FIELD-ION MICROSCOPE INVESTIGATIONS OF FINE STRUCTURES IN AS-QUENCHED
AND TEMPERED FERROUS MARTENSITE

A THESIS

Presented to

The Faculty of the Division of Graduate
Studies and Research

By

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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy in the School
of Chemical Engineering

Georgia Institute of Technology

May, 1972

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Date approved by Chairman: May 4, 1972

PREFACE

No task of this magnitude is ever accomplished without the help of others. Had it not been for Dr. Helen E. Grenga, my thesis advisor, this work would have never come to fruition. I am indebted to Dr. Robert F. Hochman for having provided me an opportunity to come to this country for pursuing my higher studies in this school; this has been an invaluable experience to me. Also, I am grateful to him for reviewing this dissertation. I would like to acknowledge the many helpful discussions I have had with Dr. Bruce G. LeFevre and also would like to thank him for reviewing this work.

The enlightening discussions I have had with Dr. Brian Ralph of Cambridge University during the dark days of my research is deeply appreciated. I have also had many useful discussions with Dr. Niels Engel and Dr. E. E. Underwood of Georgia Tech. Mr. Nirmal K. Datta helped me draw all the diagrams in this thesis and Mr. Henry G. Paris helped me in the operation of the electron microscope. Miss Margo Dunlop of Cambridge University was also helpful in the preliminary analyses of some of the results obtained in this research.

I would like to register my gratitude towards my parents who through their letters have constantly encouraged me during my tenure in this school.

This work was financially supported by AFOSR (Project Themis Contract No. F-44620-68-C-0008) and National Science Foundation.

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SUMMARY

The microstructures of as-quenched and tempered martensites in an Fe-0.8%C-0.4%Mn steel were studied with hydrogen-ion microscopy at 78°K. Information on image characteristics and contrast features as well as crystallographic and morphological data on the fine structures of these materials were obtained, and a comparison was made between microstructure and hardness during tempering.

The hydrogen-ion images of ferrite, low-carbon martensite and high-carbon martensite differed in image contrast and regularity of net plane edges. This was attributed to the change in carbon content and strain in the matrix. The iron carbides were darker in the image than the ferrite matrix, probably due to the field-induced reaction of the hydrogen image gas with the carbide particles.

Hydrogen-ion images of as-quenched martensite revealed both twinned and untwinned martensite regions. Such an observation was consistent with the recent electron microscopy investigations on high-carbon martensites. In the field-ion images twins appeared as alternate bright and dark bands, the bright bands representing the twins and the dark bands the twin interfaces. In the twinned region {112} transformation twins were 25-100 Å wide, while in the untwinned region a high density of dislocations was observed.

In the first stage of tempering, fine ϵ -carbide particles, many as small as 20 Å, having a {100} habit precipitated on dislocations and along the sub-boundaries. The contrast around the carbide particles when

they intersected a $\{110\}$ region indicated the degree of coherency of these precipitates. Both coherent and partially-coherent ϵ -carbide particles were found throughout the first stage of tempering. At peak-hardness the average particle size and density were $60 \text{ \AA}$ and 1.6×10^{17} particles/cm³, respectively, while later in the first stage of tempering the average particle size and density were $160 \text{ \AA}$ and 8.3×10^5 particles/cm³, respectively. Therefore, it was concluded that dispersion hardening contributed more than coherency hardening to the peak-hardness in the first stage of tempering. These conclusions contradicted previous ones made from observations by other techniques and demonstrated the necessity of supplementary FIM results when studying microstructures with a high density of extremely fine particles.

In the third stage of tempering, cementite particles with both $\{110\}$ and $\{112\}$ habits were observed. The pronounced softening in this stage of tempering was associated with an increase in average particle size ($600 \text{ \AA}$), a decrease in particle density (1.5×10^{15} particles/cm³) and the disappearance of twins.

CHAPTER I

INTRODUCTION

Steels belong to a select class of materials, and find a wide spectrum of applications in the modern technological era. Among the many phase transformations associated with steels, the martensite transformation¹ is probably the most important. Martensite as such finds very little use because of its brittle nature, and hence is tempered to obtain useful engineering properties. The tempering process² has stimulated keen interest among metallurgists due to its complex nature and technical and industrial importance.

Electron microscopy³ studies have shown that the fine structure of ferrous martensite consists predominantly of dislocations in low carbon steels and fine twins in high carbon steels. However, recently it has been established⁴ that the substructure of ferrous martensite consists of a mixture of dislocations and twins over a wide range of carbon concentration. Barrett and Masalski⁵ point out that precise information on individual martensite plates, rather than 'average' or 'typical' values of plates having different orientations and habits, is required for better understanding of the martensite transformation.

During tempering of martensite, ϵ -carbide and cementite are known to form, but in some cases³ identification of carbides in the early stages of tempering is difficult. The volume fraction and particle sizes are so small during initial stages of tempering that they may

escape detection by x-ray diffraction and electron microscopy techniques.

The present field-ion microscopy (FIM) investigations aim at studying the fine structure in as-quenched and tempered ferrous martensite. In FIM it is possible to obtain a magnification of 10^6 combined with a resolution of 2-3 Å, and hence its versatility in examining fine structure. Precision information on individual martensite plates is obtainable through FIM. Crystallographic as well as morphological analyses of the twins is performed and an attempt is made to explain the twin contrast observed in field-ion images of martensite. The microstructural changes occurring during the first and third stages of tempering are investigated with FIM and related to the accompanying changes in microhardness. Information is also obtained concerning nucleation and growth, habit plane, particle size, density and distribution of both ϵ -carbide and cementite. Most of the FIM studies on steels⁶⁻⁸ have centered around high purity materials while for the present studies commercial music wire (Fe-0.8% C-0.4% Mn) was chosen.

CHAPTER II

LITERATURE SURVEY

A. Field-ion Microscopy

1. Principles

Detailed reviews on the principles of FIM are available in the literature, notably those of Müller⁹, Gomer¹⁰ and Brandon¹¹, so that only a very brief description is given here.

The field-ion microscope is a high vacuum chamber evacuated to a pressure of 10^{-7} to 10^{-10} torr. The specimen is in the form of a fine tip, 100-1000 Å in radius, which is mounted within the vacuum chamber and cooled to cryogenic temperatures with liquid nitrogen (78°K), liquid hydrogen (21°K) or liquid helium (4°K) prior to imaging. An image gas, for example, helium or hydrogen, is leaked into the chamber at a pressure of about one micron, and a high positive potential of 3 to 30 kv is applied to the specimen. The image gas is ionized near the surface of the specimen by a tunneling mechanism¹², and the positive ions are radially projected onto a fluorescent screen held at ground potential. Ionization occurs at positions of highest field, which are located above the atoms protruding most from the surface of the specimen, thereby giving an image in which the bright spots correspond to individual atoms on the surface. Another important phenomenon associated with imaging in FIM is field evaporation. Removal of atoms from the surface of the specimen by the application of a positive voltage is termed field

evaporation¹², and this phenomenon makes possible the production of atomically smooth and clean surfaces. Furthermore, continued layer-by-layer field evaporation permits information about the bulk material to be obtained.

2. Application to Ferrous Materials

The majority of FIM work on iron and steels has been done by the Cambridge group^{6-8, 13-19}. These and other applications of FIM to the study of ferrous materials are summarized in Table 1.

a. Imaging Techniques. Hydrogen has been used as the image gas in most of the FIM studies on iron and steels. Imaging ferrous materials in FIM does not permit the use of helium at liquid nitrogen temperatures. The ionization field for helium is higher than the evaporation field for iron so that at the best image voltage (BIV) the image is very unstable and often the specimens fracture. This can be overcome by using an image gas of lower ionization potential, for example, neon, or much cooler specimen temperatures, for example, liquid hydrogen, or both. The BIV for hydrogen is about one half that for helium, and it is found that the image brightness and phase contrast is generally satisfactory for crystallographic and morphological analyses in steels. The low ionization potential of hydrogen makes the tip vulnerable to contamination by the residual gases, necessitating good vacuum conditions in the microscope. Also, hydrogen reacts with the specimen surface under the influence of the electric field and this causes corrosion of the specimen. The nature of this field induced corrosion is unknown¹³, but it is of no serious concern as far as the quality of the photographs is concerned, because the hydrogen-ion image is sufficiently bright, requiring

Table 1. Summary of FIM Applications to the Study of Ferrous Materials.

Alloys Studied	Type of Investigation	Reference
Fe-C Alloys	Crystallography and morphology of pearlite.	13
Iron and Fe-C Alloys	Coincidence site lattice model and crystallographic analyses of grain boundaries.	7
Fe-C Alloys	Crystallographic study of pearlite, orientation relationship between ferrite and cementite and the habit of cementite platelets.	6
Alloy Steels	Size and distribution studies of second phase particles.	14
Fe-2.0%V-0.2%C	Computer analyses of particle size and distribution.	15
Fe-2.0%V-0.2%C	Study of carbide particle coarsening-interface controlled.	16
Fe-2.0%V-0.2%C	Correlation between size and distributions of V_4C_3 and micro-hardness values.	17
Fe-2.0%V-0.2%C	Combined electron microscope and FIM study of the microstructure produced due to isothermal transformations.	8
Fe-1.4%Ti-3.4%Si	Pre-peak-hardness microstructures and particle size/hardness correlation.	18
Fe-12.0%Au	Early stages of coarsening of gold precipitates in the pre-peak and post-peak hardness ranges.	19
Fe-W(1680 ppm)	Crystallography of an incoherent twin segment.	20

Table 1. (Continued)

Alloys Studied	Type of Investigation	Reference
Fe-Mo-C	Microstructure produced by quenching and tempering.	21
Eutectoid Steels	Orientation relationship between ferrite and cementite in pearlite.	22
Fe-Cu	Early stages of precipitation.	23
Fe-0.5%Ti-0.1%C	Study of isothermal transformation.	24
Fully Nitrided Fe-3 at % Mo Alloy	FIM-Atom probe analysis of thin nitrided platelets.	25

only a few seconds exposure.

Hydrogen-promoted helium-ion imaging has also been used on ferrous materials. This technique, first introduced by Müller et al.²⁶, has been used to a limited extent in the FIM of nonrefractory materials²⁷⁻²⁹. Addition of a few percent of hydrogen to helium reduces the BIV to 70 percent of that for the pure helium image. Also, the image spots in the promoted image are much sharper than in the pure helium image.

b. Image Interpretation. Sekhar and Richman³⁰ observed many streaks running across the field-ion images of as-quenched martensite. They considered that these were the lines along which the boundaries of the transformation twins intersected the specimen surface. Further it was stated that localized electronic states existed near the vicinity of the defect and that these localized states interacted with the applied electric field causing preferential ionization to take place along the line where the defect intersected the specimen surface.

In the field-ion images of tempered martensite, it was speculated by Sekhar et al.³¹ that both ϵ -carbide and cementite appeared brighter than the matrix. However, this was at variance with the results of Morgan and Ralph⁶, who showed that in the field-ion image of pearlite the cementite phase appears darker than the ferrite matrix. Many other small second phase particles have also been observed in FIM. The carbides of Vanadium⁸ and Niobium¹⁴ imaged brighter than the ferrite matrix, while Fe_3Si ¹⁴ imaged darker. Youle et al.¹⁹ reported that the precipitates of gold imaged brighter than the ferrite matrix.

3. Advantages

FIM has many advantages over transmission electron microscopy and X-ray diffraction techniques, which can be summarized as follows:

- 1) The design and operation of the field-ion microscope are relatively simple.
- 2) It is quite easy to obtain a magnification of 10^6 times combined with a resolution of 2-3 Å; hence its versatility in studying fine structures.
- 3) The field-ion images are not complicated due to image overlapping which is inherent in electron microscopy.
- 4) In the study of very small second phase particles, FIM has many advantages^{14,19}. A very small volume of second phase particles can be detected in the field-ion microscope, whereas in electron microscopy and X-ray diffraction techniques they very well may go undetected. Modifications in the electron and X-ray diffraction patterns, such as streaking, due to the presence of very small second phase particles, makes the interpretation of these patterns extremely difficult. Also, very small second phase particles and associated high particle density, cause multiple scattering of the electron and X-ray diffraction patterns, which further complicates the interpretation of these diffraction patterns.
- 5) Both morphological and crystallographic data can be obtained effectively from a single field-ion micrograph.
- 6) Because of the high magnification that can be obtained in the field-ion microscope, it is possible to investigate individual martensite plates. Furthermore in the initial stages of tempering the particle sizes are so small, that detection and unambiguous identification of these by other techniques becomes difficult. However, these particle

sizes fall well within the range of FIM.

B. Martensite Transformation

Martensite transformations, in general, can be defined³² in terms of the existence of a lattice correspondence with no diffuse mixing of the atoms other than the shuffles needed to complete the structural change. In the case of steels, it refers to the formation of b.c.t. martensite from the high temperature f.c.c. austenite. The transformation occurs so fast that only a diffusionless process is possible and is accomplished by a co-operative movement of atoms. The background information cited in this section is primarily for ferrous martensite and is by no means intended to be exhaustive either for ferrous or nonferrous martensites.

1. Characteristics

The important features of the martensite transformation^{1,33} can be summarized as follows:

- 1) The atomic movements involved are small, co-operative and very orderly.
- 2) There is a shape change or shape deformation associated with the transformation.
- 3) Straight lines and planes in austenite are transformed into straight lines and planes in the martensite phase.
- 4) There is a definite orientation relationship between the parent and the product phases.
- 5) Usually the transformation occurs independently of time; i.e., athermally.

- 6) The amount of the product phase formed is essentially a function of the temperature.
- 7) The amount of transformation increases with plastic deformation.
- 8) The martensite crystals have a lenticular cross section, and the volume and composition changes accompanying the transformation are negligible.

2. Crystallography

Bowles and Mackenzie³⁴ observed that straight scratches purposely placed on the parent phase remained straight across the interface after the transformation. Also, when a martensite plate met the surface it remained planar, which indicated that the planes were transformed into planes. From these observations they concluded that the interface plane was an unrotated and essentially undistorted plane.

Any crystallographic theory should be able to explain the change in crystal structure, shape deformation, habit plane and the orientation relationship. Bain³⁵ showed how a b.c.t. lattice could be obtained from an f.c.c. lattice, by compression along one axis and expansion along two others. Although the Bain distortion did not explain the martensite transformation in its entirety, much of this theory has been retained in the later phenomenological theories. Jaswon and Wheeler³⁶ pointed out that the Bain correspondence was energetically the most feasible one. The Bain distortion, however, did not account for the unrotated and undistorted nature of the interface plane.

