martensitic phase, relative to the parent phase, will eventually result in mechanical instability of the parent lattice. This effect will manifest itself by the softening, that is, positive temperature dependence, of one or a combination of second-order elastic constants. Delaey et al. [46] distinguish between three classes of behavior: alloys which show no, moderate, and drastic mechanical instability approaching $M_s$. Alloys in the first class include most ferrous alloys which exhibit a negative temperature dependence of all linear elastic constants above $M_s$. Fig. 3.2 presents a compilation of elastic-constant data, for a variety of alloys, from the second and third classes [46]. Noble $\beta$-phase alloys comprise the majority of the second class for which the $C'$ constant shows a moderately positive temperature dependence above $M_s$, and extrapolates to zero at considerably lower temperatures. Iron-based invar alloys behave similarly except that $C_{44}$ also softens. $V_3Si$, Nb$_3$Sn, and In alloys are examples of materials which soften drastically, with $C'$ extrapolating to zero slightly below $M_s$. In the following discussion, the terms: elastic-softening and non-softening will refer to these differences in elastic behavior, and corresponding differences in lattice stability.

Since the magnitude of $\Delta g^{ch}$ is approximately proportional to temperature, the driving-force dependence of lattice stability, in the case of elastic-softening alloys can be modeled by assuming the following relationship for $A$:

$$A = A_0 (1 - \Delta g^{ch}_{1} / \Delta g^{ch}) = A_0 (1 - \alpha) ,$$

(3.4)

where $\Delta g^{ch}_{1}$ is the chemical driving force at instability. Note that since elastic softening alloys are those most likely to favor nonclassical nucleation paths, the above assumption concerning the form of the dependence of $A$ on thermodynamic driving force is best suited for the investigation of the potential for nonclassical martensitic nucleation.

The coefficients of $\Delta g$ are conveniently normalized by the equilibrium
Fig. 3.2: Compilation of second-order elastic-constant data for alloys in the second and third classes of materials which transform martensitically. Delaey et al. [46] proposed three classes based on elastic-softening behavior. (Compiled by Delaey et al. [46])
barrier height, \( \varphi_0 \), giving the following set of equations and definitions:

\[
\begin{align*}
A/\varphi_0 &= 16(1 - \alpha) , \\
B/\varphi_0 &= 32(1 - \alpha) - 4\alpha\beta , \\
C/\varphi_0 &= 16(1 - \alpha) - 3\alpha\beta , \\
\alpha &\equiv \Delta g_{\text{ch}}^{\text{ch}}/\Delta g_{\text{i}}^{\text{ch}} , \\
\beta &\equiv \Delta g_{\text{i}}^{\text{ch}}/\varphi_0 .
\end{align*}
\] (3.6a) (3.6b) (3.6c) (3.6d) (3.6e)

By considering the critical driving force for instability under stress at equilibrium, \( \beta \) is estimated to be equal to -3.08 \([9]\). Recall that the generalized driving-force parameter, \( \alpha \), is defined such that at \( \alpha=0 \), the lattices have an equal chemical stability (\( \Delta g_{\text{ch}}^{\text{ch}}=0 \)), and at \( \alpha=1 \), the parent lattice becomes unstable (\( \Delta g_{\text{i}}^{\text{ch}}=\Delta g_{\text{ch}}^{\text{ch}} \)).

3.2) One-dimensional Inhomogeneous Lattice Deformation

The energetics of homogeneous lattice deformation must be extended to include the influence of coherent interfaces separating strained and unstrained regions of a crystal. The reduction in energy of intermediate states accompanying the decrease in \( \varphi \) near a mechanical instability will promote diffuseness of coherent martensitic interfaces. The variation in lattice strain across a diffuse interface is best described by following a procedure which parallels the Cahn-Hilliard treatment of diffuse interfaces in diffusional transformations. In this approach, the classical volume and surface-energy contributions are replaced by a volume integral of local free-energy density and gradient energy, giving a functional of the form:

\[
\int_V [\Delta g + \kappa (\nabla \eta)^2] dV .
\] (3.7)

where \( \kappa \) is a gradient-energy coefficient and \( \Delta g \) is the local free-energy density. Note that this simple form assumes that all deformation states
lie along the path corresponding to the strain parameter, $\eta$. Roitburd [52] considered the more rigorous case involving gradients of a strain tensor.

The problem most relevant to nonclassical martensitic nucleation is the three-dimensional variation of lattice strain, along the nucleation path, within an arbitrary volume of material, constrained by the surrounding parent lattice. Applying such rigor would be extremely tedious; therefore, a simplified approach using a modified one-dimensional treatment was pursued.

Consider an infinite slab of material undergoing an invariant-plane strain (IPS), centered in the $z=0$ plane of a cartesian coordinate system. The interfaces between the strained and unstrained (parent) lattices are assumed to be coherent, invariant planes of the IPS. Fig. 3.3 illustrates the geometric aspects of this model; the dotted line depicts the displacement field for diffuse interfaces whereas the associated solid line corresponds to the sharp-interface case. The strain parameter is given by $\eta = \gamma/\gamma_r$ where $\gamma$ is the local value of lattice strain and $\gamma_r$ is the strain corresponding to the fully developed product. The normalized displacement function, $u$, is defined such that the actual total displacement relative to the $z=0$ plane is given by $u \cdot \gamma_r$. Then a natural definition for the effective-slab semithickness, $c$, based on the strain at the slab center, $\gamma_0$ and total displacement, is given by:

$$c \equiv \frac{u \cdot \gamma_r}{\gamma_0} = \frac{u}{\eta_0}. \quad (3.8)$$

where $\eta_0$ is the value of the strain parameter at $z=0$.

By symmetry, only the upper half-space of Fig. 3.3 need be considered in the energetic analysis, with proper boundary values applied at $z=0$ and $z=\infty$. Then the total free energy is given by $2F_A$, where $F_A$ takes the one-dimensional form of eqn. 3.7, with the gradient of $\eta$ replaced by
Fig. 3.3: Infinite slab of material centered in the z=0 plane, undergoing an invariant-plane-strain transformation. The displacement along the z-axis is depicted by the solid and dotted lines for a sharp and diffuse interface, respectively. The displacement function, \( u \), is defined such that the total displacement equals \( u \cdot \gamma \).

(Olson and Cohen [9])
\[ \eta' = d\eta/dz: \]

\[
F_A = \int_0^\infty [\Delta g + \kappa (\eta')^2] \, dz .
\]  

(3.8)

where \( \Delta g \) is the energy of homogeneous lattice deformation, approximated here by eqn. 3.1, and \( \kappa \) is assumed to be independent of \( \eta \). Free-energy functionals of this type, based on a Landau expansion of local free-energy density, modified by a gradient-energy term, form the basis of Landau-Ginzburg models of structural-phase transitions. Falk [53,60,61], and Barsch and Krumhansl [62] have used a similar description to model the structure of domain walls separating metastable phases.

The appropriate boundary conditions for the arbitrary variation, \( \eta(z) \), are: \( \eta = 0 \) at \( z = 0 \), and \( \eta' = 0 \) at \( \eta = 0 \). The first boundary condition sets the limit on the strain while the second ensures that the gradient energy is everywhere continuous. In addition, the total displacement across the interface must be bounded, leading to the following condition:

\[
\int_0^\infty \eta \, dz = u .
\]  

(3.9)

Variational calculus gives the minimum-energy-strain distribution, consistent with the boundary conditions and constrained by eqn. 3.9. The resulting Euler equation is written as:

\[
\frac{d\Delta g}{d\eta} - 2\kappa \frac{d\eta'}{dz} + \lambda = 0 .
\]  

(3.10)

where \( \lambda \) is a multiplier introduced by the fixed-displacement constraint. Eqn. 3.10 is a second-order differential equation in \( d\eta/dz \), and can be integrated once to give:

\[
\eta' = -\sqrt{\frac{\Delta g + \lambda \eta}{\kappa}} .
\]  

(3.11)
Further integration of eqn. 3.11 and substitution yields the following solutions:

\[ z(\eta, \eta_0, \lambda) = -\sqrt{\kappa} \int_{\eta_0}^{\eta} \left[ \Delta g + \lambda \eta \right]^{-1/2} d\eta, \quad \text{(3.12)} \]

\[ F_A(\eta_0, \lambda) = \sqrt{\kappa} \int_{0}^{\eta_0} 2\Delta g + \lambda \eta \sqrt{\frac{\Delta g + \lambda \eta}{\Delta g + \lambda \eta}} d\eta, \quad \text{(3.13)} \]

\[ u(\eta_0, \lambda) = \sqrt{\kappa} \int_{0}^{\eta_0} \frac{\eta}{\sqrt{\Delta g + \lambda \eta}} d\eta. \quad \text{(3.14)} \]

The effective semithickness \( \epsilon = u/\eta_0 \) can be used to define an effective interfacial energy:

\[ \sigma(\eta_0, \lambda) = F_A(\eta_0, \lambda) - \frac{\Delta g_0}{\eta_0} u(\eta_0, \lambda). \quad \text{(3.15)} \]

where \( \Delta g_0 = \Delta g(\eta_0) \).

Fig. 3.4 illustrates the following definition of the effective interfacial thickness: \( \delta = \eta_0 / \eta_{\text{max}} \). This quantity characterizes interfacial diffuseness, and is easily derived for the equilibrium case giving:

\[ \delta_0 = \sqrt{\kappa / \varphi_0}. \quad \text{(3.16)} \]

It is useful to consider the effective interfacial energy at equilibrium \( (\alpha = 0) \) with \( \eta_0 = 1 \). For this special case, eqns. 3.13 and 3.14 are directly integrable so that the equilibrium interfacial energy can be written as:

\[ \sigma_0 = \frac{4}{3} \sqrt{\kappa \varphi_0} = \frac{4}{3} \delta_0 \varphi_0. \quad \text{(3.17)} \]
Fig. 3.4: Schematic strain profile across a martensitic interface illustrating the definition of the effective interfacial thickness.
where eqn. 3.16 was used to eliminate $\kappa$. Using eqn. 3.17, Olson and Cohen [43] estimated $\delta_0$ to be $\sim 1$ nm. In the numerical analysis, lengths and energies were normalized to $\delta_0$ and $\phi_0$, respectively. Note that $\kappa=1$ in normalized units.

3.3) Nonclassical Nucleation Model

In the previous section, the free energy of an infinite, coherent, IPS slab, strained along the lattice deformation path leading to the martensitic structure was formulated using variational methods. This one-dimensional model was then "converted" into a model-martensitic nucleus by the introduction of additional interfaces. The martensitic nucleus was modeled as a circular cylinder or pill-box shaped particle, of radius, $r$, and semithickness, $c$, enclosed within the parent lattice. A schematic diagram showing the particle geometry is presented in Fig. 3.5. The lattice strain was assumed to be constant in sections normal to the $z$-axis; the strain distribution normal to these sections was taken to be equal to the one-dimensional variation given by eqn. 3.12.

In addition to the energy associated with the inhomogeneous change in structure (eqn. 3.13), elastic energy arising from the long-range strain field of the enclosed particle, and the energy of the circumferential interface must be included. The total free-energy change, $\Delta G$, for the formation of a nucleus can be approximated by the following equation:

$$\Delta G(r, \eta_0, \lambda) = 2\pi r^2 F_A(\eta_0, \lambda) + 2\pi r \xi A[u(\eta_0, \lambda)]^2 + 4\pi r c \sigma(\eta_0, \lambda)$$  \hspace{1cm}(3.18)

where $\xi$ is an accommodation factor. The first two terms were included in the Olson-Cohen analysis, and are sufficient for thin plates. The third term represents a first-order correction for the additional interfacial energy of the particle periphery and must be included when considering thicker plates. Evaluating $\sigma$ from eqn. 3.15 (which describes the energy of diffuse interfaces and includes the dependence of interfacial energy on driving force), the approximation is equivalent to the usual assumption of isotropic interfacial energy.
Fig. 3.5: Assumed nucleus geometry for the homogeneous nucleation calculations. The transformation shape-strain is assumed to be a simple shear IPS with the invariant plane normal to the c-direction.
The elastic-strain-energy term follows directly if $A$ and $u$ are rewritten as: $A = (1/2)\mu \gamma_r^2$ and $u = c\eta_o = c\gamma_o/\gamma_r$. The accommodation factor, $\xi$, was approximated using the Eshelby model for homogeneous elastic inclusions [63], assuming a simple-shear transformation. In the thin-plate limit, $\xi$ equals $\pi(2-v)/4(1-v)$, but in general, $\xi$ is a function of particle aspect ratio, $c/r$.

Eqn. 3.18 reveals that the total free-energy change is a function of three variables: $r$, $\eta_o$, and $\lambda$ at each level of driving force. Alternatively, since $c$ can be expressed as a function of $u$ (eqn. 3.8), and $u$ is a function of $\eta_o$ and $\lambda$ (eqn. 3.14), $\Delta G$ can be written as $\Delta G = \Delta G(r, c, \eta_o, \alpha)$. In other words, the total free-energy change may be considered to depend on nucleus size ($r$), shape ($c/r$), structure ($\eta_o$), and thermodynamic driving force ($\alpha$). The objective of this study was to determine the saddle-point free energy, $\Delta G^s$, and the corresponding critical-nucleus configuration, characterized by the critical values: $r^s$, $c^s$, and $\eta_o^s$.

As a first step in determining the saddle point of the free-energy surface, the partial derivative of $\Delta G$, with respect to $r$, was set equal to zero:

$$\frac{\partial \Delta G}{\partial r} \bigg|_{\eta_o, \lambda, \alpha} = 0 \ , \quad (3.19)$$

resulting in the following two equations for $\Delta G^s$ and $r^s$, respectively:

---

3 The multiplier, $\lambda$, effectively permits the independent variation of both $\eta_o$ and $c$; otherwise only one solution to eqns. 3.13 and 3.14 exists for each value of $\eta_o$.

4 Eqn. 3.21 gives $r^s$ as a function of the variables, $c$ and $\eta_o$. However $r^s$, as defined above, represents the critical-nucleus radius, dependent only upon driving force. The use of the symbol, $r^s$, was used here in order to keep the notation simple. The true meaning of $r^s$ should henceforth be contextually obvious.
\[ \Delta G^\infty_\Gamma = - \frac{\pi [A\xi n_0^2 c^2 + 2\sigma]^2}{2F_A} \] \hspace{1cm} (3.20)

\[ r^\infty = \frac{A\xi n_0^2 c^2 + 2\sigma}{2F_A} \] \hspace{1cm} (3.21)

\( \Delta G^\infty_\Gamma \) was then minimized with respect to \( c \) (or equivalently w.r.t. \( \lambda \)) using eqns. 3.8, 3.13–3.15, and 3.20 for fixed values of \( \alpha \) and \( n_0 \). This gave \( \Delta G^\infty_\Gamma, c(\alpha, n_0) \), which can be interpreted as the saddle-point free energy under a given driving force, for a given nucleus structure characterized by \( n_0 \). The energy change for the formation of a critical nucleus, \( \Delta G^\infty(\alpha) \), was then determined graphically, as the minimum value of \( \Delta G^\infty_\Gamma, c \), plotted as a function of \( n_0 \).

The integrals in eqns. 3.12–3.14 are elliptic and can be expressed in terms of elementary functions and standard (incomplete) elliptic integrals of the first, second, and third kinds. Therefore, one possible solution scheme requires that the original integrals be rewritten and the resulting standard elliptic integrals approximated using available computer algorithms. However, the algebra involved in expressing the integrals in the proper form is extremely cumbersome. (Those readers interested in performing this exercise should refer to ref. [64].) Furthermore, the evaluation of incomplete elliptic integrals involves infinite series which are sometimes prone to convergence difficulties. As a more direct alternative, the integrals in eqns. 3.12–3.14 were numerically evaluated using the IMSL routine, "DCADRE". Appendix 1 presents further details concerning solutions to the one-dimensional variational problem, that is, the types of solutions described by eqns. 3.12–3.14.

\[ ^5 \text{DCADRE uses an adaptive Romberg method in each subinterval of the integration interval. Status information is returned which informs the calling program of the accuracy and reliability of the result.} \]
3.4) Results and Discussion

3.4.1) Results of the Model Calculations

The results of the energy calculations for homogeneous martensitic nucleation, in accordance with the Olson-Cohen nonclassical-nucleus model described above, are summarized in Fig. 3.6. The saddle-point free-energy barrier, \( \Delta G^N(r^N,c^N) \), is plotted as a function of nucleus structure parameter, \( \eta_0 \), for a range of driving forces. The arrows in Fig. 3.6 indicate the minimum in each curve, which represents the critical free-energy barrier for homogeneous nucleation, and the corresponding critical-nucleus structure at each level of driving force, \( \alpha \). For relatively low levels of thermodynamic driving force, the critical-nucleus structure is close to the classical value of \( \eta_0=1 \); however, as the driving force increases, the critical nucleus becomes increasingly nonclassical. Hence, nonclassical-nucleation paths are energetically favored, particularly at high driving forces approaching the condition of general mechanical instability of the parent lattice.

The propensity for homogeneous martensitic nucleation to follow nonclassical paths is emphasized in Fig. 3.7, which shows the dependence of the critical-nucleus structure, \( \eta_0^N \), as a function of driving force. At low driving forces, approaching \( \alpha=0 \), the critical-nucleus structure is nearly identical to that of the fully developed product so that, under these conditions, homogeneous martensitic nucleation can be considered to be essentially classical. A distinction can be made between weakly nonclassical and strongly nonclassical behavior based on whether the nucleus structure is closer to that of the product or parent phases, respectively. Fig. 3.7 reveals that at \( \alpha=0.85 \), \( \eta_0^N=0.5 \), defining a convenient demarcation: weakly nonclassical behavior is expected at moderate driving forces up to \( \alpha=0.85 \), whereas nucleation is predicted to be strongly nonclassical when \( \alpha \) exceeds 0.85. The ultimate in nonclassical behavior occurs in the limit as \( \alpha \) approaches unity—the
Fig. 3.6: Saddle-point free-energy barriers as a function of nucleus-structure parameter, $\eta_0$. The minimum at each driving force represents the predicted critical energy barrier for nonclassical homogeneous martensitic nucleation.
Fig. 3.7: Critical-nucleus-structure parameter as a function of thermodynamic driving force.
critical-nucleus structure becomes indistinguishable from the parent structure.

The dependence of the saddle-point free-energy barrier on driving force is plotted in Fig. 3.8. It is evident that $\Delta G^m$ decreases strongly with increasing driving force. Although classical models also predict a strong dependence (typically $\Delta G^m \sim 1/(Ag_{ch})^4$), the energy barrier remains finite with increasing chemical driving force, whereas Fig. 3.8 shows that $\Delta G^m$ vanishes at the instability.

Using an Arrhenius-type rate equation, Kaufman and Cohen [14] estimated that thermally activated homogeneous nucleation can proceed at an observable rate if the critical energy barrier, $\Delta G^m$, is less than about 88kT. The inset of Fig. 3.8 indicates, by dashed lines, the room-temperature range of the normalized energy barrier which meets this criterion, assuming that $\delta_0 \approx 0.75$ nm. This range corresponds to the expected range of $\varphi_0$ (100-1000 J/mol) for the fcc-bcc transformation in metals [9]. Evidently, homogeneous martensitic nucleation can be thermally activated, only at high driving forces with $\alpha > 0.75$. While the critical driving force for this process depends on the magnitudes of $\varphi_0$ and temperature, the above analysis nevertheless suggests that general lattice instability will be precluded by homogeneous martensitic nucleation. However, even though the energy of the critical nucleus vanishes at the instability, the attempt frequency for homogeneous nucleation may limit the nucleation rate, as the critical-nucleus size diverges. Thus, it may be possible to enter the unstable region for a sufficient period of time, such that alternate, continuous transformation mechanisms may compete with the martensitic transformation.

The driving-force dependence of the computed critical-nucleus semithickness is presented in Fig. 3.9. Also included are the particle aspect ratios ($c/r$) at selected points. The dashed extension of the curve represents the results obtained in the classical limit, which agree with the nonclassical model at low levels of driving force. According to classical homogeneous martensitic models, the critical-nucleus dimensions
Fig. 3.8: Critical free-energy barrier as a function of thermodynamic driving force. The dashed lines in the inset indicate the range of the critical barrier which would lead to observable nucleation rates at room temperature assuming $\delta_0=0.75$ nm and $\phi_0=100$ to 1000 J/m$^3$. 
Fig. 3.9: Critical-nucleus semithickness, calculated as a function of driving force for nonclassical homogeneous martensitic nucleation.
should decrease as the driving force increases. In contrast, the nonclassical nucleation results indicate that as the instability is approached, the critical semithickness increases sharply as \( \alpha \) approaches unity. Coincident with this divergence from predicted classical behavior, the nucleus aspect ratio increases such that the critical nucleus becomes decreasingly plate-like. This effect reflects a reduction in the importance of elastic strain energy due to softening of the elastic shear modulus.

Incipient lattice instability has a strong influence on the effective interfacial thickness of a critical martensitic nucleus, as demonstrated in Fig. 3.10. This quantity is plotted relative to its value at equilibrium as a function of driving force. The interface apparently retains about the same degree of diffuseness with \( \delta^m/\delta_o = 1 \) until \( \alpha \) exceeds 0.9. The actual magnitude of the interfacial thickness depends on the magnitude of \( \varphi_o \) through eqn. 3.17, but it clearly increases sharply as the lattice approaches instability.

The increasing interfacial diffuseness of the critical nucleus with increasing driving force should lead to a concomitant decrease in the effective interfacial energy due to a general reduction in strain gradients leading to lower gradient energy. Fig. 3.11 shows this effect where the normalized interfacial energy is plotted versus driving force. The reduction in \( \sigma \) with increasing \( \alpha \) was observed even at low driving forces, although the interfacial diffuseness remained relatively constant.

3.4.2) Comparison with the Cahn-Hilliard Model

The treatment of nonclassical nucleation in a two-component incompressible fluid, as developed in detail by Cahn and Hilliard [51], bears many important similarities to the present model. In particular, the change in Helmholtz free energy of a metastable fluid, whose composition lay within a miscibility gap, was formulated in terms of volume- and composition-gradient-energy contributions. The saddle-point
Fig. 3.10: Effective interfacial thickness of a critical nucleus, undergoing homogeneous martensitic nucleation, computed as a function of driving force.
Fig. 3.11: Driving-force dependence of the effective interfacial energy for a critical nucleus, according to the nonclassical homogeneous martensitic nucleation model.
free-energy barrier was determined using variational methods—an approach
which was adopted for use in the present study. Apart from the fact that
the martensitic nucleation model substitutes strain for composition as the
independent variable or order parameter, the problems are quite analogous;
therefore, the solutions were expected to show similarities. However, the
martensitic nucleation model necessarily includes a strain-energy
contribution which is absent in the fluids case. This introduces a shape
dependence to the free energy which, for the assumed simple-shear
transformation strain, favors a plate-like shape with invariant-plane
interfaces.

The martensitic nucleation model is most meaningfully compared with
the special case of the Cahn-Hilliard model in which the composition of
the fluid is held fixed, lying between the stable phase boundary of the
miscibility gap and the chemical spinodal. Then the system remains
metastable with decreasing temperature until the instability temperature,
$T_1$, is reached at which point the system becomes unstable with respect to
compositional fluctuations. At temperatures near the miscibility gap, the
supersaturation, and thus, the driving force for phase separation is low.
With decreasing temperature the supersaturation and driving force
increase, with the spinodal composition approaching the bulk fluid
composition at $T_1$.

The Cahn-Hilliard model predicts that for low supersaturation (low
driving force), the composition at the center of the critical nucleus
approaches the equilibrium composition, and the radius of the critical
nucleus approaches infinity. This result agrees with the present
martensitic nucleation model which predicts that at low driving forces,
the structure and size of the critical nucleus approaches the classical
limit, as can readily be seen in Figs. 3.7 and 3.9, respectively.

According to the Cahn-Hilliard model, as the supersaturation
increases, the critical nucleus becomes progressively less classical. The
extent (size) of the critical nucleus increases, approaching infinity at
the instability, while the composition at the nucleus center approaches
the bulk composition. Clearly, under these circumstances, the interface
diffuseness must simultaneously be increasing. Coincident with this departure from classical behavior, the work required to form the nucleus, or critical energy barrier, decreases, vanishing at the instability. The homogeneous martensitic nucleation model exhibited essentially parallel behavior, with the nucleus structure replacing composition, and the instability being mechanical instead of chemical in nature. This agreement is by no means fortuitous since the underlying equations governing the behavior of the two models are almost identical with the exception of the strain-energy term in the martensitic nucleation model. But the magnitude of the strain energy is governed by the shear resistance to the transformation strain imposed by the matrix which, according to this simple model, is reflected entirely by the leading coefficient in the expansion of the free energy of homogeneous lattice deformation, $A$. Since this coefficient vanishes at the mechanical instability, the strain energy becomes increasingly significant with increasing driving force. The increase in the aspect ratio of the critical nucleus as $\alpha$ approaches unity is a direct manifestation of this effect (see Fig. 3.9).

3.4.3) Possibility of Homogeneous Martensitic Nucleation

Although nonclassical effects are expected to assist homogeneous martensitic nucleation by reducing the energy barrier to the formation of a critical nucleus, the occurrence of homogeneous nucleation necessitates the suppression of heterogeneous nucleation at lattice imperfections. To date, no clear experimental evidence of homogeneous martensitic nucleation has been reported, which may, in part, be due to the difficulty in preparing perfect crystals. Very small particles or precipitates of a metastable phase offer the greatest opportunity to produce defect-free crystals in which martensite may nucleate homogeneously. In addition, however, sufficiently high driving forces, close to the critical driving force for mechanical stability, must be attainable at a finite temperature or through the application of external fields which alter the relative lattice stability of the parent and product phases. Such conditions might be realized in Cu alloys containing Fe-Co precipitates at temperatures approaching absolute zero. Nucleation kinetic measurements would then
provide a means be which homogeneous nucleation could be distinguished from heterogeneous nucleation.

Three major assumptions in the present model are directly related to the occurrence of homogeneous martensitic nucleation: 1) the nucleus is a coherent IPS particle, 2) the lattice deformation follows a path along which the deformation resistance can be characterized by a single elastic modulus, A, which vanishes at the mechanical instability, and 3) the magnitude of A decreases linearly with driving force.

The first assumption rarely holds true in real martensitic transformations because, in general, additional lattice-invariant deformations are required to produce an invariant-plane interface\(^6\). Except in the special case that one of the three principal strains of the lattice deformation is zero, an invariant-plane interface must be semicoherent. Semicoherent interfaces produce short-range elastic fields which effectively contribute to the interfacial energy of the nucleus. As a result, the energy barrier for homogeneous nucleation would not vanish at the instability although nonclassical effects would nevertheless tend to reduce this barrier. Furthermore, this additional interfacial energy would inhibit the tendency for the critical nucleus size to increase dramatically as the instability is approached. Nevertheless, homogeneous nucleation will favor nonclassical paths although not to the extent predicted by the model. On the other hand, complete coherency requires interfacial distortions which increase the volume strain energy of the system, and thus, stabilize the parent phase against general mechanical instability at \(\alpha=1\). However, this additional strain energy may potentially be overcome by an excess driving force such that strongly nonclassical homogeneous nucleation may be postponed to higher driving forces than predicted by the model, possibly with \(\alpha>1\). The actual nature of the interface cannot be predicted without further modeling, but it is

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\(^6\)The fcc-hcp lattice deformation represents an exceptional case in which an invariant-plane interface can be generated without the inclusion of a lattice-invariant deformation.
likely that the interface of a critical nucleus will be neither fully coherent nor totally undistorted.

The second assumption listed above is also not expected to hold for real systems. Insofar as the free energy of homogeneous lattice deformation depends on elastic constants which remain finite, additional volume-energy contributions will raise the energy barrier for homogeneous nucleation at a given driving force. But as in the case of the coherency strains, an excess driving force may permit homogeneous nucleation to occur at higher driving forces than predicted by the model.

The third assumption is justified for a number of systems including the certain β-phase alloys which show a linear softening of the C' elastic constant with decreasing temperature, extrapolating to zero at a finite temperature (see Section 3.1). A nonlinear dependence of A on α is expected to influence the range of driving forces for which nonclassical effects dominate, but as long as the elastic constant which controls the lattice stability vanishes, homogeneous nucleation will favor nonclassical paths.

In summary, under conditions in which heterogeneous martensitic nucleation can be suppressed, and a sufficiently high driving force achieved at finite temperatures, thermally activated homogeneous nucleation will preclude general mechanical instability of the parent lattice. In real systems which transform martensitically, additional energy contributions will reduce the extent of nonclassical behavior, and/or increase the critical driving force for thermally activated homogeneous nucleation over that predicted by the model. Nevertheless, homogeneous nucleation is expected to favor nonclassical paths, involving structural changes during the formation of critical nuclei. This behavior is in contrast to classical nucleation paths which involve the growth of nuclei whose structure is the same as the fully developed product phase.
CHAPTER 4

HETEROGENEOUS MARTENSITIC NUCLEATION

Under the usual conditions in which martensitic transformations are observed, martensitic nucleation is predicted to be heterogeneous and follow an essentially classical nucleation path [42,43]. Apart from the potential influence of the nucleating defect, classical paths are favored at low driving forces relative to that required to promote general mechanical instability, as was demonstrated in the previous chapter. But in addition, the defect/nucleus interaction is expected to promote classical nucleus structures since the (favorable) interaction energy scales with the transformation strain.

As discussed in Chapter 2, real materials contain a spectrum of potential nucleation sites with a distribution of potencies. While classical nucleation behavior likely prevails at potent defects near $M_s$, nucleation at weak defects may exhibit some degree of nonclassical character. Indeed, it is reasonable to expect a continuous range of behavior between the extremes of homogeneous and strongly heterogeneous nucleation. The effect of defect potency on the minimum-energy nucleation path was explored by generalizing a classical heterogeneous martensitic nucleation model in order to permit nucleus-structural variations. The model employs a continuum description of heterogeneous martensitic nucleation which has been successfully applied to classical heterogeneous martensitic nucleation.
4.1) **Continuum Description of Classical Heterogeneous Nucleation**

Although the discrete-lattice description of heterogeneous martensitic nucleation via defect dissociation [2–4] provides a satisfactory geometric and mechanistic interpretation of the earliest stages of martensitic nucleation, the energetics of nucleation are more conveniently addressed using a continuum-elastic approach. In principle, one could compute the energy change associated with the formation of a martensitic nucleus through a detailed knowledge of interatomic forces. However, such a calculation is impractical because the inhomogeneous deformations involved in the transformation require the consideration of a vast number of interactions. Classical nucleation theory avoids this difficulty by formulating the free energy in terms of macroscopic quantities: typically, chemical, elastic-strain, and interfacial energies. In the case of an enclosed martensitic nucleus the elastic strain energy arises primarily from long-range elastic fields associated with interfacial dislocations and can be approximated assuming continuum elasticity. The short-range stress field and core energy of the interfacial dislocations contribute to interfacial energy; linear elasticity in conjunction with dislocation models have been used to estimate the energy of semicoherent invariant-plane interfaces [14,19,65].

Suezawa and Cook [66] modelled heterogeneous martensitic nucleation by considering an oblate-spheroidal martensitic particle interacting with the elastic field of a dislocation pile-up, approximated by that of a super-dislocation. The calculated free energy exhibited a barrier whose magnitude decreased and eventually vanished with decreasing temperature. Ling and Olson [67] obtained a similar result for the case of a square-plate shaped nucleus interacting with a finite dislocation wall. However, the calculated free energy of a lath-shaped nucleus lying along the defect, with its long dimension much greater that its height, showed no short-range barrier. Instead, the calculations predicted the formation of a stable embryo along the defect, which, at a critical driving force, could grow in a barrierless fashion, in agreement with the Olson-Cohen
defect dissociation model. Ling and Olson attribute the appearance of short-range barriers to the arbitrary constraint on nucleus shape. At small sizes when the defect/nucleus interaction is of crucial importance, a lath-shaped nucleus takes greater advantage of a favorable interaction with a group of parallel dislocations, and is therefore, more probable than a square or oblate spheroidal shaped nucleus.

As described by Ling and Olson [67], the free-energy change accompanying the formation of a martensitic nucleus in the stress field of a lattice defect can be written as the sum of the chemical free-energy change, the nucleus self energy, the defect/nucleus interaction energy, and the interfacial energy:

\[ \Delta G = \gamma \cdot A \cdot \Delta g_{ch} + E_{self} + E_{int} + d \cdot \sigma . \]  \hspace{1cm} (4.1)

In the above equation, \( \gamma \) represents the nucleus volume while \( d \) is the total interfacial area. \( E_{self} \) accounts for the increase in elastic energy due to the transformation-shape strain and can be calculated by classical continuum mechanical techniques. Eshelby [68] showed that the interaction energy can be expressed as the defect stress field multiplied by the stress-free transformation strain, integrated over the volume of the enclosed particle (nucleus):

\[ E_{int} = \int \sigma_{ij} \epsilon_{ij}^T dV' . \]  \hspace{1cm} (4.2)

where the stress-free transformation strain, \( \epsilon_{ij}^T \), is defined as the transformation-strain tensor for an unconstrained transforming volume of parent phase.

