THE STRUCTURE AND AGING OF MARTENSITE

by

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ABSTRACT

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Submitted to the Department of Metallurgy and Materials Science on August 14, 1972 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The structure and aging of virgin lath and twinned martensites were investigated by means of X-ray diffraction, transmission electron microscopy, and electrical resistivity measurements. Seventeen iron-nickel-carbon alloys with 18, 21 and 24 weight percent nickel and carbon contents from zero up to 0.62 weight percent were chosen to provide martensites of both morphologies.

The lath martensite consisted of packets of highly dislocated laths, while the twinned martensite took the form of internally twinned acicular plates, with the (112) twins spaced 60 to 100 angstroms apart. The virgin twinned martensite is found to be body-centered tetragonal with the axial ratio proportional to the carbon content. There is indirect evidence that virgin lath martensite is also tetragonal. Interstitial ordering theories are shown to be invalid in accounting for the tetragonality of virgin martensite. No indication of carbon disordering during or after martensite formation was noted.

The aging of both martensitic morphologies proceeds in four steps, depending on the temperature of aging. The first is a dislocation relaxation, which is detectable only in specimens aged below room temperature; the associated activation energy is about 3 kcal per mole. Secondly, carbon-rich clusters form in the martensite at temperatures above -30°C, the activation energy being approximately 21 kcal per mole;
this suggests that carbon diffusion is the rate-controlling process. The third step, occurring above 100°C, is the formation of ε-carbide. There is some indication that the carbide forms directly from the clusters; the corresponding activation energy of 35 kcal per mole suggests that the rate-controlling process may be the pipe-diffusion of iron atoms away from growing carbide particles. The fourth step in the sequence is the precipitation of cementite at temperatures above 200°C; here, the activation energy is the same as that for ε-carbide formation. Recovery and recrystallization follow the latter stage. No significant differences in aging behavior between the lath and twinned martensites were observed, indicating that the substructure does not play a major role in the aging phenomena.

Thesis Supervisor: Morris Cohen

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Chapter I
INTRODUCTION

Steels had been used for several thousand years before anything was known about why their properties could be changed by the application of thermal and mechanical treatments. (1) In the early part of this century, it was realized that the large increase in the strength of steel upon quenching from high temperatures is due to a transition in structure from austenite, a face-centered cubic phase, to martensite, a body-centered structure. (2) Further changes in mechanical properties upon reheating the quenched steel were explained by the discovery of a series of structures, resulting from such tempering treatments. (3-4)

Since these structures were first observed there has been substantial research activity aimed at a better description of the structures and how, when, and why they form. With the advent of more modern research techniques, such as transmission electron microscopy and Mössbauer measurements, more details of martensite formation and aging have been studied. This research is meant to provide a still more complete description of the structure of martensite and the decomposition products formed during aging.
Chapter II
LITERATURE REVIEW

2.1 Martensite Formation

Martensite is the name given to the phase produced by a diffusionless shear transformation. In iron alloys, such transformations take place when the face-centered cubic austenite is cooled sufficiently rapidly to avoid the competing isothermal reactions. The martensitic transformation begins when the temperature of the steel is cooled below $M_s$, the martensite start temperature, and it proceeds at speeds approaching that of sound in the metal. (5) Models to account for the kinetic features of the nucleation and growth of martensite have been developed by Kaufman and Cohen (6), Clapp (7), and others. A recent review of the subject was given by Kaufman. (8)

Crystallographic theories of the martensitic transformation have been developed on the basis of a phenomenological approach to the question of how the transformation from austenite to martensite is accomplished. A review of such theories was given by Dunne and Wayman. (9) The phenomenological description of the martensitic transformation is given by the matrix relationship:

$$P_1 = RBP \quad (1)$$

in which $P_1$ is the shape strain of the transformation, which is composed of three parts: $R$, the orientation relationship between the parent austenite and the martensite, $B$, the Bain strain, and $P$, an inhomogeneous shear in the martensite which accommodates the martensite to the austenite.
The cumulative effect is to produce an invariant-plane transformation.

2.1.1 Martensite Morphology

Two distinct morphologies of martensite have been observed. (10-15) One forms in alloys with relatively high $M_s$ temperatures and consists of packets of laths, with a high dislocation density. The other morphology forms in alloys with lower $M_s$ temperatures and consists of acicular plates with an internal structure of very fine twins about 60 to 100Å apart. The dislocation density of this type appears to be much lower than that of the first type. Because of the shape of the acicular plates, it is usual for much more retained austenite to be present with the twinned morphology than with the lath.* Figures 1 and 2 are optical and transmission electron micrographs of the two morphologies.

It has been proposed (10,11,16) that the inhomogeneous shear of the martensite transformation ($P$ in eqn. 1) can occur by slip or twinning. In lath martensite, which is formed at higher temperatures, this shear is accomplished by slip leading to the high dislocation density of the laths. Since twinned martensite forms at lower $M_s$ temperatures, the shear is accomplished by twinning, because twinning becomes

*The terminology used in this work will be "lath martensite" to indicate the high-$M_s$ dislocated morphology and "twinned martensite" to indicate the low-$M_s$ acicular plate martensite.
Figure 1: Micrographs of Lath Martensite in an 18Ni-0.11C Alloy.
Figure 2: Micrographs of Twinned Martensite in an 18Ni-0.4C Alloy.
relatively easier than slip at lower temperatures. Some support for this idea has come from experiments which produced changes in $M_S$ temperature by the application of high pressure or mechanical treatments resulting in a change in martensite morphology. (16-19) Davies and Magee (20-21) have extended this line of thought to a consideration of austenite ferromagnetism as a necessary condition to the formation of twinned martensite in Fe-Ni alloys. Ferromagnetic austenites are substantially stronger than paramagnetic austenites, and hence could influence the mode of deformation by which martensite forms.

Since the morphology of martensite depends on the $M_S$ temperature, the addition of alloying elements which change $M_S$ can affect the morphology of the martensite. (12-13) Figure 3 shows the morphology for Fe-Ni-C alloys. There is a range of compositions for which mixed lath and twinned structures have been observed. The breadth of this range decreases in the alloys with higher nickel contents. The $M_S$ temperature at which the lath-to-twinned change takes place is lower for alloys with larger amounts of nickel.

2.1.2 Martensite Tetragonality

Carbon occupies octahedral interstitial positions in the iron lattices of both austenite and martensite. In austenite (Fig. 4) the iron atoms forming the corners of the octahedron are equidistant from the interstitial site; hence when the site is occupied by a carbon atom the lattice is expanded symmetrically. In martensite (Fig. 5) the
FIGURE 3. THE MORPHOLOGY AND $M_s$ TEMPERATURES OF Fe-Ni-C MARTENSITE AS A FUNCTION OF COMPOSITION (AFTER WINCHELL (22))
Figure 4. fcc austenite lattice with positions of octahedral sites indicated.
FIGURE 5. BODY-CENTERED MARTENSITE LATTICE SHOWING THE THREE SETS OF OCTAHEDRAL SITES
octahedral sites have two irons closer than the other four irons, thus forming a distorted octahedron. When such a site is occupied, the lattice distortion is **asymmetrical**. 

(23-26) There are three sets of octahedral sites in bcc iron. If only one set of sites is occupied, the **asymmetric** distortions will lead to expansion in one of the three \{001\} directions and contractions in the other two.

The Bain distortion part of martensite formation (B in eqn. 1) is the collapse of the fcc austenite lattice into the body-centered martensite lattice. Due to the nature of this distortion, if there are some carbon atoms in solution they will occupy only one of the three sets of octahedral sites. The **cumulative effect of the asymmetric distortions of the occupied sites leads to the martensite being body-centered tetragonal.** Winchell and Speich (27) have offered a systematic treatment of those situations in which tetragonality may be produced in martensite as a result of asymmetric point defects. There have been a number of studies (28-30) which measured this tetragonality; the c/a ratio appears to vary linearly with carbon content.

**Tetragonal iron-carbon martensite can be thought of as an ordered solid solution, since it is the occupation of only one of three sets of octahedral sites which causes tetragonality.** Zener and others (31-35) have proposed theories to account for the ordering of carbons to one set of sites. Although the details of each theory are different, each predicts that, for a given carbon concentration, there
is a critical temperature below which the structure can minimize its free energy, and accommodate the anisotropic strain due to the interstitial atoms, by allowing them to occupy one set of octahedral sites in preference to the other two. Thus, below this critical temperature, there is a driving force for an ordering reaction that converts the bcc structure to bct. The prediction for the critical temperature for ordering is of the same order of magnitude for all the theories, namely \( T_C \) is about 1000 times the weight percent carbon in the alloy.

Owen, et al. (36) have suggested that such an order-disorder reaction may be at play in the formation of bcc martensite in alloys with low carbon contents. In such alloys \( T_C \) is lower than \( M_S \) leading to carbon disordering immediately on formation of the martensite. They cite as supporting evidence some observations of bcc virgin martensite. On the other hand, there have never been observations of actual ordering and disordering of interstitials, thus confirming the existence of a critical temperature. However, this may be due to the intervention of aging effects removing the carbons from solution before disordering could be observed. So the question of whether interstitial ordering reactions occur is still open. It would seem that the structure of martensite must be tetragonal at the moment of formation due to the inherited distribution of carbons as a result of the Bain strain, but it is not certain if any changes occur immediately afterward. There is ample evidence (28-30) that twinned martensite is
tetragonal when observed in the virgin condition, but the case of lath martensite has not been fully explored. The lower carbon contents of alloys forming lath martensite lead to high $M_S$ and low $T_C$ values, so if the ordering theories are valid it is likely that disordering will cause lath martensite to be cubic. Also, segregation of carbons to dislocation sites during the quench could deplete the lattice of interstitials and lead to the observation of cubic martensite.

2.2 Martensite Aging

The equilibrium concentration of carbon in $\alpha$-iron below 500°C is less than 0.01 weight percent. (37) Thus Fe-C martensite is a metastable phase, with much more than the equilibrium amount of carbon trapped in solution due to the diffusionless nature of the transformation. If provided with the necessary activation energy, martensite will undergo changes resulting in the formation of structures closer to the equilibrium mixture of $\alpha$-ferrite and cementite ($Fe_3C$). These changes are thermally activated, and those which occur at elevated temperatures are called tempering, while the more subtle low temperature changes have been called aging.

2.2.1 The Stages of Tempering

The tempering of steel may be divided into three stages. (3-4) Averbach and Cohen, et al. (29,38-40) have provided an extensive description of the structural changes which occur due to tempering. Their results showed that the
first stage of tempering consists of the formation of ε-carbide (41) a hexagonal close-packed structure of approximate composition Fe$_{2.4}$C, at the same time as a low-carbon martensite appears. From its c/a ratio the composition of the low-carbon martensite seems to be 0.25 weight percent carbon. Its appearance is discontinuous; that is, a second, distinct (002)$_M$ line appears on diffraction films and its intensity increases while the intensity of the original (002)$_M$ line decreases as tempering progresses. The second stage of tempering involves the transformation of retained austenite by isothermal reactions. Usually the product of the second stage is bainite, although in some steels this stage may not occur at all. The third stage was found to be the precipitation of cementite, an orthorhombic structure of composition Fe$_3$C. As tempering continues into the third stage, the ε-carbide dissolves and the carbon content of the matrix drops from 0.25 weight percent to its equilibrium value, with a concurrent loss of tetragonality. Eventually the cementite coarsens and spherodizes, and recovery and recrystallization also occur producing a structure of α-ferrite and spherodized cementite. All of the changes due to tempering are thermally activated (hence temperature- and time-dependant) so there is usually some overlap between the stages.