In order to explain the undistorted nature of the habit plane, a two shear mechanism was put forward, the first of which occurred on the habit plane, the second shear was either a slip shear or a twin shear.

Finally, a rigid body rotation made sure that the habit plane was unrotated. Thus, the transformation involved a lattice deformation to obtain the desired change in crystal structure, a simple shear or a lattice invariant shear to obtain the undistorted habit plane and a rigid body rotation to get an unrotated interface plane. As far as the mathematical treatment of the problem was concerned, the order in which these deformations occurred was immaterial.

Bowles and Mackenzie³⁴ and Wechsler, Lieberman and Read³⁷, independent of each other, adopted a matrix algebra approach to explain the crystallography of martensite transformation. The latter investigators assumed a completely undistorted habit plane whereas the former postulated a dilatation parameter assuming the presence of an isotropic distortion of 2 percent or less in the interface plane. In certain cases the experimental and theoretical values were found to agree better if the dilatation parameter was taken into account. Other approaches have been attempted, notably by Bullough and Bilby³⁸ and Bilby and Frank³⁹. A review by Bilby and Christian⁴⁰ deals competently with these theories.

3. Fine Structure

Table 2 summarizes some of the important studies on the fine structure formed in ferrous martensite and the pertinent results of these studies.

It was pointed out earlier that the second shear of the martensite transformation is either a slip shear or a twin shear. There is enough experimental evidence now to show that in steels of certain composition, the second shear is twin shear rather than slip shear.

Kelly and Nutting³ did some of the pioneering work in the

Table 2. Summary of Investigations on Ferrous Martensite

Material Studied	Technique	Results	Reference
Fe-C(0.1-1.4%) Fe-0.8%C-20%Ni 18-8 Stainless steel	Transmission Electron Microscopy (TEM)	High C and Ni steels: twinned plates; low C and 18-8 stainless steel: laths, no trace of Twinning.	3
Fe-0.57%C-23.8% Ni	TEM	Mid-rib observed, $\{112\}_m$ twins, considerable variation in twin density in a plate, thickness of twins 100-200 Å.	41
Fe-1.4%C	TEM	$\{112\} \langle 111 \rangle$ twin orientation; twinned structure not a universal feature, occasional dis- locations.	42
Fe-C(0.02-1.9%)	TEM and Light Microscopy	Mixed twinned and un- twinned structure in the range 0.6-1.0%C.	4
Fe-1.63%C Fe-1.5%C-3.0%Cr Fe-1.0%C-10.0%Cr	Tem	Transformation and mechanical twins $\{112\}$ $\langle 111 \rangle$; twins of system (101) $\{1012\}$; stacking faults; dislocations.	43
Fe-1.28%C Fe-1.82%C	TEM	1.82%C martensite: $\{112\}_m$ and $\{110\}_m$ twins, dis- location arrays and planar effects; 1.28%C martensite: $\{112\}_m$ twins.	44
Fe-1.0%C-10.0%Cr	TEM	Early states of plate martensite growth, twin habit plane same as fully grown plate.	45

Table 2. (Continued)

Material Studied	Technique	Results	Reference
Fe-1.0%C-10.0%Cr	TEM	Fully grown martensite plates: $(112)_m$ twins, $(011)_m$ planar effects, $(\bar{1}12)_m$ slip traces and lengthy dislocations parallel to $(112)_m$ and $(011)_m$.	46
Fe-1.94%Mo Fe-20.5%Pt Fe-1.3%Sn Fe-0.49%V Fe-0.31%W Fe-0.2%C	TEM	Fe-C, Fe-Pt, Fe-W, Fe-V Fe-Mo, Fe-Sn: lath martensite; high C, Ni and N binary iron alloys: plate martensite made up of fine twins and/or dislocations. Transition from lath to plate martensite influenced by alloy composition and M_s temperature.	47

transmission electron microscopy studies of ferrous martensite. They examined the fine structures of martensite formed in a number of plain carbon and alloy steels and found two types of martensite grains to be present. In high carbon steel (approximately more than 0.4%C) and in an Fe-20%Ni-0.8%C, martensite formed as plates containing stack of fine parallel twins. This supported the assumption made regarding the second shear in the phenomenological theories of crystallography of martensite transformation. They also observed that in low carbon steels (less than 0.4%C) and in an 18-8 stainless steel martensite formed as needles with no trace of internal twinning. The authors reported an average twin width of 100 Å in the Fe-Ni-C steel.

Oka and Wayman⁴⁴ investigated the martensite substructure in Fe-1.28%C and Fe-1.82%C alloys. The martensite plates had a $\{225\}_a$ and $\{259\}_a$ habit, respectively. They examined the differences in substructure of these two types of martensite plates. For the 1.82%C steel, twinning on both $\{112\}_m$ and $\{110\}_m$ planes was seen, as well as regular dislocation arrays and planar defects on $\{110\}_m$. It was suggested that in this steel the $\{110\}_m$ type twinning is caused by the accommodation distortion of the growing martensite plates. In the 1.28%C steel only $\{112\}_m$ type twinning was observed. In both cases the $\{112\}_m$ transformation twins were found to cluster around the martensite midrib region. They also pointed out that it was difficult to differentiate between the transformation substructure and that due to the accommodation distortion of the growing martensite plates. The authors reported a twin thickness of 50-900 Å in 1.28%C steel.

Marder and Krauss⁴ have shown that in Fe-C alloys a mixture of

massive (dislocated) and acicular (twinned) martensite occurred in the range 0.6-1.0%C. Electron microscopy studies⁴⁷ revealed that the substructure of plate martensite was made up of fine twins and/or dislocation arrays. Thomas⁴⁸ reported that in many fully martensitic steels the microstructures were often complex mixtures of dislocated and twinned martensites.

Pitsch⁴⁹ examined the martensite transformation occurring in thin films of iron alloys by electron microscopy. He explained the differences between austenite/martensite orientation relationships observed in thin films and that observed in massive material by considering the constraints of the surrounding matrix to the transformation, which was less in the case of thin films as compared to the massive martensite. Nishiyama and Shimizu⁵⁰ observed the presence of straight parallel fringes on the (112) plane of the martensite in an Fe-30.64%Ni alloy.

Field-ion microscopy work on martensite has been rather scarce, probably due in part to the inherent difficulties in imaging nonrefractory materials. Müller and co-workers²⁶ have obtained hydrogen-promoted helium-ion images of martensite in a high carbon steel quenched in situ from 850-900°C and then annealed for a short while. They observed a lens shaped platelet, which they interpreted as martensite. The random bright spots present all over the image were interpreted as due to interstitial carbon atoms. However, Bayuzick and Goodrich⁵¹ later showed by structural and crystallographic analyses that the lens shaped platelet actually corresponded to austenite and not martensite. Schwartz¹⁴ in a brief study of martensite in an Fe-0.8%C steel obtained hydrogen-ion images containing "straitions". He mentioned that a distinction between martensite and ferrite, specifically in terms of

crystallographic relations was unlikely due to the small amount of tetragonality in martensite. This was probably one of the very first attempts to image martensite by hydrogen-ion microscopy.

Recently Sekhar and Richman³⁰ have investigated the fine structure of martensite in an Fe-0.88%C-0.45%Mn steel using hydrogen-ion microscopy. The images they obtained also consisted of many striations, and by morphological and crystallographic analyses, these striations were attributed to the presence of twins. Both deformation and transformation twins were detected with $\{145\}_M$ and $\{112\}_M$ orientations, respectively. The twins had a width of 15-40 Å and were spaced 15-90 Å apart. The bright contrast of the striations in the micrographs was considered to be due to the intersection of twin boundaries with the specimen surface. It was also pointed out that no difference in martensite substructure was observed during the transformation of retained austenite, whether it occurred in the bulk or in the thinned down tip.

C. Tempering

Tempering has been described as essentially an ageing process, generally occurring above room temperature and below the critical temperature. This phenomenon is associated with the formation of iron carbides, such as, ϵ -carbide, Hägg carbide and/or cementite of which only cementite has been unambiguously identified. Tempering is generally divided into three stages, based on the distinct microstructural changes occurring:

- 1) Formation of ϵ -carbide ($\text{Fe}_{2.4}\text{C}$) and low carbon martensite (0.25%C), 120-200°C.

- 2) Transformation of retained austenite to bainite, 180-250°C.
- 3) Formation of ferrite and cementite from low carbon martensite and ϵ -carbide, 200-400°C.

The temperature ranges given above for the three stages are only approximate, and considerable overlapping of the various stages occurs depending on the temperature and time of tempering and the composition of the alloy. Since autotempering occurs during quenching in low carbon steels, the majority of the studies on tempering have been performed on high carbon steels. Cox² and Kurdjumov⁵² have reviewed the three stages of tempering in an extensive manner; the latter work deals with the Russian contribution to the subject. Table 3 summarizes some of the important studies on tempered martensite.

In this survey X-ray diffraction, electron microscopy and FIM studies are included with emphasis on electron microscopy and FIM studies, since fine structures are of particular interest in this investigation. Only the first and third stages of tempering are considered here, since no observations were made on the second stage of tempering in the present studies.

1. First Stage of Tempering

Jack^{53,59,60} found by X-ray analysis that ϵ -iron carbide formed in the first stage of tempering had hexagonal close-packed structure and was amorphous with ϵ -iron nitride; he also suggested that the composition was close to Fe_3C than to Fe_2C . Roberts et al.⁵⁴ from X-ray diffraction studies proposed that in the first stage of tempering, low carbon martensite with a tetragonality corresponding to 0.25%C and hexagonal ϵ -carbide of composition $\text{Fe}_{2.4}\text{C}$ were formed.

Table 3. Summary of Previous Studies on Tempered Martensite

Material	Technique	Results	Reference
Fe-1.3%C	X-ray Diffraction	Loss of tetragonality and hexagonal ϵ -carbide in the first stage of tempering. 'Two dimensional' cementite hypothesized.	53
Fe-C(0.3-1.4%), Commercial plain carbon steels.	Single Crystal X-ray Techni- que	First stage of tempering: low carbon martensite (0.25%C) and ϵ -carbide ($\text{Fe}_{2.4}\text{C}$).	54
Fe-C(0.15-1.4%)	Replica Electron Microscopy	ϵ -carbide precipitates 200 Å thick on subgrain boundaries.	55
Fe-C(0.1-1.4%) Fe-0.8%C-20.0%Ni, 18-8 Stainless steel.	Transmission Electron Microscopy (TEM)	Low carbon steel: autotempered, 3 Widmanstätten plates. High carbon steel: carbides along and perpendicular to twin planes on tempering at 200°C. At 300°C cementite along twin planes.	
Fe-0.8%C-20.0%Ni	TEM	ϵ -carbide along $\langle 100 \rangle_{\alpha}$ as thin plates. Above 200°C cementite precipitates: $\{112\}_{\alpha}$ habit when twin spacing small and $\{110\}_{\alpha}$ habit when twin spacing large. No <u>in situ</u> transformation of ϵ -carbide to cementite. Fine structures in cementite.	56
Fe-0.57%C-23.8%Ni	TEM	ϵ -carbide with $\{100\}_m$ habit. Cementite along twin interfaces. Fine structures in cementite.	41
Fe-1.4%C	TEM	First stage of tempering: randomly distributed and aligned ϵ -carbide. Heterogeneous nucleation on dislocation networks.	42

Table 3. (Continued)

Material	Technique	Results	Reference
Fe-1.0%C-4.0%Si	TEM	Low temperature tempering revealed carbon rich (3.0%C) regions.	57
Fe-0.8%C, Fe-0.5%C-19.0%Ni, Fe-0.5%C-3.9%Si.	TEM	ϵ -carbide/martensite orientation agreed with that of Jack ⁵³ .	58

In one of the earliest electron microscopy studies on tempering using the replica technique⁵⁵, it was observed that in Fe-C alloys subgrains of about 1000-2000 Å existed in martensite; the subgrains were inherited from austenite as a consequence of the hardening transformation. It was reported that ϵ -carbide having a thickness of about 8-100 Å precipitated along the martensite subgrain boundary network. It has since been established that the substructure of untempered ferrous martensites consists of twins and/or dislocations, with no further evidence of subgrain boundary networks.

Kelly and Nutting³ investigated the effect of morphology of martensite on tempering using transmission electron microscopy. In a low carbon steel (0.14%C) Widmanstätten plates or laths of carbides 100 Å wide and 1500 Å long were detected; the crystal structure and habit plane of these carbides were not identified. In a high carbon steel (1.0%C) tempered at 100°C, no change in microstructure was detected but a hardness increase from 910 to 960 DPN was found. On tempering at 200°C carbides along the twins and tiny precipitates perpendicular to the twin planes were seen. Identification of these carbides was not possible from their diffraction patterns. The authors speculated that the initial hardening in specimens tempered at 100°C was due to the formation of small precipitates probably ϵ -carbide, across the twins, locking the only remaining deformation system in an internally twinned martensite plate.

Tekin and Kelly⁵⁶ conducted an extensive investigation of tempering in an Fe-20.0%Ni-0.8%C steel. Tempering at 150°C revealed the presence of carbides in a "cross-hatched" fashion. These were found to lie

along two sets of $\langle 100 \rangle_\alpha$ directions. After tempering at 200°C the ϵ -carbide particles were 2000 Å long and 100 Å wide. They did not observe at any stage of tempering precipitation of carbides on dislocations although dislocations associated with the precipitates were found. They pointed out that the interstitial site for a carbon atom in the twin boundary was considerably larger than the corresponding interstice in the untwinned material. Therefore the carbon atoms associated with the twin boundary were more stable and less likely to precipitate than those in the matrix. Hence at low tempering temperatures there should be no precipitation along twin boundaries, according to their explanation.

Wells⁴¹ identified the presence of ϵ -carbide by selected area electron diffraction during the first stage of tempering in an Fe-23.8% Ni-0.57%C alloy. Electron micrographs showing the presence of "criss-cross" growth of ϵ -carbide having a habit close to $\{100\}_M$ were presented. The orientation relationship of ϵ -carbide/martensite was observed to be,

$$(0001)_\epsilon // (011)_M$$

$$(10\bar{1}1)_\epsilon // (101)_M$$

which agreed with that suggested by Jack⁵³.