The separation of elastic energy into self- and interaction-energy contributions is illustrated schematically in Fig. 4.1 for the dissociation of a group of evenly spaced lattice dislocations into a lath-shaped slab of martensite. The defect and nucleus is assumed to have infinite extent into the plane of the paper so that the problem is
Fig. 4.1: Schematic diagram illustrating the defect–dissociation mechanism of martensitic nucleation in the discrete–dislocation and continuum limits. (a) Discrete dislocation model. (b) Superposition of the discrete defect with the nucleus producing the nucleus–interfacial structure in (a). (c) Same as (b) except that the nucleus is treated as a continuum particle undergoing a transformation strain.
simplified as being two-dimensional. As discussed in Chapter 2, this assumption essentially neglects line-tension effects and is expected to be most valid at small separations of the bounding dislocation arrays. The nucleating defect in Fig. 4.1a is characterized by the number of dislocations, \( n_d \), their Burgers vector, \( \overline{b}_1 \), and spacing. According to the defect-dissociation model, these dislocations dissociate while their cores spread out on adjacent close-packed planes forming the nucleus depicted in Fig. 4.1a. The resulting nucleus is bounded by two dislocation arrays of total Burgers vector content \( \overline{B}_2 = n \overline{b}_2 \) and \( \overline{B}_1 - \overline{B}_2 \), where \( n \) is the number of closed-packed planes comprising the nucleus and \( \overline{b}_2 \) is the Burgers vector of the individual coherency dislocations.

The nucleus configuration of Fig. 4.1a can be formally represented as a superposition of the original defect and an isolated nucleus whose bounding interfaces possess Burgers vector contents \( \overline{B}_2 \) and \( -\overline{B}_2 \), as shown in Fig. 4.1b. Furthermore, if the interfacial dislocation arrays of the isolated nucleus are viewed as surface dislocations, the nucleus becomes equivalent to an enclosed continuum particle undergoing a shape change characterized by the \( \epsilon_{ij}^T \). This situation is depicted in Fig. 4.1c which shows a continuum martensitic nucleus interacting with the stress field of the nucleating defect; the energy of this configuration can be analyzed directly using eqn. 4.1.

In general, the top and bottom interfaces of the nucleus in Fig. 4.1 are also composed of dislocation arrays. Unless these interfaces represent invariant planes, they will produce long-range stresses which contribute to \( E_{\text{self}} \) through interfacial distortions.

4.2) Classical Heterogeneous Nucleation Model

The following analysis of classical heterogeneous martensitic nucleation is based on the Olson-Cohen defect-dissociation model [2-4]. As pointed out by these investigators, it is convenient to treat the
nucleus as a faulted region, with a fault energy composed of chemical and interfacial energy, as well as those contributions to elastic strain energy not derived from the original defect. The major portion of the elastic energy results directly from the displacements generated by defect dissociation and interaction of these displacements with the stress field of the defect. For the two-dimensional case discussed above, eqn. 4.1 can be rewritten on a per-unit-length basis for dissociation at constant nucleus thickness giving the following equation:

$$\Delta G_f = \gamma_f \cdot a + E_f^{\text{self}} + E_f^{\text{int}}.$$  \hspace{1cm} (4.3)

with the fault energy defined by [2]:

$$\gamma_f = 2\sigma + nd (\Delta g_{\text{ch}}^{\text{ch}} + g_f^{\text{str}}).$$  \hspace{1cm} (4.4)

In the above equation, \(n\) is the number of close-packed atomic planes comprising the nucleus, \(d\) is the corresponding interplanar spacing, and \(g_f^{\text{str}}\) is the portion of the total elastic strain energy which is not derived directly from dissociation of the original defect. Since defect dissociation alone produces displacements of the invariant-plane-strain (IPS) type, \(g_f^{\text{str}}\) is primarily due to shape-insensitive interfacial distortions. Consequently, \(E_f^{\text{self}}\) and \(E_f^{\text{int}}\) represent the self- and interaction-energy contributions arising from the IPS component of the transformation strain.

The fault energy can be written in terms of a normalized driving-force parameter, \(f\), defined such that barrierless nucleation can occur at constant fault thickness when \(f=1\) and \(E_f^{\text{self}} + E_f^{\text{int}}\) decrease monotonically with increasing fault width:

$$\gamma_f = 2\sigma \left[ 1 - \frac{n}{n_0} f \right].$$  \hspace{1cm} (4.5)
The defect-potency parameter, \( n_0 \), is defined as the maximum number of close-packed fault planes which can be derived from the defect consistent with a net repulsive interaction between the bounding dislocation arrays. For a nucleating defect whose Burgers vector lies in the fault plane, \( n_0 \) is determined by considering the long-range interactions between the shear components of the dislocations bounding the fault giving the following equation:

\[
n_0 = \frac{B_1}{\gamma^*} C_1(\theta_1, \theta_2) . \tag{4.6}
\]

where \( B_1 \) is the total Burgers vector content of the defect and \( \gamma^* \) is the shear component of the IPS part of the transformation strain. For a nucleus lying in the x-y plane, \( \gamma^*_z = 2[(\varepsilon^T_{13})^2 + (\varepsilon^T_{23})^2]^{1/2} \). \( C_1 \) is a geometric factor defined by:

\[
C_1 \equiv \frac{\sin(\theta_1)\sin(\theta_2) + \cos(\theta_1)\cos(\theta_2)/(1-\nu)}{\sin^2(\theta_1) + \cos^2(\theta_1)/(1-\nu)} . \tag{4.7}
\]

where the angles, \( \theta_1 \) and \( \theta_2 \), are defined such that the edge and screw components of \( B_1 \) and \( \gamma^*_z \) are given respectively by:

\[
B_{1,e} = B_1 \cos(\theta_1) , \quad B_{1,s} = B_1 \sin(\theta_1) \tag{4.8a}
\]

\[
\gamma^*_e = \gamma^*_z \cos(\theta_2) , \quad \gamma^*_s = \gamma^*_z \sin(\theta_2) . \tag{4.8b}
\]

Explicit expressions for \( E^\text{self}_f \) and \( E^\text{int}_f \) will now be presented for the special case that the IPS component of the transformation strain is a simple shear. More generally, dilational strains would contribute to \( E^\text{self}_f \) and interact with the potential climb component of the defect; however, in martensitic transformations, the shear component of the transformation strain dominates.
The nucleus self energy is readily obtained using the method devised by Eshelby [68], together with the harmonic and biharmonic potentials for the slab-shaped particle given by Lee and Johnson [69]. In the limit of a slab of width "a", and height $n \cdot d$, infinite in extent, $E_{j}^{self}$ is given by:

$$
E_{j}^{self} = \frac{\mu v_n^2 n d^2}{4\pi} \left[ \frac{\cos^2(\theta_2)}{(1-v)} g_1(w/n) + \sin^2(\theta_2) g_2(w/n) \right], \hspace{1cm} (4.9)
$$

with $w=a/d$, and the functions $g_1$ and $g_2$ defined by:

$$
g_1(x) \equiv x^2 \ln(1+x^{-2}) + \ln(1+x^2), \hspace{1cm} (4.10a)
$$

$$
g_2(x) \equiv \ln(1+x^2) - x^2 \ln(1+x^{-2}) + 4x \tan^{-1}(x^{-1}). \hspace{1cm} (4.10b)
$$

The above equation assume an infinite matrix, isotropic elasticity, and identical elastic properties in both phases.

The defect/nucleus interaction energy is computed using eqn. 4.2, superposing the contributions of the individual dislocations comprising the nucleating defect. Assuming isotropic elasticity and a simple shear transformation strain, $E_{j}^{int}$ is given by the following equation for a nucleus positioned symmetrically about the defect:

$$
E_{j}^{int} = \frac{\mu v_n^2 n_0 d^2}{4\pi C_1(\theta_1, \theta_2)} \sum_{i=1}^{\text{nd}} \left\{ \frac{\cos(\theta_1) \cos(\theta_2)}{(1-v)} \left[ g_3\left(\frac{w}{n}, \xi_1\right) - g_3(0, \xi_1) \right] + \sin(\theta_1) \sin(\theta_2) \left[ g_4\left(\frac{w}{n}, \xi_1\right) - g_4(0, \xi_1) \right] \right\}, \hspace{1cm} (4.11)
$$

where $g_3$ and $g_4$ are defined by:

$$
g_3(x, \xi_1) \equiv (1/2 - \xi_1) \ln[(x + r_o/n)^2 + (1/2 - \xi_1)^2], \hspace{1cm} (4.12a)
$$

$$
g_4(x, \xi_1) \equiv g_3(x, \xi_1) + 2(x + r_o/n) \tan^{-1} \left[ \frac{1/2 - \xi_1}{x + r_o/n} \right]. \hspace{1cm} (4.12b)
$$
In eqns. 4.12, \( r_o \) is a core-cutoff distance and \( \xi_i \) is a parameter representing the position of the \( i^{th} \) dislocation relative to the center plane of the nucleus:

\[
\xi_i \equiv \frac{m}{n} \left[ 1 - \left( \frac{n_d + 1}{2} \right) \right].
\]

(4.13)

where \( m \) is the interplanar spacing of the dislocations, defined as a multiple of \( d \).

As a final note, \( \gamma_f \), \( E^\text{self}_f \), and \( E^\text{int}_f \) all vanish in the limit as \( w = a/d \) approaches zero. This is a direct result of the implicit assumption that no change in dislocation core energy occurs during dissociation. Therefore, in order to examine the potential energetic advantage of nucleus-thickness fluctuations, an additional interfacial energy term, scaling with nucleus thickness, can be included.

4.3) Nonclassical Heterogeneous Nucleation Model

In order to assess the potential importance of nonclassical nucleation paths, the nucleus structure must be generalized to include an arbitrary variation in transformation strain within the nucleus. The appropriate strain variation can be reasonably assumed to be that which minimizes the total free energy of the system. However, even with the simplifying assumption of a lath-shaped nucleus of infinite extent, the two-dimensional strain-variational problem is prohibitively complex. In addition, solutions to the elastic continuum problems for strains which vary within the nucleus are not available in closed form. Therefore, in order to capture the essential features of nonclassical effects, while reducing computational effort to a reasonable level, a one-dimensional strain variation was assumed and the elastic-energy contributions were corrected for nonclassical structure.
The present treatment of nonclassical heterogeneous nucleation represents an extension of the Olson-Cohen defect-dissociation model, by allowing the nucleus structure to vary in a manner similar to the Olson-Cohen nonclassical-nucleus model. The assumed defect/nucleus geometry is depicted schematically in Fig. 4.2. The nucleus was treated as a continuum lath-shaped particle centered in the $x$-$y$ plane and infinitely extended along the nucleating defect in the $y$-direction. Again, the IPS portion of the transformation strain was assumed to be a simple shear; however, the strain was allowed to vary arbitrarily along the $z$-direction, normal to the fault plane. It was assumed that the most probable strain variation is that which minimizes the total energy of a one-dimensional infinite slab. As in the homogeneous nucleation model, dependence of the transformation shear on position through the nucleus thickness can be computed using variational methods, allowing the top and bottom interfaces in Fig. 4.2 to be diffuse. Furthermore, for the special case wherein $g_{f}^{\text{str}} = 0$, the fault energy, $\gamma_{f}$, can be replaced by $2F_{A}$, under the same assumptions concerning the energetics of homogeneous-lattice deformation.

A variable nucleus structure complicates the computation of the elastic-energy terms in two ways. First, the non-uniform transformation strain precludes the use of the Eshelby method in computing $E_{j}^{\text{self}}$, and greatly increases the complexity of the integrations leading to $E_{j}^{\text{int}}$. Additionally, the structural variation results in a variation in elastic properties across the nucleus, which is a consequence of the assumed nonlinear elasticity.

As a first approximation, the classical expressions for $E_{j}^{\text{self}}$ and $E_{j}^{\text{int}}$ were retained with $\gamma_{f}$ replaced by $\eta_{o} \cdot \gamma_{f}$, and nd replaced by the effective nucleus semithickness, $c$, given by eqns. 3.8 and 3.14. This assumes that the elastic energy of the nonclassical nucleus can be approximated by that of a classical nucleus with uniform transformation strain $(\eta_{o} \cdot \gamma_{f})$ and semithickness, $c$. Approximate account was taken of the
Fig. 4.2: Schematic diagram depicting the defect/nucleus geometry assumed in the classical heterogeneous martensitic nucleation model.
variation of elastic constants with strain by using $2\gamma /\gamma_r^2$ for $\mu$, consistent with the homogeneous nucleation model. In the limit of sharp interfaces these approximations becomes exact and the classical approach should be used since the expression for $F_A$ is not suitable when large strain gradients are present.

The energetic analysis followed a similar methodology as used in the homogeneous nucleation calculations, outlined in Chapter 3. The model-free-energy change can be written for a given defect/nucleus configuration as:

$$\Delta G_f = \Delta G_f(\alpha, \eta_0, c, a, \lambda) ,$$

with:

$$c = c(\alpha, \eta_0, \lambda) ,$$

preserving the definitions of $\alpha$, $\eta_0$, and $\lambda$ assigned in Chapter 3. For dissociation at constant-nucleus thickness, eqn. 4.15 uniquely determines $\lambda$ so that $\Delta G_f$ can be computed as a function of nucleus width, $a$, for a given $\alpha$, $\eta_0$ pair. Allowing thickness fluctuations, the minimum-energy thickness determines $\lambda$ via eqn. 4.14 and 4.15, which must be solved iteratively for given values of $\alpha$ and $\eta_0$ as a function of $a$. In either case, the tendency of the nucleus to adopt a nonclassical structure during defect dissociation can be assessed by computing the minimum-energy structure, $\eta_0^\text{m}$, defining the minimum-energy path:

$$\Delta G_f^\text{m}(\alpha, a) = \Delta G_f(\alpha, \eta_0^\text{m}, a, c^\text{m}, \lambda^\text{m}) ,$$

where $c^\text{m}$ is either assigned or determined by a concurrent-energy minimization, and $\lambda^\text{m}$ is the corresponding value of $\lambda$.

The numerical methods parallel those used to compute the free-energy change during homogeneous nucleation, described in Chapter 3. The following input parameters characterize the defect/nucleus configuration: $\theta_1$, $\theta_2$, $c_0 = \eta_0 d/2$, $m$, $r_0$, and $d$. The free-energy change was computed for chosen values of driving-force and nucleus-structure parameters, $\alpha$ and $\eta_0$. 
as a function of nucleus width and thickness. The normalized driving-force parameters for classical and nonclassical nucleation can be related by setting $\sigma = 0$ in eqn. 4.4, and utilizing eqns. 3.6d, 3.6e, 3.16, 3.17, and 4.5 which define $\alpha, \beta, \sigma_0, \delta_0$, and $f$, respectively, giving the following equation:

$$f = -\frac{3\alpha\beta c_0}{4\delta_0}.$$  \hspace{1cm} (4.17)

4.4) Results and Discussion

The results of the classical heterogeneous martensitic nucleation calculations will be presented before proceeding to a discussion of the results of the energetic analyses of nonclassical heterogeneous nucleation. By comparison with the similar calculations reported by Ling and Olson [67], the classical calculations served as a preliminary check on the correctness of the equations for the elastic-energy terms. In addition, the computed free-energy change accompanying nucleation via defect dissociation was compared with the results of Ling and Olson.

Proper determination of the minimum-energy path for martensitic nucleation should allow thickness fluctuations during nucleus formation since such fluctuations may lead to a reduction in total free energy. However, as discussed by Olson and Cohen [4], the difficulty of coherency dislocation generation may impose a constant-thickness constraint, particularly during the earliest stages of embryo formation. These investigators showed that the interaction of the nucleus with suitably oriented lattice-screw dislocations can lead to nucleus thickening via a pole mechanism. Whether thickness variations are energetically favorable during defect dissociation will be discussed briefly in connection with classical martensitic nucleation.
4.4.1) **Classical Martensitic Nucleation**

Ling and Olson [67] reported the computed elastic energy \((E_{\text{self}}^f + E_{\text{int}}^f)\) for the dissociation of five equally spaced lattice dislocations in the fcc structure with a spacing of two close-packed planes each. Dissociation at constant thickness was assumed, producing an hcp nucleus with a \(\{111\}_f\) habit. The elastic energy for this case, was reproduced in the present study using eqns. 4.9–4.13, with very close agreement\(^1\).

A more detailed analysis was performed for the case of a nucleating defect consisting of five lattice dislocations with a spacing of three close-packed planes. Such a defect can account for nucleation of the fcc→bcc and fcc→bct martensitic transformations in steels [3], and was also treated in detail by Ling and Olson.

In the results which follow, the free-energy change (per-unit-nucleus length) will be presented in a dimensionless form, normalized to the quantity: \(\frac{\mu v_r^2 d^2}{2}\). The resulting dimensionless elastic-energy terms then become a function of only the defect/nucleus geometry. However, the dimensionless fault energy contains a leading coefficient equal to \(4\sigma/\mu v_r^2 d^2\) (see eqn. 4.5), which takes on a value of approximately unity, assuming parameters appropriate to steels and \(\sigma \approx 0.15 \text{ J/m}^2\). This value of interfacial energy has been shown to be appropriate for semicoherent martensitic interfaces [14] and corresponds to the same value assumed by Ling and Olson.

Fig. 4.3 shows the normalized free-energy change versus nucleus width for dissociation of a defect characterized by \(n_d=5\), \(m=3\), \(n_o=15\), and \(\theta_i=0\).

\(^1\)In addition to a 35% shear along on \((111)\)–[\(\overline{121}\)]\(_f\), Ling and Olson assumed a 1% contraction normal to \((111)_f\). Therefore a self-energy term appropriate to the normal transformation strain was included since eqn. 4.9 assumes a simple shear transformation.
Fig. 4.3: Normalized free-energy change as a function of nucleus width for classical martensitic nucleation.

\[ \theta_1 = \theta_2 = 0 \text{ (edge/edge), } n_0 = 15, n_d = 5, m = 3, r_0 = d, 4\sigma/\gamma^2d^2 = 1. \]

(a) Variable-thickness (minimum-energy) case.
(b) Constant-thickness case.
Both the minimum-energy-thickness (a) and constant-thickness (b) cases are represented for a range of the driving-force parameter, \( f \). According to the definitions of Section 4.2, this defect is in pure-edge orientation with a strength capable of producing a nucleus 15 planes thick with a concomitant free-energy decrease when the fault energy becomes negative. The nucleus was also assumed to be in pure edge orientation with \( \theta_2 = 0 \). Such a defect/nucleus configuration will be referred to as an edge/edge orientation, whereas the opposite extreme (\( \theta_1 = \theta_2 = 90^\circ \)) and intermediate configurations will be termed screw/screw and mixed, respectively.

As mentioned previously, \( f \) was defined in such a way that barrierless nucleation at constant thickness (with \( n = n_0 \)) can occur when \( f = 1 \) and \( E'_s + E^\text{int} \) decreases monotonically with increasing fault width. As can be seen in Fig. 4.3, however, nucleation is not barrierless at \( f = 1 \); a somewhat higher driving force is required to eliminate a short-range barrier which persists to about \( f = 1.15 \). This is not particularly surprising for the variable thickness case depicted in Fig. 4.3a, since, for example at the local-energy minima, the minimum-energy nucleus thickness is equal to about two-thirds of the defect height. The trade-off between interaction and self energy is apparently affected by short-range geometric effects which tends to stabilize a nucleus with height, \( n > n_0 \), even though, according to eqn. 4.5, the fault energy opposes such an effect. However, as the driving force increases toward the barrierless condition (near \( f = 1.15 \) in Fig. 4.3a), the minimum-energy nucleus thickness increases, and in particular, becomes equal to \( n_0 \) at the reflection in the free-energy curve at the critical driving force.

The existence of a short-range barrier to nucleation at constant thickness is evident in Fig. 4.3b where \( n = n_0 = 15 \), in the range \( 1.15 \leq f \leq 1.15 \). Even though barrierless nucleation, in this case, requires a negative fault energy, the results remain consistent with the Olson-Cohen model since for \( n = n_0 \) the elastic energy is not a monotonically decreasing function of fault separation. In order to eliminate the short-range barrier, either the defect strength must be increased or the fault energy must be negative. For \( f < 1 \) the positive fault energy exerts a long-range
force which opposes separation beyond embryo sizes determined by the minima in the free-energy curves. This is not necessarily true when thickness fluctuations are permitted since the fault energy becomes negative when \( n \) is sufficiently large; consequently, the curves corresponding to \( f=0.9 \) and \( f=1.0 \) in Fig. 4.3a decrease at large \( w \). For \( f>1.15 \) nucleation is clearly barrierless and the nucleation rate may be controlled by interfacial processes.

It is interesting to observe that the depth of the short-range-energy minima, as well as the nucleus widths corresponding to these minima, are considerably smaller for the constant-thickness calculations. For example, when \( f=1 \), the local minimum occurs in the variable-thickness case at \( F_f \approx -13 \), \( w/d \approx 60 \), and \( n=10 \). But when constrained to follow the constant-thickness path: \( n=n_o=15 \), the minimum occurs at \( F_f \approx -5 \) and \( w/d \approx 8 \). The potential implications of this short-range barrier on nucleation kinetics will be addressed shortly.

Additional calculations predicted similar behavior for the screw/screw case, except that the appearance of short-range barriers to nucleation at constant thickness was found to depend on the choice of the cut-off radius, \( r_o \). Therefore the existence of short-range barriers could not be established when both the defect and nucleus are in screw orientation. However, edge/edge interactions do seem to promote these barriers since they were observed in calculations which assumed a range of reasonable values of \( r_o \), including \( 0.5 \leq r_o/d \leq 3 \).

In order to assess the potential for thickness variations during martensitic nucleation, Ling and Olson [70] applied their constant-thickness-energy calculations to a range of nucleus thicknesses. Specifically, the fcc-bcc transformation was treated, assuming a defect consisting of five \( a/2[110]_f \) lattice dislocations, with a spacing of three (111) fcc planes. In addition to the transformation shear strain, interfacial distortions as well as a uniform dilatational strain was included. The ensuing calculations demonstrated that prior to barrierless nucleation, a nucleus thickness matching the effective defect height
(n=15) was energetically favored. Presumably, the earliest stages of martensitic nucleation occurs at a constant thickness equal to the defect height regardless of whether the nucleus is constrained against thickness fluctuations. Furthermore, the barrierless condition was not preceded by the appearance of any type of short-range barriers.

These conclusions are in apparent conflict with the results of the present study, as indicated by Fig. 4.3, which predicts both the energetic favorability of thickness fluctuations and the presence of short-range barriers prior to the barrierless condition. The possibility that the differences are due to the omission of interfacial distortions and dilatational strains in the present study can be dismissed. Interfacial distortions contribute to $g_f^{\text{str}}$ which is actually included in the dimensionless driving force, $f$, although it is not explicitly distinguished from the chemical driving force. The dilatational strains are small compared with the shear strains and should not appreciably influence the shape of the free-energy curves.

The key difference between the Ling–Olson calculation and those described by Fig. 4.3 lies in the assumed defect strength. In the present calculation, the defect strength is characterized by $n_o=15$, which coincides with the defect height given by $n_d=15$. However, the same parameters which Ling and Olson assumed, when substituted into eqn. 4.6 for $n_o$, yields $n_o=27$ for the defect strength. Such a defect is capable of producing a nucleus nearly twice its height, under the conditions of zero fault energy. In other words, the assumed defect contained an appreciable excess strength. Consequently, the defect/nucleus interaction was stronger than the $n_o=15$ case presented above, and apparently stabilized the nucleus thickness at the defect height.

The Ling–Olson calculation was repeated according to the present model, with $n_o=27$, and using similar parameters. The defect and nucleus

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2 The actual effective value of $n_o$ is expected to be slightly less than 27 because of the (small) uniform dilatational component of the transformation strain, the displacements of which cannot be derived from the original defect.
orientations were of mixed character with $\theta_1 = 44.46^\circ$ and $\theta_2 = 69.46^\circ$.

Fig. 4.4 summarizes these calculations where the normalized free-energy change is plotted as a function of nucleus width, for defect dissociation at constant thickness. Fig. 4.4a corresponds to a driving force of $f=1$, which, as predicted by the Olson-Cohen model, enables nucleation to occur barrierlessly. However, for a nucleus thickness equal to the defect height ($n=15$ in this case), a higher driving force is necessary in order to produce a negative fault energy, consistent with eqn. 4.5 with $n \neq n_0$.

Fig. 4.4b shows the effect of increasing the driving force to $f=1.6$, which is close to the barrierless condition for $n=15$. These results indicate that at short range, the minimum-energy-nucleus thickness is very close or equal to the defect height. Thickening is energetically favored only at sizes beyond which the nucleus can grow barrierlessly, suggesting that the nucleation stages may be treated as a constant-thickness problem. This observation is in general agreement with the Ling-Olson result, although their conclusion is not altogether general. As demonstrated above, the nucleation energetics involving a defect having a similar geometry (characterized by $n_d$ and $m$), but lower strength, favor a path in which the nucleus thickness fluctuates, first decreasing and then increasing toward $n_0$, as the nucleus width increases. However, it should be emphasized that this continuum analysis does not include the potential constraints introduced by the discrete lattice, and that nucleation may indeed occur at constant nucleus thickness.

Thickness variations did introduce short-range barriers to nucleation in the $n_0=27$ case which were absent in the constant-thickness calculations with $n \neq n_0$. This is in contrast to the $n_0=15$ case which showed short-range barriers to nucleation at constant thickness which were enhanced by thickness variations. Apparently, the appearance of such barriers is sensitive to the defect strength.

Defining the driving force parameter, $f$, in terms of $n_0$ has the disadvantage that the critical driving force for barrierless nucleation depends on the defect strength. This results from the fact that $n_0$ is defined by the nature of the long-range elastic interactions and does not
Fig. 4.4: Normalized free-energy change as a function of nucleus width for classical martensitic nucleation at constant nucleus thickness.

\[ \theta_{1} = 44.46^\circ, \theta_{2} = 69.46^\circ, n_0 = 27, n_d = 5, m = 3, r_0 = d, 4\sigma / \gamma r_d^2 = 1. \]

(a) \( f = 1.0 \). (b) \( f = 1.6 \).
account for short-range effects which also influence the barrierless condition. Instead of using \( n_0 \) in eqn. 4.5, a more meaningful definition of \( f \) results when the actual nucleus thickness at the critical condition is used to characterize defect potency. This "\( n \)" could be denoted by \( n^* \) and the barrierless condition would then correspond to \( f=1 \) regardless of potency.

The existence of short-range barriers to nucleation may account for isothermal martensitic nucleation if such barriers can be surmounted by thermal activation. By analogy with the Peierls-barrier problem of thermally activated slip, the potential activated configuration probably consists of a bulge in the otherwise flat interface bounding the martensitic nucleus. The activation energy, \( \Delta G^m \), for such a bulge-formation process depends on the exact geometry of the activated state, but it is expected to scale with the magnitude of the barrier to motion of the flat interface. Fig. 4.5 shows the magnitude of this barrier (expressed in normalized units) as a function of driving force, obtained for the constant-thickness, \( n_0=15 \) case presented in Fig. 4.3b.

An order-of-magnitude estimate of the activation energy was made by assuming an effective activation length and multiplying this by the magnitude of the energy barrier (per unit length). Then the activation volume, \( V^m = \partial \Delta G^m/\partial \Delta g_{ch} \), was estimated by assuming a linear relationship between \( \Delta G^m \) and \( \Delta g_{ch} \) for \( \Delta G^m \leq 1 \) eV giving:

\[
\Delta G^m \approx \frac{1 \text{ eV}}{\Delta g_{ch}(\Delta G^m=1 \text{ eV}) - \Delta g_{ch}(\Delta G^m=0)},
\]

(4.18)

where \( \Delta g_{ch} \) is related to \( f \) through eqns. 4.4 and 4.5 giving,

\( f=n_0 d \Delta g_{ch} /2\sigma \), assuming that \( \Delta g^{\text{str}}_f = 0 \). The following values where assumed in estimating \( V^m \) from the dependence of the normalized energy-barrier height and driving force: \( \mu=70 \text{ GPa}, \gamma_r=0.2, d=0.2 \text{ nm}, \) and \( \sigma=0.15 \text{ J/m}^2 \). For an effective activation length ranging from 0.1 to 1.0 microns, the resulting activation volume was estimated to be in the range:

\( 2.2(10)^{-25} < V^m < 2.0(10)^{-24} \text{ m}^3 \). This range of predicted \( V^m \) values is 2 to 4 orders of magnitude larger than the activation volume derived from
Fig. 4.5: Dependence of the short-range free-energy barrier on driving force, for the calculations represented in Fig. 4.4b. The barrier vanishes at the critical driving force for barrierless nucleation.
isothermal nucleation experiments [40]. Therefore thermal activation over short-range energy barriers to defect dissociation is not likely to constitute the rate-controlling mechanism in martensitic nucleation, under the conditions in which isothermal martensitic nucleation is observed. Instead, thermally activated motion of the interface through short-range obstacles in the lattice represents a viable mechanism which is consistent with the observed kinetic behavior.

In summary, short-range barriers to martensitic nucleation can precede barrierless nucleation at the critical driving force defined by the condition that the fault energy vanishes. The appearance of these barriers depends on the defect strength and Burgers vector orientation, and were not observed in calculations corresponding to those performed by Ling and Olson. These short-range barriers, however, cannot account for isothermal martensitic nucleation, but raise the driving force necessary to initiate growth of metastable nuclei. Notwithstanding the possible constraints to nucleus-thickness fluctuations during defect dissociation, thickness variations are energetically favored except when the defect strength is large enough to stabilize a nucleus height equal to the effective defect height.

4.4.2) Nonclassical Martensitic Nucleation

All nonclassical nucleation calculations were carried out allowing thickness variations during nucleus formation. The classical calculations suggest that the effect of imposing a constant-thickness constraint is to reduce the depth of the short-range energy well. However, the critical driving force required to permit barrierless growth of an otherwise subcritical embryo, remains reasonably unaffected.

All of the results which will be presented were based on a defect/nucleus geometry of the edge/edge type (defined in the previous section). The interfacial thickness at equilibrium, \( \delta_0 \), was assumed to be equal to 3·d, in accordance with a previous estimate [43], and consistent with atomic-resolution studies of martensitic interfaces [71,72]. The
dislocation-core cut-off radius, \( r_0 \), was taken to be equal to \( d \).

Fig. 4.6 shows a plot of the normalized free-energy change versus nucleus width at several levels of driving force, for dissociation of a defect consisting of five dislocation with a spacing of three atomic planes, with a potency characterized by \( n_0 = 15 \). The nucleus structure corresponds to the classical value with \( n_0 = 1 \), which was found to be the minimum-energy structure for this case. Hence, nucleation at a defect of this type is predicted to follow a classical path, and Fig. 4.6 can be compared directly with the corresponding classical calculation, represented in Fig. 4.3a. The nonclassical nucleation model, in the limit of \( n_0 = 1 \), really constitutes a classical, diffuse-interface description of martensitic nucleation. It can be seen that this model gave qualitatively similar results as the previous classical model which does not explicitly include variable interfacial diffuseness. Specifically, barrierless nucleation is preceded by the formation of subcritical embryos. Fig. 4.6 indicates that barrierless nucleation can occur at a critical driving force of \( \alpha = 0.195 \), which corresponds to a classical driving-force parameter of \( f = 1.13 \) (see eqn. 4.17). This is in excellent agreement with the results of the classical nucleation model. The variation in nucleus thickness along the minimum-energy path was also found to be very similar to the previous classical results.

The assumed defect potency and geometry is consistent with the type of defects which, according to the Olson-Cohen defect dissociation model, can trigger the fcc-bcc martensitic transformation in steels at \( M_s \). The results of the present model verify the expectation that heterogeneous martensitic nucleation in steels occurs at low driving forces relative to mechanical instability, and follows a classical nucleation path. Furthermore, the results of the previous chapter indicate that, at these low levels of driving force, the interfacial diffuseness does not significantly differ from the equilibrium value.

The energetics of heterogeneous martensitic nucleation at a somewhat weaker defect with potency, \( n_0 = 9 \), are presented in Fig. 4.7. For this
Fig. 4.6: Normalized free-energy change as a function of nucleus width, plotted for several values of the normalized driving-force parameter, $\alpha$. These results were obtained using the nonclassical heterogeneous nucleation model, assuming a defect potency characterized by $n_o = 15$. The minimum-energy path follows the classical path with $\eta_o = 1$. 