Since the time that the stages of tempering were set forth, more details and refinements of the process have been explored. Wells (42) showed that orientation relationships exist between both the ε-carbide and cementite lattices and
the martensite lattice. Information about the kinetics of the various stages has been provided by a number of investigators. (29-30,38,43-44) The activation energy appears to increase during the course of tempering from initial values of about 15 kcal. per mole up to 35 kcal. per mole during stage three. It has been suggested (43-44) that tempering consists of several simultaneous or overlapping processes, each with a different activation energy. The work of Hoffman (45), Kalish and Cohen (46) and Barton (47) has questioned the idea that $\varepsilon$-carbide is in equilibrium with low-carbon martensite. They suggest that the substructure, particularly the dislocation density, of the martensite is a determining parameter for the appearance of $\varepsilon$-carbide. Recently, Hirotsu and Nagakura (48) have presented evidence that the structure of the carbide precipitated during the first stage is orthorhombic, not hcp, and call the structure $\eta$-carbide.

2.2.2 The Early Stages of Aging

Until recently most tempering experiments did not start with the martensite in its virgin state. Since the $M_s$ temperatures of most steels are well above room temperature, changes may take place while the quenching itself is going on. This phenomena has been called autotempering. Furthermore, cooling only to room temperature is not enough to prevent all aging. Calculations by Cohen (2) have shown that the jump frequency of carbon at room temperature is great enough to allow aging changes
to occur. Speich (49) has shown that even with very rapid cooling rates autotempering can take place. So in order to observe virgin martensite, alloys with low $M_s$ temperatures must be used and the quenching must be as rapid as possible to liquid nitrogen temperature (-196°C). The first systematic study of virgin martensites in this way was by Winchell and Cohen. (30) A more recent study was done by Eldis (44), who used resistivity measurements on specimens tempered at a range of temperatures from -95 to 300 °C to obtain data on the kinetics of tempering. Mössbauer measurements by Genin and Flinn (50) and by Choo and Kaplow (51) have shown that carbon atoms cluster during aging at temperatures less than 100°C. The formation of clusters correlates quite well with a resistivity peak observed by Eldis in alloys tempered at similar temperatures. Choo and Kaplow have concluded that the clusters approach the approximate composition Fe$_4$C, with an fcc structure analogous to that of Fe$_4$N. Izotov and Utevskiy (52) have reached a similar conclusion on the basis of electron diffraction data. Computer calculations by Johnson, et al. (53-54) have predicted that there is a binding energy between carbon-atom pairs as have several earlier calculations. (33,55-56) Hoffman (57-58) has calculated that a spinodal decomposition or clustering reaction of interstitial carbons would lead to a reduction in the elastic free energy of the martensite lattice. Thus, it appears that there is a driving force for the formation
of clusters of carbons and that such clusters are observed at an early stage in the aging of martensite.

Besides clustering the segregation of carbons to dislocation sites has been considered as a pre-carbide phase of aging. Speich (49) has estimated that 80 percent of the carbon in low-carbon, high-\(M_S\) steels segregates to dislocations or cell boundaries as a result of autotempering, and that further segregation occurs on tempering below 150 \(^\circ\)C before the formation of carbides. Kalish and Cohen (46) have calculated the dislocation densities required to provide enough sites for the segregation of carbons. A lath martensite whose dislocation density is of the order of \(10^{11}\) to \(10^{12}\) cm. per cc has enough sites to accommodate about 0.1 weight percent carbon without the precipitation of carbides. Eldis (44) included carbon segregation to dislocations as a step in the aging of martensite. He attributed a drop in resistivity after the peak to the segregation of 0.12 weight percent carbon to dislocation sites. However, if segregation to dislocations is an important factor then it may overlap with cluster formation, thus removing from the lattice some carbon atoms which otherwise would have found their way to clusters. It must also be pointed out that the dislocation densities of twinned martensites appear to be lower than those of lath martensites so carbon segregation should be less of a factor in the aging of this morphology.

In line with the idea of segregation to dislocations,
Lement and Cohen (59) have proposed that dislocation segregation is an important part of the formation process of $\varepsilon$-carbide. Furthermore, their model accounts for the discontinuous appearance of the low-carbon tetragonal martensite accompanying $\varepsilon$-carbide formation.

A review of the basic ideas of order-disorder, clustering and segregation of carbons in martensite has been given by Kurdjumov and Khachaturyan.(60) It is their opinion that all of these phenomena are at play in the formation and aging of martensite. They also report observations of some unusual c/a ratio increases upon aging in certain alloys.

One other phenomenon has been noted during the very early stage of aging. Eldis (44) observed a small but reproducible drop in resistivity in alloys tempered as low as $-95^\circ$C and taking only a few minutes. He suggested that this may be a result of a slight rearrangement of dislocations.
Chapter III
PURPOSE AND PLAN OF RESEARCH

In view of the fact that the structures of both lath and twinned martensites have not been well determined, this work sought to settle the question of the tetragonality of both types in the virgin condition. Also a more complete description of the fine structure of each was attempted. Furthermore, it was evident that the structures formed on aging were not well understood. It was felt that the possibility of differences in aging behavior as a result of the structural differences of the two martensitic morphologies had not been fully explored. Finally, the applicability of the ordering theories had not been tested experimentally.

The research techniques used to approach the above problems were x-ray diffraction, optical and electron microscopy and electrical resistivity measurements. The x-ray work was used to determine the crystal structure of unaged martensite and to follow changes in that structure as the martensite was aged. Microscopy was used to determine the microstructure and the fine structure of martensite at various stages of aging. The results of Mössbauer experiments performed by others (50-51) provided information about changes in atomic arrangements due to aging. Resistivity measurements tied all the structural observations together by providing kinetic data
for each change. Thus, aging changes in martensite could be followed by several different means, which allowed a more thorough understanding of the phenomena than could be achieved by the use of any single method.
Chapter IV
EXPERIMENTAL PROCEDURES

4.1 Materials

Three series of Fe-Ni-C alloys were designed for this study, and prepared by the United States Steel Company. The series had 18, 21 and 24 weight percent nickel, with a range of carbon contents such that some alloys of each series would form lath martensite and the others form twinned martensite. The nickel contents were chosen because in such alloys the transition from lath to twinned morphology occurs over a relatively small range of carbon contents (Fig. 3) and because the $M_S$ temperatures are the lowest of any alloys forming lath martensite. The latter was desirable to avoid autotempering. Table 1 lists the compositions and estimated $M_S$ temperatures of the alloys.

4.2 Alloy Processing

The alloys were received in the form of half-inch thick hot-rolled plates. Rods 2 inches long and 0.480 inches in diameter were machined from sections of the plates. Care was taken to remove all scale from the surfaces of the rods. The rods were swaged to 0.241 inches in diameter with intermediate annealings for 10 hours at 1000°C in argon filled vycor capsules as necessary. After swaging, the rods were given a homogenizing anneal at 1200°C for 24 hours and furnace cooled. Following homogenization, the rods
Table 1

COMPOSITIONS AND ESTIMATED $M_s$ TEMPERATURES
OF ALLOYS STUDIED

<table>
<thead>
<tr>
<th>U. S. STEEL HEAT NUMBER</th>
<th>C(w/o)</th>
<th>Ni(w/o)</th>
<th>$M_s$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1399A</td>
<td>0.0033</td>
<td>18.3</td>
<td>250</td>
</tr>
<tr>
<td>1399B</td>
<td>0.11</td>
<td>18.1</td>
<td>180</td>
</tr>
<tr>
<td>1400A</td>
<td>0.40</td>
<td>18.3</td>
<td>20</td>
</tr>
<tr>
<td>1400B</td>
<td>0.50</td>
<td>18.3</td>
<td>10</td>
</tr>
<tr>
<td>1400C</td>
<td>0.62</td>
<td>18.4</td>
<td>-20</td>
</tr>
<tr>
<td>1401A</td>
<td>0.0078</td>
<td>20.8</td>
<td>200</td>
</tr>
<tr>
<td>1401B</td>
<td>0.10</td>
<td>20.8</td>
<td>130</td>
</tr>
<tr>
<td>1401C</td>
<td>0.20</td>
<td>20.7</td>
<td>80</td>
</tr>
<tr>
<td>1402A</td>
<td>0.25</td>
<td>21.8</td>
<td>40</td>
</tr>
<tr>
<td>1402B</td>
<td>0.30</td>
<td>21.5</td>
<td>25</td>
</tr>
<tr>
<td>1403A</td>
<td>0.0078</td>
<td>24.6</td>
<td>110</td>
</tr>
<tr>
<td>1403B</td>
<td>0.12</td>
<td>24.6</td>
<td>50</td>
</tr>
<tr>
<td>1403C</td>
<td>0.14</td>
<td>24.7</td>
<td>35</td>
</tr>
<tr>
<td>1404A</td>
<td>0.19</td>
<td>25.5</td>
<td>10</td>
</tr>
<tr>
<td>1404B</td>
<td>0.24</td>
<td>25.5</td>
<td>-10</td>
</tr>
<tr>
<td>1404C</td>
<td>0.28</td>
<td>25.2</td>
<td>-30</td>
</tr>
</tbody>
</table>

All alloys contained less than 0.003 w/o Si and less than 0.005 w/o Mn.
were centerless ground to 0.190 inches in diameter in order to remove any scale, decarburized layer, or surface contamination due to swaging. Sections of the rods were swaged and wire drawn to 0.031 inches in diameter with intermediate annealing at 850°C for 1/2 hour in a vacuum better than $1 \times 10^{-5}$ torr, as needed.

4.3 Rapid Quenching

A rapid quenching apparatus was constructed consisting of an inconel tube inside a vertical one-inch diameter tube furnace. The tube had an inlet and an outlet for a continuously flowing argon atmosphere. A second, smaller tube inside the first held the specimen in the center of the hot zone of the furnace. This inner tube was connected to a gas reservoir, which could be filled and emptied by operating a pair of electrically activated valves. The gas reservoir was pressurized with argon at 2500 pounds-per-square-inch. When the pressure in the reservoir was released, it forced the specimen downward through an aluminum-foil membrane at the bottom of the tube and into a water-quench bath. The specimen was immediately transferred to a liquid-nitrogen bath. The time elapsed during the entire quenching operation was less than four seconds.

In practice the specimen was installed in the quencher with the furnace at room temperature, and the quencher was thoroughly purged by the flowing argon atmosphere before the heating began. It took about 30
minutes to heat up to the 850 °C austenitizing temperature, which was held for 15 minutes before quenching.

