THE STRUCTURE AND MECHANICAL PROPERTIES OF IRON-NICKEL-CARBON MARTENSITES

By

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Signature of Author
Department of Metallurgy
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Signature of Professor in Charge of Research

Signature of Chairman Department Committee on Graduate Research
ABSTRACT

THE STRUCTURE AND MECHANICAL PROPERTIES OF IRON-NICKEL-CARBON MARTENSITES

Peter Grit Winchell

Submitted for the degree of Doctor of Philosophy in the Department of Metallurgy on August 25, 1958.

The structure and mechanical properties of iron-nickel-carbon martensites containing 0.01 - 1.0 percent carbon have been investigated. In order to allow measurement of the properties and structure of the martensites prior to tempering, the nickel and carbon contents were balanced to place the Ms at about -35°C.

The structure of as-formed martensite is body-centered tetragonal with the axial ratio equal to 1.005 ± 0.045 (%C) at all carbon levels investigated. The "extra" (0.005) carbon-independent tetragonality, which disappears during aging at 100°C, can be either true tetragonality or more reasonably apparent tetragonality due to deformation faults every fortieth (211)-type martensitic plane. Precipitation of carbon commences on aging even at -40°C and results in a discontinuous decrease in the axial ratio so that after tempering at 100°C for one hour, the axial ratio is 1.008 for carbon contents between 0.2 and at least as high as 0.7 percent. During precipitation the electrical resistivity increases and subsequently decreases. Aging is similar to the first stage of tempering in iron-carbon alloys.

Potent solid-solution strengthening in as-formed martensite due to carbon, as evidenced by increasing yield stress, occurs at low carbon levels and is independent of testing temperature, suggesting that Cottrell atmosphere formation is not a hardening mechanism. Between 0.4 and 0.8 percent carbon, very little additional solid-solution hardening is observed. Further strengthening in this carbon range occurs during aging. The latter strengthening increases with increasing carbon content reaching about 50,000 psi at 0.8 percent carbon. Solid-solution hardening is thought to be due not to an increase in the strength of the atomic binding, but to the elastic interaction between dislocation stress fields and stress fields around random carbon atoms. The role of tetragonality, itself, is of secondary importance. Precipitation hardening is thought to account for hardening observed during aging.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter Number</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Figures</td>
<td>iii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>viii</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>xii</td>
</tr>
<tr>
<td>I. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>II. Literature Review</td>
<td>3</td>
</tr>
<tr>
<td>III. Experimental Procedure</td>
<td>34</td>
</tr>
<tr>
<td>A. Materials and Heat Treatment</td>
<td>34</td>
</tr>
<tr>
<td>B. Techniques and Specimens</td>
<td>40</td>
</tr>
<tr>
<td>1. Electrical Resistivity Measurements</td>
<td>40</td>
</tr>
<tr>
<td>2. Tensile Tests</td>
<td>44</td>
</tr>
<tr>
<td>3. Compression Testing</td>
<td>48</td>
</tr>
<tr>
<td>4. Hardness Tests</td>
<td>51</td>
</tr>
<tr>
<td>5. Determination of Percent Martensite</td>
<td>52</td>
</tr>
<tr>
<td>6. c/a Measurements</td>
<td>55</td>
</tr>
<tr>
<td>IV. Experimental Results</td>
<td>59</td>
</tr>
<tr>
<td>A. The Structure and the Transformation</td>
<td>59</td>
</tr>
<tr>
<td>B. Mechanical Properties</td>
<td>93</td>
</tr>
<tr>
<td>V. Discussion of Results</td>
<td>122</td>
</tr>
<tr>
<td>A. The Aging Process</td>
<td>122</td>
</tr>
<tr>
<td>B. Solid-solution Strengthening Mechanism</td>
<td>131</td>
</tr>
</tbody>
</table>
Appendices

A. Calculation of Percent Martensite from the Integrated Intensity of \( [200]_M \) and \( [220]_Y \) A-1

B. Average Burst Temperatures for Vacuum Melted Alloys B-1

C. Elastic Modulus (psi \( \times 10^{-6} \)) C-1
<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Figure Description</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Martensite start temperatures for iron-nickel-carbon alloys</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>Yield strength (0.2 percent plastic strain) for plain carbon and low alloy steel</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>Hardness vs. carbon content for untempered martensite</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>Probable tensile properties of quenched low-carbon iron-nickel alloys (0.15 percent or less carbon), Ref. 80</td>
<td>29</td>
</tr>
<tr>
<td>5</td>
<td>Sample curve of the change in electrical resistivity during martensitic transformation on cooling of 0.0C 30N</td>
<td>43</td>
</tr>
<tr>
<td>6</td>
<td>Sample curve showing the change in electrical resistivity of as-quenched martensite during aging at -22°C</td>
<td>45</td>
</tr>
<tr>
<td>7</td>
<td>Tensile specimen for elastic modulus measurements</td>
<td>47</td>
</tr>
<tr>
<td>8</td>
<td>Sub Press used for compression tests</td>
<td>49</td>
</tr>
<tr>
<td>9</td>
<td>Diameter Gauge used for compression tests</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>Percent martensite by X-ray diffraction vs. percent martensite by lineal analysis for 0.4C 23N</td>
<td>56</td>
</tr>
</tbody>
</table>
Figure Number                   Page Number
11. Martensite formed in 0.0C 31N by quenching to -90°C.  .................. 60
12. Martensite formed in 0.0C 31N by quenching to -195°C. .................. 60
13. Martensite formed in 0.2C 27N by quenching to -100°C. .................. 61
14. Martensite formed in 0.2C 27N by quenching to -195°C. .................. 61
15. Martensite formed in 0.4C 23N by quenching to -80°C ..................... 62
16. Martensite formed in 0.4C 23N by quenching to -195°C. .................. 62
17. Martensite formed in 0.6C 19N by quenching to -80°C ..................... 63
18. Martensite formed in 0.6C 19N by quenching to -195°C. .................. 63
19. Martensite formed in 0.8C 17N by quenching to -60°C ..................... 64
20. Martensite formed in 0.8C 17N by quenching to -195°C. .................. 64
21. Transformation curve for 0.0C 30N. .................. 65
22. Transformation curve for 0.2C 27N. .................. 66
23. Transformation curve for 0.4C 23N. .................. 67
24. Transformation curve for 0.6C 19N. .................. 68
25. Transformation curve for 0.8C 17N. .................. 69
<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Description</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>Banding within a deformed martensitic plate showing intersections of bands in 0.48C 20N.</td>
<td>71</td>
</tr>
<tr>
<td>27</td>
<td>Light etching phase lining sections of a tensile fracture in 0.48C 20N.</td>
<td>71</td>
</tr>
<tr>
<td>28</td>
<td>Strain-induced austenite in 0.48C 20N produced by striking a 0.070 inch diameter wire with a hammer at room temperature after quenching to -195°C. Tempered at 130°C for 5 minutes.</td>
<td>73</td>
</tr>
<tr>
<td>29</td>
<td>The same area as Fig. 28 after re-etching to -195°C, tempering at 300°C for 30 seconds, and re-etching. Transformation has occurred within the light etching phase showing that it is austenite.</td>
<td>73</td>
</tr>
<tr>
<td>30</td>
<td>A section through a tensile failure in 0.48C 20N showing highly localized shear associated with strain-induced austenite.</td>
<td>75</td>
</tr>
<tr>
<td>31</td>
<td>The c/a ratio of iron-nickel-carbon martensite as determined from polycrystalline specimens.</td>
<td>77</td>
</tr>
<tr>
<td>32</td>
<td>The c/a ratios of martensite tempered at room temperature for about one hour as determined from transformed austenite single crystals.</td>
<td>79</td>
</tr>
</tbody>
</table>
33. A positive print of an X-ray exposure showing four sets of (002) martensite spot pairs. The intensity ratio of the members of the pairs remains approximately constant from set to set. 75

34. The c/a ratio of as-formed martensite as determined from austenite single crystals transformed and X-rayed at about -100°C. 82

35. The c/a ratio of martensite after tempering at 100°C for one hour as determined from transformed single austenite crystals. 83

36. The change in (002) Martensite line position during tempering as observed on oscillation patterns, using single austenite crystals transformed to martensite. 84

37. The change in electrical resistivity during the aging of as-formed martensite at the temperatures noted, alloy: 0.02%C 30.8%Ni. 86

38. The change in electrical resistivity during the aging of as-formed martensite at the temperatures noted, alloy: 0.08%C 29.0%Ni. 87

39. The change in electrical resistivity during the aging of as-formed martensite at the temperatures noted, alloy: 0.28%C 24.5%Ni. 88
<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Description</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>40A</td>
<td>The change in electrical resistivity during the aging of as-formed martensite at the temperatures noted, alloy: 0.48%C 20.3%Ni.</td>
<td>89</td>
</tr>
<tr>
<td>40B</td>
<td>The change in electrical resistivity during the aging of as-formed martensite at the temperatures noted, alloy: 0.63%C 19.0%Ni.</td>
<td>90</td>
</tr>
<tr>
<td>41</td>
<td>The change in electrical resistivity during the aging of as-formed martensite at the temperatures noted, alloy: 0.96%C 15.1%Ni.</td>
<td>91</td>
</tr>
<tr>
<td>42</td>
<td>Change in electrical resistivity at -196°C due to aging fresh-quenched martensite three hours at the temperatures shown.</td>
<td>92</td>
</tr>
<tr>
<td>43</td>
<td>The effect of nickel on the compressive yield strength of low carbon martensite (0.01%C)</td>
<td>94</td>
</tr>
<tr>
<td>44</td>
<td>Tensile yield stress at 0.6 percent plastic strain</td>
<td>97</td>
</tr>
<tr>
<td>45</td>
<td>Compressive yield stress at 0.6 percent plastic strain for 0.0C 30N</td>
<td>98</td>
</tr>
<tr>
<td>46</td>
<td>Compressive yield stress at 0.6 percent plastic strain for 0.2C 27N</td>
<td>99</td>
</tr>
<tr>
<td>47</td>
<td>Compressive yield stress at 0.6 percent plastic strain for 0.4C 23N</td>
<td>100</td>
</tr>
<tr>
<td>48</td>
<td>Compressive yield stress at 0.6 percent plastic strain for 0.6C 19N</td>
<td>101</td>
</tr>
<tr>
<td>Figure Number</td>
<td>Page Number</td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>49.</td>
<td>Compressive yield stress at 0.6 percent plastic strain for 0.8C 17N.</td>
<td>102</td>
</tr>
<tr>
<td>50.</td>
<td>Yield stress for 100 percent martensite as a function of carbon content for tensile and compression tests, 0°C.</td>
<td>104</td>
</tr>
<tr>
<td>51.</td>
<td>The decrease in yield stress (0.6 percent plastic strain) due to a one percent decrease in martensite as a function of carbon content.</td>
<td>105</td>
</tr>
<tr>
<td>52.</td>
<td>Room temperature hardness vs. percent martensite for 0.0C 30N</td>
<td>107</td>
</tr>
<tr>
<td>53.</td>
<td>Room temperature hardness vs. percent martensite for 0.2C 27N</td>
<td>108</td>
</tr>
<tr>
<td>54.</td>
<td>Room temperature hardness vs. percent martensite for 0.4C 23N</td>
<td>109</td>
</tr>
<tr>
<td>55.</td>
<td>Room temperature hardness vs. percent martensite for 0.6C 19N</td>
<td>110</td>
</tr>
<tr>
<td>56.</td>
<td>Room temperature hardness vs. percent martensite for 0.8C 17N</td>
<td>111</td>
</tr>
<tr>
<td>57.</td>
<td>Rockwell &quot;C&quot; hardness for iron-nickel-carbon martensite at room temperature as a function of carbon content</td>
<td>112</td>
</tr>
<tr>
<td>58.</td>
<td>The effect of nickel and carbon on the modulus of elasticity of room-temperature tempered martensite</td>
<td>114</td>
</tr>
<tr>
<td>Figure Number</td>
<td>Page Number</td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>59.</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>Tensile flow stress as a function of testing temperature for as-quenched and for aged martensite.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.</td>
<td>117</td>
<td></td>
</tr>
<tr>
<td>Dependence of compressive flow stress (2 percent plastic strain) on the testing temperature for aged alloys (A) and for as-quenched alloys (Q).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>61.</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>Temperature dependence of flow stress and aging in an alloy with Ms ~ -100°C.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>62.</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>Cold Rockwell &quot;C&quot; hardness after aging three hours at temperatures shown.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>63.</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td>Estimated solid-solution hardening of martensite by carbon.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>64.</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>Elementary movement of a dislocation line in a solid solution (After Mott). Ref. 86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table Number</th>
<th>Page Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6</td>
<td>The Observed Crystallographic Relationships and Strains Developed during Martensitic Transformation in Iron-Nickel-Carbon Alloys</td>
</tr>
<tr>
<td>II</td>
<td>9</td>
<td>c/a Ratios for Iron-Nickel-Carbon Alloys</td>
</tr>
</tbody>
</table>
| III          | 11          | The Ratio of Particle Sizes in Three Directions to be Expected from a Body-Centered Cubic Metal Containing Only Twin Faults and Stacking Faults  
(38) |
<p>| IV           | 12          | The Apparent Change in the c/a Ratio of Martensite to be Expected from a Deformation Fault Probability, ( \alpha ), on the Martensite ((211), (211), (2\bar{1}1)) or ((2\bar{1}1))-Diffraction Angles and the Corresponding Axial Ratios |
| V            | 17          | Static and Dynamic Displacements of Metal Atoms in Martensite. |
| VI           | 35          | Compositions and Austenitizing Temperatures of Vacuum-Melted Chill-Cast Iron-Nickel-Carbon Alloys |
| VII          | 36          | Compositions and Austenitizing Temperatures of Vacuum-Melted Slowly Cooled Iron-Nickel-Carbon Alloys |</p>
<table>
<thead>
<tr>
<th>Table Number</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIII</td>
<td>37</td>
</tr>
<tr>
<td>IX</td>
<td>38</td>
</tr>
<tr>
<td>X</td>
<td>54</td>
</tr>
</tbody>
</table>

VIII Composition and Austenitizing Temperatures of Air-Melted Alloys
IX Heat Treating and Cold Treating Equipment
X Austenitic Grain Sizes of Alloys Used for Mechanical Testing
Acknowledgments

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I. Introduction

The hardening reaction in steel is of vast industrial importance and has received a commensurate degree of attention in the metallurgical literature. Separation of hardenability from the hardness of martensite, itself, helped indicate that carbon was the strength-determining alloying element. Nitrogen apparently plays a role very similar to that of carbon.

However, even though the alloying element primarily responsible for hardening has been identified, the mechanism by which carbon produces strengthening remains unclear. This is primarily due to three factors: (1) The structure of as-formed* martensite has yet to be unambiguously determined. (2) The temperature of formation of many low-alloy martensites on which experimental information is available is sufficiently high so that the martensite formed during quenching may be pretempered before its mechanical properties are observed. The pretempering may soften or precipitation harden martensite. (3) The mechanisms of solid solution hardening and experimental methods of distinguishing between these mechanisms are not clearly enunciated.

The present work is directed toward the determination of the mechanism by which carbon strengthens martensite. Separation of the effects of precipitation during the early

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* The martensitic transformation, being independent of diffusion, has a state immediately following transformation before independent atom movements occur. This state is termed the "as-formed" state. It is to be distinguished from the not-intentionally-tempered condition called the "as-quenched" or "untempered" state.
stages of tempering and the effect of carbon retained in solid solution is attempted by the use of high-nickel martensites in which the nickel content is adjusted so that martensitic transformation occurs only at sub-zero temperatures.

In such alloys the study of as-formed martensite appears possible, but the effect of nickel, itself, must be evaluated separately. By varying the nickel content, the $M_s$ temperature can be held constant even though the carbon content is changed. These alloys have also been used to study the lattice structure of martensite at low carbon contents.

Although no satisfactory single mechanism was found in this investigation to explain the strengthening effect of carbon, it is hoped that the problem is now more clearly defined and that a connection is established between the hardening observed in martensite and that otherwise observed in solid solutions.
II. Literature Review

The literature pertaining to the structure and properties of iron-nickel-carbon martensites and of ferrous martensites in general must be drawn from several largely diverse fields of metallurgical interest. The approach taken here has been to collect only essential information on the martensitic transformation in the particular alloys used in this investigation and to confine the more general review to the structure and properties of ferrous martensite.

The formation of martensite in iron-carbon alloys, in iron-nickel alloys, and in the ternary system has been extensively investigated.\(^{(1-13)}\) The highest temperature at which martensite forms spontaneously in stress-free austenite, Ms, is shown in Fig. 1 as a function of composition. As pointed out by Haynes\(^{(11)}\), Ms values in the region near pure iron are uncertain. The Ms obtained for pure iron by extrapolating iron-carbon values\(^{(2)}\) is 350°C lower than that obtained by Kaufman and Cohen\(^{(1)}\) on extrapolating iron-nickel Ms temperatures to pure iron.