Jackson and Krauss⁴² examined the first stage of tempering up to 200°C in an Fe-1.4%C steel by transmission electron microscopy with particular emphasis on the relationship of carbides formed to the fine structure of the tempered martensite. Specimens tempered at 150°C revealed two types of carbides, one of which was fine nodular particles

randomly distributed while the other was rods or narrow platelets aligned in preferred crystallographic directions. The latter type of distribution was similar to the "cross-hatched" pattern observed by Kelly and Nutting³ and the "criss-cross" pattern observed by Wells⁴¹; the randomly distributed nodular particles were sometimes found to be associated with dislocations. The tiny precipitates were found to precipitate at the nodes of the dislocation network, and much larger precipitates tended to align themselves parallel to one of the dislocation directions in the network. It was suggested that the dislocations in the martensite matrix acted as the heterogeneous nucleation sites. The carbide platelets distributed along preferred crystallographic directions could have represented a later stage in the carbide growth along the dislocation network. The carbides present were not identified by electron diffraction, although it was assumed that first stage of tempering occurred up to 200°C.

Murphy and Whiteman⁵⁸ found fine "cross-hatched" needles, 20-100 Å in diameter and 250-2000 Å in length; they identified the needles as ϵ -carbide by electron diffraction. The ϵ -carbide/martensite orientation relationship observed also agreed with that given by Jack⁵³. In the silicon steel ϵ -carbide grew in an $[01\bar{1}0]_{\epsilon}$ direction close to $[21\bar{1}]_m$. It was proposed that the growing carbide could minimize its interfacial energy by aligning the $(10\bar{1}0)_{\epsilon}$ planes with the $(\bar{2}11)_m$ planes and growing in the $[21\bar{1}]_m$ direction. However, since there was no carbide plane exactly parallel to this $(\bar{2}11)_m$ it was suggested that the carbide growth direction might have varied over a range of 10 degrees between the normal to the $(\bar{2}11)_m$ and the normal to the $(01\bar{1}0)_{\epsilon}$ and that this variation

might have contributed to the "wavy" nature of the carbide particles reported previously by Tekin and Kelly⁵⁶.

Kurdjumov⁶¹ suggested that nucleation and growth of ϵ -carbide required diffusion of carbon in iron. By calorimetry it was found that the binding energy of a carbon atom associated with a vacancy or a dislocation was higher than that for a carbon atom in ϵ -carbide. He also found that ϵ -carbide present in a steel tempered at 150°C, dissolved after coldworking by moving to vacancies and/or dislocations, which were introduced during the coldwork; with additional tempering ϵ -carbide was found at these sites. Thus the carbon atoms segregated to defects and ϵ -carbide formed on these; this was consistent with the observation of preferential precipitation of ϵ -carbide on dislocations⁶².

Sekhar et al.³¹ investigated the tempering phenomenon in an Fe-0.88%C-0.45%Mn steel using FIM. Tempering was performed in situ which had certain disadvantages, viz., only the approximate temperature of the specimen could be determined, and it was uncertain whether the changes occurring in bulk material and specimens thinned down to 1000 Å were the same. In this investigation only the microstructural changes occurring due to tempering were studied and no crystallographic analyses were performed. As previously mentioned in section II-B-3, the images of as-quenched martensite consisted of striated regions and regions of apparent disorder and were interpreted as twinned and untwinned martensite. In the first stage of tempering the increase in the width of the striations and also the increase in the brightness of the disordered regions were interpreted as due to the precipitation of ϵ -carbide.

However, it was not clear in this paper whether ϵ -carbide precipitation occurred along twin planes or twin boundaries.

2. Third Stage of Tempering

The third stage of tempering consists of the formation of ferrite and cementite from low carbon martensite and ϵ -carbide. Cementite has an orthogonal structure⁶³ and the cementite/ferrite orientation relationship has been found⁶⁴ to be,

$$[110]_{\text{Fe}_3\text{C}} // [\bar{1}01]_{\alpha}$$

$$[010]_{\text{Fe}_3\text{C}} // [111]_{\alpha}$$

$$[001]_{\text{Fe}_3\text{C}} // [\bar{1}2\bar{1}]_{\alpha}$$

Kelly and Nutting³ observed that cementite precipitated along the twins, and Tekin and Kelly⁵⁶ noticed the precipitation on twin boundaries. When the twin spacing was small the cementite precipitates had a $\{112\}_{\alpha}$ habit; and in untwinned regions or in areas where the twin spacing was large, the habit plane was $\{110\}_{\alpha}$. Wells⁴¹ suggested that since the habit planes of ϵ -carbide ($\{100\}_{\alpha}$) and cementite ($\{112\}_{\alpha}$ and $\{110\}_{\alpha}$) were different, the transformation of ϵ -carbide to cementite did not take place in situ, i.e., cementite did not grow directly from ϵ -carbide.

Tekin and Kelly⁵⁶ considered the effect of twin spacing on the morphology of carbide precipitation; when the twin spacing was small say less than 100 Å, growth of the precipitates perpendicular to the twins was interrupted. Thus, when the twin spacing was small, the carbides along the twin boundaries grew at the expense of small precipitates across the twins, and when the twin spacing was large the precipitates

across the twins grew to such a size that further growth then occurred at the expense of small newly formed carbides on the twin boundaries.

Internal structures in cementite have been observed by many workers^{41,56}. Tekin and Kelly⁵⁶ reported the presence of a substructure of fringes running along the length and striations 10-30 Å wide running across the precipitates. Leslie et al.⁶⁵ in a study of precipitation of cementite found dendritic carbides consisting of parallel arrays of narrow rods growing in the $[010]_{\text{Fe}_3\text{C}}$ direction. Wells⁴¹ also found that the cementite particles were composed of fine rods or needles parallel with the $[010]_{\text{Fe}_3\text{C}}$ and the $\langle 111 \rangle_m$ direction. However, according to Cox² no fine structures in cementite have been reported in later investigations, so that he proposed that the observed fine structures were due to Moiré fringes.

Sekhar et al.³¹ who investigated the third stage of tempering by FIM, proposed that the random distribution of ϵ -carbide transformed rapidly to cementite, by nucleation and growth. It was also suggested that the field etching caused the cementite particles to protrude from the surface and therefore image brighter than the ferrite matrix. However, this was at variance with the investigations of Morgan and Ralph⁶ in which they reported that the cementite phase imaged darker than the ferrite matrix. With increased tempering time the twinned structure was progressively lost and the cementite particles grew larger. Neither particle size nor crystallographic analyses were performed in this investigation.

3. Changes in Hardness During Tempering

During tempering, the hardness initially increases to a maximum

and then decreases with further tempering. In order to get an insight into the changes in hardness occurring due to tempering, the following factors which affect the strength of martensites⁶⁶ should be kept in mind:

- 1) interstitial solid solution hardening by carbon,
- 2) size of the martensite grains,
- 3) substructure - dislocation tangles or twins, and
- 4) precipitation, segregation or some other form of diffusional process involving carbon.

Kelly and Nutting³ attributed the initial increase in hardening in the first stage of tempering to be due to the formation of small, coherent ϵ -carbide precipitates. Tekin and Kelly⁵⁶ also observed an increase in hardness in the early parts of the first stage of tempering (100°C) in an Fe-Ni-C alloy. This was attributed to the precipitation of fine coherent ϵ -carbide, which was later supported by the observation⁶⁷ of strain contrast in thin foil electron microscopy of coherent interfaces around ϵ -carbide. They pointed out also that precipitation across the twins might have increased the effectiveness of the twins to hinder dislocation movement, thereby contributing to the hardness increase. They stated that the carbon depletion from the matrix due to precipitation of ϵ -carbide would have decreased the solid solution hardening, but the coherency hardening overrode this effect in the early stages of tempering. Further tempering caused an overall decrease in hardness^{55,56} due to ϵ -carbide becoming progressively incoherent and carbon continually coming out of solution. These effects became predominant in the third stage of tempering when the hardness decreased rapidly. This

pronounced softening in the third stage of tempering was attributed to the growth of carbides^{54,68}. However, Kelly and Nutting³ felt that this reasoning was dubious as no significant growth of the carbides occurred in the tempering range 200-400°C; therefore they proposed that this softening was due to the removal of the twins, by the cementite particles formed along them and also by the growth and agglomeration of these twins.

CHAPTER III

EXPERIMENTAL TECHNIQUES

A. Materials

The materials used in this research were MARZ grade iron and commercial music wire. The diameter of the iron wire was 0.005 in., and its typical composition is given in Table 4. The diameter of the music wire was 0.024 in. and its typical composition as obtained from a microprobe trace analysis is given in Table 5. The following heat treatment was given to the music wire between each draw by the manufacturer. The wire was austenitized at 1000°C and quenched in lead bath at 600°C and then slowly cooled to room temperature. This treatment was chosen to produce a microstructure containing fine pearlite along with some bainite.

B. Heat Treatments

The isothermal transformation curve for the music wire used in the present studies was not available in the literature. From the isothermal transformation diagrams published by United States Steel, curves for 0.8%C-0.8%Mn and 0.9%C-0.3%Mn steels were selected as the basis for heat treatments in these studies since these compositions were closest to those of music wire. From these curves the A_s , M_s and M_f temperatures were estimated to be approximately 775°C, 245°C and 150°C respectively.

Both martensite formation and tempering were carried out on the music wire specimens prior to thinning to form FIM tips.

Table 4. Typical Analysis of MARZ Grade Iron

Impurity Element	Content (ppm)
C	8.0
O	7.2
N	7.0
Ca	2.0
Mg	8.0
Ni	1.2
Co	0.3
Cr	0.6
K	0.2
Mn	0.1
Mo	0.2
Na	0.08
Nb	0.03
S	1.2
Si	0.5
Ti	0.5

Table 5. Typical Composition of Music Wire as Obtained from Microprobe Trace Analysis.

Element	Content (wt%)
C	0.8
Mn	0.4
Si	0.21
P	0.1
S	0.03
Cu	0.03
Cr	0.01
Ca	0.004
Zn	0.001

1. Austenitizing and Quenching

Specimens about 1.0 in. long were austenitized at temperatures between 900-1000°C for 30-90 minutes and quenched by one of the following two methods.

a. Vacuum Furnace. A vertical furnace with a vacuum of better than 5×10^{-3} torr was used for this purpose. After austenitizing the specimens for the required time, dry helium gas was let into the furnace, and the specimens were dropped vertically and quenched in iced brine, the entire quenching operation taking less than five seconds. The quenched specimens were immediately refrigerated in liquid nitrogen to ensure complete transformation to martensite.

b. Vacuum Encapsulation. In order to minimize decarburization some specimens were encapsulated in vycor tubing at a vacuum of 2×10^{-6} torr before austenitizing. After austenitizing for the required time, the specimens were quenched in iced brine by instantaneously breaking the vycor tubing to ensure efficient quenching. In this case also the quenched specimens were immediately transferred to liquid nitrogen to ensure complete transformation.

2. Tempering

The quenched specimens were tempered in the same vacuum furnace as that used in method 1 for austenitizing. The tempering temperatures and times used in these experiments are listed in Table 6.

C. Microhardness Measurements

In order to study the variation of hardness with tempering temperature and time, microhardness readings were taken on Tukon Hardness

Table 6. Temperatures and Times of Tempering

Temperature, °C	Time, Minutes
50, 100, 150, 200, 250, 300, 400	60 ^M
160	10 ^B , 20 ^M , 30 ^B , 40 ^M , 50 ^M , 60 ^B
85	60 ^T
230	60 ^T
350	60 ^T

T = specimens examined in FIM

M = specimens used for microhardness determination

B = specimens used for both microhardness measurement and FIM examination

Tester manufactured by Wilson Mechanical Instrument Co., Inc. The heat treatments used for specimens on which microhardness measurements were made are indicated in Table 6. The specimens were mounted in a cold mounting resin and their surface was prepared by taking it over graded emery papers; final polishing was carried out on billiards table cloth. The manufacturer suggested that the hardness load be such as to produce an indentation of at least 150 filar units; and in accordance with this a load of 300 gms. was used since this load was found to be necessary for minimum indentation on the hardest specimens.

D. Microscopy

1. Optical Microscopy

Metallographic examination was carried out on both the longitudinal and transverse sections of the martensite specimens. Each specimen was mounted in a cold mounting resin. The specimen surface was prepared by standard metallographic methods and was etched with 2% nital before examining under the optical microscope.

2. Electron Microscopy

Thin foils of transverse sections for examination in a Siemens Elmiskope IA electron microscope were prepared by the following method.

- 1) The wire specimens were imbedded in a suitable matrix, which in this case was aluminum. Holes of diameter 0.024 in., same as that of the wire specimens, were drilled in aluminum sheets of 0.08 in. thickness, and the wire was inserted into these holes.
- 2) The aluminum sheet along with the embedded wire specimens were then ground gradually to a thickness of about 0.004 in. by taking it over

graded emery papers. Then discs of about the same diameter as that of the electron microscope grids were punched out so that the wire specimens were approximately in the middle of these discs.

3) The specimens were then thinned by electropolishing. The interface between the wire specimen and the aluminum matrix was lacquered to avoid preferential attack of the interface during electropolishing.

The electropolishing solution consisted of 25 gms. of chromic oxide, 133 mls of glacial acetic acid and 7 mls of water. At 4 volts d.c. the preferential interface attack seemed to be at minimum, so that this voltage was used throughout the electropolishing operation. The progress of the thinning operation was monitored with the help of a light source which triggered a relay unit which in turn cut-off the d.c. power supply as soon as a small hole was formed in the foil. The lacquer was carefully peeled off, and then the thin foils were washed in distilled water and were either observed immediately or preserved in a vacuum desiccator until they could be examined.

3. Field-ion Microscopy

a. Specimen Preparation. Often it is said that specimen preparation for FIM is more of an art than science; be what it may, the entire process depends on obtaining a fine tip having a radius of curvature of about 400-1000 Å. A chromic - acetic acid solution of same composition as that used for preparing thin foils for electron microscopy was used in this case also. In the initial stages of electropolishing 22 volts d.c. was used, but in the final stages 3-4 volts d.c. was employed. At approximately the halfway mark of the electropolishing operation, the bottom portion of the specimen was lacquered; preferential thinning of the specimen was observed in a light microscope to

occur about 2 mm away from the lacquered region. Continued polishing makes the lacquered bottom portion drop off leaving a fine sharp tip.

b. Operation of the Field-ion Microscope. Two bakeable all-metal field-ion microscopes were used in the present research. In one microscope an ultimate vacuum of 2×10^{-8} torr could be obtained, while in the other the ultimate vacuum was in the 10^{-10} torr range. In both of the microscopes a fibre optic screen was used, which had the qualities of a photographic lens and facilitated contact photography.