4.4 Resistivity Measurements

Resistivity specimens were made from two-inch lengths of the 0.031 inch diameter wire by spotwelding two #24 B&S gauge pure nickel wires to each end. The diameter and length of the specimens were recorded. Then the specimens were quenched using the rapid quencher, and kept in liquid nitrogen for a minimum of one day before any resistivity measurements began. This insured that any possible isothermal transformation at liquid nitrogen temperature would have occurred before the measurements, and hence not interfere with the interpretation of the subsequent resistivity changes due to aging.

The initial resistance of each specimen was measured. The specimen was then repeatedly upquenched in an aging bath, and returned to the liquid-nitrogen bath at intervals for resistance measurements. All resistance measurements were made with the specimens at -196°C (liquid-nitrogen), with a Kelvin double bridge. The resistances could be measured with an accuracy of ±0.00001 ohms. The measured resistances were converted to resistivities by using the formula:

$$\rho = R \frac{A}{L}$$  \hspace{1cm} (2)

in which $\rho$=resistivity

$R$=measured resistance
A = cross sectional area of the specimen  
L = test length of the specimen

The accuracy of the resistivity values was ±2 percent due to the difficulty of measuring the dimensions of the specimen, with greater than this precision. However, changes in the resistivity of a given specimen by 0.1 percent or more could be accurately measured, because in this case only the sensitivity of the Kelvin bridge is important.

Various media were used for aging baths at different temperatures, Table 2. The elevated temperature baths were heated electrically. The subambient temperatures were obtained by passing cold nitrogen gas, from a liquid-nitrogen tank, through a coil immersed in the bath. Temperature control was maintained by regulating the gas flow with a solonoid valve operated by a temperature controller. Temperature variation was ±2°C for all baths.

In this way resistivity vs. aging time curves were generated for each alloy at many different temperatures, with all measurements taken at the common temperature of -196 °C.

4.5 Microscopy

Quarter-inch lengths of the 0.190-inch diameter rods were quenched using the rapid quenching apparatus. The quenched specimens were aged for one hour in the same baths as the resistivity specimens. However, only aging treatments
above room temperature were used for the microscopy, because it was impossible to prepare and examine any microscope specimens without warming them at least to room temperature. After aging the rods were cut into discs 0.015-inch thick using a water cooled carborundum cut off wheel 0.010-inch thick.

4.5.1 Optical Microscopy

A disc sample was mounted and polished in the conventional way, and then etched with one percent nital to bring out the microstructure. Some of the resistivity specimens were also prepared in the above way. Point counting was performed to determine the volume fraction of retained austenite in these specimens. A sufficient number of points were counted to insure ±10 percent accuracy of the data.

4.5.2 Electron Microscopy

The disc samples were hand-ground to 0.010-inch thicknesses using 4/0 emery paper, taking care to remove an equal amount of material from each side. The ground discs were indented electrolytically using a 25 percent nitric acid-75 percent water jet 1.5 millimeters in diameter, with the jet nozzle one centimeter above the specimen. Each side of a disc was jetted for 10 seconds at 120 volts. The indented portion of the disc was then about 0.007-inch thick. Final thinning was done by electrolytic polishing in a solution of anhydrous sodium
chromate and glacial acetic acid mixed in the ratio of one gram chromate to five milliliters acid. This operation was done in a vertical polishing set up in which the specimen was illuminated from below and viewed constantly from above through a 10 power microscope. 15 volts was applied to the well-agitated electrolytic bath. Polishing continued until a hole appeared in the specimen, usually after about 80 minutes.

After polishing the specimens were carefully washed in distilled water and air dried. Specimens were stored in an evacuated desiccator except when being observed. A Siemens Elimskop la was used for all electron microscopy. A long focal-length double-tilt specimen cartridge kept the ferromagnetic specimens out of the field of the objective lens and thus minimized spherical aberration. The microscope was equiped with a liquid-nitrogen cold trap, which helped avoid contamination of the specimen during prolonged observation.

4.6 X-ray Diffraction

4.6.1 Theory

An oscillating-crystal technique (22,61-63) was used to determine the tetragonality of virgin and aged martensite. The technique exploits the fact that crystallographic orientation relationships exist between martensite and the parent austenite. Two sets of such relationships have been observed (64): the Kurjumov-Sachs
relationship:

\[ (111)_\gamma \parallel (110)_\alpha \quad [1\bar{1}0]_\gamma \parallel [1\bar{1}1]_\alpha \] (3)

and the Nishiyama relationship:

\[ [111]_\gamma \parallel [110]_\alpha \quad [\bar{2}11]_\gamma \parallel [1\bar{1}0]_\alpha \] (4)

The two differ by a rotation of 5° 16'. A consequence of both these relationships is that martensite may form in 24 equivalent orientations in an austenite crystal. On an austenite (001) pole figure (Fig. 6), it is found that the (002)\( _\alpha \) poles are separated by 45° from the (200)\( _\alpha \) and (020)\( _\alpha \) poles. Specifically, (002)\( _\alpha \) poles are near (001)\( _\gamma \) while (200)(020)\( _\alpha \) poles are near (110)\( _\gamma \). Thus, in a single austenite crystal transformed to martensite, diffraction conditions will be fulfilled for the (002)\( _\alpha \) planes at an angle 45° from that producing diffraction from the (200)(020)\( _\alpha \) planes. This permits the recording of the diffraction of each set of planes on separate films even though the spacings of the planes are quite similar. Accordingly, the difficulty of separating the tetragonal doublet can be circumvented and the c/a ratio of martensite can be determined.

4.6.2 Specimen Preparation and Alignment

To use this "psuedo-single crystal" technique, alloys with \( M_s \) temperatures below room temperature are needed, because the parent austenite single crystal must
FIGURE 6. AUSTENITE (001) POLE FIGURE SHOWING THE (200) (020) AND (002) MARTENSITE POLES IN THE KURDJUMOV-SACHS ORIENTATION RELATIONSHIP. (AFTER WERNER (62))
be suitably oriented to produce the desired results. Hence, only some of the alloys could be used for this work.

Three-eighth inch cubes were cut from the original hot-rolled plates. The cubes were compressed to provide a small amount of plastic upset. Then the cubes were annealed at 1350°C for 24 hours in a vacuum better than 1×10^-5 torr and furnace cooled. This treatment was usually sufficient to yield some austenite grains about 3/16 inches in diameter. Occasionally it was necessary to repeat the strain-annealing process and to use up to 3-day annealing treatments in order to obtain large grains. The size of the grains was checked by etching the cubes with Marble's reagent.

The cubes were cut in half and the largest grain from one of the cut faces was selected. This grain was removed with a combination of cutting and lapping. All cutting was done with a string saw using a wire less than 0.010-inch in diameter coated with a slurry of carborundum in oil. The lapping was done with a slurry of 1000 mesh carborundum and water. After removal, the grain was cut into individual crystals about 1 millimeter square. Each crystal was etched and optically inspected to insure that it was indeed an untwinned single crystal. Where doubt existed, a wide-spot Laue exposure was made. Any imperfect crystals were discarded.

Each crystal was dissolved in warm aqua regia until it was about 1/2 millimeter in diameter. The crystal was
then glued with Duco cement to a 0.3 millimeter diameter glass capillary. The crystal was oriented with Laue exposures, and a second capillary was glued on parallel to a [100]_γ direction. Collodion cement (or Saueriesen in the case of specimens intended for aging treatments above 100°C) was used for the second gluing operation. The first capillary was removed by dissolving the Duco cement with acetone. The oriented-crystal capillary was installed in a Supper head goniometer, which formed the specimen holder for a rotating-oscillating x-ray camera. The orientation of the crystal was checked with further Laue exposures so that the (100)_γ pole of the austenite crystal was less than 1/2° from the rotation axis of the camera.

The direction of a second {100}_γ pole (i.e. perpendicular to the (100)_γ rotation axis) was determined with Laue exposures. After quenching to produce martensite, four (002)_α poles were approximately parallel to this {100}_γ and eight (200)(020)_α poles 45° from it parallel to the {110}_γ poles.

4.6.3 X-ray Exposures

The goniometer-capillary-crystal unit was mounted in a rotating camera 5.7 centimeters in diameter. The crystal could be cooled to -100°C to transform it to martensite by a jet of cold helium gas obtained by passing the helium through a copper coil immersed in liquid nitrogen. Exposures were made with Fe K_α radiation. The expected angles of the
(002)\textsubscript{\alpha} and (200)(020)\textsubscript{\alpha} diffraction spots were calculated, and the goniometer was adjusted to oscillate about one of these angles to record one or the other set of spots. Oscillation ranges of 25 and 15° were used to record the (002)\textsubscript{\alpha} and (200)(020)\textsubscript{\alpha} spots, respectively. Exposure times were 3 hours for oscillation patterns and 15 hours for complete rotation patterns. The initial exposures were made with the specimen cold except for the time required to change films and reorient the crystal for the other set of spots. Thus, virgin martensite was observed with x-ray diffraction.

After the initial exposures the crystal was aged at temperatures ranging from room temperature up to 350°C. Heating was done with air furnaces with a temperature control of ±5°C. The specimen remained in place on the goniometer during the aging treatments. At intervals the specimen was cooled to room temperature and exposures were made to follow the course of changes due to aging.

Films produced by this method were measured with a standard Debye film measuring device, and the c and a parameters of the martensite were calculated with an accuracy of ±0.01Å. This uncertainty is due to the fact that the spots were rather broad because of the strained condition of the martensite lattice. The c/a ratio of the martensite was calculated with an accuracy of ±0.003.
Chapter V
RESULTS AND DISCUSSION

5.1 Microscopy

5.1.1 Optical Microscopy

Figures 7 and 8 follow the changes in microstructure of lath and twinned martensites as a result of one-hour aging treatments at temperatures up to 350°C.

The as-quenched structure of lath martensite (Fig. 7a) consists of packets of plates, which appear to intersect one another at about 60° angles, in accordance with the reported (111) habit plane. The sample tempered at 100°C (Fig. 7b) etched more darkly compared to the as-quenched specimen, indicating that some aging reaction had taken place. When tempered at 200°C the martensite becomes still darker etching, and some very fine precipitates may be seen (Fig. 7c). Specimens tempered at 300 °C and 350 °C (Fig. 7d and 7e) exhibit fine carbide-particle dispersions.