The effect of elastic stress on the Ms has been directly related to the amount of work done by the stress during transformation.\(^{(14)}\) Since the martensitic transformation involves both shear and dilatation, any shear component raises Ms as does hydrostatic tension, but hydrostatic compression lowers Ms. The burst transformation,\(^{(15)}\) the sudden transformation of an appreciable fraction of
FIG. 1 MARTENSITE START TEMPERATURES FOR IRON-NICKEL-CARBON ALLOYS
austenite, is displaced to lower temperatures by uniaxial compression (16). Plastic deformation increases the Ms\(^{17,1}\) and produces more martensite at the deformation temperature\(^{18,19,20}\). Tension is more effective than compression\(^{19}\). Conversely, the rate of strain hardening decreases with increasing strain-induced martensitic transformation for austenitic stainless steel\(^{19}\). Prior deformation, however, may stabilize austenite with respect to subsequent martensitic transformation on cooling\(^{17,21,22}\). Martensite formed during deformation in iron-nickel-carbon alloys is reported to be similar in structure to martensite produced during cooling but to be in smaller, more regularly arranged plates\(^{13}\).

The microstructure of iron-nickel-carbon alloys with Ms below 0°C has been studied extensively, possibly because fairly well defined plates develop at all compositions and because the low Ms is experimentally convenient. Quantitative studies of the relationship of martensite to austenite are presented in Table I. The Ms is estimated from Fig. 1. The habit planes are determined by examination of relief or etch markings on two surfaces of the parent austenite crystal. The crystallographic relations are determined by the pole figure technique\(^{24,28}\) and by Laue back-reflection photographs of single martensitic plates and the austenite surrounding them\(^{25}\). The strains are determined by surface relief directly\(^{25}\) or by the movement of fiducial markings on the sample surface during transformation\(^{27}\). The habit plane remains very nearly
Table I
The Observed Crystallographic Relationships and Strains Developed during Martensitic Transformation in Iron-Nickel-Carbon Alloys

<table>
<thead>
<tr>
<th>Alloy %C %N</th>
<th>Approximate Ms (°C)</th>
<th>Habit Plane {hkl} Austenite</th>
<th>Crystallographic Relations</th>
<th>Observed Strains</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9 --</td>
<td>230</td>
<td>225</td>
<td></td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>1.4 --</td>
<td>130</td>
<td>225</td>
<td>(011)\textsubscript{M} // (111)\textsubscript{A}</td>
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<td>23</td>
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<td></td>
<td></td>
<td></td>
<td>[111]\textsubscript{M} // [10\bar{1}]\textsubscript{A}</td>
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<td>24</td>
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<tr>
<td>1.6 --</td>
<td>80*</td>
<td>259</td>
<td></td>
<td></td>
<td>23</td>
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<tr>
<td>1.8 --</td>
<td>40*</td>
<td>259</td>
<td></td>
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<td>23</td>
</tr>
<tr>
<td>2.0 --</td>
<td>20*</td>
<td>259</td>
<td></td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>1.2 11.5</td>
<td>-50</td>
<td>259 scatter</td>
<td></td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>0.8 22</td>
<td>-50*</td>
<td>259</td>
<td>(101)\textsubscript{M} within 1° of (111)\textsubscript{A}</td>
<td>0.2 shear in habit plane</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[1\bar{2}1]\textsubscript{M} 2 1/2° from [1\bar{2}1]\textsubscript{A}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3 30.5</td>
<td>-150</td>
<td>259</td>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>-- 30</td>
<td>-20</td>
<td>259</td>
<td>(101)\textsubscript{M} // (111)\textsubscript{A}</td>
<td>0.1 in[\bar{1}5\bar{6}], 27,28,29</td>
<td>27,28,29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>variant plane</td>
<td></td>
</tr>
<tr>
<td>-- 32.5</td>
<td>-100</td>
<td>259</td>
<td>[10\bar{1}]\textsubscript{M} // [1\bar{2}1]\textsubscript{A}</td>
<td></td>
<td>23</td>
</tr>
</tbody>
</table>

* Doubtful values
unchanged in the low-Ms ternary alloys,* and the variations in the crystallographic relations and observed strains are small -- possibly within experimental error. The crystallographic relationships are, therefore, not a function of the nickel-carbon ratio in the low-Ms alloys and the transformation mechanism is probably also unchanged.

Considerable evidence is available relating to the structure of iron-carbon martensites. Roberts(31) has summarized the results of lattice parameter measurements on iron-carbon alloys and plain carbon steels. The unit cell of martensite is body-centered tetragonal, and the parameters chosen by Roberts are:

\begin{align*}
(1) \quad & c = 2.861 + 0.116 \text{ (wt. \% C)} \\
(2) \quad & a = 2.861 - 0.013 \text{ (wt. \% C)} \\
(3) \quad & c/a = 1.000 + 0.045 \text{ (wt. \% C)}
\end{align*}

These equations extrapolate from the experimental data above 0.6 weight percent carbon to the parameters of body-centered cubic iron.

Kurdyumov(32) et al. state that tempering occurs during quenching in plain carbon steels having between 0.2 and 0.6 percent carbon, but that below 0.2 percent the carbon is retained in solution and the lattice is assumed to be cubic(33). Evidence for the carbon remaining in solution in the latter alloys is: (1) the \( [211]_M \) line breadth, the Rockwell "C"

* Mehl and Van Winkel(30) have investigated the change from \{225\} to \{229\} habits by the less accurate one surface analysis. They indicate that the \{259\} habit obtains in martensite formed below room temperature for iron-carbon and iron-carbon-\( 2\frac{1}{2} \) percent nickel alloys.
hardness, and the coercive force increase regularly with carbon content from 0 to 0.14 percent, and (2) additions of up to 6.5 percent manganese make no more contribution to the $\{211\}_M$ line breadth at 0.1 percent carbon than they do to the breadth at 0.01 percent carbon. Six and one-half percent manganese lowers the $M_s$ by about 200°C. According to Kurdyumov, the reason carbon is retained in solution in these low carbon steels is that the chemical driving force is too small to nucleate precipitation. On the other hand, tempering during quenching has been demonstrated in 0.13 percent carbon, plain carbon and low alloy steels (34). Thus, the regular progression of properties measured by Kurdyumov should not be taken as proof of carbon retention without further confirmation.

The loss of observable tetragonality below 0.6 percent carbon in plain carbon alloys is due to tempering during quenching (32, 35). Since the addition of alloying elements which form substitutional solid solutions with iron austenite do not usually change the c/a ratio of martensite (36), measurement of the c/a ratio of martensites with low carbon contents but with reduced transformation temperatures is possible. Such measurements are reported by Kurdyumov (32) but no values are given. Table II gives c/a values for iron-nickel-carbon alloys. The low-carbon values tend to confirm the extrapolation of the c/a values for iron-carbon alloys down to 0.3 percent carbon.

Carbon not only affects the lattice parameters of
Table II

c/a Ratios for Iron-Nickel-Carbon Alloys

<table>
<thead>
<tr>
<th>Alloy % Ni</th>
<th>% C</th>
<th>Estimated Ms (°C)</th>
<th>c/a Ratio</th>
<th>Δc/a*</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>0.57</td>
<td>220</td>
<td>1.027</td>
<td>+0.001</td>
<td>Powder pattern</td>
<td>36</td>
</tr>
<tr>
<td>5.1</td>
<td>0.75</td>
<td>175</td>
<td>1.036</td>
<td>+0.002</td>
<td>Powder pattern</td>
<td>36</td>
</tr>
<tr>
<td>10.0</td>
<td>0.75</td>
<td>100</td>
<td>1.036</td>
<td>+0.002</td>
<td>Powder pattern</td>
<td>36</td>
</tr>
<tr>
<td>4.5</td>
<td>1.06</td>
<td>100</td>
<td>1.049</td>
<td>+0.001</td>
<td>Powder pattern</td>
<td>36</td>
</tr>
<tr>
<td>19.1</td>
<td>0.32</td>
<td>80</td>
<td>1.010</td>
<td>+0.0015</td>
<td>Single austenite crystal</td>
<td>35</td>
</tr>
<tr>
<td>19.1</td>
<td>0.32</td>
<td>80</td>
<td>1.014</td>
<td>-0.0005</td>
<td>Powder pattern</td>
<td>35</td>
</tr>
<tr>
<td>18.4</td>
<td>0.43</td>
<td>40</td>
<td>1.020</td>
<td>0.000</td>
<td>Powder pattern</td>
<td>35</td>
</tr>
<tr>
<td>10.0</td>
<td>1.01</td>
<td>40</td>
<td>1.054</td>
<td>+0.009</td>
<td>Powder pattern</td>
<td>36</td>
</tr>
<tr>
<td>9.0</td>
<td>1.12</td>
<td>40</td>
<td>1.057</td>
<td>+0.007</td>
<td>Powder pattern</td>
<td>36</td>
</tr>
</tbody>
</table>

*Δc/a = c/a observed minus c/a calculated from Equation (3)
martensite, but also the broadness and intensity of the X-ray diffraction lines. Line broadening may be due to inhomogeneous strain within the coherently diffracting regions of the crystal, or it may be due to the small size of these regions (37). In addition, the size of the diffracting region may be limited by twin faults* or by deformation faults* which in turn produce additional broadening (38, 39). Twin faults and deformation faults are not expected to produce X-ray peak asymmetry or peak shifts in random body-centered cubic powder patterns, but only to produce a fictitiously small particle size which is smaller for the \{200\} peak than for the \{110\} or \{211\} as indicated in Table III.

Peak shifts from deformation faults are to be expected in X-ray powder patterns from body-centered tetragonal alloys both in random patterns where the doublets are experimentally separable and in oriented powder patterns such as those which may be obtained from martensite formed from a single austenite crystal (24, 35, 40, 41, 42). These peak shifts are such that the doublet separation may be increased or decreased. Twin faults do not produce a measurable line shift.

Table IV shows the effect on the apparent c/a ratio

* The body-centered cubic structure may be represented as \text{AB\textsuperscript{1}CA\textsuperscript{1}EC\textsuperscript{1}}\text{,} stacking of the \{211\} plane. The primed letters are one \{110\} inter-planer spacing behind the unprimed letters. A deformation fault is \text{AB\textsuperscript{1}CA\textsuperscript{1}CA\textsuperscript{1}BC\textsuperscript{1}A}. A twin fault is \text{AB\textsuperscript{1}CA\textsuperscript{1}CB\textsuperscript{1}A}. 
Table III

The Ratio of Particle Sizes in Three Directions to be Expected from a Body-Centered Cubic Metal Containing Only Twin Faults and Stacking Faults.*

<table>
<thead>
<tr>
<th>\langle hkl \rangle</th>
<th>Fictitious Particle Size Due to Stacking Faults and to Twin Faults Relative to \langle 200 \rangle</th>
</tr>
</thead>
<tbody>
<tr>
<td>\langle 110 \rangle</td>
<td>2.83</td>
</tr>
<tr>
<td>\langle 200 \rangle</td>
<td>1.00</td>
</tr>
<tr>
<td>\langle 211 \rangle</td>
<td>1.63</td>
</tr>
</tbody>
</table>
Table IV

The Apparent Change in the c/a Ratio of Martensite to be Expected from a Deformation Fault Probability, $\alpha$, on the Martensite (211), (211), (211), or (211)-Diffraction Angles and the Corresponding Axial Ratios.

<table>
<thead>
<tr>
<th>Doublet</th>
<th>Increased Doubled Separation $\theta$ in degrees</th>
<th>Apparent c/a Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>(101), (011) -- (110)</td>
<td>$5.9 \alpha \tan \theta$</td>
<td>$+0.21 \alpha$</td>
</tr>
<tr>
<td>(200), (020) -- (002)</td>
<td>$12.0 \alpha \tan \theta$</td>
<td>$+0.21 \alpha$</td>
</tr>
<tr>
<td>(211), (121) -- (112)</td>
<td>$3.0 \alpha \tan \theta$</td>
<td>$+0.10 \alpha$</td>
</tr>
<tr>
<td>(202), (022) -- (220)</td>
<td>$-3.0 \alpha \tan \theta$</td>
<td>$-0.10 \alpha$</td>
</tr>
<tr>
<td>(400), (040) -- (004)</td>
<td>$-5.9 \alpha \tan \theta$</td>
<td>$-0.10 \alpha$</td>
</tr>
<tr>
<td>(422), (242) -- (224)</td>
<td>$-1.5 \alpha \tan \theta$</td>
<td>$-0.05 \alpha$</td>
</tr>
</tbody>
</table>
of deformation faults on \{211\} type planes. The sign of the effect changes from the first order peak to the second order peak. Furthermore, the faults on the \{121\} or \{112\} type martensite planes have half the effect noted in Table IV and the sign is reversed. There is a possibility that recorded c/a values are influenced by the presence of stacking faults and that probability of stacking faults may be estimated directly from doublet separation measurements on two orders of the same reflection.

Direct information on the broadness of X-ray diffraction lines in martensite and its analysis into particle size and strain broadening is incomplete, and the values obtained by different investigators are not necessarily comparable. However, it appears from work \((35,43,44)\) done by the Warren and Averbach \((37)\) technique that the apparent particle size decreases and strain increases with increasing carbon content. The particle size in the \langle011\rangle direction decreases from 640 \((44)\) Angstrom units at 0.0 percent carbon, 22 percent nickel to 160 \((35)\) Angstrom units at 1.43 percent carbon, the balance iron. The corresponding strains are 0.0022 \((44)\) and 0.0052 \((35)\). Soviet work indicates that the particle size of martensite is about 100 to 1000 Angstrom units and that the strain is \(8 \times 10^{-2}\) according to Kurdyumov \((33)\), but the carbon dependence of these quantities is not given. Kuo \((45)\) has reviewed recent Soviet work in this area. As noted by
Hirsch and Otte\(^{(39)}\), it is often\(^{(35,42,46)}\) observed that the \{200\} diffraction is noticeably broader than would be expected on the basis of the broadening observed in the \{110\} and \{220\} lines. Identification of the source of this broadening (particle size or strain) requires the analysis of the \{200\} and \{400\} lines, and the latter (due to its low intensity) has not been studied. If this additional broadening is due to strain, it may be explained by the lower elastic modulus of alpha iron in the \langle200\rangle direction\(^{(35,43)}\), but if this broadening is due to particle size it may be explained by the presence of faults. (See Table III.)

Random displacement of atoms from their average lattice position decreases the intensity of the X-ray diffraction peaks and adds to the intensity of diffuse scattering. As presented by James\(^{(47)}\) the reduction in intensity is

\[
\frac{I}{I_0} = \exp \left( -16\pi^2 \frac{\overline{u^2} \sin \theta}{\lambda^2} \right)
\]

where \(I\) and \(I_0\) are the intensities diffracted from the lattice with and without displacements respectively, and where \(\overline{u^2}\) is the mean square displacement of any atom in a direction perpendicular to the planes reflecting at the Bragg angle, \(\theta\), for incident X-rays of wave length \(\lambda\).

The effect of thermal vibrations on the X-ray reflections is effectively described by equation 4 and
may be further approximated by

\[ \bar{u}_D^2 = \frac{3h^2T}{4\pi^2m^2k} \Phi \left( \frac{\Theta}{T} \right) + \frac{\Theta}{4T} \]

where \( m \) is the atomic mass
\( T \) is the absolute temperature
\( \Theta \) is the Debye or characteristic temperature
\( k \) is Boltzmann's constant
\( h \) is Planck's constant
and \( \Phi(\Theta) \) is a tabulated function

However, there is a possibility that displacements of atoms occur which are not related to temperature. These are called static displacements, frozen heat, or Type III strains. The temperature related, \( \bar{u}_D^2 \), and the static mean square displacements, \( \bar{u}_S^2 \), are combined

\[ \frac{\bar{u}_D^2}{\bar{u}_S^2} = \exp \left[ \frac{-16\pi^2}{\lambda^2} \left( u_D^2 + u_S^2 \right) \frac{\mu m^2}{\Theta} \right] \]

If \( \bar{u}_D^2 \) can be expressed in terms of equation 5, it is possible to determine \( \Theta \) by measuring the reduction in intensity as a function of temperature. When \( \Theta \) is known both for a sample which is suspected to contain static displacements and for an
equivalent standard specimen without static displacements, the static displacements can be obtained from equation 5 and equation 6 for the direction normal to plane \([hk1]\).

Alternately, if \(\Theta\) is known only for the sample, \(\bar{u}_s^{(hk1)}\) may be determined by measuring the reduction in intensity\(^*\) for successive orders of the same plane. For static distortions it has been assumed\(^{(46)}\)

\[
(7) \quad \bar{u}_s^x = \bar{u}_a^x \sin \alpha + \bar{u}_c^x \cos \alpha \quad \text{(static displacements)}
\]

where \(\bar{u}_a^x\) and \(\bar{u}_c^x\) are the static displacements in the \([100]\), \([010]\), and in the \([001]\) directions respectively

and where \(\alpha\) is the angle between the normal to plane \([hk1]\) and the \([001]\).