In order to avoid undesired tempering of the specimens the following precautions were taken:

- 1) The electropolishing solution was constantly stirred and maintained at approximately 0°C .
- 2) In the final stages of the electropolishing operation, the voltage was considerably lowered (3-4 volts).
- 3) The normal procedure of baking the field-ion microscope was avoided once the specimen had been mounted.

After the microscope had been evacuated to 10^{-8} torr or less, the specimen was cooled to liquid nitrogen temperature and research grade hydrogen gas was admitted to a pressure of about 1×10^{-4} torr. Other imaging techniques used for some of the specimens included hydrogen-promoted helium-ion microscopy at liquid hydrogen temperature and neon-ion microscopy at liquid helium temperature. The most convenient and satisfactory of these, however, was found to be hydrogen-ion microscopy for these studies.

CHAPTER IV

RESULTS

A. Pure Iron

Figure 1(a) is a typical hydrogen-ion image of a well annealed MARZ grade iron specimen. The important features of this micrograph are,

- 1) dark patches symmetrically distributed around the $\{110\}$ poles giving a "butterfly" pattern,
- 2) distinct $\langle 111 \rangle$ dark zone patterns between the prominent $\{110\}$ poles,
- 3) net plane edges around the low index poles are very regular, and
- 4) higher index poles are well developed, for example, $\{130\}$.

Figure 1(b) is a hydrogen-ion micrograph of the same iron specimen as in Figure 1(a), but with a small amount of air leaked into the system during imaging. The overall effect of this was to reduce the general clarity and sharpness of the image. The number of visible net plane edges around the $\{110\}$ poles was slightly reduced, but the regularity of these net plane edges was not disturbed. The "butterfly" pattern around the $\{110\}$ poles has disappeared and the dark contrast in the $\{110\}$ region has assumed an almost hexagonal shape.

B. As-received Music Wire

Figure 2(a) is a hydrogen-ion image of an "as-received" music wire specimen, which was "patented" to obtain fine pearlite and some bainite with about 35% cold work in the as-received condition. The

Figure 1. MARZ Grade Iron: (a) Hydrogen-ion Image, 78°K, 9.7 KV, (b) Corroded by a Small Amount of Air Leaked into the Microscope, 78°K, 9.8 KV.

fine dark bands in the image represent cementite and because of the cold-work many grain boundaries are also discernible.

Figure 2(b) is a hydrogen-promoted helium-ion image of the material in the as-received condition, taken at liquid hydrogen temperature. The image is irregular and it appears that only the ferrite matrix images.

C. Pearlite

A typical hydrogen-ion micrograph of a music wire specimen heat treated to produce pearlite is shown in Figure 3(a). The dark cementite platelets are 500-600 Å apart and 30-50 Å wide, which agreed with the results obtained from the electron micrographs of the shadowed replicas of these specimens which is shown in Figure 3(b). Morgan and Ralph⁶ examined pearlite formed in pure Fe-C alloys and reported a much larger thickness and wider spacing for the cementite platelets.

D. As-quenched Martensite

1. Optical Microscopy

Metallographic examination of the martensite specimens revealed a coarse grained structure in those that were austenitized at higher temperatures, for example, 1000°C, while a fine grained structure was observed in those that were austenitized at lower temperatures, for example, 900°C. The transverse sections of each of these martensite specimens revealed uniform microstructures.

2. Electron Microscopy

Preparation of thin foils of transverse sections of the wire specimens (0.024 in. diameter) presented many difficulties which may be summarized as follows:

Figure 2. As-received Music Wire: (a) Hydrogen-ion Image, 78°K, 11.2 KV, (b) Hydrogen-promoted Helium-ion Image, 21°K, 20.6 KV.

Figure 3. Pearlite formed in Music Wire: (a) Hydrogen-ion Image, 78°K, 21.8 KV, (b) Electron Micrograph of Shadowed Replica, 15,000X.

- 1) Inherent difficulties associated with the handling of such small specimens.
- 2) Progress in electropolishing could not be followed effectively since the solution (chromic-acetic acid) was opaque. Transparent solutions such as glacial acetic acid and perchloric acid were also tried; however, at lower voltages, for example, 3 volts d.c., a black deposit formed on the surface, and if an attempt was made to avoid the formation of the black deposit by polishing at higher voltages, say, 10 volts d.c., the electropolishing took place too rapidly to have control over the operation.
- 3) Preferential attack at the interface between the specimen and the aluminum matrix in which the specimens were imbedded was avoided partially by lacquering the interface.
- 4) Applying the lacquer to the interface without covering much area of the specimen surface was extremely tedious.

Of some fifty specimens that were polished only one thin foil was good enough to photograph, and a region from that foil is shown in the electron micrograph of Figure 4(a). A high density of dislocations with possible slip traces can be seen in the micrograph. In a few other cases the presence of twins was indicated⁶⁹ but no photographs were taken because of the poor quality of the foils.

3. Field-ion Microscopy

Hydrogen-ion microscopy of as-quenched martensite revealed a mixture of untwinned and twinned regions. Untwinned martensite³² refers to regions or grains of martensite in which no twins are present, but which have a complex dislocation substructure. Specimens that were

(a)

(b)

(c)

Figure 4. Untwinned Martensite: (a) Transmission Electron Micrograph, 80,000X, (b) Hydrogen-ion Image, 78°K, 21.8 KV, (c) Complex Dislocation Substructure in Hydrogen-ion Image.

austenitized at higher temperatures for longer times, for example, 1000°C for 1 hour, revealed predominantly untwinned martensite, while those that were austenitized at lower temperatures for shorter times, for example, 900°C for 15 minutes, almost always showed heavily twinned martensite. However, in a few other specimens both twinned and untwinned martensite regions were found. The results from these three types of specimens are presented separately below.

No significant differences were found in the hydrogen-ion images of specimens austenitized in the vacuum furnace and those encapsulated prior to austenitizing. Also, no significant change in the microstructure was observed in the field-ion specimens that were left within the microscope at room temperature for a period of up to ten days. As expected in high carbon steels² carbides due to autotempering were not observed.

a. Untwinned Martensite. A hydrogen-ion micrograph of untwinned martensite is shown in Figure 4(b). The image was indexed by considering symmetry and pole prominence and by calculating the interplanar angles between prominent poles⁷⁰. The c/a ratio for martensite with carbon content of 0.8% is reportedly 1.036⁷¹, and the pole prominence for planes of a b.c.t. lattice with this c/a ratio is given in Table 7. These are listed essentially in decreasing order of X-ray structure factor or d-spacing. The interplanar angles and order of prominence for the planes as seen in the image agree with those predicted; however, a distinction between (110) and (101), (112) and (211) and other planes of the same kind could not be made, as might be expected from the small differences in d-spacings of these similar planes.

Table 7. Predicted Order of Prominence for Planes of a b.c.t. Lattice with $c/a = 1.036$ on the Basis of Decreasing Order of d-spacing.

Plane	d-spacing, Å
101	2.0506
110	2.0157
002	1.4760
200	1.4250
112	1.0254
211	1.0077
103	0.9044
301	0.9013
310	0.8323

The possibility of this untwinned region being retained austenite was ruled out for the following reasons. For f.c.c. the most prominent plane is $\{111\}$, whereas for b.c.c. (b.c.t.) it is $\{110\}$. If the prominent poles in Figure 4(b) are indexed as $\{111\}$, then the angle between the zones containing these $\{111\}$ type poles should be 120 degrees indicative of 3-fold symmetry. However, from the micrograph it was found that the zones containing the prominent poles do not make 120 degrees with each other; therefore, it is not an f.c.c. structure and so cannot be retained austenite. The indexing is consistent if the prominent poles are taken as $\{110\}$.

In the martensite images the $\{110\}$ region appears almost uniformly dark and does not show the "butterfly" pattern of dark patches. Also the $\{111\}$ dark zone patterns are not sharp. The dark patches at $\{113\}$ poles are much more distinguishable than those of the ferrite image. The net plane edges around the low index poles are distorted and the higher index poles are less developed. Often complex dislocation substructures were observed, as shown in Figure 4(c).

In one specimen small crystallites were observed but this was not a common observation in the numerous specimens examined. The grain boundaries in this specimen showed dark contrast in hydrogen-ion microscopy.

b. Twinned Martensite. Figure 5 is a hydrogen-ion micrograph of a twinned martensite crystal, revealing alternate dark and bright bands or striations in the image. The bright bands are interpreted as twins and the dark bands as twin interfaces. The twin width was measured from the center of one dark band to the next. The twin width thus found

Figure 5. Hydrogen-ion Image of Twinned Martensite, 78°K, 16.9 KV.

(a)

(b)

Figure 6. Hydrogen-ion Image of Twinned and Untwinned Martensite:
 (a) In Adjacent Grains, 78°K, 14.8 KV, (b) In Same Grain,
 78°K, 12.3 KV

was 25-100 Å . Many of the twins were found to be fragmented.

A visual examination of Figure 5 shows that these striations form concentric annular discs with (121) as center. This indicates that the twins are lying on (121) planes. However, a more accurate analysis was performed as follows. The angle ' β ' between the specimen axis and the normal to the plane containing the twins was calculated by Method 2, Appendix B. The radius of curvature 'R' of the tip was 1410 Å; when a thickness 't' of 160 Å was field evaporated, the angular shift ' γ ' of the twin interface was 12 degrees. The angle ' β ' between the [110] specimen axis and the normal to the habit plane was calculated to be 28 degrees, which corresponds well with the expected angle of 30 degrees between the (110) and (121) poles. This confirms that the twins have a (121) habit.

c. Adjacent Twinned and Untwinned Martensite. Figure 6(a) is a hydrogen-ion micrograph revealing both twinned and untwinned martensite regions side by side. The untwinned region in the upper half of the micrograph exhibits all the characteristics of untwinned martensite outlined previously and is indexed as shown in the micrograph. The boundary between the twinned and untwinned regions has a 'zig-zag' shape; however, it became straight after some field evaporation. The twins were found to remain flat where they met the boundary. The twinned region in the lower half of the micrograph contains two sets of twins aligned in two different directions. The orientation of these twins was determined from Method 1, Appendix B. Both sets of twins were found to have {112} orientations within 8 degrees. The twin width was found to be 25-85 Å.

An example of a specimen that contained fine twins in an otherwise dislocated martensite crystal is represented in Figure 6(b). Such observations were quite frequent; in fact one out of every three specimens showed such a characteristic.

E. Tempered Martensite

1. Microhardness Measurements

Microhardness values of the specimens tempered for one hour at temperatures ranging from 50 to 400°C and those tempered at 160°C for times ranging from 0 to 60 minutes are given in Tables 8 and 9, respectively. Figure 7 shows graphically the hardness versus temperature for a constant tempering time of one hour. The hardness increased initially at the low temperatures, reaching a maximum at about 75-85°C, and then dropping gradually with increasing temperatures. The peak hardness value was about 43 knoop hardness units higher than the as-quenched value. Figure 8 is the hardness versus time curve at constant tempering temperature of 160°C. The hardness increased slightly to a maximum at approximately 10-20 minutes and then dropped steadily. The peak hardness value of 914 was about 39 knoop hardness units higher than the as-quenched hardness value.

2. Field-ion Microscopy

Field-ion microscopy results obtained in the later part of first stage of tempering are presented first, as the analyses and interpretation of micrographs in the early part are more complex.

a. Specimen Tempered at 160°C for 30 Minutes. Typical field-ion micrographs of a specimen tempered at 160°C for one half hour are shown

Table 8. Hardness Values of Specimens Tempered for One Hour

Temperature, °C	Knoop Hardness
As-quenched	875
50	912
75	918
100	900
150	848
200	750
250	708
300	615
400	495

Table 9. Hardness Values of Specimens Tempered at 160 ° C.

Time, minutes	Knoop Hardness
0	875
10	914
20	905
30	900
40	880
50	850
60	805

Figure 7. Isochronal Hardness Curve from the data of Table 8.

Figure 8. Isothermal Hardness Curve from the data of Table 9.

in Figures 9(a) and (b).

i) General Features of the Image: In these images the iron carbides appeared darker than the matrix. In the bright matrix $\{110\}$, $\{112\}$ and $\{100\}$ poles were discernible. The net plane edges of these poles appeared to be more regular than those of as-quenched martensite (see Figure 4(b)), but still not so regular as those commonly found in the ferrite images (see Figure 1(a)). More than one crystal of the matrix generally appeared in the image.

ii) Crystallography and Morphology of the Carbides:

Habit Plane of the Carbides: The habit plane was determined by knowing the zone that the particle intersected and the angle of inclination of the particle to the specimen axis (see Method 2, Appendix B). In the indexed image of Figure 9(b) the habit of particles 1 through 4 was found to be close to $\{100\}$ as can be seen from Table 10. All the particles for which the habit planes were thus determined were found to have a $\{100\}$ habit.

Sizes of Particles: The length and thickness of the carbides were determined from their projection sizes and image magnification. The apparent particle width was determined from the penetration depth obtained from a field evaporation sequence. The measured particle sizes were affected by the relative position of these particles and their inclination to the specimen axis¹⁵. The effect of these two factors on the thickness and length of the particles, measured directly on the micrographs, was comparatively small. The thickness and length measurements were made from one particle/matrix interface to the opposite one, and at present it is not possible to make corrections for the

(a)

(b)

Figure 9. Specimen Tempered at 160°C for 30 minutes: (a) Hydrogen-ion Image, 78°K, 10.0 KV, (b) Image after Field Evaporation of about 450 Å, 78°K, 11.4 KV.

Table 10. Habit Plane of Carbides in a Specimen Tempered at 160°C for 30 Minutes.

Particle	Measured Angular Shift, γ (deg.)	Radius of Curvature, R (Å)	Thickness Evaporated, t (Å)	Angle of Inclination to the Specimen axis, (deg.)	Expected Angle of Inclination for {100} habit, (deg.)
1	4.0	990	200	70	69
2	3.0	990	200	75	69
3	3.5	990	200	73	69
4	4.5	990	200	65	69

change in radius of curvature along the particle/matrix interface; however, the error in the measurements due to this was estimated to be only a few percent. Typical calculations for the determination of particle thickness and length are shown below:

Thickness as measured on the micrograph	= 0.1 cm
Length as measured on the micrograph	= 1.5 cm
Magnification of the image (see Appendix A)	= 5.4×10^5
Apparent particle thickness	= $\frac{0.1 \times 10^8}{5.4 \times 10^5} \text{ \AA} = 18 \text{ \AA}$
Apparent particle length	= $\frac{1.5 \times 10^8}{5.4 \times 10^5} \text{ \AA} = 268 \text{ \AA}$

The particle thickness and length in general were found to be in the range 10-20 Å and 100-300 Å, respectively.