The structure of the twinned martensite consists of acicular plates ranging in size from several hundred microns down to about 10 microns. Some of the plates have well defined midribs. Between the plates are small regions of retained austenite, amounting to about 10 volume percent. This is in contrast to the lath martensite which has little if any retained austenite. The as-quenched and 100°C temper samples appear very much alike (Fig. 8a and 8b).
Figure 7: Optical micrographs of 18Ni-0.11C Lath Martensite aged for one hour at indicated temperatures. 1% Nital etch.
(c) Tempered at 200°C, 1000X

(d) Tempered at 300°C, 1000X

Figure 7 (continued)
(e) Tempered at 350°C, 1000X

Figure 7 (continued)
Figure 8: Optical micrographs of 18Ni-0.4C Twinned Martensite aged for one hour at indicated temperatures. 1% Nital etch.
(c) Tempered at 200°C, 1000X

(d) Tempered at 300°C, 1000X

Figure 8 (continued)
(e) Tempered at 350°C, 1000X

Figure 8 (continued)
Both have some darker etching regions. It must be remembered that the as-quenched condition in the case of both optical and electron microscopy refers to samples aged at room temperature for some days as a consequence of the techniques involved. Thus, the twinned martensite might be expected to show some evidence of tempering, i.e. dark etching, when observed as-quenched, while such effects would be less apparent in lath martensite due to the lower carbon content. The results of aging the twinned martensite at higher temperatures follow the same course as that of lath martensite. After a 200°C temper (Fig. 8c), the alloy becomes darker etching, with some slight evidence of precipitation. After tempering at 300 or 350°C (Fig. 8d and 8e), the martensite is light etching and contains dispersions of carbide particles, in greater quantity than in the lath martensite due to the higher carbon content.

5.1.2 Electron Microscopy

The structure of lath martensite after various aging treatments is shown in Fig. 9. The unaged structure is made up of laths ranging in width from 500 to 5000Å, having an internal substructure of extremely dense tangles of dislocations. After aging for one hour at 100°C the structure remained unchanged (Fig. 9b); no evidence of carbide precipitation could be seen.

Two types of carbide particles precipitated on
Figure 9: Transmission electron micrographs of 18Ni-0.11C Lath Martensite aged for one hour at indicated temperatures.
(c) Tempered at 200°C, note ε-carbide and cementite particles, 32000X.

(d) Tempered at 300°C, note larger cementite particles, 44000X.

Figure 9 (continued)
tempering for one hour at 200°C (Fig. 9c). One type of carbide was present as fine needle-like precipitates a few hundred angstroms in length separated by distances of about 1000Å. The other carbide particles were much larger, roughly 2000Å long, and spaced about 5000Å apart. The finer particles conform to other observations of \( \varepsilon \)-carbide (42,48), while the larger carbides resemble cementite. (42) Because of the complexity of the structure it was not possible to obtain enough electron-diffraction information to positively confirm these identifications; however, the orientations of the particles are consistent with the conclusion that the smaller particles are \( \varepsilon \)-carbide and the larger ones cementite.

After tempering at 300°C for one hour (Fig. 9d), there are many more cementite particles, which are now up to 5000Å long. The dislocation density also seems to be somewhat reduced from that of the specimens tempered at lower temperatures. This suggests that some recovery occurs in the lath martensite tempered at or above 300°C.

Figure 10 shows the structure of twinned martensite after one hour at various temperatures. The morphology of the unaged alloy consists of acicular platelets ranging in length from less than 1 micron up to hundreds of microns (Fig. 10a). With suitable adjustment of the specimen tilt in the electron microscope, it was possible to see that each platelet is internally
twinned. Diffraction results indicate that the twins are of the \{112\} type, in agreement with previous results. (10,42) The twin spacing of 60 to 100Å can be seen in Fig. 10b. The dislocation density of the twinned martensite must be substantially lower than that of lath martensite, because no extensive tangles of dislocations can be seen anywhere in the structure. Aging at 100°C produces no noticeable change in the structure (Fig. 10c). Occasional small areas of retained austenite can be noted in Fig. 10c. This is in contrast to the electron micrographs of lath martensite, where no such regions are observed. The sample aged at 200°C had an extensive distribution of precipitates similar to the \(\epsilon\)-carbide particles observed by others. (42,48) (Fig. 10d) The carbide particles are very thin and several hundred angstroms long. As in the case of lath martensite electron diffraction data was insufficient to determine unambiguously the orientation of the \(\epsilon\)-carbide particles. However, the results are consistent with other observations (42,48) that \(\epsilon\) precipitates on \{100\} martensite planes. There seems to be no cementite present after the 200°C aging as there was in the case of lath martensite. Tempering for one hour at 300°C produces a structure containing both \(\epsilon\)-carbide and cementite (Fig. 10e). At this stage the \(\epsilon\) particles are still in the form of thin needles up to about 2000Å long, but are not present in nearly the same profusion as after
Figure 10: Transmission electron micrographs of 18Ni-0.4C Twinned Martensite aged for one hour at indicated temperatures.
(b) Tempered at 100°C, note fine twins (t) and mottling (m), 42000X.

(c) Tempered at 100°C, retained austenite (ra), 15000X.

Figure 10 (continued)
(d) Tempered at 200°C, note dispersion of $\epsilon$-carbide particles, 14000X.

(e) Tempered at 300°C, $\epsilon$-carbide and cementite particles indicated, 48400X.

Figure 10 (continued)
200°C aging. The cementite particles range in size up to 5000Å long and 500 to 1000Å wide.

A subtle feature in some of the electron micrographs of martensite is the mottled appearance in various areas of the structure. While the effect is observed in both types of martensite, it is much more evident in the twinned martensite. Possibly the dislocation substructure of the lath martensite obscures the mottling. The mottling is most prevalent in the unaged and 100°C samples, in which it can be observed throughout the twinned martensite when the diffraction conditions are suitably adjusted by tilting the specimen. In specimens tempered at 200°C and higher, mottling may be seen in some areas, but not as extensively as in the samples aged at lower temperatures. Mottled structures have been noted previously in similar alloys. Eldis (44) attributed the effect to contrast from dislocations, while others (65-66) have suggested that it is due to carbon clustering or an early precipitation step before individual carbides are resolved.

The mottling in iron-nickel-carbon martensites bears a strong resemblance to the strain-contrast effect which has been called tweed, observed by Tanner et al. (67-70) in several alloy systems during the very early stages of precipitation or ordering. The observation of the tweed structure is accompanied by an asymmetric
broadening of electron diffraction spots. It is thought that the tweed phenomenon occurs because clusters of solute atoms develop prior to the actual emergence of precipitate particles. The clusters are coherent with the matrix and the coherency strains give rise to the diffraction effects observed. When the clusters grow large enough to become precipitate particles the tweed structure gradually disappears. Substructures and diffraction effects similar to tweed are found in some systems undergoing spinodal decomposition. (71)

In order to determine whether a phenomenon similar to tweed, involving the clustering of carbon atoms, is at play during the aging of martensite, a specimen tempered for one hour at 150°C is of special interest (Fig. 11). The structure has regions with coarser mottling than seen in other specimens and areas with ε-carbide particles. Those areas with more clearly resolvable carbide particles are distinctly freer of mottling than the surrounding areas. Moreover, the texture of the mottling seems to lie parallel to the orientation of the carbide particles. The texture of the mottling in the unaged and 100°C aged specimens is also frequently observed to be consistent with a parallelism to {100}_α, planes which ε-carbide is known to form on. The spots of the corresponding electron diffraction pattern are asymmetrically distorted (Fig. 11b and 11c). Thus, the similarities to tweed are striking. However, these
Figure 11: 18Ni-0.4 Twinned Martensite tempered at 150°C for one hour. a) transmission electron micrograph, ε-carbide particles and coarse mottling (m) indicated. 38000X. b) associated (110) electron diffraction pattern suitably oriented. c) solution of diffraction pattern, note asymmetrically distorted spots.
observations alone are not sufficient to allow an unambiguous conclusion that the mottling is due to carbon clustering prior to carbide precipitation; nevertheless, they do offer some evidence that this is the case.

5.2 X-ray Diffraction Results

Exposures made on unaged martensite quenched and held at about -100°C using the "psuedo-single crystal" technique showed that the structure of virgin martensite is body-centered tetragonal. The c/a ratios obtained were combined with those obtained by Winchell (22) using the same x-ray technique. Winchell's results include many lower-carbon alloys thus extending the range of data. The c/a ratio varied linearly with carbon content (Fig. 12). A least squares fit of the data points produced the equation:

\[(c/a)_\alpha = 1.005 + 0.057(w/o\ C)\]  

The slope of this equation is somewhat higher than the slope of 0.045 previously reported for Fe-C alloys. This may be due to nickel affecting the way in which carbons expand the lattice, or it may be due to some systematic error introduced by the x-ray technique.

The a and c lattice parameters obtained from the present results also varied linearly with carbon:

\[(c)_\alpha = 2.867 + 0.122(w/o\ C)\]  

\[(a)_\alpha = 2.821 - 0.010(w/o\ C)\]
FIGURE 12 c/a RATIO OF VIRGIN MARTENSITE AS DETERMINED FROM AUSTENITE SINGLE CRYSTALS TRANSFORMED AND X-RAYED AT ABOUT -100°C
These results are in good agreement with previous measurements of martensite lattice parameters, except for the zero carbon intercept of the a parameter, which is somewhat lower than reported elsewhere. (63) This is probably due to the inherent errors of the technique, but may be a manifestation of the reported decrease (72) in lattice-parameters of Fe-Ni alloys in this range of nickel contents (18 to 24w/o).

Because the crystals must be austenitic at room temperature to allow the necessary alignments prior to quenching, only alloys with subambient $M_s$ temperatures could be used for these x-ray measurements. Unfortunately, no alloys could be found with lath martensite having subambient $M_s$ temperatures. Consequently, the lattice-parameter data are based on twinned martensites.

After aging at temperatures ranging from room temperature to 100°C, a new set of (002) spots appears corresponding to a smaller c parameter than that of virgin martensite ($\alpha'$). The intensity of the new set of spots increases with aging time, while the (002)$_\alpha'$ spots' intensity decreases and finally disappears. The complete disappearance of the (002)$_\alpha'$ spots takes up to 40 days of room temperature aging, but less than 15 minutes at 100°C. The new (002) spots are noticeably broader than the (002)$_\alpha'$ spots. The (200)(020) martensite spots broaden in the direction of a larger a-parameter during aging, suggesting that it also splits into two separate spots. The emergence
of the smaller c-parameter and the shifting of the (200)(020) position show that a low- or nil-carbon martensite forms with a c/a ratio of 1.004±0.001 independent of the alloy content. We will call this martensite $\alpha_t$, for transition, since it forms as an intermediate step in the overall decomposition:

$$\alpha' \rightarrow \alpha_{bcc} + Cm \quad (8)$$

The activation energy for the formation of $\alpha_t$ was estimated in the following way: By visual inspection of the x-ray films, it was possible to determine the aging times necessary to achieve equal intensities of the (002)$_{\alpha'}$ and the (002)$_{\alpha_t}$ spots as well as the times for the complete disappearance of the (002)$_{\alpha}$ spots. These conditions correspond to the half-way point and the completion of the formation of $\alpha_t$ respectively. A plot of natural log time vs. reciprocal aging temperature was constructed, and the slope of the plot times $R$, the gas constant, was taken to be $Q$, the activation energy, for the process. The activation energies thus obtained were 21 kcal per mole for both stages of the $\alpha' \rightarrow \alpha_t$ transformation.