$\eta_o = 1$, $n_o = 15$ for $\delta_o = 3d$
Fig. 4.7: Free-energy curves versus nucleus width for heterogeneous martensitic nucleation at a less-potent defect than in Fig. 4.6 with $\eta_0 = 9$. 

$\eta_0 = 1$, $\eta_0 = 9$ for $\delta_0 = 3d$
case the defect consisted of three dislocations spaced three atomic planes apart. Nucleation at such a defect may, for example, occur at temperatures below $N_d$ whereupon more potent defects would already have been triggered at higher temperatures. Although the range of driving forces was considerably higher than in the $n_0=15$ case, the classical path was favored even at $\alpha=0.5$. The energy minimum at $n_0=1$ for each nucleus width is a reflection of the importance of the defect/nucleus interaction energy which overrides the factors which promote nonclassical structures in homogeneous nucleation at similar driving forces. Another noteworthy effect of the reduced defect potency and resultant higher critical driving force for barrierless nucleation is the reduction in size of subcritical embryos (compare the position of the local energy minima between Figs. 4.6 and 4.7).

The free-energy change accompanying the formation of a martensitic nucleus at a considerably weak defect is shown in Fig. 4.8 for classical nucleation paths. The defect is composed of a single dislocation with a Burgers vector capable of producing a nucleus only three atomic layers thick ($n_0=3$) in the classical limit at zero fault energy. The range of driving forces indicated is well within the weakly nonclassical regime of the homogeneous nucleation model, and indeed, the calculations showed that a slightly nonclassical nucleus structure reduces the total free energy. The uncertainty in the energy calculations increases as the nucleus width approaches the core cut-off size; hence, the details of the short-range behavior could not be explored. Nevertheless, Fig. 4.8 suggests the absence of subcritical embryo formation which is a distinguishing feature of heterogeneous martensitic nucleation. It is expected that the barrier to nucleation will vanish at some finite driving force above $\alpha=0.75$, but this regime was computationally unattainable due to the uncertainty

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3 The curves of Fig. 4.8 do not pass through the origin at $a/\delta_0=0$ due to the inclusion of the interfacial energy of the nucleus sides. It is assumed that this interfacial energy is provided by dislocation-core energy of the original defect, but detailed consideration of dissociation at very small separation distances is beyond the scope of this study. In Figs. 4.6 and 4.7 the curves were forced to pass through the origin. More properly, the curves of Fig. 4.8 should be shifted downward by about 2 units.
Fig. 4.8: Same as Fig. 4.7 except that the defect potency was further reduced to \( n_0 = 3 \).
mentioned above. One might anticipate that with a decreasing defect potency, the nucleation behavior will continuously become more like homogeneous nucleation. Moreover, heterogeneous nucleation at weak linear defects may not favor a lath-shaped nucleus, and a more equiaxed geometry would probably be preferred.

The tendency for the nucleus to adopt a nonclassical structure during nucleation at this weak defect is demonstrated in Fig. 4.9, which shows constant free-energy contours as a function of \( \eta_0 \) and \( a/\delta_0 \), at a driving force of \( \alpha=0.7 \). (The dashed lines represent the region in which the calculations were prone to numerical difficulties in determining the free-energy minimum.) Careful study of this contour map reveals the existence of a saddle point as indicated by the cross. The saddle-point free energy represents the minimum barrier for nucleation at this driving force and may possibly be surmounted by thermal fluctuations. Recall that thermal activation over short-range barriers was ruled out as a possible rate-controlling mechanism in classical heterogeneous nucleation at considerably more potent defects, because the estimated activation volume did not agree with experiment. However, the situation depicted by Fig. 4.9 is somewhat different in the sense that the nucleation behavior is approaching that of homogeneous nucleation for which thermal activation likely plays an important role. Furthermore, available kinetic data were obtained for alloys which show isothermal nucleation behavior at relatively low driving forces whereby nucleation is strongly heterogeneous and classical.

The nucleus structure at the saddle point is nonclassical with \( \eta_0 \simeq 0.7 \). Furthermore, the shapes of the contour lines on either side of the saddle point suggest that the nucleus structure evolves, following a minimum-energy path over which the structure parameter increases. Thus the model predicts truly nonclassical heterogeneous martensitic nucleation, but only at weak defects, under low driving forces.

In Chapter 3 the validity of the assumptions concerning interfacial coherency, the elastic behavior of the parent phase, and the lattice-deformation path were discussed. Similar arguments hold for the
Fig. 4.9: Constant free-energy contours for nonclassical heterogeneous nucleation at a weak defect ($n_0=3$), plotted as a function of nucleus structure, $n_0$, and width, $a$, at a driving force of $\alpha=0.7$. The free-energy saddle point lies appreciably off the $n_0=1$ axis indicating an energetic advantage of nonclassical nucleation paths.
present nonclassical heterogeneous nucleation model leading to the conclusion that nonclassical effects would be reduced in real systems compared with the model system, under similar driving forces. This reinforces the conclusion that nonclassical effects are minor in heterogeneous martensitic nucleation, at potent defects.

The remaining assumptions concerning the defect/nucleus geometry should be weighed against the success of the defect dissociation model on which the present model is based. The defect dissociation model breaks down at small separations of the dislocation arrays bounding the nucleus. However, the behavior of importance to barrierless martensitic nucleation appears to occur at nucleus widths on the order of 100δ₀ (see Fig. 4.6), which is quite large compared to the dislocation core cut-off distance (r₀ ≈ 0.3δ₀). Nevertheless, the energetics of defect dissociation at small separations becomes increasingly important as the defect strength decreases; consequently, alternative approaches based on discrete atomistic models may be useful in verifying the predicted nonclassical behavior at weak defects. The present model neglects line tension effects in assuming that the defect and nucleus have infinite extent. This greatly simplifies the modeling, but the validity of this assumption should be examined. As alluded to above, the important events leading to classical heterogeneous nucleation probably take place at nucleus widths in the vicinity of the subcritical nucleus size, which is about 100δ₀ for the case represented in Fig. 4.6. Taking δ₀ ≈ 3d ≈ 0.5 nm, this size is on the order of 50 nm, or 0.05 μm. Line-tension effects should not significantly alter the results of the present study if the defect length is much greater than 0.05 μm. A reasonable effective defect length for the types of defects which are believed to be operative is about 1 μm which satisfies the above criterion. Moreover, the validity of this assumption is expected to improve as the defect strength is reduced, due to the concomitant decrease in the subcritical embryo size.

Whether nonclassical nucleation paths are favored for a particular alloy undergoing martensitic transformation depends on the magnitude of the driving force, relative to the critical driving force for which the lattice becomes unstable with respect to the homogeneous lattice
deformation. For alloys which transform over a wide range of temperature (steels, for example), sufficiently high driving forces may be attained in the later stages of transformation, well below $M_s$. Similarly, nonclassical nucleation behavior may be promoted in small particles which transform only at very large undercoolings, due to a lack of potent defects.

The alloy systems which show the greatest potential for nonclassical martensitic nucleation are those which exhibit strong elastic anomalies in the form of elastic softening above $M_s$. For example in certain In-Tl alloys, the $C'$ elastic constant, which is closely related to the lattice deformation, nearly vanishes as the transformation temperature is approached during cooling. This is the type of behavior best reflected by the present model for which lattice softening is closely associated with incipient lattice instability. Because of the uncertainty involved in accurately determining $T_o$, the driving force relative to $a=1$ in not known for this system. Nevertheless, In-Tl alloys certainly represent good candidates for nonclassical nucleation (homogeneous or heterogeneous) in either defect-free or potent-defect-free specimens.

Assuming that the necessary conditions are satisfied, experimental verification of nonclassical nucleation depends on the feasibility of measuring martensitic nucleation kinetics. In most systems, martensitic nucleation proceeds at such a rapid rate that the process can be consider to be essentially athermal. Alternatively, one might hope to observe directly, the structure of subcritical martensitic embryos. The sparseness of potent martensitic nucleation sites has thus far prevented their detection. However, recent in-situ TEM observations of martensitic nucleation at weak defects [73] suggests that direct verification of nonclassical nucleus structures is forthcoming. This is very encouraging since nucleation at weak defects is expected to favor a nonclassical nucleus structure.
CHAPTER 5

QUASIMARTENSITIC TRANSFORMATIONS

In Chapter 1 the martensitic transformation was defined as a subset of diffusionless/displacive structural phase transitions, characterized kinematically, by a deviatoric lattice distortion. In addition, the kinetics and morphology of martensitic transformations, as defined by Olson et al. [1], are dominated by strain energy. Quasimartensitic transformations share the same kinematic features of martensitic transformations, but the kinetics and morphology are not dominated by strain energy. Furthermore, the quasimartensitic transformation occurs continuously, in contrast to the martensitic transformation which requires the nucleation and growth of distinct particles. Nevertheless, a barrier to the formation of quasimartensite is anticipated at driving-force levels such that the intermediate states of the homogeneous lattice deformation produce an increase in free energy. Highlights of a simple model for the structure of quasimartensite, and the energetics of quasimartensitic nucleation will be described in the present chapter.

5.1) Quasimartensitic Continuous-Modulation Model

The one-dimensional strain-variational approach to modeling martensitic nucleation is also applicable to the problem of the formation of a polydomain structure consisting of alternating variants of transforming regions. Such an arrangement has the potential for a drastic reduction in volume-elastic strain energy over that of a single variant.
constrained by the surrounding matrix, due to cancellation of the macroscopic shape change associated with the individual transformation variants. The deviatoric component of the effective total strain of the transforming region is eliminated in the limiting case that the individual variants consist of thin plates undergoing invariant-plane-strain transformations with periodically alternating shear components. A region transforming in this manner does not qualify as being martensitic because of the lack of a net macroscopic shear strain, leading to a low strain energy, but may instead be considered to represent a form of quasimartensite.

This structural description of a volume of quasimartensite was adopted for the purpose of modeling the energetics of quasimartensite formation. In Fig. 5.1 a cross section of the model-quasimartensitic structure is illustrated in which a sample volume of quasimartensite is depicted as series of transforming plates with alternating strains (represented by variants 1 and 2). A general diffuse-interface description was employed, similar to that used in the martensitic nucleation models, for which the normalized transformation strain varies between $\eta=+\eta_0$ and $\eta=-\eta_0$ (see Chapter 3 for a definition of $\eta$). The strain variation normal to the individual quasimartensitic variants is depicted schematically in the lower portion of Fig. 5.1, which describes a continuously modulated structure.

The individual variants, or domains, were assumed to undergo simple-shear transformations with coherent, invariant-plane interfaces, and for which the strains at the centers of the domains alternate only in sign. For this model system, the total free-energy change consists of the volume free energy associated with the homogeneous lattice deformation, strain-gradient energy, and the energy of the interfaces bounding the quasimartensitic region. As a first approximation, this interfacial energy was neglected so that the free-energy change could be modeled using the same one-dimensional strain-variational formulation described in Chapter 3.
Fig. 5.1: Schematic illustration of a section of the model—quasimartensitic region, consisting of a stack of transforming plates whose transformation shears alternate in sign, between $+\eta_0$ and $-\eta_0$. 
Following essentially the same development as presented in Chapter 3, the Euler equation was written for the minimum-energy strain variation. However, instead of considering the strain-variation across an isolated particle, the quasimartensitic model was concerned with a periodic variation in strain through a modulated structure. Therefore, periodic solutions of the Euler equation were sought, which eliminated the need for a constraint on total displacement. Furthermore, since periodic solutions automatically satisfy the continuity requirement on $\eta'(z)$, the boundary condition: $\eta'(\eta=0)$ was found to be unnecessary. Instead the following boundary condition applies:

$$\eta = (-1)^n \eta_0 \quad \text{at} \quad z = n \Lambda / 2, \quad (n = \ldots -2, -1, 0, 1, 2 \ldots) .$$ \hspace{1cm} (5.1)

where $\Lambda$ is the wavelength of the periodic strain variation. The first integration of the Euler equation (eqn. 3.10 with $\lambda=0$) gives:

$$\eta' = \pm \sqrt{\frac{\Delta g + I}{\kappa}} .$$ \hspace{1cm} (5.2)

where $I$ is an integration constant. This integration constant effectively determines the wavelength at a given value of the characteristic strain or strain amplitude, $\eta_0$.

The description of the energetics of homogeneous lattice deformation parallels that used in the martensitic nucleation models (Chapter 3). The free-energy of the homogeneous lattice deformation, $\Delta g$, was approximated by an even polynomial function of degree six in $\eta$, and whose coefficients depend on the driving force parameter, $\alpha$. This represents the simplest functional form, consistent with the assumption that $\Delta g$ depends only on the absolute value of $\eta$, but which captures the essential behavior associated the metastability of the parent lattice at driving forces between $\alpha=0$ and $\alpha=1$. Following similar arguments which led to eqns. 3.6
for the coefficients of $\Delta g$ in Chapter 3, the present form of $\Delta g$ can be written as:

$$\Delta g = \tilde{A} \eta^2 - \tilde{B} \eta^4 + \tilde{C} \eta^6,$$

(5.3)

with:

$$\tilde{A} = \frac{27}{4} (1 - \alpha),$$

(5.4a)

$$\tilde{B} = \frac{27}{2} (1 - \alpha) - 3\alpha \beta,$$

(5.4b)

$$\tilde{C} = \frac{27}{4} (1 - \alpha) - 2\alpha \beta,$$

(5.4c)

where $\alpha$ and $\beta$ assume the same meanings as in Chapter 3.

Solutions to similar one-dimensional variational problems have been reported by other investigators. In particular, Falk [53,60] followed an identical approach in modeling the structure of inter-variant interfaces resulting in solitary-wave solutions or periodons. Analytic solutions to the present problem are available in terms of Jacobian Elliptic Functions. An alternative method, employed in the present study, invokes the use of eqns. 3.12 and 3.13, which can be applied over one-quarter of a wavelength, with $\lambda \eta$ replaced by the integration constant, I. Then eqn. 3.12 (inverted) gives the strain profile which, by symmetry, can be used to describe the variation of strain, $\eta(z)$, over an entire wavelength. Eqn. 3.13 gives the energy per unit area, $F_A$, for one-quarter wavelength; division by $\lambda/4$ provides the energy density, $F_V$, associated with the strain modulation.

The resulting energy density is a function of driving force, strain amplitude, and wavelength: $F_V = F_V(\alpha, \eta_0, A)$. (As noted above, $A$ can be varied by adjusting I). Results for $\alpha=0.9$ were obtained via numerical integration of the appropriately modified forms of eqn. 3.12 and 3.13. Appendix 1 gives further details concerning the nature of the solutions and the physical limits on $\eta_0$ and I.
5.2) Results and Discussion

At a driving force represented by $\alpha=0.9$, the free-energy change associated with the formation of the one-dimensional strain modulation was computed, at fixed values of wavelength, as a function of strain amplitude. As expected, the free-energy density initially increases, then decreases with increasing strain amplitude, giving rise to a finite energy barrier. A summary of the results of these calculations is presented in Fig. 5.2, which shows constant $F_V$ contours as a function of strain amplitude and reciprocal wavelength ($F_V$ and $1/\lambda$ are expressed in normalized units). The dashed line represents the locus of energy-density maxima. The magnitude of the critical energy density decreases monotonically with increasing wavelength, vanishing at infinite wavelength.

Fig. 5.3 shows strain profiles, $\eta(z)$, for two critical strain modulations corresponding to two wavelengths: (a) $\Lambda=5\delta_0$, and (b) $\Lambda=30\delta_0$. By comparing (a) and (b), it can be seen that the strain variation distorts to favor the $\eta=0$ (parent) structure at long wavelengths. Although this accounts for the vanishing of the critical energy density at infinite wavelength, the energy barrier will be nonzero for $\alpha<1$ in finite crystals.

A critical strain modulation is unstable since an infinitesimal increase in amplitude or wavelength results in a decrease in total free energy. As the lattice approaches mechanical instability ($\alpha \rightarrow 1$), the critical energy density vanishes for all wavelengths, and the transformation may be considered as a quasimartensitic instability, analogous to spinodal decomposition. Furthermore, when $\alpha<1$, thermal energy may assist in the formation of a critical modulation, resulting in a thermally assisted quasimartensitic instability. (The term, quasimartensitic nucleation is avoided since nucleation usually refers to the formation of isolated particles.) The quasimartensitic transformation may potentially compete with nonclassical homogeneous martensitic
Fig. 5.2: Normalized energy-density contours for minimum-energy strain modulations as a function of strain amplitude, $\eta_0$, and reciprocal wavelength, $1/\Lambda$, at a driving force of $\alpha=0.9$. 
Fig. 5.3: Strain profiles, $\eta(z)$, for critical strain modulations for two wavelengths at a driving force of $\alpha=0.9$.
(a) $A=5\delta_o$, and (b) $A=30\delta_o$. 
nucleation, and possibly heterogeneous martensitic nucleation, depending on the availability of potent nucleating defects.

Within the framework of traditional nucleation theory, the competition between martensitic nucleation and quasimartensite formation depends on the relative rates of these two processes. In the simplest treatment, the nucleation rate is formally expressed as the product of the density of critical nuclei, and an appropriate attempt frequency for the thermal fluctuations. The density of critical nuclei is determined by the energy density of these nuclei, relative to the thermal energy density of the crystal (often estimated by kT). The present study addresses only the energetics of martensitic nucleation and quasimartensite formation; determination of the relative attempt frequencies for the competing processes requires a consideration of lattice dynamics. Therefore, the precise circumstances for which quasimartensitic transformations may dominate over martensitic transformations, cannot be predicted by the present model. However, even if the corresponding attempt frequencies were known, such a prediction would be severely limited by the doubtful applicability of traditional nucleation theory to the formation of a large-scale modulation.

Nevertheless, the quasimartensitic transformation cannot be ruled out as a viable transformation mechanism, particularly at large driving forces. It is encouraging that evidence of the quasimartensitic transformation, in association with the martensitic transformation in In-Tl crystals, has been pointed out [1], although this evidence is based solely on a visual examination of published photomicrographs [74]. The same factors which were discussed as being favorable for nonclassical homogeneous martensitic nucleation are predicted to be potentially favorable to the quasimartensitic transformation. Therefore, those alloys which show anomalous elastic softening prior to the martensitic transformation (which includes In-Tl) are strong candidates for the quasimartensitic transformation.
The quasimartensitic problem clearly requires further theoretical study. A thermally assisted quasimartensitic instability is expected to occur within finite volumes; therefore, an appropriate model would consider the formation of a modulated, quasimartensitic region, bounded by an interface. A simple model, assuming an isolated, spherical, quasimartensitic region, has the appearance of a nucleation model for incoherent precipitates. The additional interfacial-energy contribution may act to limit the size of the critical "nucleus" in such a way that wavelength selection can be predicted.

As discussed in Chapter 3, additional energy contributions, not included in the homogeneous nucleation model, will stabilize the parent phase against homogeneous martensitic nucleation even within the unstable region ($\alpha > 1$). Under such conditions, the quasimartensitic transformation may proceed in a continuous manner, analogous to spinodal decomposition. In the case of spinodal decomposition, wavelength selection is based on mass transfer, since the order parameter (composition) obeys a conservation law. However, the order parameter, $\eta$, for a quasimartensitic instability is not conserved, so that the underlying principle determining wavelength selection is not obvious. Olson and Cohen [75] suggested that the difference between the relevant adiabatic and isothermal elastic constants may determine the maximum-growing wavelength, based on the rate of heat transfer from within the individual quasimartensitic domains to the domain walls.
CHAPTER 6

SUMMARY OF PART I

Olson and Cohen [9] proposed a model for the energetics of nonclassical homogeneous martensitic nucleation employing a diffuse-interface description and allowing a variable nucleus structure. This model was numerically evaluated for an idealized material which shows elastic softening on the shear system of the homogeneous lattice deformation. The following statements summarize the results of this part of the study.

1) Incipient mechanical instability reduces the energy barrier for homogeneous martensitic nucleation and promotes nonclassical behavior. At driving forces sufficiently close to the critical driving force for lattice instability, thermally activated homogeneous martensitic nucleation is possible at finite temperatures, and will preclude general mechanical instability.

2) Under conditions favoring homogeneous martensitic nucleation, the critical nucleus shows strongly nonclassical character. The critical nucleus structure more closely resembles that of the parent rather than the product lattice.

3) With increasing driving force near mechanical instability, the critical-nucleus structure becomes increasingly nonclassical, the critical-nucleus size diverges, and the interface becomes increasingly diffuse. These finding are in general agreement with the compositional
analogue treated by Cahn and Hilliard [51], involving nucleation in a two-component fluid near a chemical spinodal.

4) The occurrence of homogeneous martensitic nucleation requires that heterogeneous nucleation be suppressed. Small metastable particles or precipitates offer the greatest promise for obtaining defect-free crystal whereby homogeneous nucleation at sufficiently high driving forces may be revealed by nucleation kinetic measurements.

5) Additional energy contributions not included in the model, but expected to be important in real systems, will reduce the extent of nonclassical behavior and/or increase the critical driving force for homogeneous martensitic nucleation.

The nonclassical homogeneous nucleation model was extended to heterogeneous martensitic nucleation by including a nucleus/defect interaction energy. Numerical analysis employing a continuum description of the Olson-Cohen defect-dissociation model [2-4] was conducted allowing nucleus-thickness fluctuations.

Calculations indicated that heterogeneous nucleation at potent defects favors classical nucleation paths at comparatively low driving forces. Furthermore, barrierless nucleation at a critical driving force is preceded by the formation of subcritical embryos, consistent with the predictions of Olson and Cohen [2]. Nonclassical behavior is predicted for heterogeneous nucleation at weak defects when the critical driving force is sufficiently high. The subcritical embryo size decreases with decreasing defect potency, vanishing as nonclassical effects become significant.

At driving forces approaching mechanical instability, the quasimartensitic transformation may compete with martensitic transformations. The quasimartensitic structure was modeled as a continuous one-dimensional strain modulation for which gradient energy
dominates over strain energy. An appropriate form of the same variational problem used to describe the martensitic nucleus structure was adapted to explore the energetics of quasimartensite formation.

Numerical analysis revealed that as the lattice approaches mechanical instability, the energy density of critical modulations vanishes, for all wavelengths. This suggests that quasimartensitic instability may be considered to be the displacive analogue of spinodal decomposition. Prior to mechanical instability, thermal energy may assist in a thermally activated quasimartensitic instability. While a kinetic analysis of quasimartensitic instability should focus on lattice dynamics, wavelength selection may be determined by heat transfer, based on differences in the adiabatic and isothermal elastic constants.

In summary, heterogeneous nucleation controlling the martensitic transformation of typical bulk materials will be classical in nature, even in systems exhibiting strong lattice-softening (instability-precursor) behavior. In defect-free material, homogeneous nucleation becomes possible at driving forces sufficiently close to the critical driving force for lattice instability. Nucleation in this regime would be strongly nonclassical, but must compete with the alternative mechanism of quasimartensitic continuous modulation.
PART II: GROWTH OF A SINGLE MARTENSITIC PARTICLE

CHAPTER 7

INTRODUCTION TO MARTENSITIC GROWTH

Barrierless heterogeneous martensitic nucleation can be viewed as the earliest stage of martensitic growth involving the motion of a glissile interface through the parent lattice aided by the interaction between the displacement field produced by the nucleus and the stress field of the nucleating defect. Consequently, the distinction between martensitic nucleation and growth, while being somewhat arbitrary, is conveniently made based on the importance of the defect/particle interaction. This interaction diminishes as the particle size increases so that growth will be regarded as the formation process at sizes beyond which the defect/particle interaction energy is small relative to the particle self or strain energy.

In attempting to understand martensitic growth we must address the complex interactions between thermodynamic driving forces, interfacial motion kinetics, and the properties and defect structures of both the parent and product phases. Then the synthesis of these interactions into a theory for the growth of martensite will constitute a model, which must be compared to, and hopefully verified by experiment. Indeed, experimental observations provide a natural starting point in constructing such a model. The remainder of this chapter will be devoted to a discussion of experimental observations and previous theoretical studies concerning martensitic growth. The topics of martensite morphology and substructure will also be reviewed, giving emphasis to the connection between experimental observations and the formation process.
7.1) General Experimental Observations

In general, martensitic growth is extremely rapid owing to the glissile nature of semicoherent martensitic interfaces. Martensitic plates can respond to a chemical driving force or mechanical stress through the conservative glide of interfacial dislocations; thus, the martensitic transformation can be regarded as a form of plastic deformation [76]. Moreover, the rate of growth is a function of the deformation resistance of the parent lattice to the motion of the dislocations which comprise the interface. This is in contrast to the much slower diffusional transformations for which the growth rate is limited by mass transport.

The earliest successful determination of the time required for a single martensitic growth event utilized dynamic electrical resistivity measurements [77]. For Fe-30Ni, a single martensite crystal formed in about $3.1 \times 10^{-7}$ sec., or at a rate nearly one-third the velocity of shear wave propagation in iron. Indeed, the rapid growth rate manifests itself quite readily by the emission of acoustic waves during martensite formation [78], and with certain steels, audible clicks can be heard [79,27]. This high rate of growth can persist even at temperatures approaching absolute zero in steels deformed to produce strain-induced plate martensite [80,41]. Machlin and Cohen [41] proposed an explanation based on the reaction-path model discussed in Chapter 2. According to these authors, pre-existing or deformation-induced strain embryos are activated by an applied stress, so that growth can then proceed rapidly to measurable sizes. This implies that growth of plate martensite is not thermally activated and may instead occur by continuous glide of the interfacial dislocations, analogous to the continuous glide of individual lattice dislocations when the applied stress exceeds the mechanical threshold.

On the other hand, relatively slow growth of martensite has been reported in Fe-28.8Ni [81], Fe-30.2Ni [82], and Fe-21Ni-4Mn [83]. Lengthening of single martensitic units was observed to proceed at rates
ranging between 0.01 to 1.0 mm/s under the optical microscope. This growth rate is $10^{-7}$ times slower than that observed indirectly in Fe-30Ni using the electrical resistivity technique. Christian [76] suggested that this slow growth may be due to secondary factors such as thermal activation of the martensitic interface through obstacles in the lattice, whereas growth between the obstacles is expected to be very rapid. Moreover, these slow-growing martensites were observed at the specimen free surfaces, where constraints imposed by the matrix are less restrictive than in the bulk. This raises doubts concerning whether this surface transformation reflects growth behavior in the bulk.

The morphology and substructure of martensite in the Fe-21Ni-4Mn alloy, transformed under similar conditions, was examined extensively using optical microscopy and TEM [83-85]. Many of the published transmission-electron micrographs suggest that the macroscopic units are composed of smaller subunits, which have coalesced to form the larger units. Furthermore, serial sectioning revealed that martensitic units, which appeared to be single units on the specimen surface, became fragmented many microns below the surface. These observations admit the possibility that the slow-growing surface martensite (at least in Fe-21Ni-4Mn) is in fact rapidly-growing, but slowly-nucleating martensitic subunits, and that a macroscopic martensitic unit forms as a result of a chain of autocatalytic nucleation events.

Martensitic growth behavior is conveniently divided into two classes: thermoelastic and nonthermoelastic. The salient features of thermoelastic behavior have been summarized elsewhere [86,87]. In thermoelastic alloys, thin martensitic plates nucleate and then grow rapidly within individual grains, until stopped by strong obstacles such as a grain-, interphase-, or twin-boundaries. Thickening proceeds to the extent that a balance is reached between chemical and nonchemical forces, but the outstanding feature of thermoelastic behavior is the reversibility of the martensitic interface. Hence, a plate can respond to a change in driving force (chemical or otherwise) by adjusting its thickness at a rate controlled by the heating or cooling rate, preserving the thermomechanical balance. In
contrast, nonthermoelastic martensites show very little or no reversibility of interface motion. Focusing on the issue of reversibility, Olson and Cohen [88] proposed a single necessary and sufficient condition for thermoelastic behavior: the relative absence of plastic accommodation of the transformational shape change. The process of plastic accommodation and its influence on martensitic growth behavior will be a central topic in the discussions which follow.

Stepwise growth of martensite has been observed in pre-polished specimens of Fe-30.4Ni-0.39C, cooled at one end, and subsequently examined for surface relief under the optical microscope [89]. This process was repeated so that growth of individual units could be monitored. The martensite produced by this technique nucleates at the cold end of the specimen, and grows in a temperature gradient, with the chemical driving force decreasing along the specimen length. Thin martensitic plates formed, but the lengthening of these plates arrested before reaching a grain boundary, presumably due to insufficient chemical driving force being available to sustain growth. Further cooling allowed the same plates to grow further, indicating that growth, once arrested, can start up again. This stepwise growth behavior was also observed during thickening of the plates, but in this case the temperature gradient could not have been responsible. Instead, it is likely that the plates reached a state of thermomechanical balance, and that lowering the temperature allowed further thickening. The important point is that the martensite formed in this alloy, while generally categorized as nonthermoelastic, exhibits some of the same growth characteristics found in thermoelastic martensites. The same experiment was performed using Fe-32.8Ni, but stepwise growth was not observed in this alloy, suggesting that plastic accommodation is more severe during martensitic transformation in the latter case.
7.2) **Martensite Morphology and Substructure**

Direct observation of martensitic growth is greatly hampered by its extremely high growth rate. Nevertheless, martensite morphology and substructure, being direct consequences of growth, provide an indirect means by which to study the growth process. The morphology and substructure of martensite has been extensively investigated, particularly in ferrous alloys, and the reader is referred to the many excellent review articles [e.g. 90-93].

The phenomenological theory of martensitic transformations [94-96] predicts the interfacial plane between the parent and product phases, based on the requirement that this plane remain unrotated and undistorted during transformation. Treating the martensitic phase as an elastic inclusion, elastic strain energy is minimized if the particle adopts a plate shape with an invariant-plane habit [63,98]. Then the phenomenological theory can be used to predict the habit plane as well as the macroscopic shape deformation and lattice orientation relations. Thus, the expected morphology of an elastically accommodated (thermoelastic) martensitic particle is plate-like, with its planar extent determined by the distance between strong obstacles to growth in the plane of the plate. The plate thickness is limited by the thermomechanical balance mentioned in the previous section.

Generally good agreement with the phenomenological theory and "ideal" plate morphology has been reported for many alloy systems including Fe-Pt [97], Cu-Al [99,100] and other β-phase alloys, and Fe-Ni-(C) alloys which transform well below room temperature [91,101,102]. On the other hand, jagged plates and complex morphologies resembling laths and even "butterflies" are observed in ferrous alloys which transform near or above room temperature [5,91]. Furthermore, with the exception of the \{3 10 15\}_f martensite, the phenomenological theory has failed to adequately explain the observed crystallography of martensitic transformations in ferrous alloys [103]. Attempts to generalize the phenomenological theory by including multiple shears in the
lattice-invariant deformation, and/or allowing partial plastic accommodation of the shape strain have enjoyed limited success in application to martensites whose habit lies near \{225\}_f or \{111\}_f [103]. Although the admittance of general plastic accommodation can be treated in terms of additional lattice-invariant shears, the number of unknowns in the problem then increases, resulting in the need for additional assumptions concerning the individual shear systems. This reduces the predictive capability of the generalized theory and, therefore, its utility is greatly diminished.

7.2.1) Morphology of Fe-Ni Martensites

Martensitic transformations in Fe-Ni alloys have received a great deal of attention, in part, because this system shows a wide range of morphologies and substructures depending on alloy composition and transformation conditions. Alloys in the composition range Fe-(30–34)Ni (wt.-percent) exhibit a lenticular or plate morphology with a varying degree of internal transformation twinning. The arrangement of individual units forms a zig-zag pattern, effectively partitioning the grains as the transformation proceeds. Fig. 7.1 shows the microstructure of a fully-twinned plate formed in Fe-33.7Ni at 111K taken from the work of Datta and Raghavan [104]. This morphology, often referred to as "thin-plate" martensite, is characterized by relatively flat and parallel interfaces. The thin feature, or "midrib", along the plate center, represents a region of very fine transformation twinning and experimental evidence suggests that this is the first part of the plate to form [105-107]. Fig. 7.2 depicts the structure of a partially twinned martensitic plate in Fe-32.0Ni, reported by Patterson and Wayman [107]. The plate faces are much less regular in this case while the interface between the twinned and untwinned regions appears fairly flat. TEM observations revealed a high density of lattice dislocations in the untwinned region. The presence of these dislocations indicates plastic accommodation which was made even more evident by interference microscopy. As the nickel content of the alloy is further reduced, the plates become
Fig. 7.1: Optical micrograph showing a fully-twinned martensitic plate formed in Fe-33.7Ni. (Datta and Raghavan [104])
Fig. 7.2: Optical micrograph showing a portion of a partially-twinned martensitic plate formed in Fe-32.0Ni.

(Patterson and Wayman [107])
Fig. 7.2: Optical micrograph showing a portion of a partially-twinned martensitic plate formed in Fe-32.0Ni.

(Patterson and Wayman [107])
still more irregular and the proportion of twinned versus untwinned regions decreases.