Some investigators\(^{(46)}\) have determined only the sum of the mean square thermal plus mean square static displacements \((\bar{u}_a^t + \bar{u}_c^t)\) by measuring at only one temperature, and several\(^{(50, 51, 52)}\) have determined only differences as for example \(\bar{u}_c^t - \bar{u}_a^t\) through measurement of \(\frac{I_{200,020}}{I_{002}}\)** in one sample at one temperature. Investigations have also been conducted on the basis that \(\bar{u}_a^t\) and \(\bar{u}_c^t\) are approximately equal so that there is little dependence on \(hk1\) except through \(\frac{\bar{u}_c^t}{\bar{u}_a^t}\).

The results of several investigations on the static and dynamic displacements are summarized in Table V.

\* Corrected for other factors
\** The difference in between the 002, and the 200,020 is assumed to be sufficiently small to allow \(\sin\) to be approximated by the average \(\sin\).
Table V

Static and Dynamic Displacements of Metal Atoms in Martensite

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Quantities Measured</th>
<th>Results</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe C 1.57%C</td>
<td>$\frac{I(200), (020)}{I(002)} = 3.4$</td>
<td>$\overline{u_c - u_a}^2 = 0.028$ AU*</td>
<td>47 50</td>
</tr>
<tr>
<td>Fe 2.4%C, 10%Al</td>
<td>$\frac{I(200), (020)}{I(002)} = 3.0$</td>
<td>$\overline{u_c - u_a}^2 = 0.021$ *</td>
<td>48 51</td>
</tr>
<tr>
<td>1.3%C Steel</td>
<td>$\frac{I(200), (020)}{I(002)} = 3.2$ at +22°C $\frac{I(002)}{I(002)} = 3.06$ at -185°C</td>
<td>$\overline{u_c - u_a}^2 = 0.023$</td>
<td>49 52</td>
</tr>
<tr>
<td>0.98%C Steel-</td>
<td>Intensities of 110, 200</td>
<td>$\overline{u_c + u_D - u_a}^2 = 0.052$</td>
<td>46 49</td>
</tr>
<tr>
<td>Martensite ele-</td>
<td>211, 220 for specimen and</td>
<td>$\overline{u_c + u_D - u_a}^2 = 0.025$</td>
<td></td>
</tr>
<tr>
<td>treolytically</td>
<td>iron standard at room</td>
<td></td>
<td></td>
</tr>
<tr>
<td>extracted</td>
<td>temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpha iron</td>
<td>Intensity of 211 and 431, 510</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.08%C Steel</td>
<td>lines at room temperature</td>
<td>$\overline{u_c - u_a}^2 = 0.020$</td>
<td>430°K 53</td>
</tr>
<tr>
<td>0.10%C Steel</td>
<td>and -185°C</td>
<td>$\overline{u_c - u_a}^2 = 0.0034$</td>
<td>365</td>
</tr>
<tr>
<td>0.35%C Steel</td>
<td></td>
<td>$\overline{u_c - u_a}^2 = 0.0035$</td>
<td>390</td>
</tr>
<tr>
<td>0.84%C Steel</td>
<td></td>
<td>$\overline{u_c - u_a}^2 = 0.0072$</td>
<td>365</td>
</tr>
<tr>
<td>1.00%C Steel</td>
<td></td>
<td>$\overline{u_c - u_a}^2 = 0.0100$</td>
<td>360</td>
</tr>
</tbody>
</table>

* Recalculated by Equation (6).
** "Average" static displacements—physical meaning difficult to assess.
*** Listed as °C in the original.
Even though all the data are based on X-ray film measurements, and further work with a diffractometer is to be desired, the general agreement between different workers on the lower-order lines indicates that the effect is real and large in high carbon martensites. The "average" static displacements as a function of carbon content are considerably smaller. The reasons for this discrepancy are not explained.

Kurdyumov (33) also believes that static displacements occur during cold working (or from the martensitic transformation), but that these are smaller than those measured for high carbon martensites. Warren and Averbach (54) have shown that the line intensity of cold worked alpha brass is reduced during annealing for intense lines and remains about constant for weaker, high-angle lines, if one takes into account the full broadened peak in the cold-worked samples. It is not clear that cold working results in decreased diffracted peak intensity, but there is very probably a large effect due to the presence of carbon in martensite rather than to the transformation itself.

A qualitatively consistent picture of the atomic structure of iron-carbon martensite has been put forward by Petch (55). He observed that since the martensitic unit cell increases in volume as carbon is added, and since the carbon is probably interstitially dissolved in austenite (56) from which martensite is formed without
diffusion, the carbon is present in the interstices in martensite. He has considered the \textit{octahedral}, $00\overline{2}$, and the \textit{tetrahedral}, $\frac{1}{2}00$, interstitial positions. Each of these positions may be subdivided \textit{according} to their relationships to the $c$ tetragonal axis. Examination of the four cases shows that:

- Type \textit{a} tetrahedral ($\frac{1}{2} \frac{1}{2} 0$ for example) according to equations 1 and 2 becomes smaller as carbon is added and is, therefore, not a possible site for carbon atoms.
- Type \textit{c} tetrahedral ($\frac{1}{2} 0 \frac{1}{2}$ for example) becomes larger as carbon is added and is, therefore, a possible site.
- Type \textit{a} octahedral ($\frac{1}{2} 0 \frac{1}{2}$ for example) becomes smaller as carbon is added and is, therefore, not a possible site.
- Type \textit{c} octahedral ($\frac{1}{2} \frac{1}{2} 0$ for example) becomes larger as carbon is added and is, therefore, a possible site.

To distinguish between the tetrahedral type \textit{c} and octahedral type \textit{c} cases, Petch assumed that carbon atoms act directly on the metal atoms to produce tetragonality. Since the tetrahedral site is symmetric, direct interaction leads to cubic expansion, whereas the octahedral site is short in the $c$ direction and direct interaction
leads to tetragonality. The octahedral site of the type $\frac{12}{220}$ or $\frac{001}{2}$ was, therefore, chosen.

Not only do the assumed distortions by carbon atoms present in the octahedral type $c$ positions act in the correct direction to produce the average tetragonality observed in martensite, but also they act in the right direction to be sources of the anisotropic static distortions observed in carbon-bearing martensite. The movement of carbon atoms between octahedral sites in ferrite accounts satisfactorily for the $40^\circ C$ carbon damping peak ($57$). This peak is not observed in martensite ($58$) presumably because the carbon atoms are prefixed in type $c$ sites. Thus the assumption that the carbon atoms lie in type $c$ octahedral sites accounts qualitatively for the available experimental information.

Quantitative correlation of lattice parameters and carbon position has been attempted by Zener ($59$). He considers the change in free energy between an ordered martensite, i.e., one in which the carbons atoms are in type $c$ octahedral positions, and a disordered martensite in which the carbon atoms are $2/3$ in type $a$ and $1/3$ in type $c$ octahedral positions. The change in entropy is calculated directly from the change in positional entropy of the carbon atoms. The internal energy is estimated by assuming that the difference in energy between
a favored site and a disordered site is proportional to an applied tensile strain along the axis of the favored site. The stable strain, the strain at which the internal energy of the system is minimized, is assumed to be the c/a ratio observed. The difference in free energy as a function of the temperature and of the degree of order becomes zero at the critical temperature which is calculated to be

\[ T_c = 1330x \text{ (weight percent carbon)} \]

in the absence of applied stress. Above this temperature martensite is supposed to be body-centered cubic. Since tempering interferes with observation of the tetragonality at high temperatures and since no c/a ratios greater than unity have been reported below 0.30 percent carbon, no experimental test of this formula is available. That Kurdyumov also postulates the existence of a low-carbon cubic martensite has already been noted. His reasoning\(^{(41)}\) is that ferrite is body-centered cubic and must be of lower free energy than the body-centered tetragonal phase, therefore low carbon martensite must also be body-centered cubic. Fisher\(^{(60)}\) has presented a calculation similar to that of Zener but allowing for relaxation about the interstitial atom. The experimental lattice parameter data are divided arbitrarily between an elastic distortion and a uniform expansion from other causes. The
critical temperature calculated is unrealistically low:

\[ T_c = 66x \text{(Weight percent carbon)} \] (9)

Thus, no proven quantitative treatment of the lattice parameter changes with carbon content is available, and, therefore, there is no direct experimental evidence for the position of carbon atoms in martensite. The vanadium-oxygen system exhibits a body-centered cubic solid solution below 3.2 atomic percent and body-centered tetragonal between 14.7 and 21.8 atomic percent. In the latter case, the oxygen is found to occupy octahedral interstitial positions from the intensity distribution of neutron diffraction patterns. Thus, at least in this instance where the interstitial atoms are known to be in the octahedral positions and where equilibrium is obtained at a fairly high temperature, the order-disorder phenomenon appears to be operative. However, in iron-carbon martensites, there is no direct proof of either an order-disorder reaction or of the occupancy of the octahedral sites.

Directly from experimental data, however, the unit cell of martensite is body-centered tetragonal. This unit cell is repeated throughout the martensite crystal. Several crystallites may make up the martensite plate, but all of these crystallites have their tetragonal axes approximately parallel or in a twin relationship. This is a necessary consequence of the austenite-martensite parallelisms and of the fact that the martensite crystal produces a fairly well defined Laue back reflection.
photograph\textsuperscript{(25)}. The latter evidence indicates further that the amount of twin oriented material is rather small. Read\textsuperscript{(63)} has recently stated that a martensitic plate is a single crystal, thus abandoning one of the martensitic transformation mechanisms proposed\textsuperscript{(64)}.

The structure of martensite is modified by tempering. At low tempering temperatures in iron-carbon alloys (below 200\textdegree C), the reaction occurring is:

\begin{equation}
(\text{(I)}\text{)}\text{ Martensite (Carbon content of parent austenite)}
\end{equation}

\[ \longrightarrow \text{ Martensite (0.30 percent carbon) + epsilon carbide.} \]

Evidence that low-carbon martensite is formed is drawn from measurements of the change in c/a ratio during tempering. Two c/a ratios are observed together, one corresponding to the as-quenched martensite -- the reactant, and the other to the low carbon martensite $c/a \neq 1.012$\textsuperscript{(35,40,41,42)}. The X-ray line corresponding to the lower c/a ratio gradually increases in intensity while that of the higher carbon decreases and vanishes at the end of the first stage.

Evidence that a hexagonal-close-packed iron carbide forms in this reaction is based on the position of five X-ray diffraction lines from hardened and tempered high carbon steel samples and on a qualitative interpretation of their intensities\textsuperscript{(65)}. Lement\textsuperscript{(66)} has estimated the iron-carbon atomic ratio of this carbide to be 2.4 from
the total change in volume accompanying the first stage and from the lattice parameters of the phases involved.

The kinetics of the first stage have been investigated by Roberts et al. (42) using precision length measurements. He found the relation:

\[ \frac{df}{dt} = k (1-f)^{tn-1} \]

where \( f \) = fraction transformed according to equation (10)

\[ t = \text{time} \]
\[ k = \text{rate constant} \]
\[ n = \text{growth exponent, nuclei being assumed present} \]

The experimental value of the growth exponent was 0.30 ± 0.04.

The variation of the rate constant with temperature can be described by:

\[ k^{1/n} = A \exp \frac{-Q}{RT} \]

from which \( Q \), the activation energy, = 26,000 cal/mole.

These values, \( n = 0.3 \) and \( Q = 26,000 \) cal/mole, have been reinterpreted by Lement and Cohen (67) on the basis of the growth of plane front epsilon carbide with strain energy acting as the driving force for diffusion. The value of \( n = 1/3 \) is derived, and 26,000 cal/mole is considered to be the activation energy for carbon diffusion in martensite in contrast to 20,100 cal/mole given by Wert (68) for alpha iron.

Electron micrographs of iron-carbon alloys tempered in the range where other measurements indicate the presence of epsilon show a network structure. The network has been interpreted (69) as the intersection with the polished
surface of shells of epsilon carbide along martensitic subgrain boundaries and has been correlated with the kinetics\(^{(67)}\).

Some information is available on the mechanical properties of low carbon, as-quenched martensite. However, these martensites undergo tempering during the quench\(^{(34)}\) and, consequently, a fairly large scatter is observed in the tensile yield stresses, as is shown in Fig. 2. Higher carbon martensites are often too brittle to test in tension. A compressive stress-strain curve for 0.75 percent carbon martensite shows a strength of about 480,000 pounds per square inch at one percent plastic strain\(^{(74)}\).

Indention hardness measurements are numerous. Burns, Moore, and Archer\(^{(75)}\) suggested that the hardness of martensite is dependent only on its carbon content. However, the nitrogen content also affects the hardness of martensite, but it is only about one-third as effective as carbon at equal weight percentages\(^{(76)}\).* Rockwell "C" hardness of martensite is shown in Fig. 3 as a function of carbon content. The higher level of the solid points compared to the open circles and "x's" at low carbon contents is probably due to the higher alloy content (and hardenability) of the former. Although part of the hardness difference may be due to substitutional solid-solution hardening by the alloying elements, such hardening

* According to Jack\(^{(77)}\) nitrogen is present in the octahedral interstitial site in nitrogen martensite.
FIG. 2  YIELD STRENGTH (0.2 PERCENT PLASTIC STRAIN) FOR PLAIN CARBON AND LOW ALLOY STEEL AS QUENCHED
FIG. 3 HARDNESS VS. CARBON CONTENT FOR UNTEMPERED MARTENSITE
plays no part at higher carbon contents (Fig. 3). Consequently, some self-tempering or incomplete hardening of the plain carbon steels used by Kurdyumov et al. (32) (represented by "x's" in Fig. 3) must be considered likely.

Microhardness measurements within the martensitic plates were made as a function of carbon content by Sagisman (78). A maximum hardness at 0.8 percent carbon was observed. Mitsche and Maurer (74) showed, however, that the decrease in hardness observed at high carbon contents was due to deformation in the surrounding austenite, and that the microhardness of the martensite remained very nearly constant above 0.8 percent carbon.

Mechanical property data for iron-nickel alloys and for iron-nickel-carbon alloys have been collected by Marsh (80) and are presented in Fig. 4.

Several factors probably operate to produce these curves. The rapid rise in strength at low nickel contents is to be associated not only with solid solution strengthening by nickel but also with increased hardenability. The relative importance of these two quantities is difficult to assess. The rapid decrease at higher nickel contents is to be associated with increasing quantities of retained austenite. The scatter may be due to variations in retained austenite content by varying quantities of secondary alloying elements or, more probably, to the large strengthening effect of the 0.15 percent carbon content variation allowed in the results quoted.
Fig. 4.—Probable tensile properties of quenched low-carbon iron-nickel alloys (0.15 per cent or less carbon) (Ref. 80)
The general theory of solid-solution strengthening has been reviewed recently \((81, 82, 83, 84)\). The view taken is that because deformation occurs by the movement of dislocations, the interaction of dislocations with solute atoms or with solute-atom arrangements is of primary importance in determining the strengthening. In general, the mechanisms may be divided into (a) those which require preferential distribution of solute atoms before or during straining and (b) those which apply when the solute atoms are randomly dispersed. The former group includes the stress increment necessary to separate a dislocation from an atmosphere of solute atoms it has collected through elastic or electrical interaction \((85)\). Since this stress must act over only a few interatomic distances to free the dislocation, thermal vibrations can be of appreciable aid, and, consequently, the stress to move the dislocation is calculated to increase considerably with decreasing temperature.

Parker \((81)\) has particularized this concept. He regards elastic interaction of solute elements and dislocations to be most effective when the dislocations are arranged in subgrain boundaries.

The interaction of solute atoms with the faulted areas between partial dislocations \((82)\) also produces an increment in stress necessary to move dislocations. Since the stacking fault has a width of tens of interatomic distances, the stress must act over a longer distance than in the case of elastic interaction with a perfect dislocation, and little temperature dependence
of the observed stress is to be expected.

Precipitation hardening, although not strictly a mechanism of solid-solution hardening, will be considered as a member of the first group. Here the flow stress is not expected to be very temperature dependent \(^{(86)}\).

Hardening may occur from clustering or short-range order \(^{(87)}\). In this case, the creation of disorder surface energy along the slip plane is the source of strengthening. The strengthening is dependent on temperature only through the temperature dependence of the ordering energy.

Hardening by random solute atoms is often neglected \(^{(73,74,75)}\) in discussion of alloy hardening. The approximation is made that a dislocation is inflexible on an atomic scale so that solute atoms produce equal and opposite forces on the dislocation line. On the other hand, Nott and Nabarro \(^{(88)}\) have pointed out that the dislocations are bent slightly by each atom. Because statistically for any given dislocation there is an excess of bends in one direction over that in the reverse direction, a net bend will result. The reversal of this compound bend is assumed to constitute the elementary deformation process for the total length of gliding dislocations. The strengthening which results is equal to the average net force which provided the compound bend.

A solid solution can be stronger than its parent metal if the elastic constants of the solution are larger than those of the pure metal. Such an increase is reflected
in an increase of the force required to move a dislocation from its equilibrium position,\(^{(89)}\) the Peierls-Nabarro force.