The formation of $\alpha_t$ entails the redistribution of carbon atoms from the single set of octahedral sites they occupy in the virgin martensite to other positions where they do not expand the lattice in the original way. Previous observations of the formation of low-tetragonality martensite during tempering have led to the conclusion that $\varepsilon$-carbide forms simultaneously and that $\alpha_t$ is in metastable
equilibrium with the carbide. (29,38-40) This conclusion is not supported by the present data because the electron microscopy results show that ε-carbide does not precipitate on aging for one hour at 100°C. Since the formation of $\alpha_t$ is complete within 15 minutes at 100°C, the carbon atoms cannot be going into the formation of carbides when $\alpha_t$ forms. Furthermore, the activation energy for the precipitation of carbides during tempering is reported to be about 33 kcal per mole, which is much higher than that observed in the present case for the formation of $\alpha_t$.

Several other ideas about the formation of $\alpha_t$ involve carbon atoms moving to various types of sites from their initial locations in virgin martensite. These movements can be accomplished by diffusive jumps whose activation energy agrees closely with the observed 21 kcal per mole. One such mechanism is the randomization of carbon occupation among the three sets of octahedral sites, leading to a body-centered cubic structure expanded uniformly by carbon. Clearly, this is not the case because such martensite would have a c/a ratio of unity and a larger lattice parameter than the carbon-free lattice parameter of 2.866Å, neither of which is observed. Also such a process should happen continuously giving rise to a broadening of the $(002)_\alpha$ spots rather than a discontinuous separation of $\alpha'$ and $\alpha_t$ spots.

Another possible mechanism for the $\alpha' \rightarrow \alpha_t$ transition is the segregation of carbons to dislocations
or other preferred sites. The driving force for this reaction would be a reduction in the free energy due to the lattice strains caused by carbon atoms in octahedral sites. Estimates of the capacity of dislocations for such carbon absorption have shown that about 0.20 weight percent carbon can be accommodated by the dislocation densities of $10^{12}$ cm$^2$/cm$^3$ thought to be present in martensite. (46) A model proposed by Lement and Cohen (59) could account for the discontinuous appearance of $\alpha_t$ by postulating a low-carbon region surrounding dislocations which grows as aging continues. The $c/a$ ratio of 1.004 would be caused by tetragonal distortions of a small carbon concentration remaining in the matrix.

Another mechanism for the formation of $\alpha_t$ is clustering of carbon atoms. This possibility will be more fully discussed in the following sections; for the moment it will suffice to describe how $\alpha_t$ can develop as a result of clustering. The formation of clusters would remove carbons from the usual octahedral sites. This might occur by the same depleted-zone process as in dislocation segregation, thus giving the discontinuous appearance of $\alpha_t$ spots. The 1.004 $c/a$ ratio would be due to residual carbons in matrix lattice sites or to some sort of general expansion caused by the small coherent clusters themselves. Actually, both clustering and dislocation segregation could be operative simultaneously,
but as carbon content increases clustering should predominate due to the saturation of all available dislocation sites early in the transformation.

5.3 Resistivity Changes During Aging

Complete sets of resistivity vs. time curves for the five alloys of the iron-18 nickel series of alloys are presented in Fig. 13. The results obtained from the other alloys were entirely consistent with those presented here. Because of the long times required for generating the data, the curves, in most cases, were obtained in a single run. However, where duplicate runs were made, there was close agreement.

The data contained in the resistivity vs. time plots have been normalized to correct for scatter of up to ±4 percent in the initial resistivities of the specimens. The sources of such scatter were:

1. Errors of up to 2 percent in the measurements of the dimensions of the specimens.
2. The 5 to 15 percent retained austenite in the higher-carbon alloys having twinned martensite.
3. Inadvertant straining of the specimens due to deformation during quenching.

A least-squares plot of initial resistivity vs. carbon content (at 18 weight percent nickel) was constructed
FIGURE 13a RESISTIVITY VS. TIME CURVES FOR AN 18Ni-0.0033C ALLOY AGED AT INDICATED TEMPERATURES
Figure 13b: Resistivity vs. time curves for an 18Ni-0.1% alloy aged at indicated temperatures.
FIGURE 13c RESISTIVITY VS. TIME CURVES FOR AN 18Ni-0.4 C ALLOY AGED AT INDICATED TEMPERATURES
FIGURE 13d RESISTIVITY VS. TIME CURVES FOR AN 18Ni - 0.5C ALLOY AGED AT INDICATED TEMPERATURES.
Figure 13e Resistivity vs. time curves for an 18Ni-0.62C alloy aged at indicated temperatures.
yielding:

\[ \rho_i = 17.83 + 22.38 \text{(w/o C)} \]  

(9)

in which \( \rho_i \) = initial resistivity.

Then the resistivity values obtained during the aging of each specimen were multiplied by the factor:

\[ \rho_t = \frac{\rho_i}{\rho_o} \rho'_t \]

(10)

where \( \rho_i \) is obtained for each alloy from equation 9

\( \rho_o \) = initial resistivity of a given sample

\( \rho'_t \) = measured resistivity of sample after aging for time \( t \)

\( \rho_t \) = corrected resistivity after aging for time \( t \).

The corrected values, \( \rho_t \), are those used in the plots of resistivity vs. time.

Except for the 0.0033 weight percent carbon alloy, which exhibited only slight decreases in resistivity at the higher aging temperatures and long times, the behavior of all the alloys was qualitatively the same. For purposes of discussion, the curves can be divided into three regions as shown schematically in Fig. 14. Region I is characterized by a slight decrease in resistivity of short duration occurring only during aging at low temperatures. In Region II there is a resistivity peak which occurs in alloys aged in the vicinity of room temperature. Region III
consists of a continuous decrease in resistivity and constitutes the only observable behavior on tempering at 100 °C and above. The next section will show that the resistivity changes are a measure of the extent of reactions taking place in the martensite as a result of aging, and that they can provide information about the activation energy and nature of the processes involved.

5.3.1 Theoretical Background

According to the quantum model for the conduction of electrons in metals, the resistivity of a perfect crystalline metal at absolute zero temperature should be zero, because the electrons travel in the perfectly periodic potential field of the lattice. If the periodicity of the potential field of the lattice is disturbed, then scattering of electrons will occur giving rise to electrical resistivity. At temperatures above absolute zero, the atoms are not stationary but vibrate about their equilibrium positions, thus perturbing the lattice potential field and leading to the observed increase of resistivity with temperature of all metals. Aside from lattice vibrations, there are other factors which may cause increased resistivity due to interruptions in lattice periodicity. In a consideration of the resistivity of martensite during aging, we must take into account defects such as dislocations, interstitial and substitutional solute atoms as well as retained austenite
and precipitate phases. Each of these features, when present, leads to a disruption of the potential field of the iron lattice. Dislocations, solute atoms and coherent precipitate particles cause displacements of iron atoms from equilibrium positions. Retained austenite and precipitate particles (both coherent and incoherent), due to their different structures, have different electronic potential fields.

The contribution of defects to resistivity is independent of temperature as expressed by Matthiessen's rule:

\[ \rho = \rho_t + \rho_o \]  \hspace{1cm} (11)

which separates the resistivity of a metal into a thermal component (\(\rho_t\)) whose origins are lattice vibrations and a defect component (\(\rho_o\)). Since all our resistance measurements were made at -196°C, variations in resistivity must be attributed primarily to changes in \(\rho_o\) rather than in \(\rho_t\). This means that changes in resistivity observed during aging are reflections of structural changes in the martensite.

Nordheim's rule:

\[ \rho_r(x) = Ax(1-x) \]  \hspace{1cm} (12)

in which \(\rho_r(x)\) = resistivity contribution of solute atoms of concentration \(x\), and \(A\) is a constant, may be applied to
the dilute solution of carbon in martensite. Since $x$ is small the rule can be approximated as:

$$\rho_r(x) = Ax$$

which means that the resistivity of virgin martensite, with all carbons in octahedral sites, should increase linearly with carbon content. That the initial resistivities of the martensites formed in our alloys do increase linearly with carbon content is an indication that we are starting essentially from the virgin condition. Fig. 15 shows how the initial resistivities vary with carbon content for the three series of iron-nickel alloys. The resistivity at zero carbon content decreases as nickel content increases, in agreement with previous measurements at $-196^\circ$C of Fe-Ni alloys. (74)

The source of the resistivity increase due to carbon interstitials in virgin martensite is a large mean-square static displacement, $\bar{u}^2$, of the iron atom neighbors. The larger resistivity contribution per weight percent carbon as nickel content is increased may be attributed to increased iron-atom displacements around each carbon atom in the presence of nickel. The lattice parameter of iron-nickel martensite decreases with nickel content in the range of 18 to 25 weight percent nickel. (72) This means a carbon atom must displace the surrounding atoms relatively more in alloys with higher nickel. Also, the elastic constants of iron-nickel alloys decrease as
FIGURE 15. INITIAL RESISTIVITY AS A FUNCTION OF CARBON CONTENT
nickel content rises (75-76) making it easier for a carbon atom to distort the lattice.

Since the aging of martensite is largely a process of carbon-atom depletion from the iron lattice to form carbides, it is possible to follow the extent of aging by resistivity measurements. In particular, decreases in resistivity signal a reduction in iron-atom static displacements, indicating that fewer carbons remain in solution. By Nordheim's rule we may infer that such decreases are approximately linear with respect to the amount of carbon removed from solution either to form carbides or to occupy sites such as dislocations or clusters.

5.3.2 Calculation of Activation Energies from Resistivity Data

To obtain the activation energy of a thermally activated process, one procedure is to start with a general Avrami type equation:

\[ f = 1 - \exp\left[ -(kt)^n \right] \]  

(14)

in which  
\( f \) = fraction transformed  
\( t \) = time  
\( n \) = time exponent

and \( k = k_0 \exp(-Q/RT) \)  
(15)

where \( Q \) = activation energy  
\( R \) = gas constant  
\( T \) = absolute temperature
\[ k_0 = \text{a constant} \]

It is usually assumed that \( k \) and \( n \) are independent of \( f \), and by taking the natural log of both sides of the equation twice:

\[
\ln t = \frac{Q}{R} (1/T) + C(f) \tag{16}
\]

where \( C \) is a constant for any value of \( f \). Then the slope of a plot of \( \ln t \) vs. \( 1/T \) for a given value of \( f \) gives the activation energy:

\[
\frac{Q}{R} = \left[ \frac{\partial \ln t}{\partial (1/T)} \right]_{f=f_1} \tag{17}
\]

Values of \( Q \) thus obtained will be the same for all values of \( f_1 \) if the activation energy does not vary during the course of the transformation. If the activation energy does vary, then \( Q \) will represent an average activation energy for the process up to \( f = f_1 \).