Based on their observations of partially-twinned morphologies, Patterson and Wayman [107] proposed a two-step growth process, distinguished by the mode of lattice-invariant deformation. According to these authors, lateral growth is faster when the lattice-invariant deformation is accomplished by internal twinning rather than slip. They further concluded that the occurrence of plate-like martensite in Fe-Ni alloys is associated with internal transformation twinning.

As the Ni content of Fe-Ni alloys decreases below about 30.5\%Ni, a transition in morphology is observed with the plates becoming increasingly irregular in shape. Coincident with the change of plate morphology is the appearance of the "lath" morphology, typical of low-alloy carbon steels that transform above room temperature. A mixture of plates and laths is observed down to about 28.5\% Ni, below which plate-like units are no longer seen and the morphology is described as lath-like [25].

The microstructure of transformed Fe-Ni alloys, which form lath martensite, is very complex with the individual lath-shaped units being barely resolvable under the optical microscope. Marder and Marder [108] describe a hierarchy of structures in martensitic Fe-(14.8-24.5)Ni alloys. The individual laths form in aligned groups, and are separated from each other by low-angle boundaries. These groups of aligned laths form "packets", which are separated by high-angle boundaries. Under the optical microscope, the packets appear to consist of a number of parallel bands or "blocks", which apparently represent groups of laths with different orientation. TEM micrographs, reported by Speich and Swann [109], and reproduced in Fig. 7.3, show the substructure of lath martensite in Fe-12Ni (a) and Fe-20.4Ni (b). A high density of lattice dislocations is evident and the laths contain no visible transformation twins. The extreme complexity of this structure reflects a very plastic mode of growth. Although the interphase boundaries are difficult to
Fig. 7.3: Transmission electron micrograph showing the structure of groups of laths formed in Fe-12.0Ni (a), and Fe-20.4Ni (b). (Speich and Swann [109])
Fig. 7.3: Transmission electron micrograph showing the structure of groups of laths formed in Fe-12.0Ni (a), and Fe-20.4Ni (b).
(Speich and Swann [109])
discern, the size of the individual units appears to be on the order of a few microns. Evidently, the lath size is not determined by partitioning of the grains, in contrast to the higher-nickel plate-forming alloys. While autocatalytic nucleation plays an important role in determining the transformed microstructure, growth kinetics and, in particular, conditions leading to growth arrest may well limit the size of individual martensitic units.

As in the case of certain plate martensites, evidence of plastic accommodation has been reported to be associated with lath martensite. Indeed, the heavily dislocated substructures, typical of lath martensite, suggest that the martensite and/or the surrounding austenite undergo heavy deformation during lath formation. In addition, Wakasa and Wayman [110], using interferometry, found evidence of plastic accommodation associated with martensitic units on the surface of Fe-20Ni-5Mn alloy specimens. This alloy forms lath martensite while retaining an appreciable amount of austenite, thus allowing the measurement of surface relief of the martensite relative to the surrounding austenite.

7.2.2) Theories for the Morphological Transition in Steel

The plate-to-lath morphological transition represents one of the most perplexing problems to challenge researchers in the field of ferrous martensitic transformations. Numerous correlations have been made between martensite morphology and intrinsic thermodynamic variables, resulting in a variety of interesting theories. In general, increasing alloy content and decreasing transformation temperature tend to favor a plate morphology, but the matter is complicated by the fact that additions of most alloying elements to Fe alloys also depress the $M_s$ temperature. Moreover, the exact nature of the relationship between transformation temperature, composition and martensite morphology remains to be established.
Kelly and Nutting [111] concluded, after studying the morphology of martensite in Fe-C alloys, that the important factor determining morphology is the transformation temperature; the carbon content affects morphology only indirectly through its influence on the $M_s$ and $M_f$ temperatures. These authors reasoned that morphology is related to a directional dependence of growth rate which is presumably temperature dependent.

In a later investigation of martensite morphology in Fe-Cr-Ni and Fe-Mn-Cr-Ni steels with low stacking-fault energy (SFE), Kelly and Nutting [112,113] concluded that the two extreme morphologies differed fundamentally by the operative lattice-invariant deformation system which in turn is influenced by the SFE of the austenite. This conclusion, however, lacks generality since, as pointed out by Krauss and Nadler [91], Mn lowers the SFE of austenite whereas Ni raises it but both elements tend to promote plate-martensite formation in ferrous alloys.

Owen and coworkers [114] correlated martensite tetragonality in carbon steels with morphology noting that plate martensites tended to be tetragonal, whereas lath martensites were cubic. A theory was advanced based on the critical temperature for Zener ordering of the carbon atoms in the martensite, and it was proposed that this temperature also represents the transition temperature for the morphology change. This theory has received criticism [91] because it does not account for the fact that plate martensites are cubic in Fe-Ni, Fe-Pt and Fe-Mn alloys.

The conspicuous absence of transformation twins in lath martensite suggests a connection between martensite morphology and substructure. Indeed, many authors seem to distinguish lath martensite from plate martensite on the basis of internal substructure and therefore focus attention on factors which may influence the mode of lattice-invariant deformation, i.e., slip versus twinning. Thomas [90], in a critical review of this approach, lists these factors which include temperature, composition, austenite SFE, martensite strength, rate of transformation,
pressure, as well as others. The influence of these variables on the critical resolved shear stress for slip, as opposed to that for twinning, was examined in an effort to determine the conditions under which slip is favored over twinning.

Regardless of whether the mode of lattice-invariant shear determines martensite morphology, the transition from twinning to slip in partially twinned martensites represents an interesting problem in itself. Patterson and Wayman [107] suggested that the transition in deformation mode is caused by the local temperature rise at the austenite-martensite interface, based on the general observation that slip is favored over twinning, as the predominant deformation mode in α-iron, as temperature is increased. This explanation is consistent with the observed dependence of the extent of internal twinning on $M_s$, since the possibility that a temperature rise can produce a transition from twinning to slip diminishes as temperature is decreased.

Davies and Magee [115-117] observed a correlation between yield strength and martensite morphology in a series of Fe alloys, strengthened by various hardening mechanisms. Austenites with a yield strength at $M_s$ greater than about 30 ksi (207 MPa) transformed to $\{259\}_f$ plate martensite, whereas lower-strength austenites transformed to either $\{111\}_f$ lath martensite, or $\{225\}_f$ martensite, depending on the plastic resistance of the bcc phase (ferrite). These investigators postulated that the habit plane, and presumably the morphology observed in a given alloy, is the one requiring the least amount of plastic work for the lattice-invariant deformation. The three choices of habit plane were distinguished by a proposed difference in lattice-invariant-deformation mechanism, which included plastic accommodation as a generalized form of lattice-invariant shear. In the case of $\{259\}_f$ plate martensite, twinning in the martensite was assumed to accomplish the lattice-invariant deformation. At the other extreme, $\{111\}_f$ lath martensite required both slip in the martensite and slip in the surrounding austenite, while the $\{225\}_f$ habit involved twinning in the martensite and slip in the austenite. This scheme allowed the prediction of the influence of various solutes (both interstitial and substitutional) on martensite morphology, based on their relative
effectiveness as ferrite and austenite strengtheners in the base alloy. This theory was tested on a number of Fe alloys, covering a wide range of $M_s$ temperatures, and the agreement with experiment was excellent. Thus, a strong connection has been established between martensite morphology and austenite strength; this further suggests that plastic accommodation may exert a major influence on morphology.

The importance of austenite strength has also been demonstrated by Laverroux and Pineau [118,119] who induced a lath-to-plate morphological transition, via precipitation hardening in an Fe-Ni and an Fe-Ni-Co alloy. These alloys were alloyed with Ta and heat-treated in order to produce a very fine distribution of coherent particles. Hardness was controlled by the aging time and temperature after a high-temperature solution treatment. As the hardness of both alloys increased above a critical level, the martensite morphology changed from lath to plate. Remarkably, this transition took place even though the $M_s$ of the alloy was increasing, due to matrix solute depletion from precipitation.

Korenko [25] studied the effects of a high magnetic field, on the isothermal martensitic nucleation kinetics and martensite morphology in Fe-29.6Ni. The magnetic field increased the effective driving force for the transformation through a magnetic interaction, thereby reducing the activation energy and increasing the nucleation rate at a given temperature. Under zero-field conditions, the morphology was described as lath-like, but under the influence of a high magnetic field (140 kOe) at the same temperature, this alloy transformed to a mixed morphology consisting of laths and irregular plates containing a midrib. Using the magnetic field to vary driving force while keeping temperature constant, Korenko correlated the morphological transition with isothermal nucleation rate, which can be correlated with the ratio of apparent activation energy to temperature ($\Delta W_a/T$). High values of this ratio promoted a plate morphology, which implies that, at a given driving force, low temperatures favor a lath morphology. The connection between nucleation rate and martensite morphology suggests that morphology is determined very early in
the martensite formation process, possibly during thermally activated interfacial motion.

7.3) Models for the Growth of Martensite

The preceding discussion has touched upon numerous qualitative ideas concerning the mechanism of martensitic growth and the factors which control growth morphology. These ideas or theories evolved out of a need to explain experimental observations; however, certain phenomena, notably the morphological transition, have led to a number of competing theories. Quantitative modeling of the martensitic growth process is necessary in order to weigh the relative merits of each theory and to distinguish the "special cases" from truly universal behavior. Only a few attempts to quantitatively model the growth process have appeared in the literature and these will be briefly reviewed.

Knapp and Dehlinger [19] extended Frank's [18] model of a \( \{225\}_f \) martensitic interface by regarding the particle of martensite as a thin oblate spheroid, bounded by dislocation loops. These loops were predominantly of screw character with short edge components near the particle periphery. These investigators were primarily concerned with the martensitic nucleation problem, but also treated the growth process as the motion of the interfacial dislocations under the influence of an effective shear stress. This shear stress was derived from the net free-energy change (chemical and nonchemical) and increased during growth leading to rapid acceleration. By utilizing Burkhardt's [120] relationship between dislocation velocity and applied shear stress, Knapp and Dehlinger calculated the interfacial velocity as a function of particle size. From this the time of formation of a plate was computed to be \( 10^{-7} \) sec., in agreement with the measurements of Bunshah and Mehl [77].

Raghavan and Cohen [31,121] modeled the growth of a single martensitic particle starting from various sizes beyond the saddle point
in the free-energy surface. The particle shape and interfacial structure were assumed similar to those proposed by Knapp and Dehlinger. Radial growth was analyzed in terms of the expansion of existing dislocation loops together with the nucleation and subsequent expansion of new loops at the advancing particle tip. Thickening required just the motion of the interfacial dislocations normal to the plane of the thin oblate-spheroidal particle. Transformational stresses, acting on the interfacial dislocations, were defined formally in terms of the rate-of-change of total free-energy with respect to a unit growth increment. These stresses were related to interfacial velocity by application of the Gilman equation [122] under the assumption that the kinetic response of interfacial dislocations to transformational stress is similar to that of lattice dislocations to externally applied stress.

Using parameters appropriate for Fe-29.2Ni-0.20Mn, initial radial growth rate was calculated to be controlled by the rate of nucleation of new dislocation loops but soon the rate of expansion of the loops became rate-controlling. For each starting geometry, the particle tended toward the same steady-state aspect ratio until radial growth was arbitrarily stopped by an obstacle. Further thickening at constant radius resulted in a final aspect ratio of about 0.035; the total growth time was about 4.0x10^{-6} sec. Notwithstanding the doubtful accuracy of the Gilman equation [122], the model does predict some of the general features of martensitic growth. Absent, however, are the potentially important effects of plastic accommodation on the growth dynamics, therefore, the Raghavan-Cohen model represents a simulation of thermoelastic growth wherein accommodation is nearly fully elastic.

Owen, Schoen and Srinivasan [124,125] explored the influence of dissolved interstitials on the predicted mobility of martensitic interfaces in ferrous alloys which transform to lath martensite. The interface was modeled as an invariant plane containing a single set of parallel dislocations, each with identical Burgers vector. Parameters such as interfacial plane and dislocation spacing were chosen based on both experimental observations and predictions of crystallographic theory.
An analysis of the Snoek interaction between the interfacial dislocations and dissolved carbon atoms permitted calculation of the critical carbon concentration below which growth becomes kinetically unstable. At carbon concentrations above the critical value, the interface moves more slowly, dragging with it a Cottrell atmosphere of carbon atoms. The theory was compared with experimental observations of the growth rate of martensitic units as a function of carbon content in Fe-10Ni-C alloys. According to Owen et al., the observed rapid increase in growth rate as the carbon content decreased below about 0.014 (mole fraction) agrees well with the predicted critical carbon concentration. Although this approach to martensitic growth may be useful when carbon interactions with the interface control growth rate it is not believed to be generally applicable, particularly at low temperatures where carbon diffusion is slow.

Easterling and Tholen [126] proposed a mechanistic model for the growth of martensite, distinguishing plate martensite from lath martensite on the basis of the type of habit plane: rational vs. irrational. These authors envisioned the growth of martensite to involve the nucleation of dislocation loops behind a coherent plate tip in order to relieve elastic strain energy. In the case of lath martensite, forming on rational \{111\}_f austenite planes, the dislocation loops nucleate at the thickest part of the particle, and their subsequent expansion in the interface provides an "easy" thickening mechanism. In contrast, plate martensite, forming on irrational planes requires the nucleation and expansion of twinning dislocation loops immediately behind the coherent plate tip. Moreover, these twinning dislocations do not lie in the plane of the plate, so that, according to Easterling and Tholen, the thickening process is inhibited compared to the thickening of lath martensite. This conclusion appears to be based more on intuition than on fundamental principles, particularly since no quantitative analysis was provided for its support.

Meyers [127] presented an alternative viewpoint on martensitic growth, utilizing concepts taken from the field of wave mechanics in
solids. The growth process for lenticular-plate martensite was assumed to be triggered by the instantaneous formation of a critical nucleus, which generates longitudinal and transverse transformation waves. The longitudinal transformation wave propagates along the undistorted habit plane, producing a midrib region which acts as a secondary nucleus for the thickening process via transverse transformation wave propagation. This transverse transformation wave is preceded by a plastic shock and plastic shear wave. The plastic shear wave produces the lattice-invariant deformation and, presumably, any other plastic accommodation. Meyers proceeded to quantitatively analyze the wave dynamics by assuming that the longitudinal and transverse transformation waves initially travel at the velocity of elastic compressive and shear waves, respectively. The transverse wave was allowed to attenuate in proportion to the total amount of shear produced. With these assumptions, a single equation describing the position of each point on the interface was derived as a function of time. The final shape of the plate did, indeed, resemble a lens and contained a midrib, although this midrib was actually built into the model.

This wave-mechanics approach, while attractive because of its simplicity, requires further theoretical development. For example, while Meyers admits that the nucleation process cannot occur instantaneously, how rapid must the nucleation process be in order to produce a shock front? Furthermore, the energetics of the transformation process are not specifically considered; therefore, such issues as the extent of plastic relaxation and relief of elastic strain energy cannot be addressed quantitatively using this approach.
CHAPTER 8

THERMOELASTIC GROWTH

Thermoelastic martensite is distinguished from non-thermoelastic martensite by the absence of appreciable plastic accommodation of the transformational shape change. This chapter presents a model for the thermoelastic growth of a single martensitic particle in an infinite matrix. The model was evaluated, numerically, using parameters appropriate to Fe-32Ni (wt.-percent). The general approach is an extension of that proposed by Raghavan and Cohen \[31,121\], who extended the previous work of Kaufman and Cohen \[14\], and Knapp and Dehlinger \[19\]. Before presenting a detailed description of the growth model, a brief overview will be given in order to introduce its individual components.

8.1) Overview of the Thermoelastic Growth Model

Fig. 8.1 contains a flow chart summarizing the basic components of the thermoelastic growth model. Each box represents an individual component, while the connecting lines with arrows depict interactions between the components. Following classical thermodynamics, the Gibbs free energy of a system consisting of a martensitic particle embedded in an infinite matrix can be expressed as the sum of the chemical, interfacial, and elastic strain energies (a-c). The magnitude of these energies depends on particle geometry, temperature and a host of other variables. In general, the chemical free energy is the only contribution which drives the transformation from austenite to martensite—the other
Fig. 8.1: Flow chart summarizing the basic components of the thermoelastic martensitic growth model. The arrows indicate interactions between the components.
contributions act to inhibit the reaction. These three energies were combined to give the net free-energy change, or driving force, for the martensitic transformation.

The driving force was converted into a net force-per-unit-area acting on the interface (d). This force is really a virtual thermodynamic force analogous to the transformational stresses defined by Raghavan and Cohen [31]. This net force enters as input into the interface mobility relations, which gives the velocity of the interface (e). It was necessary to assume that the interfacial velocity is a single-valued function of force. The interfacial mobility, as well as the free-energy contributions mentioned above, are expected to depend on temperature. Moreover, the rapid growth of martensite is not an isothermal process; therefore, the temperature rise at the interface was modeled (f). This interfacial temperature was used directly in the mobility relations and the chemical free-energy change, but since the temperature dependence of the interfacial and elastic strain energy enters mainly through the comparatively weak temperature dependence of the elastic moduli, these latter quantities were approximated as temperature independent. Further complications arise from the the dependence of the interfacial temperature on interfacial velocity; thus, both temperature and velocity can be interchangeably viewed as either dependent or independent variables.

In addition to the interfacial forces described above, inertial forces may become important during periods of rapid acceleration. Kocks et al. [123] quantified inertial effects for individual lattice dislocations and concluded that in certain circumstances, dislocations may inertially overcome weak obstacles in the lattice. This effect probably also holds for martensitic interfaces. Furthermore, rapid deceleration at strong obstacles such as grain boundaries, requires the rapid dissipation of kinetic energy; this energy is then available to assist in autocatalytic nucleation, or other processes such as plastic deformation. In the present model inertial forces were not included.

---

1 By convention the term "force" will henceforth refer to a force acting on the interface, normalized by unit interfacial area.
The complex interactions between the energetics and kinetics of growth, combined with the variation of the dependent variable, temperature, necessitates the use of numerical methods. The final solution, obtained via computer simulation, leads to a prediction of the martensitic "growth path", that is, the size and shape of the martensitic particle as a function of time.

8.2) Particle Geometry and General Assumptions

The particle geometry was assumed to be a thin, oblate spheroid, of radius, r, and semi-thickness, c, consistent with the commonly observed plate-like morphology of martensite formed in Fe-Ni alloys with nickel contents greater than about 29.5 wt.-percent. In the following discussion, directions lying in the plane of the plate will be referred to as "radial" directions, whereas the direction normal to the plate will be termed the "perpendicular" direction. Such usage as radial growth rate and perpendicular force will be common, although perpendicular growth and thickening will be used interchangeably.

The geometric assumption imposes the constraint of an isotropic growth rate in the plane of the plate, but has the advantage of a simple solution to the elastic-inclusion problem of continuum mechanics. The macroscopic shape strain was assumed to be an invariant-plane strain (IPS) in accordance with the minimization of elastic strain energy.

The particle and matrix were treated as a continuum with no explicit regard for the details of the internal or interfacial structure. Consequently, the interface was considered to behave like an elastic membrane, moving forward under the action of the driving force, converting austenite into martensite. This interface is expected to encounter some resistance to motion since it composed of arrays of dislocations. In treating the kinetics of interfacial motion this resistance, or drag, was modeled semi-empirically, after the well-studied case of dislocation
glide. Therefore, while the continuum assumption may appear somewhat restrictive, discrete dislocation concepts have served as a guide in modeling the kinetics of growth.

8.3) Temperature of the Austenite/Martensite Interface

The release of heat due to the enthalpy change accompanying the martensitic transformation produces a local temperature rise at the martensite/austenite interface. Consequently, under conditions of rapid growth, the transformation is not isothermal; nor is it adiabatic, owing to the high thermal diffusivity of metals. The expected temperature distribution normal to the interface is depicted schematically in Fig. 8.2. In this figure, $T_i$ and $T_y$ represent the interfacial temperature and initial-austenite temperature, respectively. The maximum temperature is shown to occur at the interface, which is expected to be the case during periods of acceleration or constant growth rate.

The exact solution to the non-steady-state heat transfer problem, involving a growing enclosed particle releasing heat at its boundary, is not available in closed form. Nevertheless, the problem was treated approximately, by adapting existing solutions for somewhat simpler cases. For a thin plate, the efficiency of heat removal will differ at each point on its surface but it is expected that heat-transfer will be most efficient at the plate tip, and least efficient at the center. It was therefore convenient to treat these two regions separately, and to consider radial growth and thickening to be influenced by the temperature near the plate tip and plate center, respectively.

8.3.1) Interface Temperature Near the Plate Tip

Lyubov and Roitburd [128] applied the Ivantsov solution for growth of a needle-shaped crystal from the melt [129], to the problem of the temperature distribution over the surface of a martensitic plate modeled
Fig. 8.2: Schematic temperature profile across a martensitic interface during growth.
as a thin elliptical cylinder. The shape of the tip region was approximated as being parabolic, for which in the limit of constant velocity and steady-state, the temperature is constant over the surface [129].

The interfacial temperature for the problem of interest here was approximated by the solution to the 2-dimensional problem above. The major difference between the 2-d and 3-d cases is the divergence of heat flow in the plane of the plate in the 3-d case which is absent in the 2-d case. But since the local plate-tip radius is much smaller than the plate radius, the error in using the 2-d solution should be small. In addition, the steady-state constant-velocity limit was used, which is equivalent to assuming that the temperature distribution adjusts itself quickly to changes in growth velocity and plate shape.

Even with these assumptions, the expression for temperature is a complicated function of radial velocity and local plate-tip radius, involving exponential and error functions. In order to facilitate computational efforts the solution was fit to the following simple form with an error of less than 5%:

$$T_r \cong T^{\text{ad}} \left\{ 1.0 - \exp \left[ -1.039 \beta_r^{0.429} \right] \right\}.$$  \hspace{1cm} (8.1a)

with:

$$\beta_r \equiv \frac{\rho v_r}{\sqrt{\chi}}.$$  \hspace{1cm} (8.1b)

where $T_r$ is the interfacial temperature at the plate tip, $T^{\text{ad}}$ is this temperature in the adiabatic limit, $\rho$ is the effective local plate-tip radius, $v_r$ is the radial growth velocity, and $\chi$ is the thermal diffusivity which was assumed to be isotropic and identical in both phases. The local plate-tip radius for an oblate spheroid is given by $c^2/r$, but since the overall shape of an ellipse is sharper than that of a parabola with the same local radius of curvature, $\rho$ was reduced to $0.75 \cdot (c^2/r)$. 
The adiabatic temperature was computed using standard methods of classical thermodynamics in which the enthalpy change for the transformation of austenite to ferrite is set equal to the integral of the molar heat capacity of the product phase from the initial transformation temperature to the unknown adiabatic temperature. The enthalpy change can be determined through application of the Gibbs-Helmholz equation if the chemical free-energy difference between the two phases is known as a function of temperature.

8.3.2) Temperature of the Plate Faces

Nishiyama and coworkers [130] treated the one-dimensional problem of an infinite, flat, interface moving at constant velocity, releasing heat at a steady rate. The equations of heat transfer were solved under the assumption that the thermal properties on either side of the interface are isotropic and identical. This solution was used to approximate the interface temperature, neglecting the (mild) curvature of the interface, and end effects due to the finite plate size.

The resulting equation for the interface temperature involved exponential and error functions which were cumbersome when applied repeatedly in computer simulations. Therefore, the following equation was fit to the exact solution with reasonable accuracy:

\[ T_c \approx T_{ad} \left\{ 1.0 - \exp \left[ -1.054 \beta_c^{0.528} \right] \right\}, \tag{8.2a} \]

with:

\[ \beta_c \equiv \frac{v_c^2 \cdot t}{\chi}, \tag{8.2b} \]

where \( T_c \) is the temperature at the interface, \( v_c \) is the thickening rate, and \( t \) is time.

In an effort to adapt the above constant-velocity solution to the case in which velocity varies with time, the velocity-squared factor in
eqn. 8.2b with replaced by its time-average value, averaged over the entire growth history. This approximation, although rough, allows a gradual adjustment of temperature to changes in growth rate.

8.4) **Free-energy of the Particle/Matrix System**

The total free energy of a system consisting of a thin, oblate-spheroidal shaped, elastically accommodated particle undergoing an invariant-plane strain in an infinite matrix can be written as follows:

\[
\Delta G = \frac{4\pi}{3} r_c^2 \Delta g_{ch} + \frac{4\pi}{3} r_c^2 A + 2\pi r^2 \sigma,
\]

(8.3)

where \(\Delta g_{ch}\) is the chemical free-energy change (per-unit-volume), and \(\sigma\) is the interfacial energy. The second term represents the elastic strain energy, which assumes this simple form in the thin-plate limit. Christian [131], using Eshelby's [63] method, derived an expression for the constant, \(A\), in terms of the isotropic elastic constants (assumed identical in both phases), and the transformation shear, \(\gamma_T\), and dilatation, \(\xi_T\):

\[
A = \frac{\pi}{8} \frac{(2-\nu)}{(1-\nu)} \mu \gamma_T^2 + \frac{\pi}{4} \mu \xi_T^2
\]

(8.4)

In evaluating \(\Delta g_{ch}(T)\), the interface temperature was used since the critical processes which control growth occur at or very near the interface. As mentioned previously, the elastic and interfacial energies are expected to depend only weakly on temperature; therefore, these quantities were assumed to be temperature independent. Furthermore, in the case of thin plates, most of the elastic strain energy is stored in the matrix [63]; hence, the elastic constants were evaluated at the transformation temperature.
8.5) Interfacial Forces

The concept of generalized, virtual forces acting on defects in solids is really a statement of the second law of thermodynamics, whereby a system undergoes spontaneous change in order to minimize its total free energy. These forces then describe the magnitude and configuration of the constraint which would be required to prevent the change. In other words, any thermodynamic variable such as temperature, composition, stress, etc., which produces a tendency for a defect to change its configuration, can be said to exert a force on the defect.

A martensitic interface can be regarded as a two-dimensional crystal defect which moves in response to forces derived from the free-energy change driving the martensitic transformation. For an element of interface, the increment of work, \( \delta W \), done by dissipative processes accompanying an increment of motion, \( \delta x \), normal to the element in the \( x \)-direction is given by:

\[
\delta W = \mathcal{F}_x \cdot A \cdot \delta x = -\delta G
\]  

(8.5)

where \( \mathcal{F}_x \) is defined as the interfacial force (per unit area) in the \( x \)-direction, and \( A \) is the area of the element. As indicated, the increment of work equals the negative of the incremental free-energy change, \( \delta G \). Thus the interfacial force, as defined by eqn. 8.5, can be written in terms of the derivative of \( G \) with respect to the spatial coordinate normal to the interface:\(^2\)

\[
\mathcal{F}_x \equiv -\frac{1}{A} \frac{\delta G}{\delta x}.
\]  

(8.6)

In application to growth of a martensitic particle, modeled as an oblate spheroid, components of force in the radial direction, \( r \), and

\(^2\)In general interfacial forces are vector quantities and it is possible to have components of force lying in the interface. Eqn. 8.6 refers to the normal component and is thus written in scalar form.
thickening direction, c, were defined in terms of \( \partial \Delta G / \partial r \) and \( \partial \Delta G / \partial c \), respectively. However the interfaces in these directions are by no means flat and eqn. 8.6 applies to a flat interface or infinitesimal elements of a curved interface.. In order to overcome this apparent difficulty, effective interfacial areas, \( A_r \) and \( A_c \), were defined under the assumption that the kinetics of radial growth and thickening are governed by the resulting effective forces. For an infinite, flat, interface, the interfacial force (per unit area) due to a change in volume free energy, \( \Delta g \), is numerically equal to \(-\Delta g\). Therefore, it is reasonable to extend this result to the case of a curved interface as a method of determining the effective interfacial areas. It can easily be shown that the appropriate definitions of these effective areas are given as follows:

\[
A_r = \frac{\partial V}{\partial r} = \frac{2\pi}{3} r c , \tag{8.7a}
\]

\[
A_c = \frac{\partial V}{\partial c} = \frac{4\pi}{3} r^2 . \tag{8.7b}
\]

The individual force contributions are obtained by substituting the total free-energy expression (eqn. 8.3), into eqn. 8.6, successively replacing "x" by \( r \) and \( c \), and separating terms. The resulting chemical-free-energy interfacial forces, or chemical forces, are given by:

\[
\gamma_r^{ch} = -\Delta g_{ch} , \tag{8.8a}
\]

\[
\gamma_c^{ch} = -\Delta g_{ch} . \tag{8.8b}
\]

Likewise, the forces arising from elastic strain energy, or elastic forces, are given by:

\[
\gamma_r^{el} = -\frac{A}{2} \frac{c}{r} , \tag{8.9a}
\]

\[
\gamma_c^{el} = -\frac{4A}{3} \frac{c}{r} . \tag{8.9b}
\]

The forces due to the interfacial energy contribution to the total
free energy, or capillarity forces are written as:

\[ g_r^\sigma = -\frac{3 \alpha}{2 \epsilon} \] \hspace{1cm} (8.10a)

\[ g_c^\sigma \equiv 0 \] \hspace{1cm} (8.10b)

where \( \sigma \) is the isotropic interfacial energy. Note that eqn. 8.10b is exact in the limit of zero aspect ratio, \( c/r \).

In addition to the above "thermodynamic" forces obtained by differentiating \( \Delta G \), the intrinsic resistance to interfacial motion exerts a force on the interface. This frictional force is expected to be athermal in nature and will be designated by \( g_r^{\text{ath}} \) and \( g_c^{\text{ath}} \), for the radial and perpendicular directions, respectively.

8.6) **Interfacial Mobility Relations**

The structural model of martensitic interfaces based on discrete dislocation arrays has attained wide acceptance [38, 132, 133], but the potential kinetic similarities between martensitic interfacial motion and dislocation slip have only recently been demonstrated experimentally. Grujicic, Olson and Owen [134] investigated the mobility of martensitic interfaces in Cu-Al-Ni alloy single crystals which undergo a single-interface martensitic transformation under stress. The observed temperature and rate-dependence of the interface-frictional stress was consistent with the interpretation that martensitic interfaces interact with obstacles to motion similarly to glide dislocations. Furthermore, kinetic behavior at low velocities, ranging from \( 10^{-6} \) to \( 10^{-2} \) m/s, suggested that interfacial motion is controlled by thermal activation through obstacles in the lattice. These investigators suggested that the theory of continuous glide of lattice dislocations, involving phonon interactions, should be applicable to high-velocity interfacial motion [135].
The treatment of the kinetics of martensitic interfacial motion, based on the phenomenology of dislocation slip, therefore, has some experimental justification, at least at low velocities. At high velocities, the similarity between interfacial motion and slip kinetics is less certain, but instead, represents a working hypothesis for the purpose of modeling martensitic growth. The general approach is phenomenological in the sense that the form of the relationship between interfacial velocity and net interfacial force is emphasized rather than specific mechanisms controlling growth velocity.

Kocks, Argon and Ashby [123] have presented an excellent, comprehensive review regarding the kinetic theory of dislocation slip. Fig. 8.3 illustrates the entire range of kinetic behavior in which the average dislocation velocity is plotted schematically as a function of applied stress. At stresses below the mechanical threshold, \( \dot{\gamma} \), dislocation velocity is controlled by the waiting time at thermally surmountable obstacles. At higher stresses velocity is controlled by drag mechanisms resulting in an extended region of linear viscous behavior. These two extreme modes of kinetic behavior superpose at intermediate stress levels. Nonlinear and relativistic effects become important at extremely high stresses, leading to an asymptotic approach to the elastic shear-wave velocity, \( v_s \).

8.6.1) Thermally Activated Interfacial Motion

The form of strain-rate/stress expression commonly applied to thermally activated slip is given by the familiar Arrhenius law:

\[
\dot{\gamma} = \dot{\gamma}_0 \exp \left( \frac{-\Delta G^m}{kT} \right),
\]

(8.11)

where \( \dot{\gamma}_0 \) is assumed constant, and \( \Delta G^m \) is the activation free energy. In its simplest form, \( \Delta G^m \) can be written as a linear function of applied
Fig. 8.3: Schematic dependence of plastic strain-rate on applied stress, for crystal plasticity via slip, depicting the entire range of kinetic behavior. (Kocks, Argon, and Ashby [123])
shear stress:

\[ \Delta G^m = F_0 \left[ 1 - \frac{\tau - \tau_\mu}{\hat{\tau}} \right], \] (8.12)

where \( F_0 \) is the height of the activation barrier corresponding to the rate-controlling obstacles, and \( \tau_\mu \) is the athermal component of the applied shear stress, \( \tau \).