The direct causes for hardening of iron-carbon martensites have not been extensively discussed for many years. Sauveur\(^{(90)}\) has summarized the varied opinions held prior to 1935. They fall in general into three classes: solid-solution hardening, precipitation hardening, hardening by transformation (cold working). Experimental data were insufficient and theory too poorly developed for definite conclusions to be drawn.

Since that time Polakowski\(^{(91)}\) has concluded from indirect evidence on the work hardening characteristics of hardened steels that martensite is soft in the as-quenched condition and hardens only during flow or during low-temperature aging. He suggests that the carbon atoms are attracted to dislocations and the resulting elastic interaction produces the observed hardness. According to Kurdyumov\(^{(33)}\) and Polakowski\(^{(91)}\), Kishkin holds a similar view.

Kurdyumov, himself, considers martensite to be hard in the as-quenched condition because the strains determined from the line broadening work indicate the presence of high stresses within the structure. He does not consider the possibility that his martensites have been pre-aged during quenching or at room temperature. He states
that this hardness is due not only to structural imperfections, but primarily to the static distortions of the iron atoms caused by the presence of carbon. These distortions according to Kurdyumov increase the number of atoms slipping simultaneously and consequently allow a more efficient use of bond strength. The bond strength, itself, decreases with increasing carbon content and cannot be the cause of hardening (experimental evidence is the decrease in Debye temperature shown in Table V).

In summary, the martensitic transformation in iron-nickel-carbon alloys has been extensively investigated and the low-Ms alloys appear to transform on the same habit plane and in approximately the same orientation relationships regardless of the carbon-nickel ratio. Relatively little is known of the detailed structure of these martensites, but what is known does not deviate greatly from the information obtained on iron-carbon martensites.

The structure of iron-base martensite is estimated to be fairly highly strained body-centered tetragonal where the tetragonality is produced by elongation of the preferred (type c) octahedral sites which are occupied by carbon atoms. A martensitic plate is probably a single imperfect crystal. Quantitative calculations based on this structure are not yet checked by experiment. Carbon is primarily responsible for the hardness of martensite but the mechanism of such hardening is not clear. It is not even clear that unaged martensite is appreciably strengthened by carbon.
III. Experimental Procedure

A. Materials and Heat Treatment

All the alloys described in Tables VI, VII, and VIII were designed to have an Ms of \(-35 \pm 10^\circ\text{C}\). The austenitizing temperatures were selected to yield full carbon solution in the austenite in one hour as indicated by the c/a ratio of the martensite or by comparison of the Ms with the Ms observed after austenitizing at an extreme temperature of 1200\(^\circ\text{C}\) for one hour.

Alloys of the compositions listed in Table VI were prepared from Baker Reagent Nickel, spectrographic carbon, and Ferrovac E iron, by vacuum induction melting in recrystallized alumina crucibles. The charge was held molten for about 5 minutes and bottom-poured into a massive copper mold. The ingots were 3/4-inch in diameter and weighed between 100 and 200 grams. The ingots (except those used for single crystal stock) were radiographed, porous ingots rejected, and were quartered lengthwise. The quarters were then ground and annealed for 24 hours at 900\(^\circ\text{C}\).

All austenitizing was carried out in evacuated Vycor or fused quartz capsules. The capsules were quenched intact in water and broken only after the samples were cold. Details of the heat treating equipment are given in Table IX.
Table VI

Compositions and Austenitizing Temperatures of Vacuum-Melted Chill-Cast Iron-Nickel-Carbon Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Weight Percent Carbon</th>
<th>Weight Percent Nickel</th>
<th>Austenitizing Temperature°C</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01C 31N</td>
<td>0.01</td>
<td>31.5</td>
<td>1400 ± 30</td>
<td>Strain Anneal Single Crystals*</td>
</tr>
<tr>
<td>0.02C 31N</td>
<td>0.02</td>
<td>30.8</td>
<td>900 ± 2</td>
<td>Electrical Resistivity, Tensile Tests</td>
</tr>
<tr>
<td>0.08C 28N</td>
<td>0.08</td>
<td>28.4</td>
<td>900 ± 2</td>
<td>Electrical Resistivity, Tensile Tests</td>
</tr>
<tr>
<td>0.22C 27N</td>
<td>0.22</td>
<td>27.4</td>
<td>900 ± 2</td>
<td>Electrical Resistivity, Tensile Tests</td>
</tr>
<tr>
<td>0.28C 25N</td>
<td>0.28</td>
<td>24.5</td>
<td>900 ± 2</td>
<td>X-Ray Powder Patterns, Electrical Resistivity, Tensile Tests</td>
</tr>
<tr>
<td>0.30C 25N</td>
<td>0.30</td>
<td>25.3</td>
<td>900 ± 2</td>
<td>X-Ray Powder Patterns</td>
</tr>
<tr>
<td>0.39C 23N</td>
<td>0.39</td>
<td>22.9</td>
<td>900 ± 2</td>
<td>X-Ray Powder Patterns</td>
</tr>
<tr>
<td>0.40C 23N</td>
<td>0.40</td>
<td>23.0</td>
<td>900 ± 2</td>
<td>X-Ray Powder Patterns</td>
</tr>
<tr>
<td>0.42C 23N</td>
<td>0.42</td>
<td>23.0</td>
<td>1350 ± 30</td>
<td>Strain Anneal Single Crystals</td>
</tr>
<tr>
<td>0.48C 20N</td>
<td>0.48</td>
<td>20.3</td>
<td>900 ± 2</td>
<td>X-Ray Powder Patterns, Electrical Resistivity</td>
</tr>
<tr>
<td>0.63C 19N</td>
<td>0.63</td>
<td>19.0</td>
<td>1000 ± 5</td>
<td>X-Ray Powder Patterns, Electrical Resistivity</td>
</tr>
<tr>
<td>0.68C 19N</td>
<td>0.68</td>
<td>19.0</td>
<td>1350 ± 30</td>
<td>Strain Anneal Single Crystals</td>
</tr>
<tr>
<td>0.96C 15N</td>
<td>0.96</td>
<td>15.1</td>
<td>1000 ± 5</td>
<td>X-Ray Powder Patterns, Electrical Resistivity</td>
</tr>
</tbody>
</table>

* Crystal provided by L. Leonard of M.I.T.
Table VII

Compositions and Austenitizing Temperatures of Vacuum-Melted Slowly Cooled Iron-Nickel-Carbon Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Weight Percent Carbon</th>
<th>Weight Percent Nickel</th>
<th>Austenitizing Temperature°C</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA0</td>
<td>0.004</td>
<td>33.7</td>
<td>900 ± 2</td>
<td>Cast-Annealed Single Crystals</td>
</tr>
<tr>
<td>CA6</td>
<td>0.06</td>
<td>29.8</td>
<td>900 ± 2</td>
<td>Cast-Annealed Single Crystals</td>
</tr>
<tr>
<td>CA14</td>
<td>0.14</td>
<td>27.1</td>
<td>900 ± 2</td>
<td>Cast-Annealed Single Crystals</td>
</tr>
<tr>
<td>CA20</td>
<td>0.20</td>
<td>27.3</td>
<td>900 ± 2</td>
<td>Cast-Annealed Single Crystals</td>
</tr>
<tr>
<td>CA45</td>
<td>0.45</td>
<td>23</td>
<td>900 ± 2</td>
<td>Cast-Annealed Single Crystals</td>
</tr>
</tbody>
</table>


Table VIII

Composition and Austenitizing Temperatures of Air-Melted Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Weight Percent Carbon</th>
<th>Weight Percent Nickel</th>
<th>Austenitizing Temperature °C</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0C 31N</td>
<td>0.02</td>
<td>30.5</td>
<td>900 ± 2</td>
<td>Compression Tests, Elastic Modulus, and Hardness</td>
</tr>
<tr>
<td>0.0C 19N</td>
<td>0.01</td>
<td>19.3</td>
<td>900 ± 2</td>
<td>Compression Tests, Elastic Modulus, and Hardness</td>
</tr>
<tr>
<td>0.0C 9N</td>
<td>0.01</td>
<td>9.3</td>
<td>900 ± 2</td>
<td>Compression Tests, Elastic Modulus, and Hardness</td>
</tr>
<tr>
<td>0.2C 27N</td>
<td>0.23</td>
<td>26.8</td>
<td>900 ± 2</td>
<td>Compression Tests, Elastic Modulus, and Hardness</td>
</tr>
<tr>
<td>0.4C 23N</td>
<td>0.40</td>
<td>23.3</td>
<td>1000 ± 5</td>
<td>Compression Tests, Elastic Modulus, and Hardness</td>
</tr>
<tr>
<td>0.6C 19N</td>
<td>0.59</td>
<td>19.2</td>
<td>1100 ± 5</td>
<td>Compression Tests, Elastic Modulus, and Hardness</td>
</tr>
<tr>
<td>0.8C 17N</td>
<td>0.82</td>
<td>16.7</td>
<td>1100 ± 5</td>
<td>Compression Tests, Elastic Modulus, and Hardness</td>
</tr>
</tbody>
</table>
Table IX
Heat Treating and Cold Treating Equipment

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Equipment</th>
<th>Purpose of Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>900 ± 2</td>
<td>Resistance Tube Furnace</td>
<td>Homogenizing and Austenitizing.</td>
</tr>
<tr>
<td>1000 ± 5</td>
<td>Glo-bar Muffle Furnace with Nickel Tube</td>
<td>Homogenizing and Austenitizing</td>
</tr>
<tr>
<td>1100 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1350 ± 30</td>
<td>Glo-bar Muffle Furnace</td>
<td>Single Crystal Production</td>
</tr>
<tr>
<td>1400 ± 30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300 ± 20</td>
<td>Salt Pot</td>
<td>Darkening Martensite for Metallographic and X-Ray Examination</td>
</tr>
<tr>
<td>100 ± 2</td>
<td>Boiling Water</td>
<td>Tempering</td>
</tr>
<tr>
<td>200 ± 5</td>
<td>Forced Hot-Air Furnace with Iron Tube</td>
<td>Tempering</td>
</tr>
<tr>
<td>300 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 to 30</td>
<td>Warmed Stirred Water in a Vacuum Flask</td>
<td>Aging</td>
</tr>
<tr>
<td>-20</td>
<td>Ethyl Alcohol and Dry Ice, Stirred in a Vacuum Flask or Insulated Container</td>
<td>Aging, Martensite Formation, and Mechanical Testing</td>
</tr>
<tr>
<td>-40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-80</td>
<td>Acetone and Dry Ice, Stirred in a Vacuum Flask or Insulated Container</td>
<td>Aging, Martensite Formation, and Mechanical Testing</td>
</tr>
<tr>
<td>-120</td>
<td>Methyl Cyclohexane and Liquid Nitrogen Stirred in an Insulated Container</td>
<td>Mechanical Testing</td>
</tr>
<tr>
<td>-100 to -160</td>
<td>25% Methyl Cyclohexane, 75% Petroleum Ether (35 to 60°C), and Liquid Nitrogen, Stirred in a Vacuum Flask</td>
<td>Aging and Martensite Formation</td>
</tr>
<tr>
<td>-195</td>
<td>Liquid Nitrogen in a Vacuum Flask or Insulated Container</td>
<td>Aging, Martensite Formation, and Mechanical Testing</td>
</tr>
</tbody>
</table>
After annealing the quartered ingots were swaged to 0.25 inches in diameter, reannealed for 24 hours, and swaged with intermittent annealings to 0.090 inches in diameter. These wires were centerless ground to 0.070 inches in diameter to remove any subsurface oxide and to provide a uniform diameter for further machining.

Alloys of the compositions listed in Table VII were vacuum induction melted in 300 gram heats from the same stock but were allowed to cool slowly in insulated cylindrical recrystallized alumina crucibles. Sections were cut from the large grained circumference of the solidified heats and were annealed for 24 hours at 900°C.

One heat containing 0.27 percent carbon and 29.1 percent nickel, hereafter called 0.27C 29N, was vacuum melted as previously described, but killed with 0.10 percent aluminum and sucked up and solidified in 7 mm Vycor tubing under a purified helium atmosphere. The rods so obtained were annealed and swaged as described for the alloys in Table VII.

One vacuum-melted iron-0.96 percent carbon alloy was obtained from heat No. 126 of Roberts et al. (42), and austenitized at 1000°C for one hour, and water-quenched -- Vycor capsule broken during the quench.

The heats listed in Table VIII were melted in air from electrolytic iron, electrolytic nickel, and scrap electrode
carbon and cast into 35 pound, 3-inch square cross-section ingots by the Vanadium-Alloys Steel Corporation. They were hot forged, ground, and hot rolled to 5/8 inch diameter rod. The rod was machined into samples in the as-received condition except for electrical resistance specimens which were prepared by quartering and swaging as described above.

Single crystals were prepared from 0.68C 19N and 0.42C 23N by compressive straining to 1.3 percent. A section of the as-cast alloy 1-inch long and 3/4-inch in diameter and annealing for 24 hours at 1350°C. This recrystallized the sample and produced grains about 1/8-inch in diameter. The samples were restrained 1 percent in compression and annealed 9 hours at 1350°C. The crystals obtained were about 3/4-inch in diameter with a few thin twins in each grain.

B. Techniques and Specimens

1. Electrical Resistivity Measurements

The Kelvin double bridge described by Kaufman(92) was used to measure the ratio of the resistance of the unknown to the resistance of a 0.0342 absolute ohm shunt calibrated by B. Roessler and N. B. Smith of the Massachusetts Institute of Technology.

The samples were 0.070-inch diameter wires 3 1/2 inches long to which were spotwelded two 26-gauge nickel-wire potential leads which marked the ends of the 2 1/2 inch reference length. The specimens were austenitized after spotwelding
and quenched to room temperature. Current leads were attached directly to the ends of the sample and temporary potential contacts were made by two steel knife edges 2.00 inches apart. The sample was immersed in ice and water and its resistance measured. (The samples were austenitic at 0°C.) The knife edges were removed and the potential leads were soldered to the nickel wires. Measurement of the new resistance in ice water allowed a calculation of the effective sample length. Knowing the length and the resistance of the shunt and measuring the specimen diameter with a micrometer allowed calculation of the resistivity with an error of about 2%. The changes in resistivity in one sample could be determined with a sensitivity of about 0.1 percent. This accuracy and sensitivity were sufficient.

Two types of measurements were made:

a) **Continuous cooling runs** were conducted to determine the martensitic burst temperature and to follow the course of the transformation. The sample was immersed in a stirred methyl cyclohexane-petroleum ether solution in a vacuum flask. A calibrated copper-constantan thermocouple in the bath was read to 0.01 millivolts (0.4°C). The bath was cooled at a rate of about 3°C per minute by adding powdered dry ice or liquid nitrogen, and readings of temperature and resistance were made about every 3 degrees from about 0°C to about -120°C and at -195°C (boiling liquid nitrogen). The resistance was measured at -195°C, -120°C, and 0°C.
during reheating. A sample curve is shown in Fig. 5.

b) **Isothermal runs** were conducted to determine the change in electrical resistivity of as-formed martensite at constant aging temperature. The same standardizing procedure was used as in the continuous cooling runs. After attaching the nickel wire potential contacts, the specimens were immersed in liquid nitrogen for 5.0 minutes. At 4.0 minutes the resistance was determined. The specimen was then up-quenched in a vigorously stirred bath held at constant temperatures between 80°C and -110°C. The temperature of the bath was measured with a calibrated copper-constantan thermocouple read to 0.01 millivolts (0.4°C). The constancy of the bath temperature was measured by the deflection of a Leeds and Northrup type 2340 galvanometer with a full scale deflection of 0.0013 millivolts (0.05°C). The galvanometer was connected to read the unbalance of the potentiometer whose millivolt setting was not changed during the run. The galvanometer deflection was maintained within $\frac{1}{8}$ to 1/5 of full scale by small additions of coolant to the bath (or by electrical heating) for 3 hours. The resistance of the sample was measured periodically starting at 1.0 minute after the up-quench. Assurance that the sample had reached bath temperature in one minute was obtained by measuring the resistance of a pre-aged sample. In such a sample the resistivity was constant.
FIG. 5 SAMPLE CURVE OF THE CHANGE IN ELECTRICAL RESISTIVITY DURING MARTENSITIC TRANSFORMATION ON COOLING OF 0.0C 30N
in one minute after the up-quench onward. After 3 hours
the aging sample was requenched in liquid nitrogen and its
resistance measured. A typical curve is shown in Fig. 6.
2. Tensile Tests

a) **Small bars** of the vacuum-melted alloys in Table
VI were machined from the 0.070 inch diameter ground stock
for the purpose of determining stress-plastic strain
curves. The reduced section of these bars was 1\(\frac{1}{4}\) inches
long and 0.0425 ± 0.0005 inches in diameter and was tapered
without under-cutting to a \(\frac{3}{4}\)-inch long shoulder 0.070
inches in diameter. The end of this shoulder was threaded
(No. 1-72) for a length of \(\frac{4}{8}\) inch. The bars were austen-
tized in evacuated quartz capsules after machining.