Hillert (77) has pointed out that in the tempering of martensite, \( Q \) is not independent of \( f \), since there are several overlapping steps, each possibly having a different activation energy. Consequently, he suggested that the \( Q \) value for each step can be more accurately determined by considering the transformation rate \( (\partial f/\partial t) \) rather than only time to attain a given amount of transformation. In order to obtain the activation energy at \( f = f_1 \) Hillert considers the rate of transformation to
be a function of both $f$ and $T$:

$$\frac{\partial f}{\partial t} = G(f, T) = G_0(f)\exp\left(-\frac{Q(f)}{RT}\right)$$  \hfill (18)

Taking the natural log of each side:

$$\ln \left. \frac{\partial f}{\partial t} \right|_{f=f_1} = \ln G_0(f_1) - \frac{Q(f_1)}{RT}$$  \hfill (19)

Thus, the slope of $\ln \left. \frac{\partial f}{\partial t} \right|_{f=f_1}$ vs. $1/T$ will give $Q$ values more closely reflecting the activation energy of the process(s) going on at $f = f_1$ because

$$\frac{Q(f_1)}{R} = - \left. \frac{\partial \ln \left. \frac{\partial f}{\partial t} \right|}{\partial (1/T)} \right|_{f=f_1}$$ \hfill (20)

Clearly, the Hillert method is preferred when the nature of the data allows a determination of $\left. \frac{\partial f}{\partial t} \right|_{f=f_1}$ at several temperatures.

5.3.3 Region-I Initial Resistivity Drop

The initial resistivity drop ($\Delta \rho_I$) occurs only in specimens aged at subambient temperatures, and then only in very short times. In a given alloy $\Delta \rho_I$ decreases linearly with increasing aging temperature (Fig. 16). The drop does not occur in alloys with nil carbon, and increases as carbon and nickel content are increased. These trends may be due to autotempering since the alloys with less carbon and nickel have higher $M_s$ temperatures and hence may
FIGURE 16. VARIATION OF INITIAL RESISTIVITY DROP WITH AGING TEMPERATURE FOR Fe-18Ni ALLOY OF SEVERAL CARBON CONTENTS
undergo part of the resistivity drop during the quench. This idea is supported by considering a plot of $\Delta \rho_I$ vs. carbon content for alloys with equal $M_s$ temperatures (Fig. 17), where $\Delta \rho_I$ now becomes smaller with increasing carbon. The existence of Region I is a good indication that the martensite is in its virgin condition at the start of testing, since appreciable aging due to auto-tempering or inadvertent warming would have aged past the drop before the start of the test run.

The activation energy for the drop constituting Region I was determined by applying equation 17 to plots of log time to complete the drop or half of the drop vs. $1/T$.* A value of 3 kcal per mole was obtained, independent of alloy content. Because of the time-temperature range in which the drop occurs, only the resistivity data provides evidence of Region I, and so it is difficult to determine the cause of the drop in resistivity. Carbide precipitation or any other process involving diffusion of carbon or nickel is quite improbable because the activation energy is much too low. The possibility of retained-austenite transformation can also be discarded, because the drop occurs in lath martensite which has very little retained austenite. Furthermore, Eldis (44), who observed a similar drop, saw no change in amount of retained austenite as a result of aging in

*The data for $\Delta \rho_I$ were insufficient to apply equation 20.
FIGURE 17. INITIAL RESISTIVITY DROP VS. CARBON CONTENT FOR ALLOYS WITH A CONSTANT $M_s$ OF +10°C, AGED AT INDICATED TEMPERATURES.
this temperature range. Eldis suggested that $\Delta \rho_I$ may be due to some relaxation of the quenched-in dislocation structure of the martensite. He points out that the activation energy observed here is about the same as that found for some types of thermally activated dislocation movements. (78-80) Such relaxation should be inhibited by interstitial impurity atoms, so $\Delta \rho_I$ would be expected to decrease with increasing carbon content. Inasmuch as this is the case when alloys with the same $M_s$ temperature are compared, and since no other more likely mechanism comes to mind, the dislocation relaxation hypothesis appears to be the most appropriate explanation for Region I.

5.3.4 Region-II Increase in Resistivity

Region II, a resistivity peak, occurs in specimens aged at temperatures from 0 to 70 °C. Aging at -30 °C produces some increase in resistivity after long times. Specimens aged at 100 °C and above apparently pass the peak within 0.25 minutes of aging, because their resistivities decrease continuously with time. The height of the peak ($\Delta \rho_{II}$) increases with carbon and nickel content (Fig. 18). $\Delta \rho_{II}$ does not seem to vary in a systematic way with aging temperature, and appears to remain the same within 20 percent.

The activation energy of the process causing the peak was determined by application of equation 17 to plots
FIGURE 18. HEIGHT OF RESISTIVITY PEAK VS. CARBON CONTENT
of \( \ln t \) vs. \( 1/T \).* Values were determined at several different points on both sides of the peak as well as at the peak itself by assuming that, in samples aged at different temperatures, the attainment of equal fractions of total peak height corresponds to identical amounts of the reaction. The activation energies thus obtained vary from 18 kcal per mole during the early stages of the increase, to 21 kcal per mole at the summit of the peak, up to 24 kcal per mole during the decline. These values were found to be the same for all the alloys.

In deciding what change in the martensite is responsible for the resistivity peak, it is necessary to consider the observations of other experimental methods in the same time-temperature range. The x-ray diffraction results discussed in Section 5.2 show that a low-tetragonality martensite \((\alpha_t)\) forms during aging in this temperature range. The activation energy for this process is about 21 kcal per mole, which is in close agreement with that for the resistivity peak. Furthermore, Hillert (77) calculates the activation energy for carbon diffusion in martensite to be:

\[
Q_{\text{mart.}} = Q_{\text{ferrite}} + 3380X
\]  

(21)

where \( X \) = weight percent carbon in the martensite and \( Q_{\text{ferrite}} = 20 \) kcal per mole (44)

*The data for \( \Delta \rho_{\text{II}} \) were insufficient to apply equation 20.
Accordingly, for the carbon contents of interest, the measured Q values for the resistivity peak and for $\alpha_t$ formation are about the same as that for diffusion of carbon in martensite. Hence, the rate-controlling step in both cases appears to be carbon diffusion. On the basis of the x-ray results, the indications are that carbon atoms leave the octahedral sites occupied in virgin martensite and form carbon-rich clusters or find lower-energy sites at dislocations.

Electron microscopy has shown that micrographs of alloys aged in the temperature range of the resistivity peak have an unusual mottled appearance and electron diffraction patterns exhibit distorted spots. Both these observations can be taken as evidence of carbon clustering in light of their similarity to observations on other systems known to form solute clusters.

In addition, Mössbauer measurements (50-51) strongly suggest that aging in this temperature range causes carbon-rich clusters to form. Choo and Kaplow (51) find that the structure of the clusters resembles that of Fe$_4$N, a face-centered cubic nitride observed by Jack (81) during the aging of iron-nitrogen martensite.

The Mössbauer, electron microscopic, and x-ray observations were made on martensites aged past the summit of the peak, where the resistivity begins to undergo a steady decrease.
Since (1) the activation energy for the peak agrees with that for diffusion of carbon, (2) no peak is observed in nil-carbon alloys, and (3) peak height increases with carbon content, it is clear that carbon movements are involved in the cause of the peak. Carbide precipitation may be ruled out as the source of the peak on the grounds that no carbides are observed to form until very much later in the aging. In the present case, carbides are first seen after aging for one hour at 150 °C, a condition much past the peak. The two other possible processes involving carbon are clustering and segregation to lower-energy sites, such as dislocations.

According to the previously discussed ideas about the origin of martensite resistivity, the increase in resistivity in Region II reflects an increase in the mean-square displacements, \( \bar{\mu}^2 \), of iron atoms from their equilibrium positions. If carbon segregation to dislocations does take place, the driving proce would be a reduction in elastic strain energy. The occupation of dislocation sites by carbons produces less distortion of the lattice than occupation of octahedral sites away from dislocations. This implies that \( \bar{\mu}^2 \) should decrease with such segregation and cause a decrease in resistivity.

On the other hand, Hoffman (58) has shown that clustering may be considered to be a kind of spinodal decomposition.
in which a decrease in elastic free energy is accompanied by an increase in $\bar{u}^2$. Russian (60) investigators have suggested that a spinodal-type of clustering reaction is responsible for the distorted electron diffraction spots observed during aging. The carbon-carbon binding energies calculated by Johnson (53-54) imply that cluster formation is energetically favorable. Wilkes (82) has proposed a hypothesis which accounts for the resistivity peak during early stages of G. P. zone formation, but is generally applicable to any clustering system. He postulates a stage, reached fairly early in zone formation, when electron scattering is a maximum giving rise to a peak in resistivity. This hypothesis fits very well with the present observation that the resistivity peak occurs early in the aging compared with the aging times required to produce observable clustering effects in the x-ray, Mössbauer and electron microscopy results. According to Wilkes' suggestion, the resistivity decrease following the peak is due to the clusters exceeding some optimum scattering size. Similarly, in the Hoffman spinodal proposal, though $\bar{u}^2$ continues to increase throughout the clustering, the distribution of distortions becomes concentrated in the immediate area of clusters so that most of the atoms in the lattice are undisplaced. This would lead to a resistivity decrease during later stages of the process. Hence, the Wilkes and Hoffman proposals accounting for the resistivity peak and subsequent decrease
are qualitatively alike.

Thus clustering of carbon atoms seems to account fully for the observed phenomena and we conclude that it is the cause of the resistivity peak and the beginning phase of the subsequent resistivity decrease. Dislocation segregation, to the extent that it may occur, must involve only a small fraction of the carbons present; otherwise the peak would not be measurable. Moreover, the 18 nickel-0.11 carbon alloy would exhibit no resistivity peak if such segregation predominated since the lath martensite in this alloy should have enough dislocations to provide sites for all the carbon atoms. (46)

5.3.5 Region-III Resistivity Decrease

After achieving the peak of Region II, the resistivities of the specimens decrease steadily. Since, as was concluded in the previous section, the resistivity peaks are found fairly early in cluster formation, the subsequent decrease encompasses almost all of the decomposition of martensite (eventually) into α-ferrite and cementite. For simplicity we may consider the start of the carbide-precipitation process (f=0) to be where the resistivity is equal to its initial as-quenched value after passing the peak. It is expected that the resistivity will decrease linearly with the amount of carbon removed from solution to form carbides, and we assume that the process of martensite decomposition is complete (f=1) when
the resistivity decline levels off or reaches a plateau on aging at 300 or 350°C. This overall decrease in resistivity, which increases with alloy carbon content, is then prorated to indicated fraction transformed, as shown in the right-hand scales of Fig. 13b-e. Thus, a basic assumption in assigning values of f to points on resistivity curves is that two specimens having equal normalized resistivity changes after aging at different temperatures are at identical stages in the overall precipitation reaction.

A closer look at the shapes of the resistivity curves in Region III reveals that they can be divided into three subregions on the basis of changes in slope. In the first subregion, the resistivity decrease is a continuation of the decline from the peak. The second subregion starts when the fraction transformed is between 0.3 and 0.4; here the resistivity vs. log time curves decrease in slope. In most instances this change in slope is gradual, but some of the curves exhibit a definite elbow or break point. This second subregion lasts until f = 1, the completion of decomposition. A third subregion occurs in some specimens aged for long times at 300 or 350°C after the resistivity curves have reached the f = 1 level.