The effects of position and inclination of particles on the measured width were more pronounced, so that correction for these effects was necessary in this case. The true particle width 'w' is given by the following equation, which is modified from that given by Schwartz¹⁴ in order to take into account the movement of the center of the hemispherical surface before and after field evaporation:

$$\begin{aligned}
 w^2 = & (R_1 \sin \theta_1 \cos Q_1 - R_2 \sin \theta_2 \cos Q_2)^2 \\
 & + (R_1 \sin \theta_1 \sin Q_1 - R_2 \sin \theta_2 \sin Q_2)^2 \\
 & + (R_1 \cos \theta_1 - R_2 \cos \theta_2 + R_2 + L - R_1)^2
 \end{aligned} \tag{1}$$

where R_1 and R_2 are radii of curvature before and after field evaporation, L is the thickness over which the particle persists in a field

evaporation sequence and ϕ_1 , Q_1 and ϕ_2 , Q_2 represent the initial and final angular positions, respectively, of the particle as measured from the micrographs. The derivation of equation 1 and several examples to test its validity are given in Appendix C. The particle widths thus obtained for the precipitates in this specimen and the data used for these calculations are given in Table 11. It can be seen from the table that the true particle width in some cases was smaller than the penetration depth 'L'. If equal amounts of material were field evaporated over the entire region of the specimen, then the true particle width could never be less than the penetration depth 'L', but at best could be equal to 'L'; however, the amount of material evaporated from a field-ion specimen is not uniform, but rather decreases with distance from the apex, as illustrated in Figure 10. The particles a, b, c and d would persist over the same evaporation thickness 'L', but the true particle width of 'a' will be L, that of 'c' greater than L and those of 'b' and 'd' less than L. In the above calculations of particle width an error may have been introduced due to the fact that the center of the image might not have coincided with the specimen axis.

Density of particles: The particle density (number of particles/cm³) can be determined by counting the number of particles during field evaporation of a known volume of material. For this specimen 162 particles were found during field evaporation (from 10.0 to 11.5 kv) of 600 layers of {110} planes, the d-spacing of which is approximately 2.0 Å.

Two methods (derivations given in Appendix D) can be used to find the volume, V, of the specimen field evaporated. Firstly, if it is

Table 11. True Particle Widths of Carbides in a Specimen Tempered at 160°C for 30 minutes. (See the Text for Definitions of Symbols Used in the Table).

R_1 (Å)	R_2 (Å)	θ_1 (deg)	Q_1 (deg)	θ_2 (deg)	Q_2 (deg)	L (Å)	w (Å)
869	887	54.0	121	55.2	124	100	131
869	887	54.0	109	44.4	118	100	133
869	913	38.4	276	39.6	298	350	431
913	1000	61.2	102	44.4	90	675	522
913	1000	54.0	97	39.6	82	675	567
956	956	14.5	248	13.2	248	150	146
956	956	25.2	303	21.6	324	150	195
956	956	33.6	311	31.6	326	150	190
991	1000	43.2	309	44.4	310	200	218
956	974	22.8	301	15.6	302	100	125
974	991	24.0	336	25.2	334	175	187
991	991	18.0	236	18.5	238	75	79
991	991	14.4	240	18.5	240	25	82
974	991	54.0	123	50.4	116	175	165
991	1000	42.0	96	42.0	95	175	178
991	991	44.4	110	45.6	113	75	98
991	1000	49.2	123	43.2	124	125	85
991	1000	54.0	115	49.2	113	125	82
991	991	13.2	340	24.0	341	75	222
991	991	19.2	334	27.6	328	75	192
991	991	22.8	336	31.2	336	75	191
887	887	48.0	43	42.0	37	175	143
887	913	48.0	105	44.4	104	175	144
913	913	32.4	22	27.6	15	75	94
913	913	48.0	14	42.0	10	75	81

Figure 10. Schematic Illustration of the Effect of Particle Position on Their True Width.

assumed that equal amounts of material ($N d_{hkl}$) are removed over the entire region of the specimen, then

$$\begin{aligned} V &= \pi (R \sin \theta_p)^2 N d_{hkl} \\ &= 36.74 \times 10^{-16} \text{ cm}^3 \end{aligned} \quad (2)$$

where θ_p , the angle between the specimen axis and outer periphery of the image, is equal to 60 degrees in this case and R is equal to 943 Å.

Secondly, if a correction is made for the change in radius of curvature and for the smaller evaporation rates of material away from the apex, then

$$\begin{aligned} V &= \pi/3 [(R_2 - R_1) (1 - \cos \theta_p) + N d_{hkl}] \times (R_1^2 + R_1 R_2 + R_2^2) \times \sin^2 \theta_p \\ &\quad - \pi/3 (1 - \cos \theta_p)^2 \times (2 + \cos \theta_p) \times (R_2^3 - R_1^3) = 23.92 \times 10^{-16} \text{ cm}^3 \end{aligned} \quad (3)$$

where, R_1 and R_2 are 877 and 1009 Å, respectively. The densities thus obtained by methods 1 and 2 above were found to be 4.4 and 6.8×10^{16} particles/cm³.

Shape and Distribution of Carbides: The carbides were found to have a platelike morphology as their measured thickness and length changed very little during field evaporation. The carbide particles were distributed along preferred directions (for example, particles 1, 2, 3 and 4 in Figure 9(b)) as well as randomly (for example, particle 5 in Figure 9(b)).

Contrast Around the Carbide Particles: In many micrographs the carbides intersected {110} or other low index poles giving rise to spiral

discontinuities and in some cases deviations from smooth circular development of the pole rings. These two features are indicative of dislocations and coherency strains, which are discussed later.

iii) Presence of Cementite:

In this specimen the presence of cementite particles was indicated by the following morphological and crystallographic observations. The particles shown along the grain boundaries OA and OB in Figure 9(a), were found to have a true particle width of about $1000 \text{ \AA}$ and a thickness and length of $40\text{-}45 \text{ \AA}$ and $700\text{-}750 \text{ \AA}$, respectively. Thus the dimensions of the precipitate were suspiciously large to be ϵ -carbide. The habit plane determination by the following method was also found to be inconsistent with that of ϵ -carbide. The movement of the precipitates along with the associated boundaries OA and OB was followed through the series of micrographs in the field evaporation sequence. The six boundary traces from these micrographs were transferred to a stereographic projection shown in Figure 11. The trace moved across the image and as the field evaporation progressed it formed an arc about the $(\bar{1}21)$ and finally disappeared within a couple of degrees of $(\bar{1}21)$ indicating that its habit is $(\bar{1}21)$. The habit plane was determined also by Method 2, Appendix B. The precipitate along OA intersects the $\langle 10\bar{1} \rangle$ zone and the angle of inclination, β , of the precipitate to the specimen axis which was calculated from the following data,

Measured angular shift, γ	= 9.0 degrees
Radius of curvature, R	= $985 \text{ \AA}$
Thickness of material evaporated, t	= $100 \text{ \AA}$

was found to be 33.0 degrees. This angle of 33.0 degrees compared

well with the measured angle of 36 degrees between the center of the stereogram (Figure 11) and the $(\bar{1}21)$ pole. The precipitate along the grain boundary OB intersected the $\langle 0\bar{1}1 \rangle$ zone. The trace OB had shifted by an angle of 14 degrees when 200 Å had been field evaporated and the radius curvature was 925 Å. The angle of inclination of the trace OB was calculated (Method 2, Appendix B) to be 41.5 degrees, which compared well with the 43.0 degree angle between the center of the micrograph and $(\bar{2}11)$ pole. Thus the habit plane of OB was $(\bar{2}11)$.

b. Specimens Tempered at 160°C for 1 hour. Three specimens tempered at 160°C for 1 hour were examined by FIM, and selected micrographs from these specimens are shown in Figures 12 through 14.

i) General Features of the Image:

In the bright matrix the net plane edges of the $\{110\}$ poles appeared to be more regular than those tempered at 160°C for 30 minutes. Also, higher index poles were observed in the matrix; for example, the $\{310\}$ and $\{210\}$ in Figure 12(a).

The change in the precipitate matrix contrast was observed while gradually increasing the voltage above the BIV of the matrix. At the BIV of the matrix the contrast between the dark precipitate and bright matrix was high and the precipitate matrix interface was clearly discernible. However, with increased voltage, the entire image became brighter and the contrast between the precipitates and the matrix was reduced.

Generally the imaged part of the matrix contained more than one crystal, but in specimen 2 the matrix contained especially small crystallites, as shown in Figure 13. The crystallite size, defined as the longest diagonal of the crystallite in the projected image, varied

Figure 12. Hydrogen-ion Image of Specimen 1, Tempered at 160°C for 60 minutes: (a) Photographed above BIV, 78°K, 17.5 KV, (b) Image after Field Evaporation of about 425 Å, 17.4 KV.

(a)

(b)

Figure 13. Specimen 2, Tempered at 160°C for 60 minutes: (a) Hydrogen-ion Image, 78°K , 15.5 KV, (b) Schematic of Small Crystallites in Lower Region of Micrograph.

(a)

(b)

Figure 14. Hydrogen-ion Images, 78°K of Specimen 3, Tempered at 160°C for 60 minutes: (a) 10.7 KV, (b) 14.7 KV.

considerably in this specimen and was found from many micrographs to be 300-1100 Å. The complexity of the image due to the presence of small crystallites was revealed by the following crystallographic analysis of Figure 13(a). Crystallites A, B, C and D in the lower half of the image are shown schematically in Figure 13(b). The misorientation between the grains A and B was very small, as evidenced by the almost straight zone passing through the poles (110) - (112) - (101) , which exhibited very little distortion as it crossed the boundary between A and B. These two crystallites may have been twin related because a 180 degree rotation of $(110)_B$ about $(112)_B$ would make it coincide with $(110)_A$. The grain C was misoriented by 20 degrees with respect to grain B as a 20 degree rotation of $(112)_B$ about $(110)_B$ would make it coincide with $(112)_C$. Similarly the grain C was found to be misoriented by 30 degrees with respect to D. It should be pointed out that at best only two poles were seen in each grain and rotations about only one pole were considered in the analysis so that the results were nonsingular.

ii) Crystallography and Morphology of the Carbides:

Habit Plane of the Carbides: All of the carbide particles examined were found to have habit very close to $\{100\}$. Typical data and results for habit plane determination are illustrated in Table 12 for four particles shown in Figure 12(b).

Sizes of Carbides: The thickness and length of the carbide particles were found to be 15-25 Å and 150-450 Å, respectively. The true particle width 'w' of the precipitates in specimen 1 along with the required data are given in Table 13.

Density of Carbides: In specimen 1, 76 particles were observed

Table 12. Habit Plane of Carbides in a Specimen Tempered at 160°C for 60 minutes.

Particle	Measured Angular Shift, γ (deg.)	Radius of Curvature, R (Å)	Thickness Evaporated, t (Å)	Angle of Inclination to the Specimen axis, (deg.)	Expected Angle of Inclination for {100} habit, (deg.)
1	3.5	1513	50	61	55
2	2.5	1513	50	53	55
3	2.5	1513	50	53	55
4	3.0	1513	50	58	55

Table 13. True Particle Widths of Carbides in a Specimen Tempered at 160°C for 60 minutes. (See the Text for Definitions of Symbols Used in the Table).

R_1 (Å)	R_2 (Å)	ϕ_1 (deg)	Q_1 (deg)	ϕ_2 (deg)	Q_2 (deg)	L (Å)	w (Å)
1478	1478	33.6	246	34.8	244	75	100
1478	1478	31.2	176	30.0	177	125	113
1478	1478	26.4	164	25.2	166	125	117
1478	1478	37.2	199	38.4	204	175	211
1487	1496	24.0	141	30.0	128	275	405
1487	1522	26.4	162	24.0	142	975	978
1478	1478	48.0	214	44.4	216	125	94
1478	1478	45.6	234	42.0	236	125	97
1487	1487	8.4	221	7.2	236	125	135
1487	1487	25.6	266	25.2	254	175	217
1496	1496	40.8	160	38.4	161	75	62
1496	1496	43.2	169	43.0	167	75	80
1496	1496	48.0	157	49.2	154	75	117
1496	1496	50.4	153	49.2	151	75	68
1496	1496	49.2	145	48.0	145	75	56
1496	1496	49.2	141	48.0	142	75	60
1496	1496	20.0	121	30.0	121	25	25
1496	1496	33.6	117	33.6	117	25	25
1496	1496	32.4	234	34.8	241	75	158
1496	1504	36.0	304	39.6	309	225	306
1496	1496	32.4	268	31.2	278	75	152
1496	1496	38.4	269	36.0	277	75	141
1496	1496	38.4	259	34.8	267	75	147
1496	1496	22.8	169	24.0	171	75	94
1496	1496	37.2	221	39.6	224	125	178

over an evaporation thickness of 1500 Å. The radii of curvature before and after field evaporation were 1478 and 1522 Å, respectively and the angle ' θ_p ' was equal to 69.85 degrees. The particle densities obtained by Methods 1 and 2, Appendix D were found to be 4.8 and 8.3×10^{15} particles/cm³, respectively.

Shape and Distribution of Carbides: The majority of the carbide particles had a plate-like morphology. Tiny precipitates only a few atoms in diameters, indicated by arrows in Figure 12(b), were also observed. In some of the micrographs, for example, Figure 14(b), the distribution of carbides was analogous to the 'cross-hatched' pattern observed in electron microscopy studies⁵⁸.