A number of ferrous alloy systems exhibit isothermal martensitic nucleation kinetics which obey a temperature-dependent rate-law of the Arrhenius form. Furthermore, the experimental activation energy is observed to depend linearly on chemical driving force \([39, 40, 136-139]\). Olson and Cohen \([4, 40]\) argue that these two experimental findings strongly suggest that the rate-controlling mechanism is the thermally activated motion of partial dislocations bounding the critical nucleus. Assuming that the general character of the interface/obstacle interaction does not change after the nucleation stage, isothermal-nucleation kinetic data provide a means of estimating thermal-activation parameters for the purpose of modeling thermally activated martensitic growth.

For thermally activated interfacial motion, the interfacial velocity can be written by analogy with eqn. 8.11 as:

\[ v_{ta} = v_0 \exp \left( -\frac{Q}{kT} \right), \] (8.13)

with activation energy, \( Q \), given by:

\[ Q = Q_o - V^* \left[ \gamma^{\text{net}} - \gamma^{\text{ath}} \right]. \] (8.14)

where \( Q_o \) is assumed to be force-independent, \( V^* \) is the activation volume, and \( \gamma^{\text{net}} \) is the net force acting on the interface. Note that \( Q \) is written as a linear function of the thermal component of interfacial force by analogy with eqn. 8.12. It can be shown that this linear dependence is consistent with a linear dependence of activation energy on chemical driving force, in the early stages of isothermal nucleation. The pair of
equations, 8.16 and 8.17, relate interfacial velocity to the net force acting on the interface. These equations adequately describe interfacial-motion kinetics, at force levels well below the mechanical threshold for interfacial motion, $\mathcal{F}$.

8.6.2) Drag-Controlled Interfacial Motion

At interfacial forces considerably greater than $\mathcal{F}$, the waiting time at obstacles becomes insignificant compared with the running time between obstacles. The average dislocation velocity in this case is controlled by drag mechanisms arising from the interaction of a moving dislocation with phonons and electrons. The resulting slip behavior is often referred to as continuous glide. Electron drag is important only at very low temperatures in metals (below 100K in aluminum [140]), when lattice vibrations are relatively weak.

A variety of interactions between lattice phonons and moving dislocations have been cited [123,140,141]. Radiation scattering occurs when an incident phonon drives a dislocation into forced oscillation, causing the dislocation to radiate a cylindrical wave. Strain-field scattering arises from nonlinear elastic strains near a dislocation core. These large strains produce local changes in lattice compliance and density, resulting in phonon scattering by the core material. The average force on a stationary dislocation due to scattering of an isotropic flux of incident phonons is zero. However, a moving dislocation encounters more phonons from the forward direction than from behind, resulting in a net force resisting the dislocation motion. In addition to these scattering mechanisms, phonon viscosity also exerts a force on a moving dislocation. Phonon viscosity refers to the process by which elastic energy is converted to thermal energy, and is also responsible for the attenuation of elastic waves in solids.

The total combination of damping effects produces a net force resisting dislocation motion. For non-relativistic velocities this
force/length, $F_p$, is proportional to dislocation velocity, $v_d$, leading to the following definition of the phonon-drag coefficient, $B_p$:

$$F_p = B_p \cdot v_d$$

(8.15)

All three mechanisms lead to a drag coefficient of the same general form [123]:

$$B_p \approx \frac{bkT}{\Omega \nu_s}$$

(8.16)

where $\Omega$ is the atomic volume, $b$ is the Burgers vector, $k$ is Boltzmann's constant, and $\nu_s$ is the elastic shear-wave velocity. Following Grujicic et al. [135], and assuming that high-velocity martensitic interfacial motion is controlled by phonon interactions with interfacial dislocations, the interfacial drag coefficient, $B_a$, is related to $B_p$ through the following equation:

$$B_a = \frac{B_p}{d}$$

(8.17)

where $d$ is the spacing of the interfacial dislocations, which in the case of coherency dislocations, is given by the interplanar spacing. At steady-state, neglecting line-tension effects, the relation between phonon-drag-controlled interfacial velocity and net interfacial force, analogous to eqn. 8.15 is given by:

$$v_{pd} = \frac{1}{B_a} \left[ \mathcal{g}^\text{net} - \mathcal{g}^\text{ath} \right]$$

(8.18)

Implicit in eqn. 8.18 is the assumption that $\mathcal{g}^\text{ath}$ can be treated as a constant background resistance to continuous motion of the interface, and that the variation in lattice resistance, due to thermally surmountable obstacles, is small relative to $\mathcal{g}^\text{net}$.

As the shear-wave velocity is approached, drag mechanisms become increasingly nonlinear, and relativistic effects cause the kinetic energy
of a dislocation to increase sharply. Consequently, the shear-wave velocity represents a practical upper-limit to dislocation velocities. Taylor[142] suggested a way to account for special high-velocity effects by applying a correction to the drag coefficient. Again, assuming a similar correction for the interfacial drag coefficient, \( B_a \) becomes:

\[
B_a = \frac{B_{a,0}}{1 - \left( \frac{v_{pd}}{v_s} \right)^2}, \tag{8.19}
\]

where \( B_{a,0} \) is the uncorrected interfacial drag coefficient.

Eqns. 8.18 and 8.19 can be combined to give:

\[
v_{pd} = \frac{v_s^2 B_{a,0}}{2(\delta_{net} - \delta_{ath})} \left\{ 1 + \left( \frac{2B_{a,0}}{v_s} (\delta_{net} - \delta_{ath}) \right)^2 \right\}^{1/2} - 1 \tag{8.20}
\]

8.6.3) **Superposition of Mechanisms**

Gillis, Gilman and Taylor [142] considered the rate of dislocation motion through an array of homogeneous obstacles in an otherwise clear lattice. For obstacles with an average spacing, \( L \), in the glide plane, the average dislocation velocity is written as:

\[
v_d = \frac{L}{t_1 + t_2}, \tag{8.21}
\]

where \( t_1 \) is the average time required for the dislocation to overcome the obstacles and \( t_2 \) is the average time required to traverse the space between obstacles. Since \( L/t_1 \) corresponds to the thermally activated dislocation velocity whereas \( L/t_2 \) corresponds to the phonon-drag-controlled velocity, eqn. (8.21) states that the individual mechanisms are correctly combined in series. Assuming that this argument
also applies to martensitic interfacial motion, the interfacial velocity can be written as:

\[ \frac{1}{v} = \frac{1}{v_{ta}} + \frac{1}{v_{pd}} \]  \hspace{1cm} (8.22)

with \( v_{ta} \) and \( v_{pd} \) given by eqns. (8.13) and (8.20), respectively.

8.7) Numerical Methods

The present model aims to predict the growth path of an isolated martensitic particle, by solving the governing equations relating growth velocities to growth dimensions and time. The primary dependent variables are the plate dimensions (c and r), and effective interfacial temperatures (\( T_r \) and \( T_c \)). Time can be taken as the independent variable, so that the growth model can be represented, mathematically, as an initial-value problem, governed by a pair of coupled first-order differential equations relating interfacial velocities (\( \partial r/\partial t \) and \( \partial c/\partial t \)) with \( r, c, T_r, \) and \( T_c \). The numerical analysis was conducted using the backward Euler method [143] combined with a modified fixed-point-iteration [144] scheme.

Further details concerning the numerical methods, as well as, the algorithm used in the numerical analysis, have been included in Appendix 2.

8.8) Estimation of Parameters

The parameters defined in the thermoelastic growth model are summarized in Table 8.1. The Fe-Ni alloy system was selected for the growth simulations for several reasons. First, thermodynamic, and to a limited extent, kinetic data are available for martensitic transformations in this system. Second, choosing this system avoids potential complications due to interstitial solute-drag effects [124,125]. Finally,
# Table 8.1

**Parameter List for the Thermoelastic Growth Model**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>See Equation(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{ad}$</td>
<td>Adiabatic temperature of the martensitic phase.</td>
<td>8.1a, 8.2a</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Thermal diffusivity.</td>
<td>8.1b, 8.2b</td>
</tr>
<tr>
<td>$\Delta g_{ch}$</td>
<td>Chemical free-energy difference between the fcc and bcc structures.</td>
<td>8.3, 8.18</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Interfacial free energy.</td>
<td>8.3, 8.10</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Macroscopic transformation shear strain.</td>
<td>8.4</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Macroscopic transformation dilatation strain.</td>
<td>8.4</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson's ratio.</td>
<td>8.4</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Isotropic shear modulus.</td>
<td>8.4</td>
</tr>
<tr>
<td>$v_0$</td>
<td>Pre-exponential in the thermal-activation controlled interfacial velocity equation.</td>
<td>8.13</td>
</tr>
<tr>
<td>$Q_0$</td>
<td>Activation barrier height for thermally activated interfacial motion.</td>
<td>8.14</td>
</tr>
<tr>
<td>$V^*$</td>
<td>Activation volume for thermally activated interfacial motion.</td>
<td>8.14</td>
</tr>
<tr>
<td>$g_{ath}$</td>
<td>Athermal component of the resisting force to interfacial motion.</td>
<td>8.14</td>
</tr>
<tr>
<td>$M_s$</td>
<td>Martensite-start temperature.</td>
<td>text</td>
</tr>
<tr>
<td>$\hat{\mathcal{G}}$</td>
<td>Mechanical threshold for thermally activated interfacial motion.</td>
<td>text</td>
</tr>
<tr>
<td>$B_{a,o}$</td>
<td>Phonon-drag coefficient for drag-controlled interfacial motion. (non-relativistic)</td>
<td>8.16, 8.19</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Atomic volume.</td>
<td>8.16</td>
</tr>
<tr>
<td>$v_s$</td>
<td>Elastic shear-wave velocity.</td>
<td>8.16, 8.19</td>
</tr>
<tr>
<td>$d$</td>
<td>Slip-plane interplanar spacing.</td>
<td>8.17</td>
</tr>
</tbody>
</table>
the Fe-Ni system exhibits a transition in martensite morphology, although this transition is believed to be associated with plastic-accommodation effects, which will be included in the next chapter. Unfortunately, from the standpoint of modeling thermoelastic growth, Fe-Ni alloys show only a limited degree of thermoelastic behavior. However, the success of this model depends, in part, on the availability of data, which is very limited for strongly thermoelastic alloys. The specific alloy, Fe-32Ni (wt.-percent), was chosen for the thermoelastic growth simulations; this alloy transforms to plate martensite and was also used in the nonthermoelastic growth simulations.

The temperature of the parent phase at the start of growth was assumed to be the bulk \( M_s \) temperature. Kaufman and Cohen [145] determined this temperature to be equal to about 200 K in Fe-32Ni.

The chemical free-energy change, \( \Delta g_{ch}(T) \), was obtained from thermochemical data reported by Kaufman and Nesor [146]. As described in Section 8.3.1, application of the Gibbs-Helmholtz equation to \( \Delta g_{ch}(T) \) gives the transformation enthalpy change, which can be used to compute the adiabatic temperature, \( T^{ad} \). Approximating the thermal properties by the corresponding values for pure \( \alpha \)-Fe at 200 K, the adiabatic temperature was estimated to be: \( T^{ad} \approx 288 \) K, that is, the temperature rise at the martensite/austenite interface is limited to a maximum value of 88 K. Between \( T=M_s \) and \( T=T^{ad} \), \( \Delta g_{ch} \) is approximately linear in temperature, giving:

\[
\Delta g_{ch}(\text{Fe-32Ni}) \approx 7.08(10)^5 T - 3.08(10)^8 \text{ J/m}^3 \quad (8.23)
\]

The elastic properties were assumed to be isotropic and identical in both phases. The measurements of Goldman and Robertson [147] on fcc Fe-30Ni were used to estimate the shear modulus of Fe-32Ni at \( M_s \) resulting in: \( \mu=63.5 \) GPa. Poisson's ratio was taken to be equal to 0.3.
The transformation strain was approximated as a simple shear \((\xi_r=0)\). The magnitude of the shear was estimated to be: \(\gamma_r \approx 0.2\), based on measurements reported by Machlin and Cohen [26] on Fe-30Ni.

The interfacial energy, \(\sigma\), was estimated by: \(0.1\text{ mJ/m}^2\). Although this value represents the low end of the range, calculated for semicoherent martensitic interfaces \((0.1-0.2\text{ mJ/m}^2)\) [14]), the capillarity force was significant relative to the other interfacial forces only very early in growth.

The athermal component of the interface-frictional force, \(\mathcal{F}^{\text{ath}}\), was modeled by analogy with the corresponding value for lattice-dislocation slip. This assumes that the same mechanism responsible for dislocation-glide resistance also controls the resistance to martensitic interfacial motion—a basic working hypothesis for the present modeling of interfacial-motion kinetics. The high-temperature plateau level of the critical-resolved-shear stress gives an estimate of this athermal glide resistance [123]. Measurements conducted by Breedis and Robertson [148] give a value of 11.8 MPa for this quantity in Fe-30Ni. Multiplication by \(\gamma_r\) converts this stress into an interfacial force, effectively matching the energy dissipation between the lattice-dislocation and interfacial-motion processes. The resulting value: \(\mathcal{F}^{\text{ath}} = 2.35\text{ MPa}\), was found to be significant only during the growth start-up stages of the simulations.

The kinetic quantities characterizing thermally activated interfacial motion were estimated using the isothermal martensitic-nucleation kinetic measurements of Raghavan and Cohen [138] on Fe-29Ni. Following Olson and Cohen's [4] interpretation of the activation parameters, \(V^m\) and \(Q_o\) were estimated to be: \(3.7\times 10^{-27}\text{ m}^3\) and \(2.1\times 10^{-19}\text{ J}\), respectively. The mechanical threshold for interfacial motion was estimated by setting \(Q=0\) in eqn. 8.14 giving: \(\mathcal{F} = 59\text{ MPa}\). The pre-exponential factor, \(v_o\), is expected to scale with the atomic vibrational frequency and an activation distance. Taking this frequency to be roughly, \(10^{13}\text{ s}^{-1}\) and assuming an activation distance of a few angstroms, the product of these quantities
becomes \( \sim 3000 \text{ m/s} \), which is approximately equal to \( v_s \). Indeed, the shear-wave velocity scales with the shear modulus, which in turn influences the atomic frequency. Hence, \( v_0 \) was approximated by the shear-wave velocity, \( v_s \).

The drag coefficient for high-velocity interfacial motion was estimated using eqns. 8.16 and 8.17. The shear-wave velocity, \( v_s \), is related to the elastic shear modulus, and mass density, \( \rho \), by: \( v_s = \sqrt{\mu/\rho} \). The corresponding room-temperature values of density and lattice parameter for Fe-30Ni, reported by Hausch and Warlimont [149], were used, giving: \( B_{a,o}^{328.7T} \), in units of \( (\text{N-s/m}^3 \text{K}) \). Preliminary growth simulations indicated that the steady-state aspect ratio of a growing plate, in the phonon-drag regime, tended to be somewhat larger than anticipated, based on experimentally determined midrib aspect ratios of about one percent. Consideration of the physical and geometric aspects of the phonon-scattering process, could not justify applying a different drag coefficient for radial growth versus thickening. However, this conclusion was based on the assumption that the interfacial dislocations interact independently with lattice phonons, and that the magnitude of this interaction scales with the individual-dislocation Burgers vector. While the latter assumption is intuitive, the former is difficult to justify, particularly for coherency-dislocation arrays, whose spacing approaches atomic dimensions. Clearly, the problem of viscous drag on martensitic interfaces requires further study. Nevertheless, in the present model, it was deemed important to reproduce experimental findings; therefore, the mobility of the interface in the radial direction was enhanced relative to the perpendicular direction. This was accomplished by reducing the drag coefficient for radial growth by 50\%, while retaining the above estimate for \( B_{a,o} \) in calculating the thickening rate. The resulting plate aspect ratios then fit into the expected range of 1-3\%, corresponding to measured midrib aspect ratios.

The predicted relationship between interfacial velocity and the net effective interfacial force is plotted in Fig. 8.4 for Fe-32Ni at 200 K, and Fe-24Ni at 400 K. The curve corresponding to Fe-24Ni applies to the
Fig. 8.4: Predicted dependence of interfacial velocity on the effective interfacial force. The low-velocity regime is modeled after thermally activated dislocation slip, whereas phonon-drag mechanisms control the high-velocity growth rate.
nonthermoelastic growth model, which will be discussed in the next chapter. The low-velocity, thermally activated regime is characterized by a very strong dependence of velocity on interfacial force. The high-velocity range is dominated by the phonon-drag mechanism, while velocities near the knee of each curve are controlled by a superposition of mechanisms.

8.9) Initial Conditions—Growth Start-up

In the beginning of this chapter martensitic growth was distinguished from nucleation by the absence of significant interaction with the nucleating defect. A quantitative prediction of the plate dimensions at the start of growth, based on this definition was not pursued. Instead, the nucleation process was assumed to result in the formation of a martensitic particle whose size and shape place it beyond the saddle-point barrier of the free-energy surface defined by eqn. 8.3. This assumption was made for convenience, but it was found that the major portion of the growth simulation did not depend sensitively on the starting configuration.

The $r$- and $c$-coordinates of the free-energy saddle point are obtained by differentiation of eqn. 8.3, giving the following two equations for the critical plate radius and semithickness:

$$r^* = \frac{4\sigma A}{[A g_{ch}]}^2.$$  \hspace{1cm} (8.24a)

$$c^* = \frac{-2\sigma}{A g_{ch}}.$$  \hspace{1cm} (8.24b)

In addition to selecting initial starting dimensions such that $r > r^*$ and $c > c^*$, the particle was assumed to have an initial shape determined by
minimizing ΔG at constant volume, leading to the following equation [14,150]:

\[
\frac{c^2}{r} = \frac{a}{A}.
\] (8.25)

Then the initial values of \( r \) and \( c \) were determined such that reasonable growth rates, comparable to those encountered in barrierless nucleation-kinetic experiments, were realized in the thermally activated regime. Generally, this condition was met with \( r \) being about two times \( r^* \). Typical initial values of \( r \) ranged from 70 to 80 nm.

8.10) Growth-Simulation Results and Discussion

Figure 8.5 presents the computed growth path for a typical thermoelastic growth simulation, in which the plate radius and semithickness are plotted as a function of time. The initial plate dimensions were assumed to be: \( r=77.0 \) nm and \( c=1.78 \) nm; this may be compared with the saddle-point values: \( r^*=35.3 \) nm and \( c^*=1.21 \) nm. The apparent initial incubation period is really an artefact of the logarithmic scales; both the radial-growth and thickening rates quickly increased from their initial values of about 1 m/s. Radial growth was halted at a size of \( r=100 \) μm in order to simulate growth arrest at a strong obstacle such as a grain boundary. Thereafter, thickening continued until a thermo-mechanical balance was reached between the chemical and nonchemical forces, causing a cessation of growth.

During the radial-growth-plus-thickening stage (stage I), the plate aspect ratio decreased steadily from an initial value of 0.023, to 0.017. In contrast, Raghavan and Cohen [121], applying a similar model, found that the aspect ratio approached a steady-state value very early in growth. However, the latter calculation did not include the effect of the interfacial-temperature rise, which in the present calculation, prevented the attainment of steady-state growth. The dashed curves in Fig. 8.5 represent the results of a simulation in which the initial value of \( c \) was
Fig. 8.5: Computed growth path (r and c vs. time) for an elastically accommodated martensitic plate in Fe-32Ni.
taken to be 5 nm—nearly a three-fold increase over that assumed in the previous case. After about the first three percent of radial growth (in terms of size), the two growth paths converged, indicating that the majority of growth is insensitive to the initial plate dimensions. This result agrees with the Raghavan-Cohen calculation.

The plate aspect ratio at the end of stage I fit fairly well with the aspect ratios of the midrib portion of martensitic plates. For example Datta and Raghavan [151] presented a micrograph showing the martensitic microstructure in Fe-31.8Ni transformed at 177 K (Fig. 1b of their paper), in which the midrib aspect ratio appears to be about 0.015. As mentioned in Chapter 7, the midrib is widely believed to be the first part of the plate to form; therefore stage I of the computed growth path was interpreted as a simulation of the midrib formation process.

Following stage I, the plate thickened to a final aspect ratio of 0.028 (indicated by the dot on the right-hand side of Fig. 8.5). Datta and Raghavan [104, 151] conducted a systematic metallographic study of the dimensions of martensitic plates formed in Fe-Ni alloys. The mean value of plate aspect ratio, $c/r$, was determined to be in the range: 0.070–0.092, for alloys with nickel contents near 32 wt.-percent, transforming near 200 K. This disagreement between thermoelastic model prediction and measured aspect ratios indicates that appreciable plastic accommodation accompanies the formation of martensitic plates in Fe-32Ni. Plastic accommodation relaxes a portion of the elastic strain energy allowing the thickening process to continue in order to establish the local force balance at the interface. Discussion of the implications of plastic accommodation on martensitic growth will be resumed in the following chapter.

The total time required for stage I was found to be 0.12 $\mu$s. In the final thickening stage, about 40 percent of growth occurred within the next microsecond. Deceleration to the final thickness took nearly 43 hours. However, for most of this period, growth was under thermal-activation control, the quantitative modeling of which is subject to considerable uncertainty.
The dependence of radial-growth rate on plate radius for the same simulation described above is plotted in Fig. 8.6. Also included is the temperature of the interface in the plate-tip region, which determines the local driving force for interfacial motion. Initially, the radial velocity was controlled by thermal activation with $v_r < 500 \text{ m/s}$, but rapid acceleration almost immediately brought the plate into the phonon-drag-controlled velocity regime. Concurrently, the plate-tip temperature rose, which acted as an inhibiting factor by both reducing the chemical driving force, and increasing the phonon-drag coefficient. The magnitude of this temperature increase reached a maximum of 54 K, which is only about 60 percent of the adiabatic temperature rise. Thus, radial growth is predicted to be neither an isothermal nor an adiabatic process, but intermediate between these two extremes.

At a radius of about 1 μm, the radial velocity reached a maximum value of 940 m/s, and then steadily decreased to 790 m/s at the imposed growth-arrest size. This range of velocities corresponds to 0.34–0.28 times $v_s$, in agreement with the experimentally determined growth rate for Fe-29.5Ni, reported by Bunshah and Mehl [77] to be approximately one-third the shear-wave velocity. Prediction of the maximum radial velocity without the aid of computer simulation is complicated by the dependence of velocity on interfacial temperature, through the chemical driving force and drag coefficient, as well as the dependence of the elastic strain energy on particle shape. Had growth been assumed to be an isothermal process, the particle shape ($c/r$) would have approached a steady-state value, in accordance with the Raghavan-Cohen calculations. In this case an approach to a steady-state velocity would also have been anticipated. However, the admittance of the local temperature rise as a variable, greatly complicates the problem, precluding analytic prediction of a velocity maximum. This emphasizes the usefulness of modeling and computer simulation in the study of complex problems of importance to understanding physical processes.
Fig. 8.6: Radial growth rate and interfacial temperature near the plate tip ($\nu_r$ and $T_I$) as a function of plate radius for the thermoelastic growth simulation in Fe-32Ni.
Analysis revealed that the decrease in radial velocity was principally due to an increase in interfacial temperature in the plate-tip region. Equations 8.1 indicate that this temperature is a direct function of the local curvature of the plate tip, given by \( c^2/r \). Since the decrease in \( c/r \) was gradual compared with the rate of increase in \( c \), the local tip curvature increased with increasing plate radius producing an attendant increase in local plate-tip temperature. Physically, the increase in local plate-tip radius reduced the efficiency of heat transfer away from this advancing heat source, causing the interfacial temperature to rise. Consequently, the radial velocity declined due to the dependence of both driving force and drag coefficient on temperature.

Figure 8.7 summarizes the kinetics of plate thickening where the thickening rate is plotted versus plate semithickness, along with the interfacial temperature of the plate faces. The thickening rate experienced rapid initial acceleration, but remained under thermal-activation control throughout the growth simulation. The decline in thickening rate, after reaching a maximum value of 19.8 \( \text{m/s} \), was due to an increasing interfacial temperature. This temperature, given by eqns. 8.2 (together with the assumed averaging method), depends directly on the thickening rate (squared) and time.

The sharp decrease in thickening rate at \( c=1.65 \text{ \mu m} \) corresponds to the beginning of the thickening-only stage of growth. Further thickening produced an increasing elastic strain energy, and therefore, a decreasing net interfacial force. Eventually the elastic and chemical interfacial forces reached a balance, marking the end of growth. As expected, the interfacial temperature also decreased as the thickening rate diminished.

The maximum temperature increase along the plate face was found to be 45 \( \text{K} \), or 50 percent of the adiabatic temperature rise. Thus, thickening is also predicted to produce a local temperature rises intermediate between the isothermal and adiabatic limits.
Fig. 8.7: Thickening rate and temperature interfacial temperature along the plate faces ($v_c$ and $T_c$) as a function of plate semithickness for the thermoelastic growth simulation.
As mentioned in Chapter 7, the transition from twinning to slip as the operative mode of the lattice-invariant deformation, during martensitic transformation in ferrous alloys, has been attributed to the temperature rise at the advancing interface [107]. This argument relies on the general observation that twinning becomes the dominant mode of high strain-rate deformation in bcc structures at low temperatures. Furthermore, the proportion of twinned versus untwinned regions, comprising the substructure of plate martensite in Fe-Ni and Fe-Ni-C alloys, increases with decreasing transformation temperature. Umemoto et al. [152] studied the temperature dependence of the fraction of twinned region in martensitic plates formed in a series of Fe-Ni-C alloys. The twinned fraction was found to be a decreasing function of transformation temperature. By extrapolating their data, these investigators estimated that the transformation temperatures corresponding to the limits of no twinning and full twinning covered a range of 120 K. This range agreed with the estimated magnitude of the adiabatic temperature rise. Thus, the adiabatic temperature rise during thickening of martensitic plates was argued to be consistent with the observed behavior, and was considered to be responsible for the transition in lattice-invariant deformation mode.

In a similar experiment, conducted on a series of plate-forming Fe-Ni alloys, Datta and Raghavan [104] observed partially-twinned substructures over a transformation temperature range of more than 200 K. Estimating the adiabatic temperature rise to be 95 K, it was concluded that adiabatic heating could not account for the transition in martensitic substructure.

The present calculations reinforce this conclusion since the maximum temperature rise at the interface during thickening was computed to be only 45 K. Therefore, the interfacial temperature increase due to the release of latent heat of transformation cannot alone account for the observed transition from twinning to slip as the mode of lattice-invariant deformation during the thickening-only stage of martensitic growth. The potential influence of plastic accommodation on this transition will be discussed in the following chapter.
CHAPTER 9

NONTHERMOELASTIC GROWTH

The thermoelastic martensitic-growth model considered the kinetic response of a glissile martensitic interface to the net sum of virtual thermodynamic forces acting to move the interface forward and produce a structural change. The driving force for the martensitic transformation is the difference in chemical free energy between the parent and product phases, while the interfacial energy and elastic strain energy necessitate nucleation and reduce the net driving force for growth. The thermoelastic growth simulations suggest that once a martensitic unit nucleates, the net interfacial forces quickly increase, producing a rapid acceleration to high growth rates as the particle adopts an optimum plate-like shape. Furthermore, this shape is promoted by the dominance of elastic strain energy over interfacial energy during the growth stage of the transformation. Nonthermoelastic growth, by definition, involves some degree of plastic relaxation resulting in a reduction in elastic strain energy. Consequently, the martensitic particle does not necessarily assume a plate shape.

The assumption of total elastic accommodation of the transformation shape-strain represents a limiting case; thermoelastic growth requires that plastic accommodation play only a minor role in determining growth behavior. Indeed, thermoelastic martensitic transformations are typically characterized by a small transformation strain and/or a high resistance to plastic accommodation. The potential for nonthermoelastic growth can be assessed by considering the magnitude of the internal stresses produced by
the shape change, relative to the resistance to plastic deformation of both the parent and product phases [153]. For the case of interest—-in-plane shearing of a thin, oblate spheroidal particle—-the shear stress within the particle is constant and given by the following equation [63]¹:

\[
\tau_{23}^I = \frac{\pi (2-v)}{4(1-v)} \frac{\mu \gamma}{r}.
\]

(9.1)

retaining the same parameter definitions as in Chapter 8. By substituting the parameters estimated for Fe-32Ni, this equation predicts a stress of 242 MPa for c/r=0.01. This level of stress is much greater than the critical-resolved shear stress for slip in Fe-32Ni, emphasizing the likelihood of significant plastic accommodation during martensitic transformation in this alloy.

Nonthermoelastic martensitic growth has been modeled, based on an extension of the thermoelastic growth model presented in Chapter 8. This chapter describes the highlights of this model, and the results of computer simulation. The basic assumptions made in connection with the thermoelastic growth model were adopted and will not be repeated. As in Chapter 8, the Fe-Ni alloy system was chosen for quantitative analysis. In the present chapter, simulated martensitic growth in the plate-forming alloy, Fe-32Ni, will also be contrasted with that of lath-forming Fe-24Ni.

9.1) Overview of the Nonthermoelastic Growth Model

Figure 9.1 presents a flow chart summarizing the interactions between the basic components of the nonthermoelastic growth model. Entries (a)-(f) correspond to the thermoelastic growth model; the remaining components

---

¹Throughout this chapter, the thin, martensitic particle is assumed to lie in the x-y plane of a Cartesian coordinate system. The notation in eqn. 9.1 is consistent with a shear on this plane, in the y-direction. The transformation strain may alternatively be expressed in terms of a strain tensor as follows: \( \gamma = 2e_{23}^\gamma = 2e_{32}^\gamma \).
Fig. 9.1: Flow chart showing the basic components of the nonthermoelastic martensitic growth model. Components (g)-(j) extend the thermoelastic growth model to include plastic-accommodation effects.
represent an extension of the thermoelastic model, accounting for plastic-accommodation effects.

In general, plastic accommodation may occur both within the martensitic phase and in the surrounding austenitic phase. In the present model, plastic accommodation was considered to be restricted to the austenite, which is equivalent to assuming that the plastic resistance of the martensite is much greater than that of the austenite. Although plastic flow within the martensitic particle may appear to be the simpler case, solutions are unavailable except for very specific cases involving spherical symmetry, in the static limit. On the other hand, plastic relaxation of the highly stressed austenite in the vicinity of the particle tip shows many similarities to the crack-tip plasticity problem for which solutions are available for variety of cases. Accordingly, the plastic-accommodation process was modeled by analogy with relevant crack-tip relaxation models. The stresses in the austenite are highest near the particle tip so that plastic flow is expected to initiate in this region.

The nonthermoelastic growth model includes two additional interfacial forces arising directly from the plastic-accommodation process. Plastic accommodation involves inelastic deformation which requires an expenditure of energy in the form of plastic accommodation work, which reduces the net driving force for the transformation (component (i) in Fig. 9.1). In addition, plastic flow ahead of the moving interface is expected to produce a dislocation substructure, resulting in an energy dissipation in the form of interface-frictional work (j). The growth-inhibiting effects of these dissipations were taken into account by defining interfacial forces, which contribute to the net force acting on the interface (d).

Plastic accommodation relaxes a portion of the transformation strain, reducing the the elastic interfacial forces ($\sigma_{r}^{el}$ and $\sigma_{c}^{el}$). This effect was modeled by defining an effective transformation strain, reduced by plastic relaxation. Hence, plastic accommodation can be both growth-inhibiting and growth-enhancing; one objective of this study was to determine which effect is likely to be dominant.
Plastic accommodation is both a size- and rate-dependent process (h). The size dependence arises from the need for dislocation sources in order to produce plastic flow. The interfacial velocity effectively imposes a rate dependence on plastic accommodation through the dynamics of dislocation plasticity (g). Hence, the processes of plastic accommodation and interfacial motion interact, adding considerable complexity to the martensitic growth problem.

9.2) Plastic Accommodation Model

Martensitic growth is visualized to occur in two distinct modes—elastic and plastic growth. Initially, a microscopic martensitic particle grows elastically, but at some point, initiation of plastic accommodation may occur, marking the beginning of plastic growth. This second mode of growth does not necessarily occur in all martensitic transformations, nor is plastic growth necessarily much different from elastic growth, in all cases. However, it will be shown that plastic accommodation is, indeed, important during transformation of the two alloys chosen for the growth simulations.

As mentioned above, plastic accommodation may be delayed because of an insufficient density of normal dislocation sources near the martensitic particle. However, the stress field of the particle itself can provide an effective source for nucleating lattice dislocations. Whether dislocation nucleation is possible depends on the energetics of the process, which in turn, depends on the range and intensity of the stresses. For a given particle aspect ratio, this range scales directly with the particle radius; therefore, at small sizes dislocation nucleation may be impossible. Prior to meeting the conditions for dislocation nucleation, growth was assumed to proceed thermoelastically. Once the necessary conditions are met, plastic accommodation becomes energetically feasible.