Activation energies for various fractions transformed were calculated using Hillert's method, equation 20, and the results are presented in plots of Q vs. fraction transformed for each alloy in Fig. 19. The details of the
FIGURE 19b. ACTIVATION ENERGY VS. FRACTION TRANSFORMED FOR AN 18Ni-0.4C ALLOY
curves differ somewhat, but this may be due, at least in part, to the procedures used to normalize the data (see section 5.3) rather than to any significant difference in behavior among the alloys. The results are in reasonable agreement with those of Kerlins and Altstetter (43) and Eldis (44).

The activation energy starts at values from 20 to 25 kcal per mole during the first 30 to 40 percent of the transformation. These values are consistent with those obtained for the resistivity peak and for \( \alpha_t \) formation. Carbides can be detected by electron microscopy after three hours of aging at 100°C (45) or one hour at 150°C. This corresponds to a fraction transformed of about 0.4. Because of the similarity of activation energy, and because carbides are not yet precipitating in this first subregion of Region III we conclude that the initial part of the resistivity decline, up to about 40 percent transformation, is due to a continuation of the carbon clustering process responsible for the resistivity peak.

The activation-energy values begin to increase when the change of slope of the resistivity curves near \( f = 0.4 \) is reached. In those curves with no distinct elbows, the increase in Q begins at lower \( f \) levels and is more gradual, becoming in effect a continuous increase. Ultimately, the activation energy reaches a value between 33 and 37 kcal per mole when \( f \) is about 0.7. Since carbide
precipitation is first detected when \( f \) is about 0.4, we conclude that the increasing \( Q \) values correspond to some mixture of the activation energies of carbide precipitation and clustering. After 70 percent transformation, carbide precipitation is the predominant change occurring as reflected by the leveling off of the \( Q \) values at about 35 kcal per mole, which we take as the activation energy for carbide formation. There appears to be no pronounced difference in the activation energy for the formation of \( \epsilon \)-carbide and for cementite. The value of 35 kcal per mole for carbide precipitation is in reasonable agreement with that reported by Eldis (44), who concluded, on the basis of similar activation energies, that the rate-controlling mechanism for carbide formation is pipe diffusion of iron atoms away from the growing carbides. The present data supports this conclusion. It is interesting to consider how the two types of carbides form. The Mössbauer, resistivity and electron-microscopy results indicate that most or all of the carbon atoms in martensite are grouped in the \( \text{Fe}_4\text{C} \) clusters at the time \( \epsilon \)-carbide begins to appear. From the electron micrographs, it is seen that the \( \epsilon \)-carbide forms as a finely dispersed network of thin particles. If, as has been suggested, the mottling in the micrographs of specimens tempered at lower temperatures is a manifestation of clustering, then it is possible that the clusters act as nuclei or preferred sites for the
ε-carbide. A scheme of precipitation can be envisioned during which clusters of carbon atoms grow coherently to some critical size, after which iron atoms diffuse away by a pipe-diffusion mechanism. The remaining clusters thus become richer in carbon, perhaps approaching the Fe_{2.4}C composition of ε-carbide. An accompanying loss of coherency would then permit the hexagonal (or orthorhombic) structure of ε-carbide to form. In this sense, the clustering can be considered as a step in the formation of ε-carbide analogous to the precipitation of θ' from G. P. zones in the aluminum-copper system. On the other hand it is also possible that ε-carbide nucleates in the classical way with the clusters serving as heterogeneous nucleation sites.

In contrast cementite appears to nucleate and grow separately from the clusters or from the ε-carbide particles. However, the rate-controlling step is evidently the same as for ε-carbide precipitation, in that no difference in activation energy can be detected.

In essence, the process of martensite decomposition has two activation energies; one for the formation of clusters where the rate-controlling step is carbon diffusion, while the other is for carbide precipitation where the mechanism is probably iron-pipe diffusion.

The final drop in resistivity of specimens aged for prolonged periods at 300 and 350°C (the third subregion of Region III) is probably not due to further carbide
precipitation, since the completion of precipitation is signaled by the leveling off of the resistivity curves, at which time the overall decrease in resistivity is commensurate with the total removal of carbon from solution in the martensite. Not enough data could be obtained to determine the activation energy for the third subregion but comparison of micrographs of specimens aged for 60 minutes and 10,000 minutes at 350°C suggests that recovery and recrystallization may be responsible (Fig. 9e, 10e, and 20).
Figure 20: Optical micrographs of martensite aged for 10,000 minutes at 350°C. Compare with Fig. 7e and 8e. 1% Nital etch.
Chapter VI
SUMMARIZING DISCUSSION

6.1 The Structure of Virgin Martensite

The results of this and other studies have shown that virgin twinned martensite is body-centered tetragonal with the c/a ratio increasing linearly as a function of carbon content. Although no similar direct observations on the tetragonality of virgin lath martensite were possible, due to the relatively high $M_s$ temperatures, a strong case can be developed to show that it, too, must be tetragonal.

The face-centered cubic austenite has one octahedral site per iron atom, while the body-centered martensite has three; each of a different orientation. Thus, one of the consequences of the Bain distortion is the tripling of octahedral sites. If there are carbons present in the austenite and they do not jump from site to site during the martensitic transformation, then all the carbons will occupy one of the three sets of sites in the body-centered phase causing it to be tetragonal. This is the observed case in twinned martensite. Since the resistivity results for lath and twinned martensites are identical (except for the greater resistivity changes in the twinned due to higher carbon contents), we may infer that the difference in substructure of the two types of martensite has relatively little effect on aging.
behavior. Consequently, we may rule out segregation of carbon atoms to dislocations due to autotempering as a likely cause of the loss of tetragonality, since enough carbons remain in solution to form clusters in both types of martensite.

Another way for a nontetragonal martensite to form is by disordering of carbons such that the three sets of octahedral sites are equally populated. The occurrence of such disordering should be independent of the morphology, since the substructure does not enter into the disordering, the latter being accomplished by one or two atomic jumps. The activation energy of such a process would be about 21 kcal per mole, the same as that for cluster formation, inasmuch as the same rate-controlling step is involved. However, the total number of jumps necessary for disordering is much smaller than for clustering and so disordering should reach completion in a much shorter time.

Moreover, disordering should manifest itself by a gradual, rather than a discontinuous, decrease in the c/a ratio, and the lattice parameter of cubic, disordered martensite should be larger than that of nil-carbon iron because a hydrostatic dilatation of the lattice takes place when carbon atoms are in solution. (23) The changes observed by x-ray diffraction of twinned martensite exhibit neither a continuous decrease in c/a ratio nor a hydrostatic dilatation of the lattice after the c/a drop. Hence, we may conclude that no disordering is observed in twinned
martensite. In addition, because of the similar resistivity results for lath martensite, it appears that no disordering occurs in martensite of this morphology either.

The various interstitial ordering theories (31-35) predict that disordering of carbon atoms takes place only when the temperature of the martensite is above a critical temperature which is proportional to the carbon content of the martensite. A discussion of the theories is presented in the Appendix. On this basis, the twinned martensites might all form below their ordering temperatures and so be tetragonal, while the lath martensites might be cubic because of formation above their ordering temperatures. However, the theories predict that the critical temperature for ordering is about 1000 times the weight percent carbon in the alloy, while a slope more than sixty times as large would be needed to account for all the observations of tetragonality in virgin martensite (Fig. 21). Thus, the ordering theories are not successful at predicting tetragonality in virgin twinned martensite, and the same should hold true for the case of lath martensites.

We come to the conclusion that the structures of both twinned and lath virgin martensite are body-centered tetragonal, and any observations to the contrary are probably due to autotempering of carbons to form clusters and/or the inability of most conventional diffraction techniques to detect a closely spaced tetragonal doublet.
FIGURE 21 CRITICAL TEMPERATURE FOR ORDERING VS CARBON CONTENT SHOWING COMPOSITIONS AND TEMPERATURES WHERE TETRAGONAL MARTENSITE HAS BEEN OBSERVED
6.2 The Aging of Martensite

The results of this research have shown that both lath and twinned martensites undergo very similar changes during aging. The differences in substructural morphologies apparently have little effect on tempering behavior, because the carbon atoms cluster more rapidly than they can segregate to dislocation sites. This does not mean that dislocation segregation does not occur, merely that it is less important than cluster formation in the early aging of tetragonal martensites.

The long-standing division of the tempering of martensite into three stages can now be modified to include more detailed descriptions of each stage. An initial stage is added to include the low-temperature dislocation relaxation. The revised stages of tempering are presented in Table 2.
### Table 2

**THE STAGES OF TEMPERING**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Type of Change</th>
<th>Temperature Range</th>
<th>Q (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th</td>
<td>Dislocation Relaxation</td>
<td>below room temperature</td>
<td>3</td>
</tr>
<tr>
<td>1st</td>
<td>Clustering, $\alpha' \to \alpha_t$</td>
<td>-30 to 100°C</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>$\alpha' \to \alpha_t$ immediately followed by precipitation of $\varepsilon$-carbide</td>
<td>above 100°C</td>
<td>21 increasing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>to 35</td>
</tr>
<tr>
<td>2nd</td>
<td>Isothermal conversion of retained austenite</td>
<td>above 200°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(not observed in these experiments)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3rd</td>
<td>Precipitation of $\varepsilon$-carbide and cementite, followed by resolution of the $\varepsilon$ leading to the equilibrium mixture of $\alpha$-Fe and cementite</td>
<td>above 200°C</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Recovery and recrystallization</td>
<td>above 300°C</td>
<td></td>
</tr>
</tbody>
</table>
Chapter VII
CONCLUSIONS

1. The virgin structures of both lath and twinned martensite are body-centered tetragonal with a c/a ratio increasing with carbon content according to:
\[ c/a = 1.005 + 0.057(w/o\ C) \]

2. While the substructures of the two martensitic morphologies are quite different, both exhibit very similar behavior during aging.

3. The changes during the aging of virgin martensite can be divided into the following overlapping steps:
   a) Dislocation relaxations occur during aging below room temperature. The activation energy for such relaxations is about 3 kcal per mole.
   b) The formation of carbon clusters (of approximate composition Fe$_4$C) takes place when martensite is aged at temperatures from -30 to +200°C. The rate-controlling process for such clustering is the diffusion of carbon interstitials in martensite with an activation energy of 21 kcal per mole.
c) $\varepsilon$-carbide particles precipitate during aging above 100°C; the corresponding activation energy is about 35 kcal per mole suggesting that the rate-controlling process is pipe diffusion of iron atoms away from the growing carbide particles. There are strong indications that the carbon clusters formed earlier are a precursor to the $\varepsilon$-carbide precipitation.

d) Cementite particles nucleate and grow at aging temperatures above 200°C. The activation energy is the same as that for $\varepsilon$-carbide formation, suggesting that the same rate-controlling process is at play in both instances.

e) Recovery and recrystallization occur when martensite is aged at temperatures above 300°C.