These bars were threaded into stainless steel grips,
surrounded by a container which was filled with a liquid
maintained at the testing temperature, and were tested
in an Instron tensile machine at a crosshead speed of
0.020 inches per minute. The stress was measured by a
strain gauge load cell which was calibrated before each
test. The strain was determined from cross-head motion.
Measurable plastic strain was shown to be confined to
the gauge section by observing the displacement of fiducial
markings on the gauge section and on the shoulders before
and after plastic straining.

b) **Larger**, 0.252 inch diameter, tensile bars of the
SAMPLE CURVE SHOWING THE CHANGE IN ELECTRICAL RESISTIVITY OF AS-QUENCHED MARTENSITE DURING AGING AT –22°C
air melted alloys in Table VIII were machined from hot rolled stock for the purpose of determining elastic moduli. The specifications of these bars are given in Fig. 7. They were austenitized in evacuated Vycor capsules filled with crushed Vycor to provide support against sagging at the higher austenitizing temperatures used. They were oil quenched to room temperature, the capsule being broken during quenching. At room temperature two SR 4 - A D 1 electric resistance strain gauges were attached by Duco cement to opposite sides of the gauge length. Two similar gauges were attached to a ½-inch diameter dummy bar. Separate lead wires were soldered to each gauge so that the strain could be measured in each gauge independently or the average reading could be measured directly by connecting the leads in series. The specimens were tested at room temperature and at liquid nitrogen temperature in equipment described by G. T. Hahn (93) on a hydraulic 60,000 pound tensile machine whose low scale reads from 0 to 6000 pounds. Strain readings were taken at fifty pound load increments between 0 and 250 pounds for austenitic samples and between 0 and 1400 pounds in martensitic samples. A preload cycle to 1500 pounds was applied to martensitic samples to assure that plastic deformation did not occur during the step-loading experiments.

Several runs showed that even with large deviations from axiality, large differences in the strain on opposite
FIG. 7 TENSILE SPECIMEN FOR ELASTIC MODULUS MEASUREMENTS
sides of the specimen, did not affect the elastic modulus obtained from the average strain.

3. Compression Testing

Cylindrical compression specimens were machined from the air-melted alloys listed in Table VIII. For determination of yield stresses, 0.400 inch diameter, 0.90 inch long specimens were used. For determination of stresses at two percent plastic strain, 0.350 inch diameter, 0.90 inch long specimens were used so that fracture would occur below one-half the rated capacity of the 60,000 pound hydraulic machine used. No bars fractured. The diameters of the specimens were centerless ground to 0.0001 inches and the ends were surface ground to be perpendicular to the specimen axis within 0.05 degrees. The specimens were austenitized and oil quenched to room temperature after machining. They were cleaned thoroughly with Lakeseal Glass Cleaner and the ends were polished lightly on a velvet wheel until a clean, shiny surface was obtained.

Compression was carried out without lubricant between polished clean tungsten carbide plates in the subpress shown in Fig. 8. The strain was determined by the diameter gauge shown in Fig. 9. The output of the MP-1 Microformer was fed directly into a Baldwin-Lima-Hamilton Microformer Recorder. The latter, being mechanically linked to
Fig. 8 Sub-Press Used for Compression Tests
Fig. 9 Diameter Gauge Used for Compression Tests
the load indicator, produced a force-diameter curve which could easily be converted to true stress-true strain by the empirically determined ratio, change in diameter to change in microformer output.

The lower two-thirds of the subpress and the sensing arms of the diameter gauge were immersed in a bath which was held at the testing temperature. Prior to each compression test the sample was preloaded to 2000 pounds and the diameter gauge base adjusted in position until the minimum microformer output was reproducibly obtained. The test then started at 2000 pounds load.

The elastic slope (which was somewhat variable and less than is to be expected from the elastic constants) was determined after plastic straining by unloading to the 2000 pound load and then reloading to just under the maximum load applied.

The sensitivity of the process was about 0.1 percent plastic strain. For this reason 0.6 percent plastic strain was used as a basis for the compressive yield stress.

4. Hardness Tests

Room temperature Rockwell hardness readings were taken on the cylindrical surfaces of 0.400 inch diameter compression specimens after these specimens had been strained to about 1%. The "C" scale was used for carbon contents above 0.02 percent carbon and the Rockwell "B" scale for the 0.02 percent carbon alloy.
Rockwell "C" hardness tests were also conducted on samples immersed in liquid nitrogen. For this purpose an insulated metal cup was placed on a bakelite block which rested on the anvil of the hardness testing machine. The sample was placed inside the cup, which contained liquid nitrogen, on the end of a brass cylinder. All surfaces between the specimen and the anvil were surface ground. The 5/3-inch diameter x 1/4 inch high specimens were surface ground top and bottom before austenitizing. Ten readings were taken on each sample and were usually within 0.5 Rockwell "C" units of the average. The assembly was taken apart, warmed and dried before testing the next sample.

The average readings were corrected for the small (0.5 Rockwell "C" units) variations in the readings of standard blocks taken after each group of four to eight samples.

5. Determination of Percent Martensite

Two methods were used to determine the percent martensite. X-ray diffraction was used when the austenitic grain size was sufficiently fine and lineal analysis was used for coarse-grained alloys. Sample preparation was the same for both techniques. Longitudinal sections were cut from compression samples and the shoulders of small tensile bars. The carbon-bearing martensites were tempered at 300°C for 30 seconds to darken the martensite and to decrease carbon content of the martensite. The sections were carefully mechanically polished and etched with 4
percent Nital with 1% Zephiran Chloride\(^{(94)}\). Little if any martensite was formed during polishing as is evidenced by the lack of light etching martensite in the structures and by the fact that 100 percent austenitic samples were successfully polished without difficulty at all compositions.

In the X-ray technique the \{200\} martensitic and \{220\} austenitic reflections were recorded on a hand-operated Geiger counter diffractometer using crystal monochromated cobalt K\(\alpha\) radiation according to the method of Averbach\(^{(95)}\). In this technique most of the martensite line intensity together with the underlying background was recorded at one counter angle. The process was repeated for the austenite line. The background intensity was recorded for the Bragg angle midway between the reflections and was subtracted from the intensities of both reflections. This one-shot technique was feasible because the background intensity was low compared to that of the peaks and because it was not very sensitive to diffraction angle. Because the austenitic grain size was always considerably larger than that of most hardened steels (see Table X), the samples* were oscillated by hand \(\pm 7\) degrees to bring more grains into diffracting position while counting the austenite peak. Oscillation

* In six determinations which were run on an automatic spectrometer the samples were not oscillated.
Table X
Austenitic Grain Sizes of Alloys
Used for Mechanical Testing

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Austenitizing Temperature°C</th>
<th>Austenite Grain Size After Austenitizing for One Hour (ASTM No.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02C 31N</td>
<td>900</td>
<td>5-6</td>
</tr>
<tr>
<td>0.08C 28N</td>
<td>900</td>
<td>5-6</td>
</tr>
<tr>
<td>0.22C 27N</td>
<td>900</td>
<td>5-6</td>
</tr>
<tr>
<td>0.26C 29N</td>
<td>900</td>
<td>(not determined)</td>
</tr>
<tr>
<td>0.28C 25N</td>
<td>900</td>
<td>5-6</td>
</tr>
<tr>
<td>0.0C 31N</td>
<td>900</td>
<td>5</td>
</tr>
<tr>
<td>0.2C 27N</td>
<td>900</td>
<td>5</td>
</tr>
<tr>
<td>0.4C 23N</td>
<td>1000</td>
<td>4 and 2</td>
</tr>
<tr>
<td>0.6C 19N</td>
<td>1100</td>
<td>1</td>
</tr>
<tr>
<td>0.8C 17N</td>
<td>1100</td>
<td>1</td>
</tr>
</tbody>
</table>
during recording of the martensite peak had no effect on the scatter of intensities obtained nor on the average intensity.

The percent martensite was calculated as shown in Appendix A. The values were estimated to be ± 2 to 5% martensite, increasing with decreasing percent martensite.

Lineal analysis was conducted by one operator directly on the sample at visual magnification of 1000 using a Hurlbut Counter as described by Howard and Cohen (96). The length of line traversed was about 0.3 inches. Correlations of the results of this technique with those of X-ray diffraction was attempted for one heat and the results are shown in Fig. 10. Little scatter is observed but there is a consistent trend away from equality at high martensite levels. In addition, forty 1000x photomicrographs were taken of the highest martensite sample and lineal analysis was conducted on the prints. The result verified the direct lineal analysis determination.

It is believed that the X-ray determinations are in error possibly because the martensite peak is not adequately recorded in one Geiger counter position. This error would be considerable less important at low carbon levels. Lineal analysis values were used. X-ray determinations for 0.2C 27N were corrected according to Fig. 10. X-ray determinations for heat 0.0C 31N were used uncorrected.

6. c/a Measurements

a) Powder pattern samples were prepared from austen-
FIG. 10 PERCENT MARTENSITE BY X-RAY DIFFRACTION VS PERCENT MARTENSITE BY LINEAL ANALYSIS FOR 0.4C - 23N
tized 0.70 inch rods by etching in aqua regia or by electro-polishing in perchloric acid-acetic acid. The final diameter was about 0.015 inches.

Exposures were made using unfiltered iron and filtered cobalt radiations in a 5.7 inch diameter Debye-Scherrer camera with Straumanis mounting. Exposures using monochromated cobalt Kα radiation in a similar 5.7 cm. camera were also made.

b) Single crystals of austenite transformed into martensite according to the orientation relationships given in Table I have clusters of \( (001)_M \) poles about each \( (100)_A \) pole and clusters of \( (100)_M \ (010)_M \) poles about each \( (110)_A \) pole. By suitable choice of oscillation angles, the (002) reflection can be recorded on a separate film from the (200) (020) reflection(35, 40, 41, 42) and hence, measurement of the c/a ratio is possible even at values approaching unity.

Single crystal specimens were cut from the cast-annealed crystals whose compositions are listed in Table VII and from the strain-annealed crystals listed in Table III. Specimens were preoriented so that a \( \{100\}_A \) austenite pole was approximately parallel to the long axis of a tetragon about 0.07 inches square in cross-section. They were etched in aqua regia to about 0.030 inches in cross-section, mounted on a three-circle goniometer with Duco cement, and
oriented to within 2 degrees using Laue back-reflection photographs.

The technique used was the same as that described by Werner et al. (35), except that line positions were measured directly on the film and microphotometer traces were made for illustrative purposes only. An attachment was constructed that allowed a small stream of cold nitrogen gas to be directed on the sample so that an exposure could be made of martensite at about -100°C before that martensite had been heated to room temperature. All tempering treatments above room temperature were done with the crystal still attached to the goniometer. The goniometer could easily be replaced in the camera within 1 degree of its previous position.

Thus, the tetragonality of martensite could be determined as-quenched to subzero temperatures, and after tempering at room temperature or up to 100°C for any carbon content with an accuracy of ±0.002.
IV. **Experimental Results**

A. The Structure and The Transformation

The microstructures of the martensites investigated are shown on Figs. 11 through 20. These photomicrographs were taken after the samples had been compressed to about one percent plastic strain, but little microscopic evidence of the deformation is visible. The martensite is plate-shaped at all carbon contents; however, as the carbon content is raised the plate width apparently decreases. This phenomenon may be related to the gradual decrease in the total extent of transformation with increasing carbon content shown in Figs. 21 through 25.

The extent of transformation near the burst temperature is obtained by extrapolating the curve of the martensite contents of the compression specimens back to the burst temperature, the latter being observed during continuous cooling. This extrapolation fits the data well but does not represent the course of transformation in any individual specimen. Each individual specimen probably starts to transform in a burst, (often the burst was audible) and in this way acquires an appreciable quantity of martensite at a single temperature. This behavior was always found during continuous cooling experiments. Chemical banding in the compression specimens probably helped to increase the range of percent martensite attainable.
Fig. 11. Martensite formed in 0.0C 31N by quenching to -90°C

Fig. 12. Martensite formed in 0.0C 31N by quenching to -195°C
Fig. 13. Martensite formed in 0.20 27N by quenching to -100°C

Fig. 14. Martensite formed in 0.20 27N by quenching to -195°C
Fig. 15. Martensite formed in 0.4C 23N by quenching to -80°C

Fig. 16. Martensite formed in 0.4C 23N by quenching to -195°C
Fig. 17. Martensite formed in 0.6C 19N by quenching to -80°C.

Fig. 18. Martensite formed in 0.6C 19N by quenching to -195°C.
Fig. 19. Martensite formed in 0.8C 17N by quenching to -60°C

Fig. 20. Martensite formed in 0.8C 17N by quenching to -195°C
FIG. 21 TRANSFORMATION CURVE FOR 0.0C - 30N
Figure 22: Transformation Curve for 0.2C-27N

- Percent Martensite after 5 min at Temperature
- Burst Temperature during Continuous Cooling

Quenching Temperature °C

Volume Percent Martensite
After 5 min at Temperature Burst Temperature during Continuous Cooling

Volume Percent Martensite

-200 -160 -120 -80 -40
Quenching Temperature °C

Percent Martensite After 5 min at Temperature
 Burst Temperature during Continuous Cooling

FIG. 23 TRANSFORMATION CURVE FOR 0.4C - 23N
FIG. 24 TRANSFORMATION CURVE FOR 0.6C - 19N
FIG. 25 TRANSFORMATION CURVE FOR 0.8C - 17N
Similar metallographic structures and transformation curves were obtained for the vacuum-melted alloys used for tensile testing. The $M_s$ values observed for these heats are tabled in Appendix B.

Three deformation effects were noted in the microstructure of the martensite-austenite complexes studied.

1. Strain-induced martensitic transformation occurred.
2. Banding was observed in the martensitic plates.
3. Strain-induced austenitic transformation occurred.

Transformation during tensile testing could be observed on the automatic load-record of the Instron tensile machine as an erratic increase and decrease in load during testing of high-austenite samples. This tendency seemed to increase with increasing carbon.

In tensile testing, strain-induced transformation at $-195^\circ$C was used to increase the percent martensite attainable by 4 to 7 percent. In compression testing, however, appreciable flow accompanied a much smaller strain-induced transformation, about two percent, and the yield strength of such samples was greater than would be expected from the percent martensite they contained.

Banding in the martensitic plates was observed on metallographic sections of heavily deformed samples. Fig. 26 shows such banding in 0.48C 20N after deformation in tension. Two sets of bands are shown intersecting in one
Fig. 26. Banding within a deformed martensitic plate showing intersections of bands in 0.48C 20N

Fig. 27. Light etching phase lining sections of a tensile fracture in 0.48C 20N
plate. The wider set carries the narrower through a uniform strain. A requirement for simple twinning on the composition plane -- that the composition plane bisect the angle between crystallographic planes in the twin and in the parent -- is approximately satisfied for the traces of the narrow set. This photomicrograph provides some evidence that the banding revealed by the etching of deformed martensite is probably caused by twinning as previously hypothesized by Greninger and Troianc\(^{25}\).

Metallographic sections through fracture surfaces of tensile bars tested at 0\(^{\circ}\)C showed a white phase lining part of the fracture surface, Fig. 27. This phase could be made to transform partially upon cooling to liquid nitrogen temperature and was, therefore, austenite, Figs. 28 and 29. From its microscopic arrangement, it is also identified as austenite formed during deformation. (See, for example, Fig. 30 where a section of a tensile bar has sheared toward the tensile failure.)

Strain-induced reversal of the martensitic transformation in iron-nickel alloys occurs at temperatures above \(A_d\)^\(1\). Generalizing this to iron-nickel-carbon alloys, since the strain-induced austenite is observed at average sample temperatures below \(A_d\), the section of the sample which transformed must have been heated to that temperature by the work done during local deformation. In addition, mechanical energy must supply the heat required
Fig. 28. Strain-induced austenite in 0.48C 20N produced by striking a 0.070 inch diameter wire with a hammer at room temperature after quenching to -195°C. Tempered at 130°C for 5 minutes.