Plastic flow in the austenite surrounding the martensitic particle was considered to occur within separate regions or plastic zones. Furthermore, a distinction was made between plastic accommodation in the locality of the
particle-tip region, as opposed to accommodation along the broad faces, based upon anticipated fundamental differences between the mechanics of plastic flow between these two regions. Plastic flow near the particle tip produces a radial plastic zone, whereas plastic flow along the particle faces takes place within perpendicular plastic zones. Finite-element methods are well-suited for the study of elastic/plastic continuum problems, and could be used to determine the size and shape of the plastic zones, as well as the strain distribution with these zones. Moreover, these methods are applicable to dynamic problems, and presumably, offer an attractive means by which to model plastic accommodation during growth. However, in the interest of developing a fairly simple model, alternative approximate methods were employed in the modeling of plastic accommodation.

9.2.1) Energetic Criterion for the Initiation of Plastic Accommodation

Ashby and Johnson [154] modeled the nucleation of lattice dislocation loops at the interface of a misfitting, spherical inclusion, undergoing a pure dilatational strain. A similar approach was adopted for application to the problem of plastic-flow initiation in the stress field of the model-martensitic particle. The general description and treatment of this problem essentially parallels that proposed by Ashby and Johnson, and further details of the dislocation-generation process can be obtained by referring to their publication [154].

The present model is concerned with the energetics of dislocation-loop nucleation in the intense stress field just outside of the shearing martensitic particle. This process is the most energetically favored in regions of highest shear stresses. Preliminary calculations, revealed that the shear stresses are a maximum in the plane of the particle, at circumferential positions for which the shear strains are closest in character to anti-plane strain. Generally, the nucleation process should be considered to occur on crystallographic slip-planes of the parent lattice. However, for the case of interest here, the slip plane lies at a fairly shallow angle to the habit, and so the dislocation was treated as forming in the plane of the particle.
Fig. 9.2 shows a schematic illustration of a dislocation loop, with radius, \( r_f \), partially lying in the interface of the model-martensitic particle, viewed from above the habit plane. The Burgers vector of the dislocation loop was assumed to be parallel to the shear direction of the particle. Although the equilibrium loop shape can be computed, a circular shape was assumed, which was found to be a good approximation in the case considered by Ashby and Johnson.

The total energy change of the system during loop expansion is given by the sum of the work done by the stress field of the particle and the self energy of the loop. The work is given by the area-integral of the product of shear stress and Burgers vector. This integration was simplified by assuming a box-shaped loop of width, \( r_f \), having a similar area. The self energy was approximated by that of a fully circular dislocation loop, for which Chou and Eshelby [155] derived an appropriate expression.

The calculated total energy change showed a classical barrier versus loop radius, which was computed as a function of particle dimensions. The energy barrier decreases with increasing particle radius and aspect ratio. The former dependence is due the increase in the range of the stress field, while the latter arises primarily from the increase in intensity of the stresses. The limiting case of athermal nucleation, for which the energy barrier vanishes, was adopted as a criterion for dislocation-loop formation, potentially leading to the initiation of plastic accommodation. The conditions meeting this criterion are depicted in Fig. 9.3, where the critical particle radius for the above process is plotted as a function of aspect ratio. For a given aspect ratio, elastic growth is predicted up to a radius given by the indicated demarcation line. When the particle radius exceeds this critical value, plastic accommodation becomes energetically possible. Thus, a necessary energetic condition for the initiation of plastic accommodation has been determined in terms of the particle geometry which determines intensity and range of the stress field in the vicinity of the particle tip. However, it will be shown that this nucleation condition is not necessarily sufficient for plastic flow, and that mobility factors also play an important role in determining the onset of plastic accommodation.
Fig. 9.2: Schematic illustration depicting nucleation of a lattice-dislocation loop, in the stress field at the tip of a martensitic particle.
Fig. 9.3: The critical combinations of particle radius and aspect ratio, necessary to nucleate dislocation loops, athermally, in the stress field at the tip of the model-martensitic particle.
9.2.2) **Radial Plastic Zone**

The radial plastic zone (RPZ) was modeled by analogy with the elastic/plastic mode III shear-crack problem. This approach is justified by the similar nature of the stress field in the crack-tip region compared with the stress field near the tip of the model-martensitic particle. The connection between these stress fields can be demonstrated by considering the related 2-dimensional case involving a shearing particle in the shape of an infinite elliptical cylinder. Fig. 9.4 schematically illustrates this connection. Fig. 9.4a depicts the elliptically-shaped particle, enclosed within an infinite matrix, undergoing a shear in the x-y plane, with the shear direction being normal to the plane of the figure. The lower part of (a) shows schematically the in-plane elastic stress field, in which the (constant) stress within the particle is represented by $\tau'$. Fig. 9.4b shows the analogous mode III shear crack in which an elliptical cavity, having the same shape as the particle, is embedded in an infinite matrix with a shear stress equal to $-\tau'$ applied at infinity. Fig. 9.4c shows an oppositely stressed homogeneous continuum body of infinite extent. The in-plane elastic stress field of (a) can be approximated by the superposition of the corresponding stress fields of (b) and (c) establishing the connection between the shearing enclosed particle and the blunt mode III shear crack.

The stress field outside of the particle in Fig. 9.4a can be computed using the Eshelby method [156], and is given by the following equation:

$$\tau_{23} = 2\mu D_{2323} \varepsilon_{23}^I,$$

(9.2)

where identical isotropic elastic behavior is assumed for both the particle and matrix. The quantity, $\varepsilon_{23}^I$, is defined as the stress-free transformation strain ($\varepsilon_{23}^I = \gamma / 2$ in the previous notation). Mura [157] has provided an expression for $D_{2323}$, which is a function of spatial coordinates and particle shape.
Fig. 9.4: Schematic diagram illustrating the connection between the in-plane stress fields of an enclosed, shearing, elliptically-shaped inclusion particle, with that of a blunt, mode III shear crack.
As discussed above, the crack-tip stress field and the particle stress field is approximately related by a stress-shift whose magnitude equals the internal stress of the particle. According to crack-tip-relaxation models, in the small-scale-yielding limit, the plastic-zone size is related to the yield distance, defined by the position for which the stress field equals the matrix flow stress, \( \tau_f \). The stress ahead of the crack-tip in Fig. 9.4b, at a distance given by the yield distance for the enclosed particle, is approximately equal to \( \tau_f + |\tau'| \). Therefore, for the purpose of estimating the RPZ size for the enclosed particle, existing mode III shear-crack solutions were used, but appropriately modified, with the external applied stress replaced by the stress within the particle, and the matrix flow stress replaced by the sum of the flow stress and the particle stress.

A further modification was found to be necessary for application to an oblate spheroidal-shaped particle of interest to the growth model. The in-plane stress field for the elliptically-shaped particle, given by eqn. 9.2, was compared with the in-plane stress field for the oblate spheroidal geometry, along the direction normal to the shear direction. For the same value of the transformation shear, the intensity of the former field was observed to be about twice that of the latter field. A correction was made in order to account for this difference.

In summary, the plastic-zone size was estimated by adapting analogous mode III shear-crack solutions. These solutions involve the external applied stress and flow stress of the matrix, and the following substitutions were found to be necessary for application to the shearing oblate spheroid case:

\[
\begin{align*}
\tau_f & \rightarrow \tau_f + \frac{1}{2} \tau_{23}^I, \\
\tau_{23}^A & \rightarrow \frac{1}{2} \tau_{23}^I.
\end{align*}
\] (9.3a)

(9.3b)

where \( \tau_{23}^I \) is the stress within the oblate spheroidal-shaped particle, and \( \tau_{23}^A \) is the externally applied stress in the crack-tip case. Next, the specific plastic-zone solutions will be presented.
Hult and McClintock [158] solved the elastic/plastic mode III shear-crack problem under the assumptions of perfect plasticity (no strain hardening) and elastic isotropy. The corresponding plastic-zone size $R_o$ is given by the following equation:

$$\frac{R_o}{a} = \frac{2}{\pi} \frac{(1 + \lambda^2)}{(1 - \lambda^2)} E\left[\frac{1}{2}, \frac{2\lambda}{1 + \lambda^2}\right]. \quad (9.4a)$$

with $\lambda$ defined by:

$$\lambda \equiv \frac{\tau_{23}^A}{\tau_f}. \quad (9.4b)$$

In eqn. 9.4a, "a" is the crack length, and $E$ is the elliptic integral of the second kind. This expression for the plastic-zone size was used to estimate the RPZ size for the case of the model-martensitic particle, after applying substitutions 9.3, and replacing "a" by the particle radius, $r$.

The resulting plastic-zone geometry is presented schematically in Fig. 9.5 which shows a cross section of the particle-tip region. The locus of $R$ as a function of the angle, $\alpha$, defines the plastic-zone boundary. Hult and McClintock showed that this boundary is circular in the small-scale yielding limit. The radial-plastic-zone shape was assumed to have a circular cross section, and to "wrap" around the circumference of the particle, forming a torus shape.

The plastic-strain distribution within the RPZ was assumed to be identical to that of the crack-tip case, which is given by [158]:

$$\gamma_p = (\tau_f/\mu) \left( \frac{R}{r_p} - 1 \right) = (\tau_f/\mu) \left[ \frac{R_o \cos(\alpha)}{r_p} - 1 \right] \quad (9.5)$$

where $R$, $r_p$, and $\alpha$ are defined in Fig. 9.5.

The solutions represented by eqns. 9.4 and 9.5 are appropriate for a sharp cracks; however, the model-martensitic particle has a finite tip radius. Therefore, plastic relaxation at a blunt crack-tip is a more appropriate analogue to the problem at hand. Fortunately, extension of the
Fig. 9.5: Schematic illustration of a cross section through the model-martensitic particle particle showing the assumed radial plastic-zone shape.
sharp-crack solution to the blunt-crack case is quite simple. Hult [159] has shown that inasmuch as the root radius of the crack tip is small in comparison to the crack length, the plastic-zone size remains unaffected by blunting. Furthermore, eqn. 9.5 for the plastic-strain distribution holds for a blunt crack, except with the origin shifted ahead of the crack tip by an amount equal to the local root radius. This is equivalent to applying a cut-off distance in the strain equation, much like the core cut-off used in dislocation problems. By analogy, the local particle-tip radius was used as a plastic-strain cut-off distance for the model-martensitic particle.

The plastic-accommodation-work calculation involves the average plastic strain within the RPZ. This average plastic strain was obtained by integrating eqn. 9.5 over the RPZ volume, giving:

\[ \bar{\gamma}_p^R = \frac{\tau_f}{\mu} \]  \hspace{1cm} (9.6)

Although the plastic-accommodation model does not include strain hardening, the rapid rate of martensitic growth necessitates a consideration of rate-dependent plastic flow, leading to "strain-rate hardening". The plastic-flow model (described in Appendix 3) gives the flow stress as a function of strain rate. In order to include rate effects, an effective strain rate was defined for the purpose of computing an effective plastic flow stress, denoted by \( \bar{\gamma}_p^R \), which was used in the above equations, replacing \( \tau_f^R \). The effective plastic strain rate in the RPZ was defined in terms of the plastic strain gradient at the center of the RPZ, and the radial growth velocity, giving the following equations:

\[ \bar{\gamma}_p^R \equiv - V_r \frac{\partial \gamma_p^R}{\partial x} \bigg|_{x=\frac{R_o}{2}} = -4V_r \frac{\tau_f}{\mu} \frac{1}{R_o} \]  \hspace{1cm} (9.7)

Inclusion of a rate-dependence in the flow stress only partially accounts for dynamic effects during plastic accommodation of a growing martensitic particle. It was recognized that the use of the above static solutions, during the incremental analysis, might result in plastic unloading of certain regions due to changes in the variables which
determine the RPZ size. This physically unrealistic condition was prevented by not allowing plastic-zone "shrinkage" in the computer algorithm. Although a rigorous treatment of the dynamic plastic-accommodation process would represent a major refinement to the present growth model, the complexity of this problem would certainly require a major computational effort, and was not attempted here.

9.2.3) Perpendicular Plastic Zone

Recall that the perpendicular plastic zone (PPZ) refers to the region of plastically accommodated material adjacent to the broad faces of the particle. Ling [160] used the Eshelby method to derive stress-field equations for the same geometry and type of transformation strain assumed in the present model. Using these equations, the PPZ thickness, C, was estimated by the yield distance along the direction normal to the plane of the particle. The resulting equation, relating C to \( \frac{\tau_{23}^I}{\tau_f} \) and \( \tau_f \), is rather complex; therefore, a simpler form was obtained by applying a curve-fitting technique, giving the following equations for the PPZ thickness:

\[
\frac{C}{r} \approx 0.3279 \left[ \ln \left( \frac{\tau_{23}^I}{\tau_f} \right) \right]^{0.8171} \quad \text{if} \quad \tau_f \leq \tau_{23}^I, \quad (9.8a)
\]

and:

\[
\frac{C}{r} = 0 \quad \text{if} \quad \tau_f > \tau_{23}^I. \quad (9.8b)
\]

The PPZ thickness was assumed to be constant along the particle faces. Fig. 9.6a shows this assumed plastic-zone geometry, in which a cross-section of a plate-like martensitic particle is drawn schematically, together with a PPZ of thickness, C.

The plastic-strain distribution within the PPZ has not been previously modeled, and its determination probably requires numerical modeling of the plastic-accommodation problem as a whole, including plastic flow near the particle tip. The present model assumed the simplest form for this strain distribution. The plastic-strain gradient, within the PPZ, was assumed to
Fig. 9.6: Schematic illustration of a cross section through the model-martensitic particle showing the assumed perpendicular plastic-zone shape.
scale inversely with the particle radius. This dependence is consistent with the expectation that in the limit of infinite particle radius, the situation reduces to that of homogeneous straining for which the strain gradient is zero. Fig. 9.6b schematically illustrates the resulting plastic-strain distribution, where the plastic strain within the PPZ is denoted by $\gamma^C_p$. Note that this assumed plastic-strain distribution is a linear function of distance away from the interface. The plastic strain as a function of the coordinate, $z' \equiv z - c$ (see Fig. 9.6b) can be written as follows:

$$\gamma^C_p = \frac{\beta C}{r} \left[ 1 - \frac{z'}{C} \right], \tag{9.9}$$

where $\beta$ is a proportionality constant.

The average value of $\gamma^C_p$ was used to compute the plastic-accommodation work. This average plastic strain in the PPZ is given by the following equation:

$$\overline{\gamma^C_p} = \frac{\beta C}{2r}. \tag{9.10}$$

Strain-rate hardening was accounted for in the same way as in the RPZ case, by utilizing a rate-dependent flow stress in eqn. 9.8. For the assumed form of plastic-strain gradient, the corresponding effective plastic strain rate is given by the following equation:

$$\overline{\gamma^C_p} = -\gamma_c \frac{\beta}{r}. \tag{9.11}$$

which is simply the negative of the thickening rate times the plastic-strain gradient. Furthermore, the PPZ was not permitted to decrease in size during growth simulations, thus avoiding the (unphysical) possibility of plastic unloading.
9.2.4) **Interfacial Forces**

As mentioned in Section 9.1, plastic accommodation introduces two types of interfacial forces in addition to those necessary to describe thermoelastic martensitic growth. These additional forces are due to energy dissipations arising from plastic-accommodation work and interfacial friction. Another way in which plastic accommodation may alter growth behavior, relative to the thermoelastic case, is through the modification of the stored elastic energy of the system. The following sections outline the approach used in modeling these effects.

9.2.4.1) **Plastic-Accommodation Work**

The interfacial forces due to the dissipation of plastic-accommodation work were defined in the same manner as the forces arising from the thermodynamic potential (see eqn. 8.6). However, in certain cases it was necessary to approximate the partial derivatives by finite-increment ratios. The following expressions define these forces in terms of the rate of energy dissipation accompanying an increase in \( r \) (at constant \( c \)), or an increase in \( c \) (at constant \( r \)):

\[
\begin{align*}
g_r^p & \equiv \frac{1}{A_r} \left[ \frac{\delta W^p}{\delta r} \right]_c \approx \frac{1}{A_r} \left[ \frac{\delta W^p}{\delta r} \right]_c, \quad (9.12a) \\
g_c^p & \equiv \frac{1}{A_c} \left[ \frac{\delta W^p}{\delta c} \right]_r \approx \frac{1}{A_c} \left[ \frac{\delta W^p}{\delta c} \right]_r. \quad (9.12b)
\end{align*}
\]

where the effective interfacial areas, \( A_r \) and \( A_c \), were defined in eqns. 8.10.

Equation 9.1 shows that an increase in particle radius, at constant thickness, generally reduces the stress within the particle, so that both \( R_0 \) and \( C \) remain unchanged, since these plastic-zone sizes were not allowed to decrease. However, the RPZ and PPZ volumes increase, simply by virtue
of the geometric changes in the circumference and area of the particle. The incremental work due to this effect was approximated by the product of three quantities: 1) the average plastic strain, 2) the effective flow stress, and 3) the incremental plastic-zone-volume change, for the corresponding plastic zones. In addition, plastic work is done during advancement of the RPZ as the particle radius increases. This work was computed by integrating the product of the effective flow stress and the incremental increase in plastic strain within the RPZ. The volume of integration was restricted to only those regions which experience an increase in plastic strain during RPZ advancement, which corresponds to $|\alpha| < \pi/4$ in Fig. 9.5.

An increase in particle thickness, at constant radius, results in an increase in $\tau_{23}^I$, according to eqn. 9.1. Thus, in addition to PPZ advancement, both the PPZ and RPZ expand in size. The incremental work done during PPZ advancement was computed similarly to that accompanying RPZ advancement, except that the integration was performed over the entire PPZ volume. The derivative entering the definition of interfacial force was obtained as:

$$\frac{\partial W^P}{\partial c} = \frac{\partial W^P}{\partial R_o} \frac{\partial R_o}{\partial c} + \frac{\partial W^P}{\partial C} \frac{\partial C}{\partial c}.$$  (9.13)

The derivatives, $\partial W^P/\partial R_o$ and $\partial W^P/\partial C$, involve the average plastic strain and effective flow stress in the corresponding plastic zones. The small-scale-yielding limit of eqn. 9.4a for $R_o$ was used to compute $\partial W^P/\partial R_o$.

The dependence of the internal stress on particle thickness, $\partial \tau_{23}^I/\partial c$, was needed to form the remaining derivatives ($\partial R_o/\partial c$ and $\partial C/\partial c$) in eqn. 9.13. The thermoelastic limit was used to approximate this dependence, by applying eqn. 9.1, which does not include plastic-relaxation effects.
The resulting interfacial forces can be written as follows:

\[ g^P_r = -\left[ \frac{3\pi^2}{16} \frac{R_o^2}{rc} \frac{\tau^R_f}{\gamma_p} + \frac{3\pi}{2} \frac{c}{c} \frac{\tau^C_f}{\gamma_p} + \frac{3\pi}{4} \frac{R_o}{c} \frac{\tau^C_f}{\gamma_p} \ln \left( \frac{R_o}{r_0} \right) - 0.06 \right] \], \hspace{1cm} (9.14a)

\[ g^P_c = -\left[ 3\tau^C_f \frac{\gamma_c}{\gamma_p} + 0.8c \frac{\tau^C_f}{\gamma_p} \left( \ln \left( \frac{I}{\tau^C_f} \right) \right)^{0.2} + \frac{3\pi R_o}{c} \frac{\tau^R_f}{\gamma_p} \frac{\tau^R_f}{\gamma_p} \frac{\tau^R_f}{\tau_{23}} \left( \frac{R_f}{\tau^2_{23}} \right)^3 \right] \], \hspace{1cm} (9.14b)

where \( r_0 \) is the local radius of the particle tip, used as a cut-off distance in the plastic-strain equation (eqn. 9.5). The superscripts, R and C, distinguish between quantities in the RPZ and PPZ, respectively. The order in which the terms in the above equations are written, corresponds to the order in which they were described above.

9.2.4.2) Interface-Frictional Work

Dislocation debris produced in the austenite ahead of an advancing martensitic interface during plastic accommodation is expected to impede interfacial motion through interaction with the interfacial dislocations. This effect is quite analogous to strain hardening during plastic deformation of single crystals via the forest-dislocation-cutting mechanism, but with two important exceptions. First, the measured increase in macroscopic flow strength during plastic deformation of crystals represents an average of many interactions of varying intensity, and does not reflect the maximum local interaction between dislocations. Furthermore, individual dislocations gain assistance from bowing and cross-slip processes in overcoming strong obstacles, effectively permitting the dislocations to seek paths of least resistance to slip. In constrast, interfacial dislocations are constrained to lie in the interface, and must pass through obstacles in their path, produced by plastic deformation of the adjacent austenite. Therefore, strain hardening can be expected to be more effective in inhibiting interfacial motion than in raising the flow strength of crystals.
Interaction between the interfacial dislocations and the dislocation substructure adjacent to the interface may be regarded as a source of increased resistance to interfacial motion, producing an energy dissipation in the form of interface-frictional work. This work reduces the net-available driving force for interfacial motion, effectively imposing a resisting interfacial force. This force was added to the intrinsic athermal frictional force, introduced in the thermoelastic growth model, during the plastic-growth stage of the growth simulation.

The radial and perpendicular forces due to dislocation interactions will be influenced by the detailed nature of the substructure within the respective plastic zones. However, even if such information were available, prediction of the interfacial forces would require knowledge of the interface/dislocation interaction. While the mechanics of this specific interaction have not been modeled, recent efforts to model the interaction between martensitic interfaces and discrete particles [134,135] suggest that the general nature of the interaction is similar to that of individual dislocations.

In the present study, a phenomenological approach was used, in which the interface/dislocation interaction was assumed to be proportional to an effective interfacial plastic strain in the plastic zone ahead of the interface. Thus, the radial and perpendicular interface-frictional forces, due to interface/dislocation interactions were defined by the following equations:

\[
\begin{align*}
\gamma_r^d &= -\theta_i \hat{\gamma}_p^R, \\
\gamma_c^d &= -\theta_i \hat{\gamma}_p^C,
\end{align*}
\]  

(9.15a)

(9.15b)

where \(\theta_i\) is a constant, characterizing the magnitude of the interaction, and \(\hat{\gamma}_p^R\) and \(\hat{\gamma}_p^C\), are the effective interfacial plastic strains in the RPZ and PPZ, respectively. \(\hat{\gamma}_p^C\) is given by eqn. 9.9 with \(z'=0\):

\[
\hat{\gamma}_p^C = \frac{\beta C}{r}.
\]

(9.16)
For the assumed plastic-strain distribution in the RPZ (eqn. 9.5), the locus of maximum plastic strain corresponds to straight lines along $\alpha = \pm \pi/4$. Since plastic unloading was not allowed, these strains are preserved in the "wake" left behind by the advancing plastic zone, through which the interface must pass. Accordingly, the effective interfacial plastic strain in the RPZ was obtained by averaging the plastic strains, given by eqn. 9.5 with $\alpha = \pi/4$, along the line defined by $\alpha = \pi/4$ in Fig. 9.5. This average was taken from the RPZ cut-off distance to the point on this line, at a distance above the plane of the particle defined by an effective particle semithickness. This latter quantity was defined by: $2c^{\text{eff}} = \frac{A_r}{2\pi r}$, that is, by considering the equivalent pill-box shaped particle having the same radius and effective radial interfacial area as the model-martensitic particle. Application of this procedure resulted in the following equation:

$$
\gamma_p^R = \frac{\tau_f}{\mu} \left[ \frac{3\sqrt{2}}{4} \frac{R_0}{c} \ln \left( \frac{2\sqrt{2} c}{3 r_0} \right) + \frac{3r_0}{2c} - \frac{\sqrt{2}}{2} \right]. \quad (9.17)
$$

9.2.4.3) Elastic Strain Energy

Plastic accommodation relaxes a portion of the stored elastic energy and reduces the internal stresses within the martensitic particle. The effect of relaxation on the elastic interfacial forces, $\mathcal{g}_r^{\text{el}}$ and $\mathcal{g}_c^{\text{el}}$, was modeled by generalizing these forces from the thermoelastic case, giving the following modified definitions (compare with eqns. 8.4 and 8.12):

$$
\mathcal{g}_r^{\text{el}} = -\frac{A^{\text{eff}}}{2} \frac{c}{r^{\text{eff}}}, \quad (9.18a)
$$

$$
\mathcal{g}_c^{\text{el}} = -\frac{4A^{\text{eff}}}{3} \frac{c}{r^{\text{eff}}}, \quad (9.18b)
$$

with:

$$
A^{\text{eff}} = \frac{\pi}{8} \frac{(2-v)}{(1-v)} \left[ \gamma_r^{\text{eff}} \right]^2. \quad (9.19)
$$
Relaxation due to RPZ formation was modeled by using an effective particle radius, \( r_{eff} > r \), in the computation of the elastic forces. PPZ formation results in the direct cancellation of displacements, which was conveniently modeled by assuming an effective transformation strain, \( \gamma_{eff} < \gamma_r \). The internal stress, given by eqn. 9.1, was modified in a similar manner, substituting \( \gamma_{eff} \) for \( \gamma_r \), and \( r_{eff} \) for \( r \).

Although it is clear that plastic relaxation ahead of a martensitic particle relaxes the elastic stresses, modeling the magnitude of this effect represents a complex problem. The similar problem concerning the redistribution of stresses due to plastic relaxation ahead of a tensile crack was addressed by Irwin [161,162], who introduced the concept of an equivalent elastic crack length, increased over the actual crack length by an amount equal to the yield distance. This plastic-zone correction factor accounts for elastic-stress relaxation within the plastic zone such that the stress-intensity factor of the actual crack is equivalent to that corresponding to the corrected crack length. For small-scale yielding, the plastic-zone size is equal to twice the yield distance so that the plastic-zone correction factor is equal to half of the plastic-zone size. These results were adopted by analogy to the problem of plastic relaxation of a martensitic particle. Specifically, plastic relaxation in the RPZ, leading to a reduction in the elastic interfacial forces, was approximately accounted for by assuming that the effective particle radius is given by:

\[
r_{eff} = r + R_O / 2.
\]

Displacements within the PPZ directly cancel those displacements produced by the transformation strain. The total displacement across the PPZ was obtained by integrating the displacements along the particle normal, from the interface to the PPZ boundary. The effective reduction in the transformation strain was defined as the total displacement divided by the particle semithickness, \( c \). Subtraction of this quantity from \( \gamma_r \) results in the following equation for the effective transformation strain:

\[
\gamma_{eff} = \gamma_r - \frac{\beta c^2}{2 rc}.
\]

(9.20)
Two additional corrections to the transformation strain were made in order to account for incorporation of plastic displacements into the growing particle, as the interface sweeps through the deformed austenite. Consideration of the nature of the deformation in the RPZ and PPZ leads to the conclusion that the plastic strains contribute to an increase, and, decrease, respectively, in the effective transformation strain. During each growth increment, the effective interfacial strains, $\gamma^R_p$ and $\gamma^C_p$, were appropriately averaged into correction factors for the effective transformation strain.

9.2.5) **Kinetic Criterion for the Initiation of Plastic Accommodation**

A constitutive model for plastic flow in Fe-24Ni and Fe-32Ni, is described in detail in Appendix 3. This model gives the flow stress corresponding to an imposed plastic strain rate, which enters into the appropriate expression for strain rate (eqn. 9.7 or 9.11). However, there is no guarantee that a solution exists, between the constitutive equations, and the equations describing the kinematics of flow in the plastic zones. Indeed, it was found that at sufficiently-high radial growth rates, the equations giving the strain rate in the RPZ (defined by eqn. 9.7), and the constitutive equations could not be simultaneously satisfied.

The existence of solutions is illustrated in Fig. 9.7, in which strain rate is plotted versus flow stress. The solid lines depict the constitutive response of the two alloys, at their respective transformation temperatures (200K for Fe-32Ni; 400K for Fe-24Ni), based on the flow model presented in Appendix 3. The dashed lines represent solutions to eqns. 9.4 and 9.7, for two different ratios of the radial velocity to particle radius, $v/r$, such that $(v/r)_1 > (v/r)_2$. Of course, the solutions do not depend solely on $v/r$, but for a given particle shape ($c/r$) and effective transformation strain, solutions lie approximately along the dashed lines. Solutions consistent with the kinetic flow behavior are represented by the intersection between the dashed and solid lines. Due to the shapes of these curves, intersection occurs at either one or two points. In the case of two intersections the lower-strain-rate solution is
Fig. 9.7: Flow curves (solid) for Fe-32Ni at 200 K and Fe-24Ni at 400 K, predicted by the slip-kinetics model, presented in Appendix 3. Also included are solutions to the radial-plastic-zone model (dashed), corresponding to two ratios of \( v/r \), where \( v \) is the radial growth rate. \((v/r)_1 > (v/r)_2\).
more physically appealing, since it leads to strain rates which decrease with decreasing growth rate.

Referring to Fig. 9.7, \((v/r)\) corresponds to a case in which no solutions exist, which was interpreted to result from an insufficient dislocation mobility, leading to an inability to maintain plastic-zone formation. In other words, the plastic-zone formation process was considered to depend critically on the existence of simultaneous solutions to the kinematics of plastic accommodation, and the kinetics of plastic flow. As the ratio, \(v/r\), decreases, a critical condition is eventually reached, whereby the dashed and solid curves meet at a point near the knee of the flow curve. This condition will be referred to as the kinetic criterion for the initiation of plastic accommodation. Prior to meeting this condition, for example at small sizes and high radial velocities, radial growth was assumed to proceed elastically, with satisfaction of the kinetic criterion being a necessary condition for RPZ formation. Note that for \((v/r)\), the kinetic criterion has been met for Fe-24Ni, but not for Fe-32Ni. This is due primarily to the higher dynamic flow strength, and lower temperature for Fe-32Ni; both of these factors strongly influence the shapes of the flow curves.

9.3) Estimation of Parameters

With the exception of \(\beta\) and \(\Theta\), the parameters for the nonthermoelastic growth model are identical to those introduced in Chapter 8, and listed in Table 8.1. The following parameters were assumed to be the same for both Fe-24Ni and Fe-32Ni: \(\chi, \sigma, \gamma, \xi, v, v_0, Q_0, v^w, G_{\text{th}}, \Omega, v_s,\) and \(d\). These parameters are either insensitive to the difference in composition, or represent rough estimates for which a distinction is not warranted\(^2\). The remaining parameters in Table 8.1 are: \(M_s, Ag^{\text{ch}}, T^{\text{ad}}, \mu, B_{a,o}\).

\(^2\)The transformation-strain parameters, \(\gamma\), and \(\xi\), were estimated for Fe-32Ni based on data for Fe-30Ni. This strain is expected to be approximately the same for these two alloys because they show similar morphologies and habit planes. However, Fe-24Ni differs in both morphology and habit from Fe-30Ni and Fe-32Ni; consequently, the assumption of identical transformation strain, carries a greater degree of uncertainty.
As in the thermoelastic growth model, the temperature of the austenite at the start of growth was taken to be equal to the bulk $M_s$ temperature. Kaufman and Cohen [145] determined this temperature to be about 400 K in Fe-24Ni.

Kaufman and Nesor [146] reported thermochemical data for Fe-24Ni giving $\Delta g_{\text{ch}}^c$ as a function of temperature. The adiabatic temperature was computed to be: $T^{\text{ad}} = 526$ K, using the method described in Chapter 8. For this calculation, the thermal properties of the martensitic phase were approximated by those of pure $\alpha$-Fe at 400 K. For the temperature range: $M_s \leq T \leq T^{\text{ad}}$, $\Delta g_{\text{ch}}^c$ is approximately linear in temperature:

$$\Delta g_{\text{ch}}^c(\text{Fe-24Ni}) \approx 9.30(10)^5 T - 5.34(10)^8 \text{ J/m}^3 \tag{9.21}$$

The isotropic elastic shear modulus for Fe-24Ni at 400 K was approximated by that of fcc Fe-25.1Ni-0.26C, measured by Goldman and Robertson [147]. The resulting value: $\mu = 67.1$ GPa, is slightly greater than that estimated for Fe-32Ni at 200 K (63.5 GPa).

The drag coefficient depends linearly on temperature, so that the major difference between $B_{a,0}$ for the two alloys is due to the difference in transformation temperature. Therefore the expression for $B_{a,0}$, given in the previous chapter for Fe-32Ni: $B_{a,0} \approx 528.7 T$ N·s/m$^3$·K, was also used to compute the drag coefficient for Fe-24Ni. This value of the drag coefficient was applied to the thickening rate; radial growth was again enhanced by adjusting the drag coefficient as described in Chapter 8.

Recall that the coefficient, $\beta$, determines the plastic-strain gradient in the perpendicular plastic zone through eqn. 9.9. As discussed in Section 9.2.3, this single-parameter strain function is the simplest form, consistent with the expected limiting behavior. Since the magnitude of $\beta$ determines the amount of strain-energy relaxation for a given PPZ size, eqn. 9.20 gives an upper limit to $\beta$ for which the effective transformation strain vanishes:

$$\beta_{\text{max}} = \frac{2\gamma rc}{C^2} \tag{9.22}$$
This parameter can be determined experimentally by precise measurement of the surface relief produced by fully-developed martensitic units. For example, interferometry can be used to determine surface displacements: the curvature of interference fringes crossing a unit gives a direct measure of the strain gradients. By measuring the average curvature of these fringes in the austenite at the interface, a value can be estimated for $\beta$.