Contrast Around the Carbide Particles: Many of the carbide particles which intersected a $\{110\}$ pole exhibited spiral discontinuities and deviations from smooth circular development of the pole rings, indicative of dislocations and strains associated with the precipitate, respectively.

iii) Presence of Twins:

The field-ion micrographs of specimen 2 revealed an unstriated region initially; then after field evaporation of about 1800 atomic planes of $\{110\}$, there was a gradual appearance of a striated region, as shown in Figure 13(a). The striated region occupied a maximum of about one third of the image during the entire field evaporation sequence of this specimen. The striated region finally disappeared after a field evaporation of approximately 600 additional atomic layers of $\{110\}$. In the striated region the alternate dark and bright bands and the size of these bands suggested that these were twins. However, that these

striations did represent twins was confirmed by the following crystallographic analysis. The striated region was indexed by examining many micrographs in the series. The habit of these striations was found by Method 1, Appendix B to be $\{112\}$ within 8 degrees. The twin width was measured from the center of one dark band to the next and was found to be 25-125 Å.

iv) Presence of Cementite:

Particles 1 and 2 in Figure 14(a) were found to have a thickness of 25 and 75 Å and a length of 600 and 950 Å, respectively. The misorientation between grains A and B was small as can be seen from the almost straight zone passing through (011) - (121) - (110) planes. By Method 1, Appendix B the habit plane of particle 1 was found to be within 3 degrees of $\{112\}$ and that of the particle 2 within 8 degrees of $\{112\}$. This confirmed that particles 1 and 2 were cementite precipitates.

c. Specimen Tempered at 160°C for 10 Minutes. A series of photographs were taken of a specimen that was tempered at 160°C for 10 minutes, and representative micrographs from this series are presented in Figures 15(a) and (b).

i) General Features of the Image:

Large number of dark precipitates were found to be present in the bright matrix, and low angle boundaries were of common occurrence. In the image of the matrix the $\{110\}$ and $\{112\}$ poles were discernible.

ii) Crystallography and Morphology of the Carbides:

Habit Plane of the Carbides: The fine carbide particles were found to have a habit close to $\{100\}$. None of the carbides were found to have either $\{110\}$ or $\{112\}$ habit.

(a)

(b)

Figure 15. Hydrogen-ion Images, 78°K, of a Specimen Tempered at 160°C for 10 minutes: (a) 10.9 KV, (b) Image after Field Evaporation of 160 Å, 11.3 KV.

Sizes of Particles: Majority of the carbide particles were very fine in this case. The thickness of the particle was found to be about 8-10 Å; the length of the particle varied considerably and was found to be generally in the range of 30-150 Å. However, the true width of the particles did not fluctuate as much as the length as can be seen from Table 14.

Density of Particles: Since many of the particles were very small, counting the particles was time-consuming. In order to minimize the human error involved in counting, an average of five counts was taken as the representative value. A total of 152 particles were observed in an evaporation thickness of 650 Å. The radii of curvature before and after field evaporation were 717 Å and 760 Å, respectively, and ϕ_p was 63 degrees. The particle densities determined by Methods 1 and 2, Appendix D, were 1.14 and 1.69×10^{17} particles/cm³, respectively.

Shape and Distribution of Carbides: The majority of the carbide particles were found to have a plate-like shape. However, some tiny nodular precipitates and some particles with irregular shapes were also observed.

Tiny precipitates of about 20-30 Å in size were found along the sub-grain boundaries as shown in Figure 15(a).

Contrast Around the Carbide Particles: In this specimen carbide particles frequently intersected the prominent {110} pole. The net plane edges close to the precipitates were found to be heavily distorted (see Figure 15(b)) and spiral discontinuities in the net plane edges were also observed.

d. Specimens Tempered at 85°C for 1 hour. Three specimens tempered

Table 14. True Particle Widths of Carbides in a Specimen Tempered at 160°C for 10 minutes. (See Text for Definition of Symbols Used in the Table).

R_1 (Å)	R_2 (Å)	ϕ_1 (deg)	Q_1 (deg)	ϕ_2 (deg)	Q_2 (deg)	L (Å)	w (Å)
717	717	42.0	341	42.0	343	20	24
717	717	18.8	151	18.5	150	10	10
717	717	10.8	278	10.8	275	30	31
717	717	15.6	301	16.8	303	30	38
717	717	30.0	196	31.0	195	20	29
760	760	9.6	90	10.8	89	20	28
760	760	14.4	40	15.6	42	30	38
760	760	12.0	40	14.4	52	30	60
760	760	44.4	32	42.0	26	30	60
760	760	54.0	25	54.0	18	30	81

at 85°C for 1 hour were examined in the field-ion microscope. Only one of these was successfully imaged; typical micrographs of this specimen are presented in Figures 16(a) and (b). The hydrogen image gas was contaminated so that the quality of the micrographs was not very good. However, this did not prevent obtaining the data given below.

i) General Features of the Image.

In the image of the matrix the $\{110\}$ and $\{112\}$ poles were discernible, whereas the high index poles were not.

ii) Crystallography and Morphology of the Carbides.

Habit Plane of the Carbides: All the carbide particles examined exhibited a habit close to $\{100\}$.

Sizes of Particles: The thickness and length of the carbide particles were found to be 8-10 Å and 40-150 Å, respectively. The true particle widths of the carbides are given in Table 15.

Density of Particles: A total of 267 particles, obtained from an average of five counts, were observed in an evaporation thickness of 1000 Å. The radii of curvature before and after field evaporation were 921 Å and 1017 Å, respectively, and ϕ_p was 50 degrees. The particle densities determined by Methods 1 and 2, Appendix D are 1.2 and 1.55×10^{17} particles/cm³, respectively.

Shape and Distribution of Carbides: The majority of the carbide particles had a plate-like morphology; however, some particles with irregular shapes were also observed. Some small precipitates were found across the twins as shown in Figure 16(b).

Contrast Around the Carbide Particles: The $\{110\}$ poles were almost always intersected by precipitates (see Figure 16(b)). The net

Figure 16. Hydrogen-ion Images, 78°K, of a Specimen Tempered at 85°C for 60 minutes: (a) 9.5 KV, (b) 10.8 KV.

Table 15. True Particle Widths of Carbides in a Specimen Tempered at 85°C for 60 minutes. (See Text for Definitions of Symbols Used in the Text).

R_1 (Å)	R_2 (Å)	ϕ_1 (deg)	Q_1 (deg)	ϕ_2 (deg)	Q_2 (deg)	L (Å)	w (Å)
930	939	33.0	73	27.5	64	50	104
930	939	38.5	45	37.0	44	50	40
930	930	40.7	31	40.7	31	10	10
930	930	46.2	20	46.2	20	10	10
930	930	49.5	7	49.5	7	10	10
956	965	36.3	7	29.5	11	50	98
965	965	70.7	90	11.0	95	40	75
965	973	28.6	22	17.6	39	60	200
965	973	25.2	1	17.6	21	60	168
1008	1017	22.0	210	20.8	195	20	99

plane edges close to the particles were found to be distorted.

iii) Substructure.

Twins having a habit close to $\{112\}$ as determined by Method 2, Appendix B were found in one of the three specimens examined. The twins were found to be uniformly distributed, as shown in Figure 16(a), and had a width of 150-250 Å. These twins were found to change contrast across the $\langle 111 \rangle$ zone, and alternate twins had the same contrast on either side of the $\langle 111 \rangle$ zone.

e. Specimen Tempered at 230°C for 1 hour. Figure 17 is a typical micrograph from a specimen tempered at 230°C for 1 hour.

i) General Features of the Image:

The net plane edges around the $\{110\}$ pole were more regular than those observed in the first stage of tempering. Also, the dark zone patterns between prominent $\{110\}$ poles were observed. Generally, in the image of the matrix more than one grain was present.

ii) Crystallography and Morphology of the Carbides:

Habit Plane of the Carbides: The habit plane of the carbides was found to be $\{112\}$ by Method 1, Appendix B.

Sizes of Particles: The particle sizes of the carbides varied considerably. The thickness and length of the carbides were in the range 60-160 Å and 300-1500 Å, respectively.

Shape and Distribution of Carbides: The particles were found to have a plate-like morphology. In Figure 17 the carbide particles were distributed along the grain boundaries (particles 1 and 2) as well as within the grains (particles 3 and 4).

f. Specimen Tempered at 350°C for 1 hour. Representative

Figure 17. Hydrogen-ion Image of a Specimen Tempered at 230°C for 60 minutes, 78°K, 12.5 KV.

(a)

(b)

Figure 18. Hydrogen-ion Images, 78°K, of a Specimen Tempered at 350°C for 60 minutes: (a) 15.1 KV, (b) Image after Field Evaporation of 800 Å, 16.5 KV.

micrographs of a specimen tempered at 350°C for 1 hour are given in Figures 18(a) and (b).

i) General Features of the Image:

In the bright matrix the regularity of the net plane edges around the {110} poles was comparable to that observed in the ferrite image. The dark zone pattern between the prominent {110} poles and the butterfly contrast around the {110} poles were discernible. Also, many high index poles were observable in the matrix, for example, {130} and {120}. Generally, the image of the matrix contained more than one grain.

ii) Crystallography and Morphology of the Carbides:

Habit Plane of the Carbides: The carbides were found to have either a {110} or a {112} habit. For example, the habit planes for particle 1 in Figure 18(a) and particle 2 in Figure 18(b) were found to be {112} and {110}, respectively, by Method 1, Appendix B. The data and results for the habit plane determination for these two particles is given in Table 16.

Sizes of Particles: The thickness and length of the particles were found to be 100-200 Å and 800-1800 Å, respectively. The true particle widths 'w' of the carbides were also calculated and are given in Table 17.

Density of Particles: Seven particles were observed in an evaporation thickness of 1148 Å. The radii of curvature before and after field evaporation were 1270 and 1460 Å, respectively, and θ_p was 60 degrees. The particle densities determined by Methods 1 and 2, Appendix D, respectively, were found to be 1.56 and 1.46×10^{15} particles/cm³.

Shape of the Carbides: The carbides in the specimen tempered at 350°C for 1 hour were found to have a plate-like morphology.

Table 16. Habit Plane of Carbides in a Specimen Tempered at 350°C for 60 Minutes.

Particle	Measured Angular Shift, γ (deg.)	Radius of Curvature, R (Å)	Thickness Evaporated, t (Å)	Angle of Inclination to the Specimen axis, (deg.)	Expected Angle, (deg.) and Habit
1	1.2	1300	60	65	60-{112}
2	2.4	1375	150	88	90-{110}

Table 17. True Particle Widths of Carbides in a Specimen Tempered at 350°C for 60 minutes. (See the Text for Definitions of Symbols Used in the Table).

R_1 (Å)	R_2 (Å)	ϕ_1 (deg)	Q_1 (deg)	ϕ_2 (deg)	Q_2 (deg)	L (Å)	w (Å)
1305	1435	24.0	44	8.4	16	1148	1110
1305	1340	6.0	154	6.0	151	50	51
1305	1340	38.4	286	38.4	284	50	68
1325	1435	22.8	267	23.6	281	970	997
1360	1435	48.0	93	38.4	42	600	946
1325	1375	42.0	97	24.0	90	450	408

CHAPTER V

DISCUSSION

A. Characteristics and Contrast of Hydrogen-ion Images

1. Image Features of Ferrite, As-quenched Martensite and Tempered Martensite.

Distinct differences in contrast and regularity of net plane edges were observed between the images of pure iron and as-quenched martensite. Hydrogen-ion images of high purity iron wire revealed very regular net plane edges except occasionally when a dislocation intersected this region. A distinct $\langle 111 \rangle$ dark zone pattern and a "butterfly" contrast around the $\{110\}$ poles were present. Also, in the ferrite images many higher index poles were discernible. For as-quenched martensite with 0.8% C, however, the image exhibited very distorted $\{110\}$ net plane edges, a diffuse dark region around the $\{110\}$ poles, and no distinct $\langle 111 \rangle$ dark zone pattern. Complex dislocation substructures were also frequently observed in these images, and only low index poles were discernible.

These differences in image features for pure iron and martensite with 0.8% C could arise for several reasons. Of these, the most probable ones are background vacuum, tip radius and orientation, carbon content and lattice strain. However, background vacuum, tip radius and orientation can be ruled out; the background pressure was essentially the same for a number of experiments and the contrast features cited for

each of the cases were persistent over a wide range of tip voltages and for tips of different orientations. Therefore, the most likely explanation is the difference in carbon content and lattice strain.

At present, there is no detailed theory which can satisfactorily explain the contrast features, such as dark or bright zones and regions in the FIM images of metals. However, it is reasonable to assume that a dark region results from a lower field-ionization rate in this area. This could arise from a higher local radius of curvature, and therefore lower field, due to faster evaporation rates on certain crystal regions; or it could result from a lower ionization probability on certain regions or zones on the surface. In the martensite image the $\{110\}$ region is darker than the $\{111\}$ region; this at least in part, is due to a faster evaporation rate of $\{110\}$ region compared to that of the $\{111\}$ region. However, the lack of a pattern similar to that of pure iron within this $\{110\}$ dark region of martensite is not explained by differences in local radii of curvature.

Similar contrast features around certain crystal regions as well as along certain zones have been discussed for several metals by Knor and Müller⁷² in terms of directional surface bonding orbitals and by Moore and Brandon⁷³ in terms of the number and type of nearest neighbors of the surface atoms. It is therefore suggested here that the pattern of dark regions around the $\{110\}$ poles, called the "butterfly" pattern, results from the surface electronic characteristics, whether they are described by surface orbitals or by atomic environment, and that the addition of 0.2-0.8% C to iron changes this electronic structure in such a way as to eliminate the "butterfly" pattern in $\{110\}$ regions. This

effect of carbon may be an indirect one on the surface electronic structure produced by randomness of evaporation, which is used to explain the poor development of low index poles and the absence of high index poles in alloy images¹², or it may be due to a more direct effect of carbon on the surface electronic distribution, which has been used to explain contrast effects arising from interstitial atoms⁷⁴, or some combination of both. The former effect of random evaporation, is supported in part by the lack of development of higher index poles as well as the visibility of fewer $\{110\}$ net plane edges in the martensite image. An irregular or less perfect surface produced by random evaporation might also eliminate other sharp contrast differences such as the dark zones between the $\{110\}$ poles. The latter effect of change in the surface electronic distribution due to the presence of carbon may be the result of the transfer of sp-electrons from the carbon atoms to the iron atoms. Such a concept of charge shift from one species to the other and their possible effect on the field ion images has already been discussed by Müller and Tsong¹². The difference in crystal structure of martensite (b.c.t.) and ferrite (b.c.c.) could also lead to some differences in the image contrast.

The effect of strain in the matrix would be primarily on the regularity of the net plane edges, although some small effect on contrast may also be operative. The strain present in the lattice due to the martensite transformation causes a slight deviation from the circular development of the low index net plane edges as found in ferrite images. Also, the higher density of dislocations in martensite gives rise to additional and even more pronounced irregularities which are clearly

seen around the low index poles.

If the large differences in the image features of iron and high carbon martensite are attributable to carbon content and lattice strain, as proposed above, then in the first stage of tempering the image features of the matrix phase, which is low carbon martensite (0.25% C), should be intermediate between those of pure iron and high carbon martensite. This, in fact, was observed. The matrix image in these specimens revealed that the $\{110\}$ net plane edges were more regular than those in the martensite image but less regular than those in the ferrite image. Also, the $\langle 111 \rangle$ dark zone pattern was not so sharp as in the ferrite image; the $\{110\}$ regions were somewhat less diffuse than in the high carbon martensite image, but did not show the distinct "butterfly" pattern of the pure iron image. In some of the micrographs higher index poles were discernible. Therefore, the image features of low carbon martensite were intermediate between those of pure iron and high carbon martensite.