Fig. 29. The same area as Fig. 28 after requenching to -195°C, tempering at 300°C for thirty seconds, and re-etching. Transformation has occurred within the light etching phase showing that it is austenite.
for reversal. Consequently, for adiabatic local shear, \( \gamma \):

\[
\gamma = K \left( \frac{C_v (A_d - T) + \Delta H}{\gamma} \right)
\]

where the thermodynamic values are taken from an iron-nickel alloy with an Ms of \(-30^\circ C\)\(^{(1)}\)

\(K = 37\) inch-pounds per calorie

\(C_v = \) specific heat of martensite at constant volume

\(\approx 14\) cal/in\(^3\)

\(A_d = \) the lowest temperature at which martensite is observed to reverse during isothermal deformation

\(\approx 250^\circ C\)

\(T = \) testing temperature

\(= 0^\circ C\)

\(\Delta H_{\alpha'\gamma} \Delta E_{\alpha'\gamma} = 1500\) cal/in\(^3\)

\(\gamma = \) the shear stress

\(\approx 300,000\) p.s.i. estimated from 0.75 percent carbon, low alloy steel\(^{(74)}\)

This estimates \(\gamma\) to be of the order of 0.5. Zener\(^{(98,99)}\)

has found adiabatic failure in punching operations and in armour-plate piercing by projectiles, and has discussed the nucleation and propagation of such failure. He claims that homogeneous deformation is unstable under adiabatic conditions when a pronounced temperature dependence of the flow stress is present. Transformation from a hard phase to a soft phase would fulfill this condition adequately.
Fig. 30. A section through a tensile failure in 0.480 20N showing highly localized shear associated with strain-induced austenite

Fig. 33. A positive print of an x-ray exposure showing four sets of (002) martensite spot pairs. The intensity ratio of the members of the pairs remains approximately constant from set to set.
However, a highly localized strain applied at a very rapid rate is prerequisite. In Zener's cases (and in the hammered specimens, Fig. 28, 29) these were provided by the loading conditions. In slowly strained test bars, they must be provided by microscopic inhomogeneity of strain. A previously started failure is a probable cause, but the possibility of other localized strain by twinning or even possibly by slip cannot be overlooked. In any case, it appears likely that failure will accompany the formation of strain-induced austenite.

The c/a ratios determined from polycrystalline samples are shown in Fig. 31. The measurements are derived from (002), (020)-(002) and (211), (121)-(112) doublet positions. The (110) and (220) doublets were often not useful because of the presence of the austenite (111) and (222) lines. One determination was also made for an iron-carbon alloy, 0.96 percent carbon. The determinations indicate that in iron-nickel-carbon alloys with subzero transformation temperatures, the c/a ratio is higher than is observed in straight iron-carbon alloys and in steels. The difference is about 0.005 and appears to be independent of carbon content.

The present results agree with those of Nishiyama (36) but not with those of Werner et al. (35). A possible source of disagreement is that, in the latter case, a rather low (850°C) austenitizing temperature was used. Carbon not
FIG. 31 THE c/a RATIO OF IRON-NICKEL-CARBON MARTENSITE AS DETERMINED FROM POLYCRYSTALLINE SPECIMENS
in solution usually appears as graphite in these alloys, and small quantities of graphite are difficult to detect metallographically.

The lower limit in observation of c/a at about 0.3 percent carbon in the powder pattern technique is set not only by the overlapping of the doublet peaks but also by the alloys themselves through the presence of a second (002) line which makes separation of the "doublet" impossible at low carbon levels. The use of austenite single crystals transformed to martensite eliminates the uncertainty due to overlapping. This technique yielded the c/a ratios shown in Fig. 32 when applied to iron-nickel-carbon martensites at room temperature directly following subzero quenching. Between 0.2 percent carbon and 0.4 percent carbon, two c parameters exist together, which is a most unusual result for as-quenched martensite. The larger of the two c parameters divided by the single a parameter produces a c/a ratio which varies with carbon content according to the line drawn through the powder pattern values. The smaller c/a ratio is about 1.005 at all carbon levels at which it is observed.

A typical film showing the (002)M reflections for such a case is presented as Fig. 33. Four sets of double (002) spots are present. Each set has a different intensity because different numbers of martensitic plates
FIG. 32 THE c/a RATIOS OF MARTENSITE TEMPERED AT ROOM TEMPERATURE FOR ABOUT 1 HR. AS DETERMINED FROM TRANSFORMED AUSTENITE SINGLE CRYSTALS.
contribute to each. However, the intensities of the two peaks vary together, for example one set is nearly invisible for both members. This strongly indicates that the two \( c \) parameters corresponding to the two (002) peaks exist together in the same martensitic plate. Furthermore, since the peak breadth does not appear greatly different, the particle size of the lower \( c \) parameter martensite is probably* of the same order of magnitude as that of the higher \( c \) parameter martensite unless a large difference in faulting or strain is present. The last two alternatives are considered unlikely.

The lower end point of the carbon range in which double \( c \) parameters occur is marked by inability to resolve the two \( c \) parameters. The upper end point, beyond 0.5 percent carbon, is marked by broadening and decreased intensity of the lower \( c \) peak.

Exposures of the (002) martensite peak were carried out at about \(-100^\circ C\) on martensite produced during cooling to \(-100^\circ C\). Specimens were then reheated to room temperature, the cassette reloaded, and specimen recooled to \(-100^\circ C\) for exposure of the (200) (020) martensite peak. Additional exposures on other crystals indicated that little change in the position of the (200) (020) spots had occurred during aging at room temperature. The results, given in

* This statement assumes that particle size broadening makes an appreciable contribution to the broadening of the (002) peak.
Fig. 34, show that only the high c/a ratio is present in as-formed martensite. Therefore, the lower c/a ratio material has appeared during reheating to room temperature and during exposure at room temperature (approximately one hour). Furthermore, the variation of c/a with carbon content according to:

\[ \frac{c}{a} = 1.005 + 0.045 \text{ (weight percent carbon)} \]

is verified to very low carbon levels. This represents the line constructed through the powder pattern measurements (Fig. 31).

Specimens were tempered to temperatures up to 1000°C for one hour. The c/a ratios determined at room temperature after tempering at 100°C for one hour are given in Fig. 35. These data indicate that the martensite is predominately of low tetragonality, c/a now about 1.008. The results further indicate that the "extra" tetragonality has been lost at low carbon contents. The c/a now passes through 1.000 at 0.001 percent carbon within experimental uncertainty. However, the increase in the c/a ratio of low carbon martensite is apparently directly in proportion to the carbon content at low carbon levels after tempering for one hour at 100°C. Fig. 36 shows pictorially the change in the (002) peak which occurs during step-heating of the crystal from -100°C to +100°C. It is noted, at least qualitatively, that 0.68C ¹⁹N goes
FIG. 34 THE c/a RATIO OF AS-FORMED MARTENSITE AS DETERMINED FROM AUSTENITE SINGLE CRYSTALS TRANSFORMED AND X-RAYED AT ABOUT -100°C
FIG. 35 THE c/a RATIO OF MARTENSITE AFTER TEMPERING AT 100°C FOR 1 HR. AS DETERMINED FROM TRANSFORMED SINGLE AUSTENITE CRYSTALS
FIG. 36 THE CHANGE IN (002) MARTENSITE LINE POSITION DURING TEMPERING AS OBSERVED ON AN OSCILLATION PATTERN USING SINGLE AUSTENITE CRYSTALS TRANSFORMED TO MARTENSITE
through approximately the same stages as 0.42C 23N but a higher temperature is needed in the former case.

The data indicate directly that as-formed martensite in low-Ms iron-nickel-carbon alloys is body-centered tetragonal with a tetragonality that varies with carbon content according to equation (14). Above about 0.2 percent carbon, this martensite is directly observed to produce a lower tetragonality martensite during aging which gradually consumes the higher tetragonality phase. Furthermore, the process probably occurs within individual martensite plates.

The aging of martensite formed during quenching to -195°C is accompanied by a change in electrical resistivity. Electrical resistivity aging curves are presented in Figures 37 through 41. At low temperatures and at temperatures above about 20°C, the electrical resistivity decreases during aging. At intermediate temperatures, an increase in resistivity is observed, the magnitude of which is directly dependent on the carbon content of the as-formed martensite. The overall change in resistivity from the original value at -195°C to the value at -195°C after three hours aging at an elevated temperature is shown in Fig. 42. as a function of aging temperature for several alloys. The increase in resistivity is shown again to be dependent on the aging temperature and carbon content of the alloys. The magnitude of subsequent decrease
FIG. 37—THE CHANGE IN ELECTRICAL RESISTIVITY DURING THE AGING OF AS-FORMED MARTENSITE AT THE TEMPERATURES NOTED

ALLOY  30.8 % Ni  
  0.02 % C
FIG. 38 THE CHANGE IN ELECTRICAL RESISTIVITY DURING THE AGING OF AS-FORMED MARTENSITE AT THE TEMPERATURES NOTED
Alloy 29.0% Nickel
0.08% Carbon
FIG. 39 THE CHANGE IN ELECTRICAL RESISTIVITY DURING THE AGING OF AS-FORMED MARTENSITE AT THE TEMPERATURES NOTED. Alloy 24.5% Ni, 0.28% C.
FIG. 40A THE CHANGE IN ELECTRICAL RESISTIVITY DURING THE AGING OF AS-FORMED MARTENSITE AT THE TEMPERATURES NOTED

ALLOY 20.3% Nickel
0.48% Carbon
Fig. 40B: The change in electrical resistivity during the aging of as-formed martensite at the temperatures noted.

Alloy 19.0% Nickel, 0.63% Carbon, 0.33% Chromium.
FIG. 41 THE CHANGE IN ELECTRICAL RESISTIVITY DURING THE AGING OF AS-FORMED MARTENSITE AT THE TEMPERATURES NOTED

Alloy 15.1% Nickel
0.96% Carbon
FIG. 42 CHANGE IN ELECTRICAL RESISTIVITY AT -196°C DUE TO AGING FRESH-QUENCHED MARTENSITE THREE HOURS AT THE TEMPERATURES SHOWN
in resistivity is also dependent on carbon content.

The decrease in resistivity at low temperatures seems to be associated with the extent of isothermal martensitic transformation in iron-nickel alloys. There is no reason why this explanation should not apply equally well to iron-nickel-carbon alloys in the low temperature range. In plain carbon steels, tempering is found to decrease the electrical resistivity. It, therefore, seems likely that the high temperature aging is due to tempering. A discussion of possible causes of the increase in resistivity in the intermediate temperature range is presented in the discussion of results.

B. Mechanical Properties

Nickel is expected to contribute solid-solution hardening to the ternary alloys being studied. The effect of nickel on the compressive (0.6 percent) yield stress is shown in Fig. 43. The measurements were made on three low-carbon heats at room temperature after tempering at 100, 200, and 300°C. Tempering had no effect on the yield strength. The martensitic transformation is assumed complete in 0.0C 9N (Ms 500°C) at room temperature and in 0.0C 20N (Ms 200°C) after quenching to -195°C. The yield strength of 0.0C 31N was corrected to one hundred percent martensite as indicated below (Fig. 45). To decrease variations in carbon content from alloy to alloy, the three heats had been annealed in the same Vycor tube.
FIG. 43 THE EFFECT OF NICKEL ON THE COMPRESSION YEILD STRENGTH OF LOW CARBON MARTENSITE

(O.01% C)
for 5 days at 1100°C. For such a treatment, \( \sqrt{Dt} \), the 
characteristic diffusion distance, is about 0.3 inches for carbon\(^{(101)}\) and about 0.001 inches for nickel\(^{(101)}\). After 
the treatment, 0.025 inches were machined from the contact-
ing ends of the compression specimens. The specimens were 
all less than 0.02 percent carbon before and were assumed* 
to be of nearly equal carbon content after treatment. Fol-
lowing the 1100°C treatment, the specimens were quenched 
to produce martensite, reaustenitized separately for one 
hour at 900°C, and then quenched.

The results of the compression tests show that nickel 
affects the yield stress by less than 10,000 psi over the 
nickel range used in this investigation. Comparing these 
values with those in Fig. 4 shows that the short plateau 
in Marsh's collected data\(^{(80)}\) is, as expected, extended 
considerably by controlling the percent martensite present 
in the alloys. There may, however, be an appreciable solid 
solution hardening in the lower nickel range (below 10 per-
cent nickel). For example, Lacy and Gensamer\(^{(102)}\) found 
1, 2, and 3 atomic percent nickel each raised the tensile 
strength of ferrite by about 6,000 psi. Such hardening 
would tend to raise the results of this investigation uni-
formly above those on plain carbon steels, but the hard-
ness and strength variations of the alloys studied here 
may be regarded as independent of the nickel content.

* The activity coefficient of carbon in austenite probably 
varies with nickel content, but since this enters as a 
multiplying factor it is not expected to produce much 
absolute change in the carbon content.
In order to determine the mechanical properties of martensite at any given carbon level and test temperature, martensite must either be present in sufficient quantity so that the effect of austenite is insignificant, or the effect of austenite must be corrected for in the results. The first alternative applied for the two high-Ms alloys. However, for the alloys with Ms at approximately \(-30^\circ C\), cooling to \(-195^\circ C\)* produced appreciably less than total transformation. (See Figs. 21 through 25.) For a testing temperature of \(0^\circ C\), each alloy was tested at various percentages of martensite. Tensile bars were tested to failure and compression specimens were strained to about one percent permanent strain. The percent martensite and Rockwell "C" hardness were determined for each specimen.

The 0.6 yield stress (at 0.6 percent plastic strain) is shown as a function of percent martensite in Fig. 44 for the tensile tests, and in Fig. 45 through 49 for the compression tests. The higher carbon tensile test series show a very large scatter. The scatter is reduced in the compression series. Care was taken in the compression series to age the specimens 3 3/4 hours in ice water before testing, but the aging time at \(0^\circ C\) was not controlled for the tensile tests. The increased scatter in the latter case is thought to be due in part to uncontrolled aging. Tensile tests were also conducted at

* Cooling to \(-269^\circ C\) does not produce appreciably more transformation than does cooling to \(-195^\circ C\).
FIG. 44 TENSILE YIELD STRESS AT 0.6 PERCENT PLASTIC STRAIN
FIG. 45 COMPRESSIVE YIELD STRESS AT 0.6 PERCENT PLASTIC STRAIN FOR 0°C - 30N
FIG. 46 COMPRESSIVE YIELD STRESS AT 0.6 PERCENT PLASTIC STRAIN FOR 0.2C -27N

Testing Temperature
0°C
Aged 3 3/4 hr. at 0°C
FIG. 47 COMPRESSIVE YIELD STRESS AT 0.6 PERCENT PLASTIC STRAIN FOR 0.4C-23N
FIG. 48 COMPRESSION YIELD STRESS AT 0.6 PERCENT PLASTIC STRAIN FOR 0.6C-19N
FIG. 49 COMpressive YIELD STRESS AT 0.6 PERCENT PLASTIC STRAIN FOR 0.8C-17N

Testing Temperature 0°C
Aged 3 3/4 hr at 0°C
0.4 and 0.5 percent carbon but insufficient plasticity was present at high martensite levels and results are, therefore, not reported.

A least mean square line was fitted to the experimental data, and the standard deviation of the intercept and slope were calculated\(^\text{(103)}\) assuming that perfect data would be exactly linear. The intercept at 100 percent martensite is taken as the yield strength of martensite aged and tested at 0°C. This quantity, along with its calculated standard deviation, is plotted in Fig. 50 as a function of carbon content. The slope of the yield stress vs. percent martensite line is shown in Fig. 51 as a function of carbon content. In both cases the agreement between the tensile results and the compression results is usually within the random error in these measurements. However, there may be a systematic error in the retained austenite measurements. If the X-ray data were used and the lineal analysis results corrected to conform to them according to Fig. 10, the yield strength of 100 percent martensite would rise between 20,000 and 30,000 psi for each compression test series except that of 0.0C 31N. Large divergence between the compression tests and the tensile tests is not expected because (a) rather slender specimens were used, (b) only low strains were attempted, and (c) appreciable barreling did not occur. However, frictional effects
FIG. 50

YIELD STRESS FOR 100 PERCENT MARTENSITE AS A FUNCTION OF CARBON CONTENT FOR TENSILE AND COMPRESSION TESTS 0°C
FIG. 51  THE DECREASE IN YIELD STRESS (0.6 PERCENT PLASTIC STRAIN) DUE TO A ONE PERCENT DECREASE IN MARTENSITE AS A FUNCTION OF CARBON CONTENT
at the ends of compression specimens would tend to raise the apparent flow stress.

The Rockwell "C" hardness was determined at room temperature on the curved surface of each compression sample. The results are plotted as a function of martensite content in Figs. 52 through 56. The 100% martensite intercept of the smooth curve drawn through the points is corrected for the curvature of the sample and plotted as a function of carbon content in Fig. 57. The value for 0.0C31N has been converted from Rockwell "B" to "C" by assuming that near Rc 20 one Rockwell "C" unit corresponds to one Rockwell "B" unit and using the experimentally determined equivalence of 97Rb ≈ 20Rc for this alloy. The values so obtained are approximate, but show that the present alloys are appreciably softer at higher carbon levels than fully hardened plain carbon steels. (Compare Fig. 57 with Fig. 3.)