4. Interstitial ordering theories are not successful in predicting whether or not virgin martensite is tetragonal or cubic. There is no evidence that disordering of carbon atoms takes place to cause the formation of body-centered cubic martensite.
Chapter VIII
SUGGESTIONS FOR FURTHER WORK

1. The tetragonality of virgin lath martensite has still not been determined by direct observation. Perhaps closer-spaced compositions or more sophisticated specimen preparation could allow the pseudo-single crystal method to be used for such measurements.

2. The nature of the carbon clustering during the early stages of aging should be more fully explored. This can be done by a combination of x-ray, electron microscopy and Mössbauer experiments. It would be desirable to show more definitely whether \( \varepsilon \)-carbide nucleates heterogeneously near the clusters and grows at their expense or whether the clusters themselves gradually develop into \( \varepsilon \)-carbide. Also of interest is the 1.004 axial ratio of \( \alpha_t \), and its relation to the clusters. The exact cause of this low tetragonality during aging remains to be established.

3. More accurate values for the activation energy of each step of aging could be obtained by additional resistivity runs at smaller temperature intervals. Combined with structural observations, this information could lead to a more detailed understanding of the mechanisms of tempering. Furthermore, such resistivity data could lead
to an improved theory of the resistivity of clustered and multiphase alloys.

4. The theories of martensite strengthening should be re-examined in the light of the clustering stage of aging.

5. Experiments with very high-carbon alloys would be of interest because the structure of martensite and the phenomena of aging should be easier to observe in such alloys than in alloys with less carbon.
APPENDIX

Application of Interstitial Ordering Theories to Fe-Ni Alloys

The theories concerning interstitial ordering reactions (31-35) were originally developed for the case of carbon atoms in solution in pure body-centered iron. However, the experimental data in this thesis available to test the applicability of these theories were for Fe-Ni alloys containing between 20 and 30 weight percent nickel. Consequently, it was necessary to take the addition of nickel into account in the ensuing calculations.

The calculations of the critical temperature for interstitial ordering in all theories can be affected by the addition of nickel to the alloy in two ways: 1) The lattice parameters of Fe-Ni alloys decrease as nickel content increases, in the nickel range of interest, thus requiring larger distortions of the lattice to accommodate carbon interstitials, and 2) the elastic constants of Fe-Ni alloys decrease as nickel content increases, thus making it easier for carbon atoms to expand the lattice. Clearly, these effects work in opposing directions. However, the elastic constants drop by as much as 35 percent in going from zero to 30 percent nickel (76) while the variation in lattice parameter is only a tenth as much. (72) Therefore, only
the change in elastic constants was considered in the calculations to be discussed here.

To obtain the Fe-Ni elastic constants of interest, values for the bulk elastic constants $E$ (Youngs Modulus) and $G$ (shear modulus) for $\alpha$-phase alloys were obtained from Marsh (76). Then, using the Reuss averaging expressions for bulk elastic constants and $J = 0.601$ (the compliance anisotropy factor for pure iron) (83) the elastic compliances and constants were calculated. It was assumed that the elastic anisotropy of Fe-Ni alloys is the same as that of pure Fe. The elastic constants obtained are listed in Table A1.

1. Polder (32) considers the contribution to the free energy of the strain energy produced by distributions of carbons among the three sets of octahedral sites, and concludes that in the absence of applied stress, carbon atoms will populate all three sets of sites equally. This means no critical temperature for ordering exists because tetragonal martensite is not considered to be thermodynamically stable. Polder suggests that the reason carbon atoms in tetragonal martensite remain ordered at room temperature may be due to a much slower diffusion of carbon in martensite than in $\alpha$-Fe.

2. Zener (31) has derived an interstitial ordering theory based on the energy change associated with moving a carbon atom from a disordered to an ordered site, the strain
Table A2
ELASTIC CONSTANTS OF BCC Fe-Ni ALLOYS

<table>
<thead>
<tr>
<th>Constant</th>
<th>Pure Fe</th>
<th>Fe-20Ni</th>
<th>Fe-30Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>2.08*</td>
<td>1.72*</td>
<td>1.52*</td>
</tr>
<tr>
<td>G</td>
<td>0.81*</td>
<td>0.67*</td>
<td>0.59*</td>
</tr>
<tr>
<td>$s_{11}$</td>
<td>0.760†</td>
<td>0.821√</td>
<td>0.898√</td>
</tr>
<tr>
<td>$s_{12}$</td>
<td>-0.287†</td>
<td>-0.289√</td>
<td>-0.311√</td>
</tr>
<tr>
<td>$s_{44}$</td>
<td>0.893†</td>
<td>1.010√</td>
<td>1.215√</td>
</tr>
<tr>
<td>$c_{11}$</td>
<td>2.42†</td>
<td>1.974√</td>
<td>1.761√</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>1.465†</td>
<td>1.072√</td>
<td>0.931√</td>
</tr>
<tr>
<td>$c_{44}$</td>
<td>1.12†</td>
<td>0.99√</td>
<td>0.85√</td>
</tr>
</tbody>
</table>

all units are $10^{12}$ dynes/cm² except $s_{11}$, $s_{12}$ and $s_{44}$ which are in $10^{-12}$ cm²/dyne

* Marsh (76)
† Hirth and Lothe (83)
√ calculated
energy produced by the expansion of the lattice, and the variation in entropy with the degree of interstitial order. A critical temperature is predicted because at low temperatures the entropy contribution to free energy (G) is small and so G is minimized when the atom configuration with the lowest combination of chemical and strain energies is achieved. At higher temperatures the entropy term predominates and the disordered configuration of atoms posses the lowest free energy. The Zener prediction of the critical temperature is:

\[ T_c = 0.243N E_{100} \lambda^2 / k \]  

in which \( N = 3.92 \times 10^{21} \text{ (w/o C)} \), the number of carbon atoms per unit volume \( E_{100} = 1/s_{11} \), Young's Modulus in the [100] direction \( \lambda = 1.2 \times 10^{-23} \), the strain of transferring one carbon per unit volume from a disordered to an ordered site \( k = \text{Boltzmann's constant} \)

3. The Fisher theory (33) is derived by computing the elastic energy of an interstitial atom through a detailed consideration of the displacements of the 32 iron atoms nearest to a carbon interstitial. An expression for the free energy is developed, and conditions for its minimum are derived from which an equation for the critical
temperature for ordering is obtained:

$$T_c = \frac{n(f_1a^2e_0)^2}{12k(c_{11}-c_{12})}$$ (A2)

where $n =$ number of interstitials per cm$^3$
$a = 2.866 \times 10^{-8}$ cm, the lattice parameter of iron
$e_0 = 0.19$, the dipole strain of an interstitial
estimated from the tetragonal lattice
parameters of martensite
$k =$ Boltzmann's constant
$c_{11}, c_{12} =$ elastic constants
$f_1 =$ force on the two nearest-neighbor iron atoms
necessary to maintain equivalent distortion
of an interstitial; this is a function of
both the elastic constants and the displacements
of the 32 irons surrounding the interstitial
site

4. The treatment of interstitial ordering by
Nowick and Heller (34) considers the interactions of the
distortion dipoles of occupied interstitial sites. The
underlying idea is that as the concentration of
interstitials is increased, mutual interactions lead to the
ordered configuration having the lowest free energy. The
critical temperature predicted by this theory is:
\[ T_c = \frac{c_0 v_0 (\lambda_1 - \lambda_2)^2 (c_{11} - c_{12})}{3k} \]  \hspace{1cm} (A3)

in which  
- \( c_0 = \) mole fraction of interstitials  
- \( v_0 = a^3/2 = (2.866 \times 10^{-8})^3/2 = \) molecular volume  
- \( c_{11}, c_{12} = \) elastic constants  
- \( k = \) Boltzmann's constant  
- \( (\lambda_1 - \lambda_2) = 1.06, \) obtained from anelastic measurements on single crystals, where \( \lambda_1 \) and \( \lambda_2 \) describe the strain around the interstitial site

5. Khachaturyan (35) derived his interstitial ordering theory from a treatment of the elastic interactions of pairs of interstitials, an approach similar to that of Nowick and Heller. The expression for the critical temperature is:

\[ T_c = \frac{c(3-c) v (c_{11} - c_{12})^2 (\gamma_1 - \gamma_2)^2}{9(1-c)^2 k \frac{c_{11} - c_{12} + c_{44}}{c_{11} - c_{12}}} \]  \hspace{1cm} (A4)

in which  
- \( c = \) atom fraction of carbons  
- \( v = \) molecular volume of iron  
- \( k = \) Boltzmann's constant  
- \( c_{11}, c_{12}, c_{44} = \) elastic constants  
- \( \gamma_1 = -0.117 \)  
- \( \gamma_2 = 0.917, \) representing the rate of change of the a and c lattice parameters, respectively, with the addition of carbon
The critical temperatures as recalculated using the elastic constants listed in Table A1 are presented in Table A2. It is evident that the predictions of the various theories are quite similar. It is difficult to decide which approach is on the firmest theoretical grounds. However, all of the theories contain the obviously invalid assumption that linear elasticity holds true for the very large distortions around interstitial carbon atoms. A more serious short-coming is that these order-disorder theories are all refuted by the available lattice-parameter measurements which clearly show (Fig. 21) that Fe-Ni-C martensites remain tetragonal at temperatures well above critical temperatures deduced from Table A2.
Table A2

CRITICAL TEMPERATURES FOR CARBON ORDERING

\[ T_c \, ^\circ K = M(w/o \, C) \]  \hspace{1cm} (M values are tabulated)

<table>
<thead>
<tr>
<th>Theory</th>
<th>Fe</th>
<th>Fe-20Ni</th>
<th>Fe-30Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zener</td>
<td>1298</td>
<td>1204</td>
<td>1098</td>
</tr>
<tr>
<td>Fisher</td>
<td>823</td>
<td>744</td>
<td>572</td>
</tr>
<tr>
<td>Nowick and Heller</td>
<td>1413</td>
<td>1335</td>
<td>1224</td>
</tr>
<tr>
<td>Khachaturyan</td>
<td>1165</td>
<td>1140</td>
<td>1081</td>
</tr>
</tbody>
</table>
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BIOGRAPHICAL NOTE

Andrew Michael Sherman was born in Cleveland, Ohio on October 28, 1945. He attended public schools in Cleveland Heights through ninth grade, and then entered Windsor Mountain School, Lenox, Massachusetts from which he graduated in 1963. Starting in September 1963 he attended the Massachusetts Institute of Technology, where he obtained an SB degree in Metallurgy in June 1967. During the summers of 1965, '66 and '67 he was employed at the Lewis Research Center of NASA in Cleveland as a summer trainee in the Materials and Stresses Division.

Since September 1967 he has been enrolled as a graduate student in Physical Metallurgy at MIT. During his first two years of graduate study he held the position of Part-time Instructor in the Department of Metallurgy and Materials Science. In June 1969, he received a fellowship sponsored by the Climax Molybdenum Company of Michigan. Following the completion of his studies for the PhD degree he expects to pursue a career of research in private industry.

His interests include music, violin making and playing, art sports, literature, and the pyramids of Egypt.