In the third stage of tempering the matrix image contained regular $\{110\}$ net plane edges without any distortion. In some micrographs the $\langle 111 \rangle$ dark zone pattern and the "butterfly" contrast around the $\{110\}$ poles were discernible indicating that the matrix phase is ferrite, as expected in this stage of tempering, and that 0.01-0.02% C has no appreciable effect on image characteristics. Therefore, the image characteristics (contrast and net plane edge regularity) depend on the carbon content and lattice strain, so that a careful examination of the field-ion images with particular reference to the image features should aid in identifying the matrix phase for heat treated steel specimens in

FIM studies.

It should also be mentioned here that the degree of tetragonality in these materials cannot be used reliably to aid such an identification. The acute angle between the zones passing through the $\{110\}$ planes is related to the amount of tetragonality (c/a ratio) in the matrix. For 0.8% C martensite, this angle on (110) centered stereographic projection would be 73 degrees, compared to 72 degrees for pure iron. However, it is known that field-ion micrographs deviate from a stereographic projection by as much as several degrees so that the experimental error is larger than the expected angular difference due to tetragonality in these materials.

2. Twin Contrast

Twins in field-ion images of as-quenched martensite revealed alternating bright and dark band contrast (see Figures 11 and 12). Sekhar and Richman³⁰ speculated that the bright bands represented the intersection of twin boundaries with the specimen surface. To support this they cited a paper by Ranganathan et al.⁷⁵ in which the latter authors observed streaking (narrow bright bands) at grain boundary interfaces when the voltage was raised above the BIV. Ranganathan et al. reported that the streaks from these grain boundaries might arise from either a geometrical step where the interface intersects the surface or some electronic perturbation. Sekhar and Richman were apparently extending this argument to twin boundary contrast and reported that the stresses around the twin boundaries caused the observed image streaking. However, such an argument would appear doubtful when applying it to the twins with $\{112\}$ habit planes since the stress associated with the

coherent twin interfaces is very small compared to that at grain boundaries. Furthermore, it has not been established that streaking is a universal feature for all grain boundaries; in fact, the hydrogen-ion images of iron in the present studies showed dark contrast at the grain boundaries. Ranganathan et al. mentioned that extreme care should be exercised in interpreting streaking in field-ion images.

It is postulated by the present author that the bright bands, in general, do not correspond to streaks but instead represent the twins, while the dark bands represent the intersection of twin interfaces with the specimen surface. The following observations support this postulate:

1. Generally the bright bands were much wider than the dark bands. This is consistent with the fact that the width of the twin is larger than the twin interface. In the initial stages of the field evaporation sequence the dark bands were narrow, so that it was difficult to detect their presence. After some field evaporation the dark bands increased in width. Therefore, the dark bands seen in an image after reasonable amounts of field evaporation do not represent the exact width of the twin boundary, which is expected to be only a few angstroms.
2. Distinct image spots were seen in the bright bands and poles were clearly identified. Therefore, these bright bands do not correspond to streaks as described by Ranganathan et al.⁷⁵ for grain boundaries.
3. In a specimen in which the twins were inclined at an angle to the specimen axis, a large bright region was centered about the (121) pole (see Figure 5) and was separated from the next bright region by a dark band. As the former bright region was removed by field evaporation, the dark band between the two bright regions was removed simultaneously,

and the next bright band filled out a similar large region around the (121) pole. This again is consistent with bright contrast for the twins and dark bands representing the twin boundaries.

3. Precipitate Contrast

Emphasis is given here to hydrogen-ion images of the field evaporated end forms of carbide precipitates in a ferrite matrix. It has been observed¹⁴ that V_4C_3 and NbC particles image brighter and Fe_3Si darker than the ferrite matrix. In the present studies both Fe_3C and ϵ -carbide particles were found to image darker than the ferrite matrix. Possible explanations for these observations are discussed below.

Schwartz¹⁴ suggested that the bonding strength within the particle is different from that in the matrix which causes the radius of curvature over the particle to be raised or lowered due to evaporation rates, and this in turn makes the precipitate image darker or brighter than the matrix. For example, a particle with a lower bonding energy than the matrix will preferentially field evaporate and assume a larger radius of curvature, thereby giving a lower field over the particle and a darker image. The bonding energies of the above mentioned compounds can be compared by their melting points. Vanadium carbide and niobium carbide have melting points higher than that of ferrite and therefore image brighter, while Fe_3Si has a lower melting point compared to ferrite and so images darker. The melting points of ϵ -carbide and Fe_3C , however, are unknown.

Bonding energies can also be compared by the number and type of bonds. According to Engel's theory^{76,77} the electronic configuration of Fe_3C can be derived as follows. The electronic configuration of

α -ferrite and carbon in the solid state are $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ and $1s^2 2s^2 2p^3$, respectively. Since α -iron, ϵ -carbide and Fe_3C are ferromagnetic, the kernel of these should be the same as far as the electronic configurations are concerned. Therefore, all the sp-electrons of carbon would go to the outermost shell of iron, increasing the number of sp-bonds in ϵ -carbide and Fe_3C compared to α -iron, the d-bonds remaining the same in both cases. According to Engel's theory, the d-bonds give the major contribution to bonding energy while the sp-bonds have a much smaller effect on bonding energy and primarily determine the crystal structure. Therefore, according to this theory, the bonding strength of ϵ -carbide and Fe_3C should be marginally higher than that of α -ferrite. Also, according to Pauling⁷⁸, a comparison of sublimation energies indicates that Fe_3C has a higher bonding energy than elementary iron.

Since it is experimentally observed, however, that ϵ -carbide and cementite image darker than the ferrite matrix in the field evaporated end form, it appears that some consideration other than the bonding energy is necessary to explain this contrast. Two possibilities which should be examined are the ionization efficiency for hydrogen and the field-induced chemical reactivity of α -iron, ϵ -carbide and ferrite.

1. Preferential Field Ionization: The probability of field ionization over ϵ -carbide and Fe_3C particles may be less than that of the ferrite matrix; this would lead to a dark appearance of ϵ -carbide and Fe_3C in the field-ion images. While it is not possible to evaluate fully this mechanism at present, it might be mentioned that the greater number of sp-bonds expected in ϵ -carbide and Fe_3C along with Müller's theory¹² that

field ionization is related to overlap of atomic orbitals from the image gas and the metal would together suggest preferred field-ionization over ϵ -carbide and Fe_3C rather than ferrite. In fact, the initial images of pearlite prior to any significant field evaporation revealed bright Fe_3C platelets¹³, which is consistent with preferential field ionization over Fe_3C . However, the Fe_3C platelets showed dark contrast when the field evaporated end form was produced¹³.

2. Field-induced Chemical Reactivity: The melting point of gold (1063°C) is lower than that of ferrite; therefore, according to the previously mentioned hypothesis of preferential field evaporation, gold should image darker than ferrite. However, gold particles have been observed¹⁹ to image brighter than the ferrite matrix in hydrogen-ion microscopy.

In order to explain the above contrast of gold precipitates, the field-induced chemical reactivity of the image gas with the precipitates should be considered. Gold being a noble metal should react very little with the hydrogen image gas; these particles would therefore stay proud of the surface and image brighter. By analogy, field induced corrosion of ϵ -carbide and Fe_3C particles would lead to a slight depression over these precipitate regions causing them to image darker than the matrix.

Support for such an argument might be found in the above hypothesis for preferential field ionization, that is, according to Engel's theory the number of unfilled orbitals in ϵ -carbide and Fe_3C is more than that in ferrite, and therefore the overlap of hydrogen orbitals with ϵ -carbide and Fe_3C orbitals may be more than that with ferrite. This would not only lead to preferential field ionization as indicated above, but should also aid the chemical attack by hydrogen of ϵ -carbide and Fe_3C under the influence of the electric field. Furthermore, the metastability of the ϵ -carbide and cementite phases could contribute to their preferential removal.

4. Observations on the Degree of Coherency of the Particle/Matrix Interface.

It has been demonstrated^{17,19} that useful information regarding the degree of coherency at a particle/matrix interface can be deduced from the field-ion images although certain complications in image analysis arise due to other factors. Generally such an analysis is facilitated when the particle intersects a low index region, for example, {110} regions in the hydrogen-ion images of iron. A particle can be defined as coherent when the lattice planes are continuous through the precipitate and the matrix, while the interface of a partially coherent particle consists of a fairly simple array of structural dislocations⁷⁹.

For a coherent particle in FIM, the net plane edges of the pole which the precipitate intersects should be continuous across the interface between the precipitate and matrix and should show distortion or deviation from a smooth circular development away from the interface due to the resulting strains in the matrix. While the continuity of lattice planes across the precipitate cannot be seen in the dark region representing the carbide particle, the lattice strain in the matrix can clearly be seen, as shown in the micrographs in Figure 19 (particles 1 and 3). The continuity of matrix rings from one interface to the other indicates the absence of dislocations (Figure 19(b), particle 3).

For a partially-coherent particle, structural dislocations relieve the accumulated strain due to misfit at the interface as coherency is lost. Therefore, less strain should be evident in the net plane edges of the pole which a partially-coherent particle intersects; and spiral discontinuities, representing dislocations, should be found in the net

(a)

(b)

(c)

Figure 19. Carbides Intersecting $\{110\}$ region: (a) Specimen Tempered at 160°C for 10 minutes, (b) Specimen Tempered at 160°C for 30 minutes, (c) Specimen Tempered at 160°C for 60 minutes.

plane edges at the particle-matrix interface. An example of a partially coherent particle showing these features is given in Figure 19(a) (particle 2).

A complication which arises in the above analysis is the identification of the origin of dislocations observed at the particle/matrix interface, that is, whether the dislocations were formed at the interface to relieve strains or were the original dislocations on which nucleation occurred or perhaps even were trapped by the carbide particles. It would seem, however, that any dislocation at the interface, regardless of its origin, should serve to relieve some of the misfit strain. Therefore, the degree of distortion in the net plane edges of the pole which they intersect should be a better indication of the degree of coherency than the observation of dislocations at the particle/matrix interface in FIM studies.

The interpretation of degree of coherency is further complicated by the presence of 'split pole' contrast as shown in Figure 19(c). Similar contrast observed for gold particles in a ferrite matrix has been attributed¹⁹ to preferential field evaporation of the matrix on one side of the particle, resulting in discontinuities in the net plane edges due to surface geometry and thereby obscuring any effects of strain or dislocations at the interface.

B. Microstructure of As-quenched Martensite

1. General

In the present FIM studies both twinned and dislocated regions have been observed. Though ferrous martensites have been well

characterized microscopically into laths and plates, complications arise when individual martensite crystals are to be analyzed. Therefore, when we are dealing with individual martensite plates, as in FIM, it is suggested, that the fine structure should be discussed with reference to twinned and dislocated martensite and not in terms of laths and plates. In many recent investigations, as pointed out in the literature survey, twinned and dislocated martensite regions have been observed to be present simultaneously.

Recently, Thomas⁴⁸ has reviewed the factors responsible for controlling the martensite substructure. Those factors which are related to plain carbon steels and their effect on the substructures of martensite are given as follows:

1. Twinning is promoted by increasing the carbon content. Below 0.3% C mainly dislocated laths form, while above 0.6%C primarily twinned plates form. However, fine twins have been frequently observed⁴⁷ in the lath martensite and dislocations in plate martensite⁴⁸. Also in plain carbon steels in the composition range 0.6-1.0% C both twinned and dislocated martensite have been found to occur simultaneously⁴.
2. Twinned martensite forms in steels with lower M_s temperatures, and dislocated martensite forms in steels with higher M_s temperatures. For plain carbon steels it has been reported⁴⁷ that then the M_s temperature is in the range of 400-600°F both dislocated and twinned martensite forms.
3. Local variations in carbon composition and M_s temperature could give rise to nonuniform transformation substructures.
4. It has been suggested⁴⁸ that the strength of martensite, i.e., the relative magnitudes of the critical resolved shear stresses for twinning

and slip at a given temperature for a particular composition, is the single most important factor which determines the substructure of martensite.

It can be concluded from the above considerations that music wire with carbon content of 0.8% and an M_s temperature of 475°F, should contain both twinned and dislocated martensite as was observed in these studies.

2. Crystallography and Morphology of Twins.

Results of previous studies on the crystallography and morphology of twins in martensite were included in Table 2. The twins in the as-quenched martensite in this research were found to have a $\{112\}$ habit consistently. This agrees with the previous FIM and electron microscopy studies for the habit of transformation twins. Oka and Wayman⁴⁴ reported the observation of twins with $\{110\}$ habit in an Fe-1.82% C alloy, but no such twins have been identified in the present research.

Sekhar and Richman³⁰ reported the presence of $\{145\}$ deformation twins in the central regions of their FIM images; they concluded that these twins were formed due to the high field stress acting on the specimen. However, in the present FIM studies no such deformation twins were observed. Sekhar and Richman did not indicate the techniques used in the crystallographic analyses, which appears to be the only way the two types of twins could be distinguished in field-ion images. Also, the indexing of their field-ion micrographs appeared to be erroneous according to results from the present studies.

The twin width observed in the present investigation was in the range of 25-85 Å which agrees well with the previous FIM and electron microscopy studies. Generally, the regions examined in FIM revealed a

uniform density of twins. Also, in the present research many of the twins were found to be fragmented. Such fragmented twins have been observed previously by Wells⁴¹.

C. Microstructure of Tempered Martensite

1. Shape of the Carbide Particles

In the present FIM investigations the majority of the carbide particles were found to have a platelike shape, while a few irregular shaped and tiny nodular precipitates were also found in the first stage of tempering. Previous investigators have reported the precipitation of platelike carbides^{80,81} as well as fine nodular carbide particles⁴² in specimens tempered below 200°C.

Since the music wire used in the present studies contained approximately 0.4% Si, Fe_3Si might be expected to precipitate along with the iron carbides. The shape of the Fe_3Si precipitates has been established¹⁴ to be spherical; no particles of such shape and reported size were found in the present investigations, except possibly in the very early stages of tempering. However, the diffusion rate of silicon is very much slower than that of carbon so that no Fe_3Si would be expected in these initial stages of tempering; therefore, the co-precipitation of Fe_3Si can be ruled out.