The elastic modulus was determined for 100 percent austenite at room temperature, for as-formed martensite plus retained austenite at -195°C, for room-temperature-aged martensite plus retained austenite at room temperature, and for room-temperature-aged martensite plus retained austenite at -195°C. The modulus of elasticity was calculated for martensite aged at room temperature using the approximate relationship:
FIG. 52  ROOM TEMPERATURE HARDNESS VS. PERCENT MARTENSITE FOR 0.0 C—30N
FIG. 53 ROOM TEMPERATURE HARDNESS VS PERCENT MARTENSITE FOR 0.2C - 27N
FIG. 54 ROOM TEMPERATURE HARDNESS VS. PERCENT MARTENSITE FOR 0.4C-23N
FIG. 55 ROOM TEMPERATURE HARDNESS VS. PERCENT MARTENSITE FOR 0.6C-19N
FIG. 56 ROOM TEMPERATURE HARDNESS VS. PERCENT MARTENSITE FOR 0.8C-17 N
FIG. 57 ROCKWELL C HARDNESS FOR IRON-NICKEL-CARBON MARTENSITE AT ROOM TEMPERATURE AS A FUNCTION OF CARBON CONTENT
(15) \[ 100 \frac{E}{E} = (\text{Percent Martensite}) E_M + (\text{Percent Austenite}) E_A \]

which should hold closely if \[ \frac{E_A - E_M}{E_M} \] is small compared to unity.

This condition was fulfilled for the present alloys. As in the yield strength experiments, transformation of 0.0C 9N and 0.0C 20N was assumed to be substantially complete. The room temperature values of elastic modulus for iron-nickel alloys are shown by the solid points in Fig. 58 while those for the iron-nickel-carbon alloys are open circles. The iron-nickel curve falls within the scatter band given by Marsh (105). (In this case, the percent martensite is a much less important variable than in the case of yield strength.) The iron-nickel-carbon values fall below the iron-nickel curve. The observed modulus values are given in Appendix C.

The temperature dependence of the flow stress at two percent plastic strain was determined both in tension and in compression at temperatures between 0°C and -195°C. All specimens were quenched to -195°C to form the maximum quantity of martensite by the cooling transformation. The tensile bars were prestrained about one percent plastic strain at -195°C to further lower the retained austenite content. After prestraining, the bars were up-quenched to the testing temperature and tested within 15 minutes of reaching temperature. In addition, duplicate bars were prestrained at -195°C, allowed to age for three hours at 0°C, quenched to the testing temperature,
FIG. 58 THE EFFECT OF NICKEL AND CARBON ON THE MODULUS OF ELASTICITY OF ROOM TEMPERATURE TEMPERED MARTENSITE
and tested. The results are presented in Fig. 59. No difference in flow stress between aged and as-formed martensite was observed in 0.02C 31N. However, a difference of approximately 30,000 psi was observed in 0.22C 27N at low testing temperatures. As the testing temperature was increased, the difference in strength between the aged and unaged samples decreased. This is probably due to aging occurring in the unaged samples at the testing temperature. The stress difference was independent of the flow stress at which it was measured.

The possibility that the austenite was becoming stabilized (on aging at 0°C) with respect to subsequent strain-induced transformation was tested using a pair of 0.22C 27N samples which had not been prestrained and consequently had more retained austenite. The resulting points are shown as squares in Fig. 59. If stabilization were responsible for the effect of aging, the strengthening should be more pronounced in the higher austenite samples. The reverse was found to be true and stabilization was ruled out. It was also noted that in the aged samples the strengthening produced by increasing the carbon from 0.02 to 0.22 was very nearly independent of the testing temperature.

The tensile results were substantiated by the compressive flow stresses as a function of testing temperature, as shown in Fig. 60. The samples were not prestrained
FIG. 59 TENSILE FLOW STRESS AS A FUNCTION OF TESTING TEMPERATURE FOR AS-QUENCHED AND FOR AGED MARTENSITE

(A) Aged 3 hrs at 0°C
(Q) Aged 1/4 hr at Testing Temperature

- ■ Not Prestrained, Aged
- □ Not Prestrained, Not Aged

Flow Stress at Two Percent Plastic Strain psi

Testing Temperature °C
FIG. 60 DEPENDANCE OF COMPRESSIVE FLOW STRESS (2 PERCENT PLASTIC STRAIN) ON THE TESTING TEMPERATURE FOR AGED ALLOYS (A) AND FOR AS-QUENCHED ALLOYS (Q)

(A) Aged 3 hrs. at 0°C
(Q) Aged 1/4 hrs. at Testing Temperature
before compression testing, and, therefore, contain more austenite, but the treatment was otherwise the same.

The possibility that as-formed martensite was not being tested at any of the testing temperatures because of concomitant aging was considered. Since the Ms was about \(-30^\circ C\), aging might have occurred during quenching to \(-195^\circ C\). To check this possibility, 0.26\%C 29N was tested in tension in the same manner as 0.22\%C 27N. The Ms for this heat was approximately \(-100^\circ C\). The results, Fig. 61, show that this heat was considerably stronger than 0.02\%C 31N at all testing temperatures and, in particular, that the flow-stress for the unaged martensite showed the same temperature dependence as the \(-30^\circ C\) Ms alloys and, thus, indicated that the Ms temperature or the cooling rate through the transformation range was not interfering with testing of as-formed martensite at low temperatures.

In order to follow the effect of aging on mechanical properties, Rockwell "C" hardness measurements were made at \(-195^\circ C\) on specimens which had been quenched to \(-195^\circ C\), aged for three hours at a constant temperature between \(-195^\circ C\) and \(+100^\circ C\), and requenched to \(-195^\circ C\). The results are shown in Fig. 62. The hardness peak occurred at higher temperatures for higher carbon contents. It is difficult to make a general statement on the size of the peak because (1) the amount of austenite retained varied from
FIG. 61 TEMPERATURE DEPENDANCE OF FLOW STRESS AND AGING IN AN ALLOY WITH $M_S \sim -100^\circ C$
FIG. 62  COLD ROCKWELL C HARDNESS AFTER AGING THREE HOURS
AT TEMPERATURES SHOWN
alloy to alloy and (2) the correspondence between units of hardness and units of strength properties changes with the hardness. However, it is evident that the hardening process was carbon-dependent; hardening was practically absent at 0.02 percent carbon.

Examining the mechanical property results presented here shows that carbon appreciably strengthens iron-nickel-carbon martensite. The strengthening is particularly potent for carbon contents below about 0.2 percent. This hardening, however, is not entirely characteristic of as-formed martensite. An appreciable amount of strengthening is acquired during the aging of martensite at temperatures below room temperature. The strengthening produced during aging is dependent on the presence of carbon and probably increases with carbon content. The effect of carbon on the inherent strength of as-formed martensite will be discussed later.
V. Discussion of Results

A. The Aging Process

The c/a ratio of martensite decreases during aging. The decrease occurs discontinuously at carbon levels higher than 0.2 percent. Below 0.2 percent carbon, the path of the change is not amenable to experimental study by the X-ray diffraction technique used, but the initial state and the state after aging at 100°C for one hour are given by

\[ c/a = 1.005 + 0.045 \%C \]  
and

\[ c/a = 1.000 + 0.045 \%C \quad \%C < 0.18 \pm 0.05 \]
respectively within the experimental uncertainty.

Discussion of this change must hinge on a discussion of the "extra" 0.005 carbon-independent tetragonality observed in as-formed martensite in these alloys.

The "extra" tetragonality may be either true tetragonality or it may be a peak shift due to deformation faults on the (211) type martensite planes. The first alternative refutes the assumption that martensite and ferrite have identical lattices at very low carbon contents. Atomistic reasoning to explain such a difference does not appear feasible at the present time. The second alternative would mean that deformation faults are pre-
sent every 40 (211) type planes. (See Table IV).* In either case the "extra" tetragonality would be expected to vanish during aging.

The formation and growth of martensite of low c/a ratio is observed directly in alloys containing more than 0.2 percent carbon. It involves a larger change in tetragonality than 0.005. Consequently, interpretation of this change must be based on the supposition that carbon-dependent tetragonality is disappearing. Two processes are considered:

(1) Tetragonality is being lost in certain portions of martensite because carbon atoms are moving to interstitial positions in which they produce less net tetragonality. The case which has been seriously considered (59,60) is that of carbon atoms redistributing between octahedral interstitial sites leaving a degree of preference for 00\(^1\) and \(\frac{1}{2}\)0, type "c", sites as necessary to produce minimum free energy. The transformation considered is

\[ \text{order} \rightarrow \text{partial order}. \]

According to Zener (59) and Fisher (60), the critical temperature should obey an equation of the form

\[ T_c (\text{OK}) = K \text{ (percent carbon)} \]

* Experimental testing of this hypothesis, although theoretically possible through measurement of the doublet separation of the (002)-(020) (200) and (004) -(040) (400), was not experimentally attainable because of the low intensity of the \{004\} reflections.
Disorder should occur and proceed to the largest extent at low carbon contents and high temperatures. Fig. 35 shows that after aging at 100°C for 1 hour, 0.06 percent carbon martensite is tetragonal and has approximately the same carbon-dependent tetragonality as is exhibited by the as-formed condition. Then, in equation 17, \( K \) is restricted to

\[
(18) \quad K = \frac{273}{0.06} \approx 4500.
\]

Since disordering of carbon atoms does not occur at 0.06 percent carbon, i.e., at low carbon contents where the driving force is greatest, disordering will not be present at higher carbon contents in the martensites under consideration.

The arguments for the disordering reaction are sufficiently general so that the specific test given here can serve to limit the applicability of the theory for ferrous martensite in general. For example, on the basis of the \( M_s \) values for iron-carbon alloys, the possibility of quenching disordered martensite is confined to carbon contents below 0.1 percent carbon. Furthermore, since the mean time of stay of carbon atoms is short (approximately one second for ferrite) at room temperature, reordering may be expected at room temperature. Consequently, X-ray observations of \( c/a \) ratios at room temperature should be unaffected by disordering if more than
about 0.5 percent carbon is in solid solution, and therefore, determination of the carbon content of tempered martensite by c/a measurements is justified.

(2) Since disordering can be ruled out, the lowering of the c/a ratio can be interpreted as the loss of carbon-dependent tetragonality at carbon levels above 0.2 percent through the removal of carbon from solution. Carbide formation is, by analogy with low alloy steels, the most likely sink for this carbon. The reaction involved is:

(19) Martensite (percent C of the Austenite ----> Martensite (percent C of c/a=1.008) + Carbide

Since the carbon-independent tetragonality has vanished by tempering at 100°C, the c/a of 1.008 must be referred to equation (3) to determine the carbon content left in solution. This indicates 0.18 percent carbon.

Equation (19) indicates a process of carbide precipitation which is similar to the first stage of tempering, equation (10), but which produces a martensite of lower carbon content.* The c/a ratio of the low-carbon martensite so produced apparently increases during aging from 1.005 to 1.008. This represents an increase of 0.07 percent carbon according to equation (3). A temperature dependence of the c/a ratio at the end of the first stage

* This is the same conclusion drawn by Werner et al. (35)
was found by Roberts et al. (42) but not by Werner et al. (35) in iron-carbon alloys.

The electrical resistivity changes significantly during aging. Below -80°C a decrease in resistivity occurs due to isothermal martensitic formation. Above -40°C in carbon-containing alloys, an increase in resistivity is observed. The magnitude of this increase varies directly with carbon content. The increase is followed by a decrease in resistivity whose magnitude is also a direct function of carbon content. Tempering, according to equation (19), is thought to be responsible for both the increase and the subsequent decrease in resistivity.

The argument can be carried out by a process of elimination. Broom (106) has reviewed the changes in resistivity which are expected and which occur during recovery of homogeneous cold-worked metals and alloys. With the exception of the growth of stacking faults due to chemical segregation (84) and the removal of strain-induced order, (107) the electrical resistivity decreases during recovery. Stacking fault growth is considered unlikely in body-centered cubic metals because of the high energy of the fault interface. Order-disorder has been excluded on the basis of X-ray results.

* Both processes are used to account for a small increase in resistivity observed during room temperature annealing of gold-silver alloys deformed at -80°C and -190°C (107).
On the other hand, precipitation often produces an increase in resistivity during its early stages. The time dependence of this increase can be quite similar to that indicated in Figs. 37 through 41. The later stages of precipitation, and the tempering of plain-carbon steels in particular, exhibit a decrease in resistivity. It is concluded that precipitation is likewise occurring during the aging of martensite, and that carbon is intimately involved.

The observation of an increase in resistivity during isothermal aging in 0.08\%\text{C} 29\%\text{N} suggests that precipitation takes place from as-formed martensite even at a carbon content of 0.08 percent. It, therefore, appears that part of the decrease in tetragonality at low carbon contents is due to removal of carbon from solid solution. This observation represents some evidence against a metastable chemical equilibrium between carbide and low-carbon martensite obtaining at the end of the first stage of tempering.

However, if stacking faults are present and if a metastable chemical equilibrium between 0.2 percent carbon martensite and carbide applies, transient precipitation of carbide from carbon segregated to stacking faults might still occur. The precipitation of such carbon would provide an increased driving force for stack-
ing fault removal and might occur at very low carbon levels because of the high energy of the faulted area. However, as the faulted areas recede, the martensitic matrix left behind would be undersaturated with respect to the carbide. Carbide would tend to redisolve leaving martensite of the original carbon content.

The initial and final states postulated above agree with the X-ray data, Fig. 34 and Fig. 35, and the postulated mechanism produces precipitation which accounts for the increase in resistivity observed, Fig. 38. Furthermore, Fig. 35 can be directly interpreted according to metastable chemical equilibrium. Since the "extra" tetragonality has vanished, the c/a ratio is directly convertible to carbon content according to equation (3). The carbon content of martensite originally containing less than 0.2 percent carbon is unchanged -- no precipitate is present because the martensite is undersaturated with respect to the carbide. The supersaturation of higher carbon as-formed martensite with respect to the carbide, and the consequent precipitation of carbide holds the carbon content of the depleted martensite at 0.2 percent -- independent of its original carbon level.

Age hardening should be observed as a consequence of the precipitation process described above. Fig. 62
shows that it is present and that it follows the trends indicated by the electrical resistivity results. (Compare Fig. 42 and Fig. 62.) The peak hardness occurs about 50°C higher than the maximum increase in electrical resistivity.

Precipitation hardening is observed during the low-temperature tempering in high carbon iron-carbon alloys (69). However, an increase in resistivity is not observed (100). In order to determine whether the increase in resistivity reported here should be observable in iron-carbon alloys, the temperature dependence of the resistivity increase was estimated. The resistivity was taken to be proportional to the $1/3$ power of time (67) and then three times the logarithms of the slopes so obtained were plotted against the reciprocal temperature. From the resulting straight line (corresponding to an activation energy of 18,000 calories per mole*), the rate of resistivity increase was estimated at higher temperatures. The results indicate that a resistivity increase in iron-carbon alloys would be observable only for carbon contents above one percent, and then only if measurements were started within a few minutes of reaching room temperature. These calculations are not included because the

* Similar calculations were carried out for the decrease in resistivity. In this case the activation energy was 24,000 calories per mole for carbon contents larger than 0.2 percent and decreased to approximately zero for 0.02C 31N.
same conclusions can be drawn directly from the experimental data (Figs. 37 through 41).

The X-ray data (see Fig. 36) indicate that at lower carbon contents (higher nickel contents) tempering proceeds more rapidly in the iron-nickel-carbon alloys. Part of this may be due to the effect of nickel, or the low transformation temperature, on the rate of tempering. This is probably the cause of the more rapid tempering observed here for 0.68C 19N than was observed by Roberts et al.\(^42\) for iron-carbon alloys of similar carbon content. But within the alloys considered here, separation of the effect of nickel and carbon is not possible. Considering that less carbide need be formed to produce observable X-ray diffraction effects in the lower carbon alloys, carbide formation may be, as indicated in Fig. 42, proceeding at a constant rate over an appreciable carbon range (nickel range), but the apparent end point is reached more rapidly in lower carbon (higher nickel) alloys.

In summary, the c/a ratio of the iron-nickel-carbon as-formed martensite is given by equation (14) between 0.01 and 1.0 percent carbon. The "extra" tetragonality of 0.005 (which may be either true tetragonality or an effect of (211) deformation faults) is independent of carbon, and disappears during tempering at 100°C for one
hour. Tempering as-formed martensite containing more than 0.2 percent carbon at temperatures as low as $-40^\circ C$ results in the formation of a low-carbon martensite, the carbon probably precipitating as a carbide. This process may also occur at carbon contents below 0.2 percent. Precipitation is accompanied by hardening and by an increase and subsequent decrease in electrical resistivity.

B. The Solid-Solution Strengthening Mechanism

The strength of 100 percent as-formed martensite has not been directly observed. The $0^\circ C$ yield strength of martensite aged at $0^\circ C$ for $3\frac{3}{4}$ hours is shown in Fig. 50. The increase in flow stress acquired on aging martensite-austenite mixtures at $0^\circ C$ for 3 hours is shown in Figs. 59 and 60 for the testing temperatures at which it can be observed. If the age hardening of the austenite-martensite mixture is assumed to equal that of the 100 percent martensite alloy and is assumed to be the same at 0.6 and at 2 percent strain, an estimate of the solid-solution strengthening can be obtained. The approximate curve is presented in Fig. 63. Intense solid-solution strengthening is present but is confined to carbon contents below about 0.3 percent. Practically no additional strengthening is observed from 0.4 to 0.8 percent carbon.
FIG. 63 ESTIMATED SOLID-SOLUTION HARDENING OF MARTENSITE BY CARBON
Over this entire range of compositions the elastic modulus for the carbon-bearing alloys is below the modulus line for iron-nickel alloys. This is in agreement with the statements of Kurdyumov and with his experimental observations on the decrease of the Debye temperature of martensite with increasing carbon content for plain-carbon steels (see Table V).