Patterson and Wayman [107] presented interference micrographs showing surfaces relief near martensitic plates in Fe-32Ni. Analysis resulted in an estimated of $\beta$ in the range: 0.2 to 0.4. However, preliminary growth simulations showed that this estimate was as much as one order-of-magnitude greater than the maximum allowed value, given by eqn. 9.22. Notwithstanding the oversimplified nature of the PPZ model, other factors contributed to this apparent discrepancy. The size of the plate used to estimate $\beta$ was very difficult to determine, and a number of plates appeared to be interacting, producing a complex strain pattern. Moreover, the resolution of the interference fringes was not high enough to permit an accurate determination of their local curvature at the interface.

Careful high-resolution microinterferometry on isolated martensitic units might lead to a reasonable estimate of $\beta$. In addition, finite element methods could be used to assess the validity of the assumed plastic-strain distribution, and to calculate an effective value for $\beta$. In the present study, $\beta$ was treated as an adjustable parameter.

In Section 9.2.4.2, $\Theta_1$ was defined as a strain-hardening coefficient, which characterizes the interaction between the interface and the dislocation substructure produced in the plastic zone. This coefficient, multiplied by the effective interfacial plastic strain, gives the corresponding interface-frictional force (see eqns. 9.15). The following experimental investigation provides insight into the magnitude of $\Theta_1$.

Knorovsky [29] performed a series of experiments in which the martensitic transformation in single crystals of Fe-31Ni was observed in temperature-gradient specimens. The transformation propagated up the
temperature gradient by autocatalytic nucleation and growth, but at a critical temperature, growth of individual plates arrested spontaneously. Assuming that the growth arrest was produced by the interaction of the interface with a radial plastic zone, the driving force at the maximum growth temperature gives the following estimate for the interface-frictional force: $\tau^d_r \approx 0.13$ GPa. Simulations using the present growth model resulted in $\hat{\nu}_r^p \approx 0.16$ when the radial plastic zone formed giving: $\Theta_1 \approx 0.8$ GPa. This value is equal to about $\mu / 80$, which is considerably greater than the stage II strain-hardening rate for multiple slip in single crystals [163], consistent with expectation (see Section 9.2.4.2). The above estimate for $\Theta_1$ is very approximate, and serves only as an order-of-magnitude guide. In practice, $\Theta_1$ was also treated as an adjustable parameter.

9.4) Growth-Simulation Results and Discussion

The starting configuration for the nonthermoelastic growth simulations was chosen based on the procedure described in Section 8.9. Accordingly, the initial particle dimensions for the Fe-32Ni were assumed to be: $r=77.0$ nm and $c=1.78$ nm, the same as in the thermoelastic growth simulation described in the previous chapter. For Fe-24Ni, slightly different starting values were used because of the small difference in the position of the free-energy saddle point; the initial dimensions were taken to be: $r=75.6$ nm and $c=1.72$ nm. In both cases, the initial temperature of the parent and product phases was assumed to be the $M_s$ temperature.

Due to the energetic restriction on plastic accommodation arising from the incapability of lattice-dislocation generation at small sizes (Section 9.2.1), the initial stage of growth is elastic, that is, the transformation strain is elastically accommodated. The kinetic criterion for the initiation of plastic accommodation was modeled for the case of radial-plastic-zone (RPZ) formation, and therefore, does not apply to plastic yielding in regions adjacent to the particle faces. Consequently,
the perpendicular plastic zone (PPZ) might possibly form prior to RPZ formation. In the growth simulations two distinct cases were considered. In the first case, the PPZ was envisioned to develop by the "spreading" of plasticity back away from the particle-tip region, once the energetic criterion for dislocation nucleation was met. This process was regarded to occur even before fulfillment of the kinetic criterion for RPZ formation. While this assumption is somewhat arbitrary, it represents a limiting case in which dislocation sources are produced near the particle tip, though full scale radial plasticity is not dynamically sustainable. In the second case, RPZ formation was assumed to be a necessary requirement for PPZ formation.

9.4.1) Computed Nonthermoelastic Growth Behavior

The computed growth paths during the initial period of elastic growth were similar to the results described in Chapter 8 (in the case of Fe-32Ni the results were necessarily identical). However, plastic accommodation was found to have a dramatic affect on growth, the details of which differed substantially between the two alloys.

Figure 9.8a summarizes the predicted martensitic-growth dynamics for Fe-24Ni and Fe-32Ni, where the radial interfacial velocity is plotted as a function of particle radius. The corresponding rises in interfacial temperature at the particle tip are plotted in Fig. 9.8b. The two parameters, $\Theta_1$ and $\beta$, characterizing the interfacial/plastic-zone interaction, and the strain-field intensity in the PPZ, respectively, were assumed to be: $\Theta_1=1.0$ GPa and $\beta=0.001$. As in the thermoelastic growth simulations, the radial growth rate rapidly accelerated into the phonon-drag controlled regime, reaching a maximum value. The radial velocity then decreased at a much lower rate. Recall that the maximum growth velocity is determined by a combination of factors including the dependence of interfacial temperature on growth rate and local tip radius, as well as the temperature dependence of the chemical driving force and the phonon-drag coefficient. As can be seen in Fig. 9.8b, the interfacial
Fig. 9.8: Predicted radial-growth behavior of a single martensitic particle in Fe-24Ni transformed at 400 K. and Fe-32Ni transformed at 200 K. $\Theta_i = 1.0$ GPa; $\beta = 0.001$.

a) Radial growth velocity versus particle radius.
b) Interfacial temperature at the particle tip.
temperature increased even while the interfacial velocity decreased, similar to the thermoelastic case. The decrease in radial velocity was primarily due to this rise in interfacial temperature. In addition, the radial velocity for Fe-24Ni was considerably lower than that of Fe-32Ni due to the difference in initial temperature (400 K versus 200 K), since the phonon-drag coefficient is proportional to temperature (eqn. 8.16).

The arrows in Fig. 9.8a indicate the point at which the energetic criterion for plastic-flow initiation was satisfied. This occurred at r=3.8 μm for Fe-24Ni, and r=3.2 μm for Fe-32Ni, with c/r being about 0.02 in both cases. However, the kinetic criterion region was not satisfied at this radial velocity and particle size, for either alloy. The ratio of \( v_r / r \) was too great to permit a solution between the plastic-zone kinematics and the kinetics of plastic flow; therefore, elastic radial growth continued beyond this critical condition. However, plastic accommodation was allowed to occur along the particle faces leading to PPZ formation. The initial PPZ size for Fe-24Ni and Fe-32Ni was found to be: C/r=0.61 and C/r=0.32, respectively, which is quite large, particularly in the case of Fe-24Ni which has a lower flow stress than Fe-32Ni. However, with the assumed low value of \( \beta \), plastic relaxation arising from cancellation of displacements in the PPZ was minimal, with \( v_r^{\text{eff}} \) being reduced by less than 5% in both cases. The rather small magnitude of \( \beta \) resulted in very small plastic strains in the PPZ (for example \( v_p^{C}=0.0003 \)). Consequently, the forces due to plastic work in the PPZ and interfacial friction were negligible compared with the chemical and elastic interfacial forces. The effect of increasing \( \beta \) was explored in a separate calculation, and will be presented shortly.

Elastic radial growth was interrupted for Fe-32Ni at a radius of 123 μm, at which point the kinetic criterion for RPZ formation was satisfied, marking the initiation of radial plasticity ahead of the particle tip. In Section 9.2.5 it was pointed out that for a given aspect ratio and effective transformation strain, the kinetic criterion corresponds to \( v_r / r \) decreasing to a critical value. For the assumed value
of Θ_i, the radial interface-frictional force caused immediate radial growth arrest. This force was comparable in magnitude to the chemical force. Due to relaxation, the radial elastic force decreased by more than a factor of two, greatly reducing its significance. Also the forces due to plastic work in the RPZ, and interfacial energy were found to be small compared with the other forces.

A similar set of circumstances was realized in the Fe–24Ni growth simulation; however, occurring at a much smaller radius of 20 μm. At this particle size, the kinetic criterion for RPZ formation was met resulting in a precipitous drop in radial velocity from 520 m/s to 5(10)^{-8} m/s. Very similar observations concerning the relative magnitudes of the interfacial forces were made in this case; the radial elastic force dropped severely, while the interface-frictional force became comparable to the chemical force. Furthermore, the plastic work and interfacial energy made negligible contributions to the net radial force.

Following the near radial growth arrest (with Θ_i=1.0 GPa), the radial velocity increased to a maximum value of 30 m/s before gradually decreasing. This behavior is indicated in Fig. 9.8a by the dashed curve. Unfortunately, this portion of the growth simulation was considered to be unreliable because of the extensive degree of plasticity resulting from the reduced dynamic flow stress at the low radial growth rate. The computed plastic strain rate in the RPZ resulted in a flow stress close in magnitude to the athermal stress, which was estimated to be only 8 MPa—smaller than the internal stress within the particle. The computed RPZ size corresponding to this plastic radial growth exceeded five times the particle radius. The plastic-zone model is not capable of dealing with such large-scale plasticity; therefore, the nonthermoelastic growth model is considered to be limited to the prediction of the onset of plastic accommodation in such plastically soft alloys.

In a similar calculation with Θ_i=1.2 GPa, the onset of plastic accommodation ahead of the particle tip produced immediate radial growth arrest. Although the Fe–32Ni alloy required a slightly lower value of Θ_i to produce arrest, the difference in not considered to be significant.
The major difference in the predicted radial-growth behavior between Fe-32Ni and Fe-24Ni is the extent of the elastic radial-growth event prior to plastic accommodation ahead of the growing martensitic particle. For a strain-hardening coefficient, $\Theta_1$, in excess of 1 GPa, this plastic accommodation process is predicted to result in immediate radial-growth arrest, with the final particle radius of the two alloys differing by a factor of six. The reason for this difference lies in the vastly different dynamic flow behavior predicted for these two alloys. As can be seen in Fig. 9.7, the flow-curve shape, and in particular, the position of the distinct knee, determines the critical ratio of $v_r/r$ for which plastic-zone solutions exist (see Section 9.2.5). The position of the knee in each curve is influenced by temperature (primarily through the drag coefficient), and the magnitude of the threshold stress. Of these two factors, the threshold stress is more important in determining the critical ratio. The dynamic flow model predicts a much lower threshold stress for Fe-24Ni compared with Fe-32Ni, and therefore, a higher critical ratio. Thus, for comparable radial growth rates, radial plasticity is expected to occur earlier (at a smaller particle size) in Fe-24Ni. The extent of elastic radial growth is further reduced in Fe-24Ni, compared with Fe-32Ni, because of the lower radial growth rate, which results in a smaller ratio of $v_r/r$ at a given radius.

The nonthermoelastic martensitic growth model therefore predicts that for a sufficiently strong plastic-zone/interface interaction, characterized by $\Theta_1$, radial growth arrest will occur immediately upon formation of the RPZ. The critical condition for RPZ formation is determined primarily by the mechanical threshold stress of the austenite, and the radial growth rate of the martensitic particle. The potential implications of these findings on the lath-to-plate morphological transition in ferrous alloys will be discussed in the following section.

The above calculations assumed that plastic accommodation in the austenite adjacent to the martensitic particle begins once the energetic criterion for dislocation generation is met. With an assumed value of $\beta=0.001$, the effect of this accommodation was inconsequential, since the
resulting plastic strains were very small. Therefore, the growth event prior to plastic-zone formation ahead of the particle may be considered to be completely elastic in those calculations. However, it was found that for larger values of $\beta$, the effect of this perpendicular plasticity can be significant.

The effect of increasing $\beta$ was explored by repeating the calculation for Fe-32Ni, with the same value of $\Theta_i$, but with $\beta$ increased by a factor of 25 to $\beta=0.025$. Upon formation of the PPZ at $r=3.2 \, \mu m$, the effective transformation strain relaxed by about 25%. This relaxation produced an almost 50% decrease in the radial elastic force; it might have been anticipated that this would lead to an enhancement in the radial growth rate. However, the plastic work in the PPZ was appreciable for this value of $\beta$, causing the radial force due to the dependence of the PPZ volume on particle radius to more than compensate for the reduction in the elastic radial force. Consequently, the radial velocity actually decreased from 925 m/s to 901 m/s when the PPZ formed. Following PPZ formation, elastic radial growth continued until RPZ formation at a particle radius of 190 $\mu m$, considerably greater than in the corresponding simulation assuming $\beta=0.001$. Although the increase in $\beta$ resulted in a slight decrease in radial velocity, the critical ratio of $v_r/r$ depends on the effective transformation strain which was reduced by relaxation in the PPZ. Therefore elastic radial growth persisted to a larger particle size.

For the simulation assuming $\beta=0.001$, the thickening behavior in Fe-32Ni prior to the onset of radial plasticity was not significantly different from the thermoelastic case described in the previous chapter. As in the thermoelastic growth simulation, the interfacial temperature rose to a maximum of 254 K---60% of the adiabatic limit. In Fe-24Ni the thickening rate was lower due to the difference in low-velocity interfacial kinetic behavior, as depicted in Fig. 8.4. The maximum thickening rate in Fe-24Ni was 11.4 m/s compared with 19.8 m/s in Fe-32Ni. Because of the lower velocity in Fe-24Ni, the interfacial temperature increased to only 24% of the adiabatic limit.
Figure 9.9 summarizes the computed thickening behavior for a growth simulation in Fe-32Ni with $\Theta_1=1.0$ GPa and $\beta=0.025$; the thickening rate is plotted as a function of particle semithickness. The initial period of rapid acceleration matched the behavior predicted for thermoelastic growth. The arrows in Fig. 9.9 indicate the point at which the energetic criterion for plastic accommodation was met; the PPZ was then allowed to form. In contrast to the $\beta=0.001$ case, the more intense plastic-strain gradient resulted in a significant degree of relaxation with the effective transformation strain decreasing by 25% to $\gamma_{eff}=0.15$. As mentioned above, the radial velocity immediately decreased from 925 m/s to 901 m/s. Concurrently, the thickening rate immediately dropped from 18.5 m/s to 10.2 m/s due to the perpendicular interfacial forces derived from plastic work ($\mathcal{F}_P^p$) and interface-frictional work ($\mathcal{F}_c^d$), even though the elastic strain energy decreased by a factor of two. The thickening rate continued to decline reaching a minimum of 9 m/s, and then increased as $\mathcal{F}_P^p$ and $\mathcal{F}_c^d$ decreased due to a decline in the characteristic PPZ strains, $\gamma_P^p$ and $\gamma_c^p$. The effective transformation strain initially increased, due to the incorporation of PPZ displacements into the particle, reaching a maximum of 0.17 at c=1 $\mu$m, before decreasing monotonically to 0.147 at c=3 $\mu$m. Although the details of this process are strongly dependent on the rather approximate plastic-zone model, the results of this calculation serve to demonstrate the complexity of the interactions introduced by plastic accommodation.

Further thickening prior to the onset of radial plasticity at c=3 $\mu$m was considerably more "well-behaved" as the velocity gradually declined in response to an increasing interfacial temperature. Upon RPZ formation at c=3 $\mu$m, relaxation in the RPZ produced a three-fold decrease in the perpendicular elastic restraining force, resulting in a large boost in the thickening rate from 11.3 m/s to 565 m/s. The significance of this enormous increase in thickening rate is unclear, but it may partially account for the persistence of twinning as the mode of the lattice-invariant deformation during the thickening stage of growth. At this point, the growth simulation was stopped due to the excessive degree of radial plasticity relative to small-scale yielding.
Fig. 9.9: Predicted thickening behavior of a single martensitic particle in Fe-32Ni transformed at 200 K. The thickening rate is plotted as a function of particle semithickness. $\theta_1=1.0$ GPa; $\beta=0.025$. 
The effect of delaying perpendicular plasticity until the onset of radial plasticity was found to be insignificant for $\beta=0.001$. In both alloys, a higher value of $\beta=0.025$ did not change the particle radius at which the initiation of radial plasticity was observed.

One of the initial objectives of this study was to simulate plastic growth following the onset of plastic accommodation ahead of the particle tip. Such a study is needed in order to predict the final aspect ratio of plate martensite, which undergoes appreciable plastic relaxation. However, as pointed out above, the reduction in dynamic flow strength accompanying the reduction in radial velocity resulted in large-scale plasticity, which the current radial-plastic-zone model is incapable of handling. This limitation is most severe in the final thickening growth stage because the flow stress reduces to the athermal limit, while the stresses within the particle increase. Future improvements of the martensitic growth model should be concentrated in the area of large-scale plastic accommodation.

Throughout these calculations, the martensitic phase was assumed to be elastically accommodated; plastic accommodation was considered to occur only in the surrounding austenite. Observations on the substructure of both plate and lath martensite in Fe-Ni alloys [107,109] suggest that the martensite does experience severe plastic deformation. However, plastic accommodation in the martensite may be inhibited during the initial rapid radial-growth event due to strain-rate effects, similar to the case of plastic accommodation in the austenite. Nevertheless, the possibility that the martensite undergoes plastic accommodation even during the early stages of growth cannot be ruled out. The major effect of plastic accommodation in the martensite would be to relax elastic strains, reducing the stored elastic strain energy. The resulting dislocation debris, however, would not interact directly with the advancing interface, distinguishing this type of plastic accommodation from that occurring in the austenite. Therefore, the potential for growth arrest depends chiefly on plastic accommodation in the austenite, and plastic relaxation of the martensite would only influence the details of this process. A discussion of the potential role of plastic accommodation in the martensite on the thickening behavior of plate martensite will be presented in Section 9.4.3.
In summary, the nonthermoelastic growth simulations predict that elastic radial growth at microscopic particle sizes is stabilized because of an inability to generate dislocations in the highly stressed region ahead of the particle tip. At larger sizes, radial plasticity is delayed by dislocation-mobility factors related to the growth-rate dependence of the plastic strain rate. The large difference in dynamic flow behavior and growth rate between the alloys Fe-24Ni and Fe-32Ni produced a large difference in the extent of elastic radial growth. The onset of radial plasticity occurred much earlier in Fe-24Ni compared with Fe-32Ni. Furthermore, assuming the same set of parameters ($\Theta_1=1.0$ GPa, $\beta=0.001$), radial plasticity resulted in immediate radial-growth arrest in Fe-32Ni, whereas in Fe-24Ni, the onset of radial plasticity was followed by a highly plastic mode of radial growth. The implications of these differences in growth behavior on the lath-to-plate morphological transition will be discussed in the following section.

9.4.2) Radial-Growth Arrest and the Morphological Transition

In Chapter 7 a brief description was presented concerning the various martensitic-product morphologies that are observed in ferrous alloys. In general, alloys which transform at very low temperatures exhibit a plate morphology resembling that predicted for thermoelastic martensitic transformations. Those alloys which transform above room temperature, typically show what is referred to as a lath morphology. Within a given alloy system such as Fe-Ni, a lath-to-plate morphological transition is frequently observed with increasing alloy content, and decreasing transformation temperature. However, these two variables—temperature and composition—are not necessarily fundamental variables directly controlling the transition.

Lath martensite has been associated with extensive plastic accommodation; the resulting microstructure is very complex owing to a combination of highly plastic growth and autocatalytic nucleation. One simple characteristic distinguishing lath martensite from plate martensite is the relative size of the transformation units. In the case of plate
martensite the size of the unit is determined by the free path between strong obstacles to growth, such as grain boundaries and other plates. In striking contrast, individual laths in the lath-martensitic structure do not partition grains as do plates, but instead, typically form packets, with the size of the laths being much smaller than the grain size. This strongly suggests that the laths undergo premature growth arrest. The association of lath martensite with extensive plastic accommodation further suggests that the mechanism of growth arrest is closely related to the plastic-accommodation process itself.

The results of the nonthermoelastic growth model offer a plausible explanation for the observed lath-to-plate morphological transition. Initially, radial growth is elastic, with the extent of elastic growth determined by the dynamic flow behavior of the austenite, as well as the radial growth rate. During elastic radial growth the martensitic particle tends toward a plate-like shape due to the direct dependence of the elastic strain energy on particle aspect ratio. The elastic radial-growth event may be considered to be stabilized by rate effects which act to delay the formation of a plastic zone ahead of the advancing particle tip. Radial plasticity produces a dislocation substructure which interacts with the interface—a process analogous to strain-hardening. For a sufficiently strong interaction, immediate radial-growth arrest will take place. This suggests the possibility that the lath morphology is a direct result of early radial growth arrest due to plastic accommodation ahead of the martensitic particle. Alternatively, the onset of radial plasticity may not produce immediate growth arrest, but instead may lead to a highly plastic mode of growth with arrest occurring soon afterward. In either case, the onset of radial plasticity is regarded to be the key factor influencing martensite morphology.

The martensitic growth simulations indicate that the above process occurs at much smaller particle sizes in the lath-forming alloy, Fe-24Ni, as opposed to plate-forming, Fe-32Ni. For a strain-hardening coefficient, $\theta_1$, near 1 GPa, radial-growth arrest was predicted at $r=20\mu m$ for Fe-24Ni, and $r=123\mu m$ for Fe-32Ni, although these values are sensitive to prior plastic accommodation in the regions adjacent to the plate. In reality,
the observed lath size is considerably smaller than this, and the plate size extends to larger sizes in coarse-grained austenites. However, perfect agreement is not expected, considering the approximate nature of the growth model. The significant finding is that the onset of radial plasticity and the potential for radial-growth arrest occurs at much smaller sizes in Fe-24Ni compared with Fe-32Ni.

Although the present calculations did not address the highly plastic growth behavior which results when radial plasticity does not produce immediate radial-growth arrest, the plastically softer Fe-24Ni alloy is expected to show a greater degree of plasticity that Fe-32Ni. This suggests a distinction between three modes of growth. Elastic growth applies to thermoelastic alloys, and the thermoelastic growth model predicts a plate morphology. At the other extreme, plastic growth is associated with the lath morphology, in which the individual unit corresponding to a single nucleation event grows in a highly plastic manner, undergoing early growth arrest. An intermediate mode of growth shows both elastic- and plastic- growth behavior. This elastic/plastic mode produces a plate morphology in which an initial rapid elastic-growth event is follow by plastic accommodation.

The essential factors controlling the onset of radial plasticity and the potential for premature radial-growth arrest are predicted to be: 1) the radial growth rate, and 2) the mechanical threshold stress. It was found that both a high growth rate and high mechanical threshold stress promote elastic growth. These same factors are expected to exert a major influence on martensite morphology. Accordingly, it is proposed that a plate morphology is promoted by rapid radial growth and a high mechanical threshold stress. A reduction in growth rate and/or the mechanical threshold can potentially result in a transition to a lath morphology, due to plastic accommodation at comparatively small sizes, resulting in premature radial-growth arrest.

This conclusion is consistent with the correlation between austenite flow strength and martensite morphology in steels. Davies and Magee [115-117] observed that a plate morphology is favored when the
austenite yield strength exceeds 30 ksi (207 MPa); below this critical strength lath martensite forms. The predominant role of strength over temperature was demonstrated by making observations on many alloys, strengthened by a variety of mechanisms (including invar strengthening), and covering a wide range of transformation temperatures. Laverroux and Pineau [118,119] reported a similar correlation between hardness and morphology in precipitation-hardened Fe-Ni and Fe-Ni-Co alloys with a transition from a lath morphology to a plate morphology occurring at a critical hardness level.

These correlations were based on low strain-rate yield-strength measurements. The present model cites the mechanical threshold stress as an important factor determining the extent of elastic radial growth, and therefore, martensite morphology. While the mechanical threshold reflects high strain-rate dynamic flow behavior, it is reasonable to expect that any strengthening mechanism which produces a substantial increase in the resistance to dislocation motion at low strain rates will also result in an increased threshold stress.

The conclusion that rapid radial growth promotes a plate morphology is also consistent with experimental observations conducted by Korenko [25] on the effect of a high-intensity magnetic field on martensite morphology in Fe-29.6Ni. Under zero-field conditions, this alloy transformed to a lath-like morphology at 271 K. However, in a 140 kOe magnetic field at the same temperature, the transformation produced a mixture of laths and plates. It was estimated that the magnetic field enhanced the driving force for the transformation by about 11%. Under the present interpretation, the increased driving force led to an increase in the martensitic growth rate, which promoted elastic radial growth. This, in turn, promoted a plate morphology by delaying the onset of radial plasticity, allowing the martensitic units to grow elastically to large sizes.
9.4.3) The Internal Structure of Plate Martensite

A perplexing problem associated with the final thickening stage of plate-martensitic growth is the transition from twinning to slip as the operative mode of the lattice-invariant deformation (LID). As reviewed in Chapter 7, the internal structure of plate martensite in ferrous alloys typically consists of a central, finely twinned midrib, surrounded by a somewhat more coarsely twinned plate-shaped region, which is itself surrounded by a highly dislocated untwinned region. The present study most effectively modeled growth of the midrib which apparently results from rapid elastic radial growth (with concurrent thickening) during the initial stage of plate formation. The other two distinct regions form during the final thickening stage. The change in internal substructure from twinned to untwinned suggests that a transition in the LID mode occurs during thickening. In Fe-Ni and Fe-Ni-C alloys, the fraction of twinned versus untwinned material within a plate depends on the transformation temperature. As the transformation temperature decreases, the relative proportion of twinning increases until at very low temperatures a fully twinned structure is observed. Recent work by Datta, Ghosh, and Raghavan [164] suggests a possible connection between plastic accommodation and the transition from twinning to slip.

After an extensive metallographic study on the dimensions of martensitic plates formed in Fe-Ni [151] and Fe-Ni-Mn [139], Datta et al. [164] observed that the aspect ratios were greater than that predicted by a simple thermoelastic force balance. They concluded that the disagreement was due to plastic accommodation resulting in a release of stored elastic strain energy. By applying an equation proposed by Olson and Cohen [88] describing thermoelastic equilibrium, these authors defined a plastic-accommodation factor (PAF) as being the fraction of stored elastic energy released by plasticity during the transformation.

The dependence of the PAF on transformation temperature is reproduced in Fig. 9.10 for Fe-Ni alloys and one Fe-Ni-Mn alloy. It can be seen that the degree of plastic accommodation increases with increasing transformation temperature. This can be anticipated from the current model
Fig. 9.10: Plastic-accommodation factor as a function of transformation temperature for Fe-Ni alloys and one Fe-Ni-Mn alloy.

The plastic-accommodation factor is defined as the fraction of stored elastic energy released by plastic accommodation of the transformation strain during martensitic transformation.

(Datta, Ghosh and Raghavan [164])
in the case of radial plasticity. For a given alloy, the threshold is fixed. Growth velocities diminish with increasing temperature due to the lower chemical driving force and the increased phonon drag. This promotes earlier plasticity, and presumably, the degree of plasticity. Fig. 9.11, also taken from the work of Datta et al., shows the dependence of the fraction of the untwinned versus twinned region on the PAF (\(\bar{c}\) and \(\bar{c}_r\) refer to the mean semithicknesses of the total and twinned portion of the plates, respectively). As the PAF increases, so does the relative proportion of the "outer rim" region. This suggests a correlation between plastic accommodation and the LID transition from twinning to slip.

The growth simulations were conducted under the assumption that plastic accommodation along the particle faces begins once dislocations are capable of being generated in the particle-tip region. The availability of dislocation sources probably plays an important role, and dislocation nucleation may be required in order to produce the necessary sources. The possibility that thickening of the highly twinned region surrounding the midrib proceeds elastically is supported by the lack of evidence of a dislocation substructure within the highly twinned region. If plastic accommodation occurs in the austenite during this stage of thickening the dislocation substructure would be inherited by the martensite. On the other hand, the untwinned region contains a high density of dislocations indicating plastic accommodation regardless of whether it takes place ahead or behind the interface.

As pointed out in Chapter 8, the temperature range over which a mixed internal structure is observed exceeds the adiabatic temperature rise for the martensitic transformation; therefore, local heating alone cannot account for the transition in the LID mode. A possible alternative is that dislocations produced during plastic accommodation in the austenite adjacent to the interface cause the change in LID mode. Olson and Cohen [65] suggested that interfacial energy considerations should favor slip as the mode of LID, and that kinetic factors such as interfacial mobility may favor twinning. Grujicic et al. [135] modeled thermal-activation-controlled martensitic interfacial motion and predicted a greater mobility when the LID mode is twinning. Whether this is true in
Fig. 9.11: The mean value of the relative fraction of untwinned versus twinned region within martensitic plates as a function of the plastic-accommodation factor in Fe-Ni alloys.

(Datta, Ghosh and Raghavan [164])
drag-controlled interfacial motion remains an open question. Nevertheless it is plausible that twinning persists during elastically accommodated thickening until conditions are favorable for the initiation of accommodation slip in the austenite. The reduction in thickening rate due to the interaction between the interface and the accommodation dislocations, combined with the general availability of slip dislocations, may then allow a transition in LID mode to slip, with a concomitant reduction in interfacial energy. Hence, a critical condition for the transition may be the onset of perpendicular plasticity, which may occur during a later stage of thickening than originally assumed in the growth model.

In rationalizing the dependence of both the PAF and the twinned fraction on transformation temperature, it must be recognized the final amount of plastic accommodation is determined by the static flow properties of both the austenite and martensite. In the case of Fe-Ni invar alloys, both the fcc austenitic phase and the bcc martensitic phase show a strong (negative) dependence of the static flow stress on temperature. Therefore, even without knowing the relative amounts of plastic accommodation in the austenite and martensite, the degree of plastic relaxation is expected to decrease with decreasing transformation due to an elevation in the flow strength of both phases. Furthermore, since plastic accommodation during thickening likely takes place only after the transition from twinning to slip as the operative LID mode, the relative proportion of twinning within a plate will decrease with increasing temperature due to the attendant increase in the degree of plastic accommodation. Therefore, under the assumption that plastic accommodation along the plate faces triggers the transition from twinning to slip, the final amount of plastic accommodation, as measured by the PAF, as well as the final twinned fraction within a plate can be rationalized in terms of the temperature dependence of the static flow properties of both phases.
CHAPTER 10

SUMMARY OF PART II

A model for the dynamics of thermoelastic martensitic growth was developed based on the kinetic response of the martensitic interface to forces derived from thermodynamic potentials. The mobility of the interface was modeled after the kinetic behavior of slip dislocations. Incremental solutions to the governing equations were obtained using appropriate parameters for Fe-32Ni. Although Fe-32Ni does not transform thermoelastically, very little thermodynamic and kinetic data are available for thermoelastic alloys. The computed results represent a first approximation to the growth behavior in thermoelastic transformations, as well as the initial elastic-growth stage of ferrous plate martensites. The following observations and conclusions were drawn from this part of the study:

1) The radial growth rate initially accelerates to a maximum velocity of 940 m/s, determined by the interaction between interfacial forces, particle shape and heat transfer. The mobility of the martensitic interface at this high growth rate is controlled by phonon drag.

2) After reaching the peak velocity, radial growth slowly decelerates due to a temperature rise in the plate-tip region producing a decrease in chemical driving force and an increase in the interfacial drag coefficient. The range of computed radial velocities (790-940 m/s) is consistent with experimental measurements [77] of the growth rate of Fe-Ni plate martensite.
3) The maximum temperature rise at the plate tip is calculated to be 54 K, or only 60 percent of the adiabatic limit. Therefore, radial growth occurs neither adiabatically nor isothermally, but intermediate between these two limits.

4) The thickening rate also initially accelerates, reaching a maximum velocity of 19.8 m/s—well within the thermal-activation-controlled regime of interfacial motion kinetics.

5) The maximum interfacial temperature along the plate faces is computed to be 45 K, or 50 percent of the adiabatic limit. Therefore, thickening is also intermediate between isothermal and adiabatic. This prediction reinforces the conclusion of Datta et al. [104] that the temperature rise alone cannot account for the transition in the lattice-invariant deformation mode during thickening of plate martensite.

6) Following radial-growth arrest at an imposed obstacle, thickening continues until a thermomechanical balance is reached between the chemical and nonchemical interfacial forces, with a final plate aspect ratio of 0.028.

The thermoelastic growth model was extended to include plastic-accommodation effects. The following observations and conclusions summarize the results of the modeling efforts and computer simulations:

1) Plastic accommodation of the transformational shape-strain potentially can have both growth-enhancing and growth-inhibiting influences. Enhancement originates from the relaxation of the elastic strain energy, thereby reducing the elastic restraining forces. The inhibiting effects are due to the interaction between the interface and the dislocation substructure produced during plastic accommodation, and the dissipation of plastic accommodation work.
2) The highly stressed region near the particle tip is predicted to be an effective source for nucleating lattice dislocations. At microscopic particle sizes the energetics of dislocation nucleation are unfavorable, promoting elastic growth.

3) Dislocation mobility plays an important role in determining the extent of the elastic radial-growth event. At sufficiently high radial growth rates radial plasticity is inhibited; the model predicts a critical ratio of radial-velocity-to-particle-radius necessary to initiate plastic flow in the particle-tip region.