The strengthening in these alloys cannot be ascribed to any solid-solution hardening process which requires prior segregation of the solute atoms. In particular, carbon-atmosphere formation by elastic interaction between dislocations and carbon atoms is not a likely strengthening mechanism because the solid-solution hardening is present in as-formed martensite. This type of hardening would also lead to a large temperature dependence of the solid solution strengthening. This is not observed.

The decrease in elastic modulus from pure iron-nickel to iron-nickel-carbon indicates that the Peierls-Nabarro force is not increasing rapidly. Because only the elasticity modulus was measured and because the expression for the Peierls-Nabarro force is approximate, no proof can be offered, but it appears that strengthening caused by carbon is not due to an increase in the lattice binding.

The interaction between random solute atoms and dislocations as visualized by Mott and Nabarro has
been specialized by Petch and Cracknell\textsuperscript{(112)} for interstitial carbon and nitrogen atoms in iron. The mechanism is as follows:

The dislocations, which glide during deformation, bend slightly at each solute atom along their length. If \( \Lambda \) is the separation between solute atoms, the average amplitude of such a bend of length, \( \Lambda \), is:

\[
(20) \quad A = \frac{F\Lambda}{8\alpha\mu b^2}
\]

where \( F \) is the average force exerted by the atom on a dislocation at a distance \( \Lambda/2 \),

\( \alpha \) is about 0.5,

\( \mu \) is the shear modulus,

\( b \) is the Burgers vector of the dislocation

On the average, no excess force and consequently no excess bending of the dislocation can be predicted in a specified sense along the slip direction; but it is likely that with \( n^2 \) such small loops, approximately \( n \) will be in excess in one sense (unspecified). These \( n \) excess bends will produce a net amplitude of the compound bend, Fig. 64, of

\[
(21) \quad A_n = \frac{(nF)(n^2\Lambda)}{8\alpha\mu b^2}
\]

The elementary slip process, according to this mechanism, is to reverse the sign of the amplitude of
Fig. 64. Elementary movement of a dislocation line in a solid solution. (After Mott.) (Ref. 86)
the compound bend by producing n excess individual bends in the opposite sense.

A difficult point to establish is how long a compound loop to consider. The shorter the loop, the more extreme the hardening predicted. Cracknell and Petch determined the length by requiring the amplitude of the compound loop to be \( \Lambda \), the distance between solute atoms.

The compound loop is then regarded to be sufficiently long so that it may be reversed independently of the next loop. The stress for this reversal is determined by the force opposing the reversal

\[
\left( \frac{22}{2} \right) \frac{\tau}{2} = \gamma = \frac{nF}{n^2 \Lambda} \frac{1}{b}
\]

The average force, \( F \), is evaluated by averaging the gradient of the elastic interaction energy (85) in the slip direction, over all the angles between solute atoms and dislocations and over solute-atom–dislocation distances between \( \Lambda/2 \) and \( \nu \), the core radius of the dislocation.

Assuming that \( \Lambda = \text{(number of carbon atoms per unit volume)}^{-1/3} = \frac{N^{-1/3}}{N} \)

\[
\sigma = \left\{ \frac{N^{2/9}}{(4\pi)^{1/3} b \Lambda} \left[ \frac{16 A}{\pi} \log \frac{1}{2 + \frac{1}{N^{1/3}}} \right]^{1/2} \right\}_N
\]

where \( A = 1.5 \) to \( 3.0 \times 10^{-20} \) dyne cm\(^2\)
The number within the braces varies quite slowly with $N$. In engineering units for carbon contents $0 < \%C < 0.3$:

(24) \( \sigma \text{(psi)} \simeq 100,000 \) (weight percent carbon)

Some aspects of the derivation outlined above are worthy of particular note. The calculation of the stress exerted by a carbon atom on a dislocation is based on the interaction of the hydrostatic stress and the volume change due to inserting a carbon atom. A large shear component, which is difficult to approximate, is very likely present in the distortion caused by interstitially dissolved carbon atoms. Since the shear stress is probably of the same order of magnitude as the hydrostatic stress, an appreciable contribution to $\sigma$ is expected. In addition, it is to be noted that throughout the derivation, elasticity theory is assumed. This theory can be expected to break down when the separation of the dislocation and the carbon atom equals the core radius of the dislocation. This condition is approached at 0.3 percent carbon, and above this carbon level the derivation has no physical meaning. At this carbon content, solid-solution hardening is observed to level off.

The strengthening predicted by the theory is about an order of magnitude too low. The effect of shear interaction might improve the agreement, but at least a factor of five is expected to be left.
The experimental evidence of Cracknell and Petch\(^{(112)}\) is of interest also. They found that carbon and nitrogen strengthened ferrite according to

\[(25) \sigma (\text{psi}) = 6 \times 10^5 \text{ (weight percent carbon)}\]

which is about half the strengthening rate observed in low-carbon martensite. The higher rate of solid-solution hardening in martensite compared to ferrite may be related to the tetragonality of the martensite. The preferred positioning of carbon atoms in the octahedral sites of martensite might allow a larger shear-stress interaction between carbon atoms and dislocations than is present in ferrite.

Heslop and Petch\(^{(113)}\) investigated the temperature dependence of this strengthening. It is independent of temperature which is also the case observed in martensite.

The Mott-Nabarro mechanism of solid-solution strengthening as presented above is not in good agreement with the experimental observations, but predicts qualitatively the carbon content over which hardening is observed. Qualitatively, it seems to correspond to Kurdyumov's\(^{(33)}\) greater simultaneity of slip in that stress-fields of the carbon atoms hold back the progress of slip, and therefore, require a larger applied stress to produce deformation. It is in direct opposition to
the hypothesis of Polakowski\(^{(91)}\) that aging is required to obtain strength in martensite.

In summary, the mechanism of solid-solution hardening in interstitial body-centered cubic and body-centered tetragonal solid solutions has not yet been explicitly stated. The experimental work described here may be regarded as a critical experiment to test whether randomly distributed carbon atoms will produce solid-solution hardening and thus to provide a guide for the development of such a theory. Solid-solution hardening does occur, but it decreases in potency very rapidly with increasing concentrations. It appears that hardening is confined to solute concentrations where elastic interaction is important.

Precipitation hardening also plays an appreciable role in determining the strength and hardness of martensite. This role extends to carbon levels lower than 0.2 percent, but solid-solution hardening is more important at these low carbon levels. Considering the small decrease in hardness observed during the first stage of tempering in hardened plain-carbon steel and the large decrease in carbon in solid solution, solid-solution strengthening is also probably confined to a similar carbon range in martensitic steels.
The present alloys are appreciably softer than martensitic steels at carbon contents larger than 0.3 percent. A greater contribution by precipitation hardening in plain-carbon steels may be the reason for this difference, but no evidence is available on which to argue the point.
Conclusions

1. Iron-nickel-carbon martensites with an Ms of about -35°C offer an opportunity to study as-formed martensite.

2. As-formed martensite is body-centered tetragonal, with \( c/a = 1.005 + 0.045 (\%C) \).

3. The 0.005 "extra" tetragonality may be either true tetragonality or more reasonably apparent tetragonality caused by deformation faults every 40 (211)-type martensitic plane.

4. Aging commences at temperatures as low as -40°C and is evidenced by increasing yield strength, hardness, and by an increase and subsequent decrease in electrical resistivity.

5. During aging the excess tetragonality disappears; the c/a ratio of martensite aged for one hour at 100°C may be described by
   \[
   \begin{align*}
   c/a &= 1.000 + 0.045 & \%C \leq 0.20\% \\
   c/a &= 1.008 & \%C \geq 0.20\%
   \end{align*}
   \]

6. The aging process is similar to the first stage of tempering in iron carbon alloys and is given by
   \[
   \text{As-formed Martensite} \rightarrow (0.2\%C) \text{Martensite} + \text{Precipitated Carbide}
   \]

7. The aging data indicate that metastable equilibrium between 0.2 percent carbon martensite and precipitated carbide is possible.
8. The yield strength of martensite (below 0.3 percent carbon) is primarily determined by the yield strength of the as-formed martensite. The yield strength of as-formed martensite is probably due not to increasing atomic bond strength but to the strengthening effect of random carbon atoms and may be qualitatively related to the strengthening produced by carbon atom-dislocation elastic interaction. For carbon levels higher than 0.4 percent, little additional solid-solution strengthening occurs.

9. The additional strengthening observed in 0°C tempered martensite, at least for carbon contents greater than 0.3 percent, is due to precipitation hardening.

10. The strengthening of martensite by carbon is independent of the temperature of testing for testing temperatures which are low enough to prevent aging, suggesting that Cottrell atmosphere formation is not an important strengthening mechanism.
Suggestions for Future Work

1. The probability of the occurrence of stacking faults in martensite should be investigated, using different diffractometer techniques on martensite formed in austenite single crystals.

2. The nature of the carbide formed at low tempering temperatures should be determined.

3. The effect of the structure of prior austenite on the mechanical properties should be investigated.

4. The nature and kinetics of the aging process at carbon levels below 0.2 percent should be investigated.
References


45. Kehsin Kuo, "Recent Progress in the Study of the Structure of Martensite and its Decomposition Products in Carbon Steels", Jern. Annaler 140 no 11 (1956) 854 (in English)

46. Laurence Leonard, Private Communication


48. Ibid. pg. 219.


53. G. V. Kurdyumov, V. K. Kritskaya, and N. M. Nodia, "Influence of Carbon on the Bonding Forces and Static


66. B. S. Lement, Appendix B of Reference 42


   *Special Purpose Alloys*, First Edition, McGraw Hill,
   New York (1933) 384.

81. Earl R. Parker, "Modern Concepts of Flow and Fracture",
   Trans. ASM 50 (1958) 52.

82. Hideji Suzuki, "The Yield Strength of Binary Alloys",
    *Dislocations and Mechanical Properties of Crystals*,
    Fisher, Johnston, Thomson, Vreeland, Editors: J.

83. Earl R. Parker and Thomas H. Hazlett, "Principles of
    Solid Solution Hardening", *Relation of Properties to

84. A. H. Cottrell, "Interactions of Dislocations and Solute
    Atoms", ibid. 131.

85. A. H. Cottrell, "Effect of Solute Atoms on the Behavior
    of Dislocations", *Conference on the Strength of
    Solids*, University of Bristol Report, N. F. Mott, Editor,


88. N. F. Mott and F. R. N. Nabarro, "Dislocation Theory
    and Transient Creep", *Conference on the Strength of Solids*,
    University of Bristol Report, N. F. Mott, Editor,


95. B. L. Averbach, "Retained Austenite Determinations by X-ray Methods", Trans. AIME 196 (1953) 87.

96. R. T. Howard and M. Cohen, "Quantitative Metallography by Point Counting and Lineal Analysis", Trans. AIME 172 (1947) 413.


Biographical Note

Peter Grüt Winchell was born on July 27, 1929 in Ossining, New York. He attended New York State Public Schools through the tenth grade. He attended the University of Chicago from 1945 to 1949, receiving an A.B. degree in 1948. He attended Purdue University for one year, worked as a metallurgical observer for the Republic Steel Corporation for one year, and entered the Massachusetts Institute of Technology in 1951, where he received a B.S. degree in metallurgy in June, 1953. He entered graduate school in 1953 and instructed physical metallurgy laboratory in 1954 and 1955, was a research assistant in metallurgy in 1956 and 1957, and Universal-Cyclops Steel Corporation Fellow in 1958.
Appendix A

Calculation of Percent Martensite from the Integrated Intensity of \( \{200\}_M \) and \( \{220\}_\gamma \)

For a spectrometer

\[
(A - 1) \quad I^A_{1} = k^A R^A V^A,
\]

where \( I_1 \) = integrated intensity of peak 1;

\( k \) = constant dependent on the instrument;

\( V^A \) = volume of phase A contributing to peak 1;

and

\[
(A - 2) \quad R^A_1 = \frac{1}{(\bar{\mu})^2} \frac{F^A_1}{N_1} \frac{1 + \cos^2 2\Theta_m \cos 2\Theta_1}{\sin \Theta_1, \sin 2\Theta_1} e^{-2M_1}
\]

where \( V^A \) is the unit cell volume for phase A

\( \bar{\mu} \) is the average absorption coefficient

\( F^A_1 \) is the structure factor of phase A at \( \Theta_1 \) corrected for dispersion

\( N_1 \) is the multiplicity of plane 1

\( \Theta_m \) is the Bragg angle for the monochromating crystal

\( \Theta_1 \) is the Bragg angle for plane 1

\( M_1 \) is the Debye factor for \( \Theta_1 \)

Then:

\[
(A - 3) \quad I \{220\} = k R \{220\} V^\gamma
\]

\[
(A - 4) \quad I \{200\} = k R \{200\} V^M
\]
also

\[(A - 5) \quad V^M + V^Y = V\]

correspondingly:

\[(A - 6) \quad \text{Volume Percent Martensite} = \frac{100}{1 + \frac{I_{\{220\}}^M}{I_{\{200\}}} \frac{R_{\{220\}}^M}{R_{\{200\}}}}\]

using:

\[\theta_m = 15.5^\circ \quad \text{(quartz crystal);}\]

\[\text{cobalt \( k \alpha \) radiation;}\]

\[\text{Debye Temperature for the alloys \( 420^\circ K; \)}\]

and the lattice parameters given in Table A-1:

the desired \( R \) ratios were:

<table>
<thead>
<tr>
<th>% C</th>
<th>% Ni</th>
<th>( \frac{R_{{200}}^M}{R_{{220}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>21</td>
<td>0.689</td>
</tr>
<tr>
<td>0.30</td>
<td>25</td>
<td>0.689</td>
</tr>
<tr>
<td>0.00</td>
<td>31</td>
<td>0.698</td>
</tr>
</tbody>
</table>

Table A-1

<table>
<thead>
<tr>
<th>% C</th>
<th>% Ni</th>
<th>( a_Y )</th>
<th>( a_m )</th>
<th>( c/a_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>21</td>
<td>3.588</td>
<td>2.850</td>
<td>1.028</td>
</tr>
<tr>
<td>0.3</td>
<td>25</td>
<td>3.583</td>
<td>2.855</td>
<td>1.019</td>
</tr>
<tr>
<td>0.00</td>
<td>31</td>
<td>3.573</td>
<td>2.861</td>
<td>1.005</td>
</tr>
</tbody>
</table>
Appendix B

Average Burst Temperatures for Vacuum Melted Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Burst Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02C 31N</td>
<td>-46</td>
</tr>
<tr>
<td>0.08C 28N</td>
<td>-27</td>
</tr>
<tr>
<td>0.22C 27N</td>
<td>-38</td>
</tr>
<tr>
<td>0.28C 25N</td>
<td>-39</td>
</tr>
<tr>
<td>0.30C 25N</td>
<td>-38</td>
</tr>
<tr>
<td>0.39C 23N</td>
<td>-31</td>
</tr>
<tr>
<td>0.40C 23N</td>
<td>-30</td>
</tr>
<tr>
<td>0.48C 20N</td>
<td>-31</td>
</tr>
<tr>
<td>0.63C 19N</td>
<td>-37</td>
</tr>
<tr>
<td>0.96C 15N</td>
<td>-56</td>
</tr>
</tbody>
</table>
## Appendix C

Elastic Modulus (psi x 10⁻⁶)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Y at Room Temperature</th>
<th>% Martensite</th>
<th>Y and Martensite (as-formed) at -195°C*</th>
<th>Y and Martensite at room temperature</th>
<th>Y and Martensite (Tempered) at -195°C*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>31N</td>
<td>23.6</td>
<td>88</td>
<td>20.0</td>
<td>21.0</td>
</tr>
<tr>
<td>0.2C</td>
<td>27N</td>
<td>25.1</td>
<td>84</td>
<td>22.0</td>
<td>22.8</td>
</tr>
<tr>
<td>0.4C</td>
<td>23N</td>
<td>27.2</td>
<td>86</td>
<td>23.9</td>
<td>24.2</td>
</tr>
<tr>
<td>0.6C</td>
<td>19N</td>
<td>27.6</td>
<td>81</td>
<td>25.5</td>
<td>24.8</td>
</tr>
<tr>
<td>0.8C</td>
<td>17N</td>
<td>27.0</td>
<td>79</td>
<td>26.2</td>
<td>25.5</td>
</tr>
<tr>
<td>0.0C</td>
<td>19N</td>
<td>--</td>
<td>100</td>
<td>--</td>
<td>25.2</td>
</tr>
<tr>
<td>0.0C</td>
<td>9N</td>
<td>--</td>
<td>100</td>
<td>--</td>
<td>28.7</td>
</tr>
</tbody>
</table>

* Not corrected for change in SR⁴ - ADI gauge factor.