4) Two critical factors control the onset of radial plasticity:
   a) the radial growth rate, and
   b) the mechanical threshold stress.
Elastic radial growth is promoted by a large radial growth rate and high mechanical threshold.

5) Depending on the strength of the plastic-zone/interface interaction, radial plasticity will either result in immediate radial-growth arrest or a highly plastic mode of growth. Under conditions favoring radial-growth arrest, the growth simulations predict that the onset of plastic accommodation leading to radial-growth arrest occurs at much smaller particle sizes in (lath-forming) Fe-24Ni compared with (plate-forming) Fe-32Ni. This behavior was primarily due to lower values of the mechanical threshold stress and radial growth rate for Fe-24Ni which promoted earlier radial plasticity.

6) It is proposed that the lath-to-plate morphological transition is related to premature radial-growth arrest due to the onset of radial plasticity. A plate morphology is promoted by rapid radial growth and a high mechanical threshold stress. This conclusion is consistent with the experimentally observed correlation between martensite morphology and austenite yield strength. The influence of growth rate explains the observation of a transition in morphology induced by a high-intensity magnetic field.
7) A plausible explanation for the transition in the mode of lattice-invariant deformation (LID) in plate martensite is proposed based on interface-mobility factors. The transition in LID mode may be triggered by the onset of perpendicular plasticity during thickening, causing the thickening rate to decrease favoring slip over twinning.

8) The temperature dependence of the amount of plastic accommodation, as reflected by the final aspect ratio of martensitic plates, as well as the temperature dependence of the twinned fraction within a plate, can be explained in terms of the static flow properties of both the austenite and martensite. Since the twinned portion of martensitic plates appears not to experience appreciable plastic deformation, plastic accommodation is probably confined to the untwinned portion of the martensitic plate, and the austenite. Therefore, the total amount of plastic accommodation should depend inversely on the static flow stress of both phases, which depends inversely on temperature. Furthermore, since the amount of plastic accommodation increases with temperature, the relative fraction of twinned versus untwinned material within a plate should decrease with increasing temperature. These predictions are consistent with experimental observations on the substructure of plate martensite.
CONCLUSIONS

1) Nonclassical martensitic nucleation paths are energetically favored only at sufficiently high driving forces approaching the critical driving force for lattice instability. Such high driving forces may be realized for heterogeneous nucleation at weak defects, and in defect-free crystals whereby homogeneous nucleation becomes possible. Under these conditions, the critical-nucleus structure deviates from that of the product phase, approaching the parent structure in the limit of strongly nonclassical nucleation.

2) At high driving forces favoring nonclassical martensitic nucleation the alternative mechanism of quasimartensitic continuous modulation will compete with the martensitic transformation. The quasimartensitic transformation may be considered to be the displacive analogue of spinodal decomposition.

3) Individual martensitic units initially grow elastically with plastic accommodation of the transformation shape-strain inhibited by the inability to generate accommodation slip dislocations, and the limited mobility of lattice dislocations.

4) High growth rates and a high dynamic flow stress promote elastic radial growth which leads to a plate martensite morphology. In ferrous alloys, early plasticity producing either immediate radial-growth arrest or a highly plastic mode of growth results in a lath morphology in which the size of the individual units is not determined by grain partitioning.

5) Adiabatic heating cannot account for the transition in the lattice-invariant-deformation mode during thickening of plate martensite. Instead, this transition may be triggered by the onset of plastic accommodation ahead of the advancing interface, causing the thickening rate to decrease favoring slip over twinning.
1) While many refinements to the nonclassical nucleation model are possible, the most fruitful extension would involve a fully 3-dimensional variational formulation in which the transformation strain could also be generalized to include additional shears and dilatations. The general results are not expected, however, to differ substantially from those reported here.

2) In order to quantitatively apply the nonclassical nucleation model, the energetics of homogeneous lattice deformation should be computed for each system of interest. In addition, the interfacial-thickness parameter, \( \delta_0 \), should be estimated by high-resolution TEM on martensitic interfaces.

3) The potential for nonclassical nucleation paths is greatest in alloys such as In-Tl which show strong elastic softening above \( M_s \). For non-softening alloys, such as Fe-based alloys, nonclassical effects will nevertheless dominate near a lattice instability. Preliminary electronic calculations indicate that the critical driving force for lattice instability is about 3000 cal/mol in pure Fe [168]. Although such a high driving force cannot be achieved at finite temperatures in Fe, the Fe-Co system shows the potential for becoming unstable above 0 K. Nucleation-kinetic experiments on small metastable particles or precipitates may reveal nonclassical nucleation behavior at driving forces approaching lattice instability. The population of weak nucleating defects may be high enough to permit their detection in the TEM. Under conditions favoring weakly nonclassical heterogeneous nucleation, pre-existing embryos may be stable and the structure of these embryos is expected to show a slight deviation from that of the product structure. Direct observation may confirm this prediction.
4) Further theoretical work on the energetics and kinetics of the quasimartensitic transformation is suggested. Extension of the model presented in Chapter 5 to include the additional interfacial energy arising from the formation of a modulated structure in a finite region may better clarify the competition between the quasimartensitic and martensitic mechanism of structural change near a lattice instability. In addition, fundamental studies of the lattice dynamics leading to the formation of continuous strain modulations may reveal the kinetics of quasimartensitic transformation which can then be compared with experiment.

5) Experimental observation of the quasimartensitic transformation is most likely to be possible in strongly elastic-softening alloys such as In-Tl and V₃Si. Considerable experimental work has already been reported for these systems; these studied should be re-examined in light of the quasimartensitic transformation mechanism.

6) The martensitic growth model represents a first attempt to incorporate into a single model, all of the important effects which influence the growth of an isolated martensitic particle. Although each component of the model would benefit from refinement, efforts to do so are somewhat limited by a lack of necessary kinetic data. Unfortunately, kinetic data on martensitic interfacial motion is not readily obtainable, except in the case of single-interface transformations, so that one must rely on modeling to determine the necessary kinetic parameters. The kinetic similarities between martensitic-interfacial and lattice-dislocation motion should be further explored, particularly in the high-velocity drag-controlled regime.

7) The mechanics of plastic accommodation should be modeled using finite-element methods. Although static elastic/plastic solutions would be interesting, and may have some relevance to the final state of the martensitic particle, ultimately the dynamic interactions between martensitic growth and plastic-zone formation should be explored. Finite-element models are capable of dealing with dynamic problems, and
therefore, offer the opportunity to more accurately model plastic growth behavior. However, in order to model dynamic plastic accommodation in specific systems, high-strain-rate plastic-flow data is needed which could be obtained through dynamic-impact experiments.

8) Direct observation of the plastic strains associated with fully developed martensitic units should be attempted using microinterferometry. This experimental technique permits the accurate determination of surface relief produced by the transformational shape change. Such experiments may confirm the hypothesis that the internally twinned portion of martensitic plates does not experience appreciable plastic accommodation. Furthermore, examination of the tip region of martensitic plates may reveal the radial-plastic-zone size and shape. This latter experiment should be performed on isolated plate tips which could be obtained in single crystal specimens transformed in a temperature gradient.

9) The substructure of martensite has been examined extensively by TEM, but the defect structure of the surrounding austenite has received considerably less attention. Further studies aimed at exploring the regions immediately adjacent to martensitic units may provide clues concerning the interaction between accommodation dislocations and the martensitic interface. In addition, cold-stage experiments on thin-plate martensites may reveal, directly, the limited degree of thermoelasticity expected to be associated with minimal plastic accommodation.
APPENDIX 1

SOLUTIONS TO THE ONE-DIMENSIONAL VARIATIONAL PROBLEM

The proposed models for martensitic nucleation and quasimartensitic strain modulations, utilized solutions to the minimum-energy one-dimensional strain-variational problem, presented in Chapter 3. This appendix presents further details concerning the types of solutions that have been investigated in connection with the spatial dependence of the transformation strain.

A1.1) Martensitic Nucleation

Eqn. 3.12 represents an integral equation which can be inverted to give the minimum-energy strain profile, \( \eta(z) \), for a fixed total displacement, subject to the boundary conditions: \( \eta(0) = \eta_0 \) and \( \eta'(\infty) = 0 \). Actually, the extent of the strain variation is finite, so that the second boundary condition is properly written as: \( \eta'(L) = 0 \), where \( L \) is the position where \( \eta \) reaches zero, i.e., \( \eta(L) = 0 \). Eqn. 3.11 gives the strain gradient as a function of strain:

\[
\eta' = -\sqrt{\frac{\Delta g + \lambda \eta}{\kappa}}.
\]  \hspace{1cm} (A1.1)

The form of this equation suggests a useful construction which facilitates in the visualization of solutions.
This construction is illustrated schematically in Fig. A1.1 for the three types of solutions which are relevant to the martensitic nucleation problem. Focusing attention first on Fig. A1.1a, $\Delta g(\eta)$ and $-\lambda \eta$ are plotted schematically as a function of $\eta$, for assumed values of $\eta_0$ and driving force. A schematic showing the corresponding strain profile is included; when applied to the nucleus structure, the nucleus center plane is located at $z/L=0$. According to eqn. A1.1, the local strain gradient is proportional to the square root of the distance between the $\Delta g$ and $-\lambda \eta$ curves. This imposes a restriction on the magnitude of $\lambda$, namely, the range of permissible $\lambda$ values corresponds to the condition: $\Delta g + \lambda \eta > 0$ for $0 \leq \eta \leq \eta_0$. For the value of $\lambda$ chosen in Fig. A1.1a, $\eta'$ is non-zero at $z=0$.

As $\lambda$ is decreased, holding $\eta_0$ constant, $\eta'(0)$ decreases until $\lambda$ reaches its minimum allowable value, $\lambda_0$, for which $\eta'(0)=0$. This case is depicted in Fig. A1.1b. Although eqn. 3.12 indicates that $L$ is a maximum for this limiting value of $\lambda$, the nucleus may thicken further by adopting a strain profile resembling a slab of material, with a constant strain of $\eta_0$, bounded by the strain profile of Fig. A1.1b. This "piecewise" solution obeys the continuity requirement on gradient energy.

A third type of solution results when $\eta_0 \geq \eta_t$, where $\eta_t$ is defined by the point of tangency between the $\Delta g$ and $-\lambda \eta$ curves. The corresponding value of $\lambda$: $\lambda_t$, is unattainable when $\eta_0 \geq \eta_t$ since $L$ would be then be infinite. Fig. A1.1c illustrates the case where $\lambda$ is close to $\lambda_t$; the strain gradient at the origin is non-zero, and the strain tends to concentrate near $\eta_t$. As $\lambda$ approaches $\lambda_t$, the nucleus thickness increases without a significant change in the normalized strain profile. For the assumed form of $\Delta g(\eta)$, the smallest value of $\eta_t$ (corresponding to $\alpha=1$) is equal to $8/9$. Therefore, the third type of solution is only encountered when the nucleus structure is nearly classical ($\eta_0 \approx 1$).
Fig. A1.1: Schematic diagram illustrating the three types of solutions to the strain-variational problem as applied to martensitic nucleation.

(a) The strain gradient is non-zero at the origin.
(b) $\eta'$ is zero at the origin; piecewise solutions are allowed.
(c) $\eta'$ is nonzero at the origin and the strain tends to concentrate near $\eta_t$. 
A1.2) Quasimartensitic Strain Modulations

As discussed in Chapter 5, the quasimartensitic structure was modeled as a periodic strain variation, normal to a stacking of martensitic variants, whose characteristic structure alternates between $\eta_0$ and $-\eta_0$. The first integration of the Euler equation leads to the following equation for the strain gradient:

$$\eta' = \pm \sqrt{\frac{\Delta g + \frac{1}{\kappa}}{\kappa}}.$$  \hspace{1cm} (A1.2)

The integration constant, $I$, determines the wavelength of the variation, the limits of which depend on the magnitude of $\eta_0$. As pointed out in Chapter 5, the eqns. 3.12 and 3.13 of Chapter 3 are applicable to the present case, with $\lambda \eta$ replaced by $I$. For instance, by setting $z=A/4$ and $\eta=0$ in eqn. 3.12, the wavelength can be written in terms of the strain amplitude, $\eta_0$, and $I$:

$$\Lambda = 4\sqrt{\kappa} \int_0^{\eta_0} \left[ \Delta g + I \right]^{-1/2} \, d\eta.$$ \hspace{1cm} (A1.3)

A convenient construction, illustrating the nature of the solutions to the strain-variation problem, is presented in Fig. A1.2. Here the free energy of homogeneous lattice deformation is plotted, schematically, against normalized strain for a particular driving force. The radical of the square-root function in eqn. A1.2 is proportional to the distance between the free-energy curve and the horizontal line located at $\Delta g=I$ ($I \geq 0$). Since $\eta'$ is real, the limits on the permissible range of $\eta_0$, for a given value of $I$, is determined by the requirement that $\Delta g(\eta_0)+I \geq 0$.

At a given level of driving force (with $\alpha > 0$) and wavelength, the critical structure, clearly, must correspond to a decrease in free energy with increasing $\eta_0$; therefore, the minimum critical structure is given by the condition: $\Delta g(\eta_0) < 0$. As a result, the constant $I$, must be nonzero. As the value of $I$ approaches zero, the wavelength of the strain variation
Fig. A1.2: Free energy of homogeneous lattice deformation, plotted schematically as a function of $\eta$, at a driving force potentially favorable for the transformation of the parent structure ($\eta=0$) to the product structure ($\eta=1$). The integration constant, arising from the solution of the Euler equation under the prescribed boundary conditions for the quasimartensitic strain-modulation model, is indicated on the diagram.
increases toward infinity, as can be seen from eqn. A1.3, noting that \( \Delta g(\eta=0)=0 \). The significance of this limiting behavior is discussed in Chapter 5.
APPENDIX 2

COMPUTER ALGORITHM FOR THE GROWTH CALCULATIONS

This appendix presents the algorithm which was used to compute approximate solutions to the martensitic growth model. The mathematical formulation of the model can be represented by an initial-value problem, involving a pair of coupled, nonlinear differential equations. For thermoelastic growth these equations can formally be written as:

\[ v_r = \frac{dr}{dt} = f(r, c, T_r, T_c) \]  \hfill (A2.1a)

\[ v_c = \frac{dc}{dt} = g(r, c, T_r, T_c) \]  \hfill (A2.1b)

Due to the complex interrelationships between the dependent variables, the functions, \( f \) and \( g \), cannot be written explicitly. Moreover, in the case of nonthermoelastic growth, these functions are further complicated by their dependence on plastic-accommodation parameters. Therefore, numerical solutions were obtained using the backward Euler method [143]. This method utilizes the simplest numerical algorithm for solving differential equations, and was chosen based on its practical computational-speed advantage over other methods.

Numerical solutions were obtained incrementally, using either selected time increments and computed velocities to determine growth increments, or using selected growth increments and computed velocities to determine time increments. For example, in the time-incremental method (the former method), the discretized solution can be represented by the
following pair of simultaneous equations:

\[ \begin{align*}
  r^{n+1} &= r^n + \Delta t \cdot v_r^n, \\
  c^{n+1} &= c^n + \Delta t \cdot v_c^n.
\end{align*} \tag{A2.2a,b} \]

relating growth dimensions in the \((n+1)^{th}\) time increment to the growth dimensions and velocities in the \(n^{th}\) time increment. The growth algorithm was designed such that the user selects either the time- or growth-incremental method of solution, as well as, the number of increments to be used until the next increment update and data output. In general, time increments were found to be more practical during periods of rapid acceleration or deceleration. Within each increment, the simultaneous equations were solved using a modified fixed-point-iteration scheme \([144]\).

In what follows, stage 1 refers to the radial-growth-plus-thickening mode of growth, whereas, stage 2 refers to the thickening-only mode. For both cases, reverse growth was not permitted. In addition, plastic-zone shrinkage was deemed to be physically unrealistic, therefore, steps were taken to prevent this during growth.

The following outline summarizes the the major features of the program logic. Operations embedded within brackets \(\{\ldots\}\) apply only to nonthermoelastic growth. Table A2.1 lists the symbols used in the outline, along with their corresponding definitions.
Table A2.1

List of Symbols Used in the Growth-Algorithm Outline

\( r \)  Plate radius.
\( c \)  Plate semithickness.
\( \Delta r \)  Radial growth increment, entered as input in the growth-incremental method of solution in stage 1 of growth.
\( \Delta c \)  Thickening increment, entered as input in the growth-incremental method of solution in stage 2 of growth.
\( \Delta t \)  Time increment, entered as input in the time-incremental method of solution.
\( n \)  The number of growth or time increments, entered as input, until the next data output, and update of the increment type and size.
\( v_r \)  Radial growth velocity.
\( v_c \)  Thickening rate.
\( D_{nuc} \)  Logical variable. Dnuc is "true" if the lattice-dislocation-nucleation condition has been met, signaling the initiation of plastic accommodation. Otherwise, Dnuc is "false".
OUTLINE OF THE MARTENSITIC-GROWTH ALGORITHM

--Open input and output channels.
--Input parameters and initial values of variables.
--Compute or assign values to constants and flags.

--Enter INCREMENT INPUT/CONTROL SECTION.

--If Stage 1 growth: Input Δr or Δt, and n. Radial growth may optionally be halted.
--Else (Stage 2 growth): Input Δc or Δt, and n. Thickening may optionally be halted.

--Enter MAIN COMPUTATIONAL SECTION.

--Repeat n times:

--Repeat, iterating until convergence:

--Compute the stress within the plate.

--If Stage 1 growth:
  --If growth-incremental method: Set Δt=Δr/v_R.
  --Else (time-incremental method): Set Δr=Δt*v_R.
  --Set r=r+Δr, c=c+Δt*v_c.
  --Set t=t+Δt.
  --{If Dnuc="false": Check dislocation-nucleation condition.}
  --{If Dnuc="true": Compute plastic-zone sizes and plasticity parameters. The plastic zones may not necessarily form due to kinetic factors discussed in Chapter 9}.
  --{Compute the effective transformation strain}.
  --Compute the temperature of the plate tip.
  --Compute the temperature of the plate faces.
  --Compute the net force for radial growth.
  --Compute v_R.
  --Compute the net force for thickening.
  --Compute v_c.

Else (Stage 2 growth):
  --If growth-incremental method: Set Δt=Δc/v_c.
  --Else (time-incremental method): Set Δc=Δt*v_c.
  --Set c=c+Δc.
  --Set t=t+Δt.
  --{If Dnuc="false": Check dislocation-nucleation condition.}
(If Dnuc="true": Compute plastic-zone sizes and plasticity parameters. The plastic zones may not necessarily form due to kinetic factors discussed in Chapter 9).

--{Compute the effective transformation strain}.
--Compute the temperature of the plate faces.
--Compute the net force for thickening.
--Compute \( v_c \).

--Check convergence behavior. Repeat until convergence is met.

--If Stage 1 growth:
   --If radial-growth arrest (spontaneous or due to an imposed obstacle): Set \( v_r = 0 \), output data, and loop back to the increment input/control section for Stage 2 growth.
   --Else (no arrest): Repeat computations for the next increment.
--Else (Stage 2 growth):
   --If thickening arrest: Output data and exit program.
   --Else (no arrest): Repeat computations for next the increment.

After \( n \) growth increments, output data and loop back to the increment input/control section, for an update on \( n \), and either \( \Delta r \), \( \Delta c \), or \( \Delta t \).
APPENDIX 3

DISLOCATON-SLIP KINETICS FOR THE MODEL ALLOYS

The austenite flow properties enter directly into the equations describing the plastic-accommodation model, through the effective flow stress, which is a function of both the average plastic strain, and the effective plastic strain rate, within the plastic zones. A kinetic description of dislocation slip has already been presented in Chapter 8, in a form appropriate to the kinetics of interfacial motion. This appendix presents the form necessary to describe plastic-flow behavior, leading to constitutive equations for rate-dependent flow. In addition, the procedures used to estimate parameters appropriate to Fe-24Ni and Fe-32Ni, will be summarized.

The modified forms of eqns. 8.14, 8.19, 8.21, and, 8.25, giving the strain rate as a function of applied stress, are listed below:

\[ \dot{\gamma}_{ta} = \dot{\gamma}_0 \exp\left[ -\frac{\Delta G^*(\tau)}{kT} \right] . \]  \hspace{1cm} (A3.1)

\[ \dot{\gamma}_{pd} = \frac{\rho_m b^2}{B_j} \left[ \tau - \tau_\mu \right] . \]  \hspace{1cm} (A3.2)

\[ B_j \equiv \frac{b kT}{\Omega v_s} . \]  \hspace{1cm} (A3.3)

\[ \frac{1}{\dot{\gamma}} = \frac{1}{\dot{\gamma}_{ta}} + \frac{1}{\dot{\gamma}_{pd}} . \]  \hspace{1cm} (A3.4)

where \( \tau \) is the applied shear stress, \( \tau_\mu \) is the athermal component of the
flow resistance, and, $\rho_m$ is the mobile dislocation density. The remaining parameters in the above equations have the same meaning as in Chapter 8. In deriving the above equations, the relation between average dislocation velocity and strain rate was approximated by the usual expression: $\dot{\gamma} \approx \rho_m b \dot{\nu}_d$. A relativistic correction was applied to the drag coefficient, analogous to eqn. 8.22, but with strain rates substituting for velocities.

Equations A3.1-A3.4 were combined and inverted to give the dependence of flow stress on the imposed plastic strain rate. The martensitic growth model is concerned with plastic flow, on a size-scale smaller than the grain size. The measure of flow stress, appropriate to this microscopic scale, is the critical-resolved shear stress (CRSS). A limited amount of CRSS data is available for Fe-Ni crystals, deformed at low strain rates. Unfortunately, high strain-rate data is not available (at least to the author's knowledge) for these alloys; this is the major reason for applying eqn. A3.3 to estimate the drag coefficient. The following sections summarize the application of the above constitutive model to microscopic plastic flow in Fe-32Ni and Fe-24Ni.

A3.1) Fe-32Ni

Kocks et al. [123] proposed the following form for the stress dependence of the activation energy, in thermally activated slip:

$$\Delta G^m(\tau) = F_o \left[ 1 - \left( \frac{\tau - \tau_\mu}{\hat{\tau} - \tau_\mu} \right)^p \right]^q,$$  \hspace{1cm} (A3.5)

where $0 < p < 1$, $1 < q < 2$, $F_o$ is a constant, and $\hat{\tau}$ is the mechanical-threshold stress. By substituting this equation into eqn. A3.1, and rearranging,
the following equation results:

\[
(\tau - \tau_{\mu})^p = (\hat{\tau} - \tau_{\mu})^p - (\hat{\tau} - \tau_{\mu})^p \zeta T^{1/q},
\]  

(A3.6a)

with:

\[
\zeta = \left[\frac{k \cdot \ln(\dot{\gamma}_0 / \dot{\gamma})}{F_0}\right]^{1/q}.
\]  

(A3.6b)

If \( \zeta \) is assumed to be constant, then a plot of \((\tau - \tau_{\mu})^p\) versus \(T^{1/q}\), gives an estimate of \(\hat{\tau}\). Although this is really amounts to an extrapolation of stress to absolute-zero temperature, the parameters, \(p\) and \(q\), can be adjusted to give a good fit, over the temperature range in which data is available.

Figure A3.1 summarizes a collection of published data, giving the temperature dependence of the CRSS, for three ferromagnetic Fe-Ni invar alloys, as well as, a paramagnetic Fe-Ni-Cr alloy. The invar effect influences low-temperature plastic-flow behavior, leading to a strong temperature dependence of the CRSS, relative to that of Fe-25Ni-16Cr. Recent progress in modeling invar strengthening suggests that invar anomalies affect thermally activated flow, chiefly, through a strongly temperature-dependent athermal stress \([167]\). Nevertheless, the above phenomenological description, which assumes a constant athermal stress, was used, taking full advantage of the limited available data.

Because the martensitic transformation offers an alternate deformation mechanism, reliable CRSS data for metastable austenites can only be obtained at temperatures well above \(M_s\). Fortunately, the data for compositions in the range represented in Fig. A3.1, fall within a fairly narrow band, suggesting that invar strengthening is more important than solid-solution strengthening at low temperatures. Therefore, the combined behavior of the Fe-Ni alloys was assumed to reflect that of Fe-32Ni, and in particular, permit an estimation of the parameters in eqn. A3.5.
Fig. A3.1: Compilation of critical-resolved shear-stress data for four ferromagnetic Fe-Ni invar alloys, with Ni contents in the range: 30–36.1 wt.–percent Ni, and paramagnetic (non-invar) Fe–25Ni–16Cr. Invar strengthening strongly affects plastic-flow behavior below the Curie temperature for Fe-Ni austenites in this composition range.
The approximate linear dependence of the CRSS on temperature, below about 300 K, is consistent with \( p=q=1 \) in eqn. A3.6a. Therefore, the mechanical threshold, \( \hat{\tau} \), was estimated by extrapolating to 0 K, the best-fitting line for the Fe-Ni data below 300 K, giving: \( \hat{\tau} \cong 250 \) MPa. The data in Fig. A3.1 shows a distinct plateau in the high-temperature range; the athermal stress was approximated by this plateau stress, resulting in: \( \tau_{\mu} \cong 11.8 \) MPa.

According to Kocks et al. [123], the pre-exponential factor, \( \dot{\nu}_0 \), should fall within the range: \( 10^5 \leq \dot{\nu}_0 \leq 10^{10} \) s\(^{-1}\). Assuming a value of \( \dot{\nu}_0 \cong 10^7 \) s\(^{-1}\), \( F_0 \) was determined using eqn. A3.1 and A3.5, substituting \( \dot{\nu}_{ta} = 10^{-4} \) s\(^{-1}\), and the value of \( \tau \) at 200 K, obtained directly from Fig. A3.1. This led to the result: \( F_0 \cong 1.5(10)^{-19} \) J (0.92 eV).

The drag coefficient, \( B_\beta \), was estimated using eqn. A3.3, substituting the same parameters that were estimated in Chapter 8, in connection with drag-controlled interfacial motion. Both the equation for \( \dot{\nu}_{pd}(\tau) \), and the relativistic correction factor, involve the mobile dislocation density. A value of \( \rho_m \cong 10^{12} \) m\(^{-2}\) was taken as an order-of-magnitude estimate for this quantity.

A3.2) Fe-24Ni

Since Fe-24Ni transforms near 400 K, low-temperature CRSS data is not available for this alloy. However, the thermally activated slip behavior is expected to be similar to other paramagnetic, fcc austenites, such as Fe-25Ni-16Cr, which is stable against martensitic transformation on cooling to 4 K. CRSS data for this alloy is included in Fig. A3.1. This data was assumed to also apply to Fe-24Ni, with the stress corrected by the difference in the athermal stress between the two alloys. The athermal stress for Fe-24Ni was assumed to be the same as that estimated for Fe-32 Ni (11.8MPa); Fig. A3.1 shows that the CRSS for Fe-25Ni-16Cr levels off at the higher temperatures giving an athermal stress of 15.9 MPa.
Applying a curve-fitting technique, the CRSS data for Fe-25Ni-16Cr was found to be adequately described by eqn. A3.6a, with \( p=1/2 \) and \( q=5/4 \). This analysis gave a value of 83 MPa for the mechanical threshold for Fe-25Ni-16Cr, which was corrected as described above, resulting in an estimate of \( \dot{\gamma} \approx 79 \) MPa for Fe-24Ni. Estimating (as above) a value of \( 10^7 \) s\(^{-1} \) for \( \dot{\gamma}_o \), \( F_o \) was determined by eqns. A3.1 and A3.5, substituting CRSS data at 400 K, giving: \( F_o \approx 2.4(10)^{-13} \) J (1.5 eV).

As with Fe-32Ni, \( \rho_m \) was estimated to be \( 10^{12} \) m\(^{-2} \) for Fe-24Ni. Eqn A3.3 was used to estimate the drag coefficient, using the parameters estimated in Chapter 9.

3.3) Predicted Flow Curves

Table A3.1 summarizes the parameters estimated for Fe-32Ni at 200 K, and Fe-24Ni at 400 K. Fig. A3.2 shows the dependence of strain rate on stress for these two alloys computed using eqns. A3.1-A3.5, and the parameters in Table A3.1. At stresses below the threshold, the strain rate is a very strong function of stress, typical of thermally activated slip in metals. The knee of each curve occurs roughly at the mechanical threshold, wherein thermal-activation- and phonon-controlled kinetics superpose. At higher stresses, the phonon-drag drag mechanism dominates, and strain-rate is much less stress-sensitive. This model does not permit supersonic dislocation velocities, since the relativistic correction forces an asymptotic approach of \( \dot{\gamma} \), to \( \dot{\gamma}_s \), at high stresses.

The major differences in the predicted deformation response of Fe-32Ni and Fe-24Ni, are due to their different values of threshold stress and drag coefficient. The drag coefficient is mainly determined by temperature, whereas, invar strengthening greatly enhances the mechanical threshold stress for Fe-32Ni, over that of Fe-24Ni. These two factors contribute to the drastic difference in the position of the knees in the flow curves.
Fig. A3.2: Predicted slip kinetics for the austenites: Fe-32Ni at 200 K, and Fe-24Ni at 400 K. These curves describe the response of a crystal to an applied stress; inversion of the governing equations gives the flow stress as a function of imposed strain rate.
Table A3.1

Estimated Parameters for the Kinetic Equations of Plastic Flow

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fe-32Ni at 200K</th>
<th>Fe-24Ni at 400K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau$</td>
<td>252 MPa</td>
<td>79 MPa</td>
</tr>
<tr>
<td>$\tau_\mu$</td>
<td>11.8 MPa</td>
<td>11.8 MPa</td>
</tr>
<tr>
<td>$F_0$</td>
<td>$1.5(10)^{-19}$ J</td>
<td>$2.4(10)^{-19}$ J</td>
</tr>
<tr>
<td>p</td>
<td>1</td>
<td>1/2</td>
</tr>
<tr>
<td>q</td>
<td>1</td>
<td>5/4</td>
</tr>
<tr>
<td>$\dot{\gamma}_0$</td>
<td>$10^7$ s(^{-1})</td>
<td>$10^7$ s(^{-1})</td>
</tr>
<tr>
<td>$\rho_m$</td>
<td>$10^{12}$ m(^{-2})</td>
<td>$10^{12}$ m(^{-2})</td>
</tr>
<tr>
<td>$B_p$</td>
<td>$2.1(10)^{-5}$ N·m(^{-2})·s</td>
<td>$4.3(10)^{-5}$ N·m(^{-2})·s</td>
</tr>
<tr>
<td>$\ddot{\gamma}_s$</td>
<td>$7.5(10)^5$ s(^{-1})</td>
<td>$7.5(10)^5$ s(^{-1})</td>
</tr>
</tbody>
</table>

$\ddot{\gamma}_s$ is needed to compute the relativistic correction factor, given by eqn. 8.22, with $v/v_s$ replaced by $\dot{\gamma}/\dot{\gamma}_s$, where $\dot{\gamma}_s = \rho_m b v_s$. 
BIBLIOGRAPHY


26 Machlin, E.S. and Morris Cohen, Trans. AIME 191 (1951) 1019.

27 Machlin, E.S. and Morris Cohen, Trans. AIME 191 (1951) 746.


32 Kurdjumov, G. and G. Sachs, Z. Physik 64 (1930) 325.


41 Machlin, E.S. and Morris Cohen, Trans. AIME 194 (1952) 489.
60 Falk, F., in Proc. ICOMAT-82, Leuven, Belgium, J. de Physique, vol. 43, suppl. no. 12, 1982, C4-203.


Ling, H. and G.B. Olson, reported by: Olson and Cohen [9].


Olson, G.B., Private communication concerning the interpretation of ref. [71].


88 Olson, G.B. and Morris Cohen, Scripta Met. 9 (1975) 1247.


113 Kelly, P.M., Acta Met. 13 (1965) 635.
120 Burkhardt, W., Diplomarbeiten, Stuttgart, 1954.


137 Magee, C.L., Met. Trans. 2A (1971) 2419.


144 Ibid. p. 88.


161 Irwin, G.R., in *Seventh Sagamore Ordinance Materials Research Conf.*, 1960, p. IV-64.
164 Datta, R., G. Ghosh and V. Raghavan, private communication; to be published.
167 Grujicic, M., unpublished research.
168 Krasko, G. and G.B. Olson, unpublished research.
BIOGRAPHICAL NOTE

The author was born in Detroit, Michigan where he attended elementary and secondary schools. He gained a respect of nature and wildlife through active participation in a local Boy Scout troupe. His scientific education began at the Michigan Technological University in the Department of Metallurgical Engineering. During his sophomore year the author was awarded a General Motors Corporation scholarship which included summer internships at the General Motors Research Laboratories. Shortly after graduating from Michigan Tech, he married Pat Comas and enrolled in the Department of Materials Science and Engineering at M.I.T.