Langer⁸² examined transverse sections of cylindrical specimens of tempered steels by electron microscopy using carbon replica technique. He observed an angle of 90 degrees between ϵ -carbide particles and 70 degrees between cementite particles. He did not, however, specify the grain orientation, which should influence the observed angles; for

example ϵ -carbide particles on $\{100\}$ planes observed in the $[110]$ direction would intersect at 90 degrees, while those observed in the $[111]$ direction would intersect the surface at 60 degrees. It is not clear why he consistently observed the above angles unless a fiber texture was present in these specimens. In FIM, the situation is further complicated by the spherical surface of the specimen and the stereographic projection of this surface in the image; that is, not only would the angle of intersection of the particles at the surface vary with the projection orientation, but also the measured angle on the field-ion micrograph would depend on the particle position in the specimen. Consistent with this, the angles between ϵ -carbide particles and those between cementite precipitates varied considerably in the present FIM studies.

2. Habit Plane of the Carbides

The identification of the carbide particles was performed crystallographically by determining their habit planes. It should be emphasized here that crystallographic identification of carbides is probably the most conclusive one possible in FIM. In the first stage of tempering the ϵ -carbide particles were found to have $\{100\}$ habit. In the later stages of tempering cementite having both $\{112\}$ and $\{110\}$ habits were observed. These habit planes observed for ϵ -carbide and cementite in the present investigation agrees with those reported previously (see Table 3).

3. Comparison Between Microstructure and Microhardness Values

From the microhardness curves given in Figures 7 and 9, it can be seen that in the first stage of tempering the hardness increases to a peak value and then drops slowly. With the onset of the third stage of

tempering the hardness decreases more rapidly. The correlation between these microhardness values and microstructures is discussed below in terms of the degree of coherency of the carbide particles, particle size and density, subgrain and twin boundaries and solid solution effects.

The change in hardness occurring during tempering should be considered in terms of the following four hardening mechanisms:

- 1) Coherency hardening: A coherent precipitate with its surrounding field of strained matrix offers greater resistance to the motion of dislocations than an incoherent precipitate⁵³. The initial increase in hardness in the first stage of tempering has been attributed^{3,56} to the precipitation of fine coherent ϵ -carbide and the subsequent decrease in hardness with further tempering to the loss of coherency of these particles.
- 2) Dispersion hardening: Cohen⁸³ has described the increase in hardness in the first stage of tempering as due to dispersion hardening on the supposition that it is due to dislocation pinning by an early form of carbide precipitation. The subsequent decrease in hardness with further tempering may then be due to particle coarsening or an increased inter-carbide spacing.
- 3) Substructure: The presence of twins and sub-boundaries could impede the motion of dislocations, thereby contributing to hardness.
- 4) Solid solution hardening: Interstitial solid solution hardening in unaged martensite is caused by the carbon atoms trapped in interstitial positions and imposing severe displacements on two of the six nearest neighbor iron atoms⁸⁴. The contribution of solid solution hardening by carbon to the overall hardening in tempered martensite decreases continuously from a maximum value in the unaged martensite due to the

precipitation of carbides and the ensuing depletion of carbon from the matrix.

In the present investigation it was observed that the peak hardness in the first stage of tempering (160°C for 10 minutes and 85°C for 60 minutes) was not entirely due to coherent precipitates, since many of the particles were found to be only partially coherent. If the dislocations present adjoining these precipitates were due to the relaxation of coherency strains, then a slight decrease in hardening could be expected. Furthermore, many coherent as well as partially coherent particles were found in specimens tempered throughout the first stage of tempering well beyond peak hardness.

The variation in particle size and density with tempering treatment along with other microstructural observations are summarized in Table 18. Here the true particle width is assumed to be representative of the particle size in a specimen. From the table it is seen that the particle density was found to be highest (10^{17} particles/cm³) and the particle size least (40-80 Å) at peak hardness. Therefore, it appears that the contribution of dispersion hardening of fine carbide particles to peak hardness is significant.

The presence of twin and subgrain boundaries were observed in one of the specimens that was tempered to peak hardness. In this specimen precipitation of carbides across the twins was also detected; this could increase the effectiveness of the twin boundaries to impede the motion of dislocations. No twins were found in specimens tempered for longer times except in one tempered at 160°C for one hour; in this case, no carbide precipitation was found across the twins.

Table 18. Variation in Particle Size, Particle Density and other Microstructural Features with Tempering Treatment.

Tempering Treatment		Average Particle	Particle	Other Microstruc-
Temperature, °C	Time, Minutes	N Size ($\sum_{i=1}^N w_i/N$), Å	Density, Particles/ cm ³	tural Features Observed
160	10	39	1.69×10^{17}	Coherent ϵ -carbide, partially-coherent ϵ -carbide, sub- boundaries
160	30	194	6.8×10^{16}	Primarily partially- coherent ϵ -carbide
160	60	164	8.3×10^{15}	Primarily partially- coherent ϵ -carbide, twin and sub-bound- aries
85	60	81	1.55×10^{17}	Coherent ϵ -carbide and partially-co- herent ϵ -carbide, precipitation of carbides across the twin
350	60	596	1.46×10^{15}	No twins or sub- boundaries, in- coherent Fe_3C

It was pointed out by Chilton and Kelly⁶⁶ that solid solution hardening due to carbon is an important contributing factor to the strength of unaged martensite. Cohen⁸⁵ reported that the decrease in solid solution hardening in the first stage of tempering was very little, as concluded from the flow stress of 0.25%C martensite, which was well over 90% of the maximum value reached at the high carbon levels; therefore, solid solution hardening does contribute in a major way to the strength of tempered martensite. However, this contribution continuously decreases during the first stage of tempering due to carbide precipitation.

The relation between microstructure and microhardness in the first stage of tempering can therefore be summarized as follows. The gradual decrease in hardness immediately following the first stage of tempering peak hardness was observed to be associated with an increase in particle size and a decrease in particle density, thereby reducing the contribution of dispersion hardening. Some additional loss in coherency of the carbide particles was observed, which reduced the contribution of coherency hardening. The decrease in hardness appears not to be associated with the absence of twin or sub-boundaries, since both of these were found even in the later first stage of tempering. The decrease in solid solution hardening might not be significant, as in the first stage of tempering the 0.25%C martensite matrix is persistent.

In the third stage of tempering a rapid decrease in hardness was observed. Kelly and Nutting³ attributed this decrease in hardness to the disappearance of twins. They, however, felt that the pronounced softening in the third stage of tempering was not due to the growth of

carbides, since they did not observe a significant growth in the tempering range of 200-400°C. In the present investigations disappearance of twins as well as considerable increase in particle size of the carbides was observed between the specimen tempered at 160°C for 1 hour (164 Å) and that at 350°C for 1 hour.

In summary the change in hardness due to tempering may be schematically represented as shown in Figure 20 for each of the above hardening mechanisms.

4. Kinetics of Tempering from Microstructural Features

Some of the qualitative observations concerning the kinetics of tempering are summarized below. It was observed that in the first stage of tempering the thickness of the carbide particles did not change significantly, while the length and the width did increase considerably until a certain stage in the tempering process.

The ratio of length to width in the first stage of tempering was found from individual particle measurements to increase generally from 1:1 to about 1:5.

Within the third stage of tempering the thickness, length and width were all found to increase considerably. However, the relative increase in thickness was greater than that for both the length and the width. In this stage of tempering the thickness was found to increase by a factor of four or five, while the ratio of length to width increased from 1:1 to about 1:2.

From the above observations it is concluded that in the first stage of tempering edgewise growth of the carbide particles is important, while in the third stage of tempering the growth of carbide particles primarily occurs sideways.

Figure 20. Probable Contribution of Various Hardening Mechanisms to the Variation in Overall Hardening Occurring During Tempering.

5. Mechanism of Tempering from Microstructural Features

The following two stage mechanism of tempering has been proposed⁸²,

Untempered Martensite $\rightarrow$ Low Carbon Martensite (0.25%C)

The present studies confirm this two stage mechanism. In the first stage of tempering low carbon martensite probably formed as very small subgrains about 400-600 Å in size, and ϵ -carbide precipitated along the sub-boundaries (see Figure 13).

In specimens that were tempered at 160°C for increasing times the particle sizes first increased and then decreased. In those specimens which showed a decrease in particle size, cementite along with ϵ -carbide was detected. Therefore, the decrease in particle size and simultaneous presence of cementite indicates that before the precipitation of cementite occurs, dissolution of ϵ -carbide takes place, as previously proposed⁸².

Figure 21 represents graphically the tempering treatments which produced ϵ -carbide and/or cementite. This illustrates that the precipitation of different carbides during tempering is dependent on both temperature and time. It can be seen from this figure that both ϵ -carbide and cementite coexist over a wide range of temperatures and times; this indicates that the disappearance of ϵ -carbide and the appearance of cementite do not take place suddenly but occur very gradually. However, it is clear whether dissolution of ϵ -carbide or nucleation of cementite

Figure 21. Carbide Precipitation During Tempering

is the rate controlling mechanism⁸². Also, the difference in habit planes for ϵ -carbide and cementite indicates that the transformation from ϵ -carbide to cementite does not take place in situ.

6. Nucleation of Carbides

In the first stage of tempering dislocations associated with the precipitates were almost always observed. Although some of the dislocations might have been introduced after the precipitation of the carbides to relieve some of the coherency strains, the presence of original dislocations on which precipitation occurred cannot be ruled out. This is supported by the fact that a high density of dislocations were observed in the untempered martensite. Also, the precipitation of very small particles of about 20-30 Å in width, was observed along the sub-boundaries. This confirms the previous electron microscopy studies^{42,82}, which reported the precipitation of ϵ -carbide on dislocations and on sub-boundaries.

In the initial stages of tempering the particle density was very high but steadily decreased with continued tempering. Therefore, it appears that nucleation takes place within short periods of tempering, and no nucleation sites were created with further tempering, but instead agglomeration and growth of the already existing particles occurred.

Cementite precipitated on the twin boundary and grew along the twin interface. Precipitation of cementite within the grains was also observed.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1) Identification of matrix phase: Certain image features, such as regularity of the $\{110\}$ net plane edges, 'butterfly' contrast around the $\{110\}$ pole, $\langle 111 \rangle$ dark zone pattern and development of high index poles, change gradually when going from high-carbon martensite to low-carbon martensite to ferrite; these features facilitate the identification of the matrix phase.

2) Substructure of as-quenched martensite: Hydrogen-ion images of as-quenched martensite in an Fe-0.8%C-0.4%Mn steel revealed both twinned and untwinned regions; in the twinned region twins were 25-100 Å wide and had a $\{112\}$ habit; in the untwinned region a high density of dislocations was observed.

3) Twin contrast: In hydrogen-ion images the twins appeared as alternate bright and dark bands; the bright bands represented the twins and the dark bands the twin interfaces.

4) Contrast of iron-carbides: In hydrogen-ion microscopy both ϵ -carbide and cementite appeared darker than the ferrite matrix. The field-induced reaction of hydrogen with the carbides seemed to be the most probable reason for this.

5) Substructure of tempered martensite: In the first stage of tempering twins with a width of 150-250 Å and a $\{112\}$ habit were present. Very fine (often 20 Å) ϵ -carbide particles of $\{100\}$ habit were found in

the early part of the first stage of tempering. Also, in this stage of tempering the low-carbon martensite matrix consisted of many small crystallites. In the third stage of tempering cementite particles of $\{110\}$ and $\{112\}$ habit as large as $1000 \text{ \AA}$ were present. The particle density decreased from $10^{17} \text{ particles/cm}^3$ in the early first stage of tempering to $10^{15} \text{ particles/cm}^3$ in the third stage of tempering.

6) Degree of coherency of particle/matrix interface: From the distortion around the net plane edges (suggesting coherency strain) and the spiral discontinuities (indicating dislocations) when a particle intersected a $\{110\}$ region, information regarding the degree of coherency of the particle was deduced. The strain associated with a coherent particle was high, while the partially-coherent particle was associated with dislocations. Both coherent and partially-coherent particles were found throughout the first stage of tempering.

7) Microhardness and microstructure: At peak-hardness in the first stage of tempering the contribution of dispersion hardening appeared to be greater than that of coherency hardening. The decrease in hardness immediately following the peak-hardness was due to increase in particle size, decrease in particle density and additional loss in coherency. The pronounced softening in the third stage of tempering was due to a large increase in particle size and the removal of twins.

8) Mechanism of tempering: The following two stage mechanism of tempering was confirmed,

$$\text{high-C martensite} = \text{low-C martensite} + \epsilon\text{-carbide} = \text{ferrite} + \text{cementite}$$

B. Recommendations

The following FIM studies are recommended for better understanding of the martensite transformation and the tempering process at an atomic level.

1) Further FIM of twinned martensite should be performed with neon or hydrogen-promoted helium-ion microscopy in order to determine the atomic arrangements at the interface.

2) The effect of carbon content on the fine structure of martensite should be examined.

3) By choosing an appropriate ferrous alloy the austenite/martensite orientation relationship should be investigated.

4) The microstructure of tempered martensite prior to peak-hardness should be examined by FIM.

5) The second stage and the fourth stage of tempering should be studied.

6) Higher resolution FIM techniques, such as neon and hydrogen-promoted helium-ion microscopy should be used to examine the particle/matrix interface in tempered martensite.

APPENDIX A

MAGNIFICATION OF A FIELD ION IMAGE

The magnification, M , of a field-ion image is given by

$$M = L/r,$$

where, L is the tip to screen distance and r is the radius of curvature of the tip. The radius of curvature can be found¹⁰ from

$$F = v/kr,$$

where F is the field on the surface of a sphere, taken as the ionization potential of the image gas, v is the applied voltage to the specimen and k is a slowly varying function of radius.

For hydrogen the ionization field is $2.28 \text{ v/\AA}$ and k for a field-ion tip¹⁰ is 5. By substitution into the above equations of these values along with the applied BIV and the measured specimen to screen distance the image magnification can be found.

APPENDIX B

DETERMINATION OF THE HABIT OF A PLANAR FEATURE

Method 1

The habit of a planar feature can be determined from any single micrograph⁸⁶. The projection of a planar feature onto the field-ion image is generally a small circle, as shown in Figure 22. This small circle, after being transferred to the stereographic projection is completed by extending outside the projection circle, if necessary. A diameter of the small circle is so chosen that it passes through the center of the stereographic projection; the two ends of this diameter of the small circle are then joined to the south pole of the projection circle. The angle subtended by the diameter of the small circle at the south pole is then bisected, and the intersection of the bisector with the diameter of the small circle gives the pole 'p' of this small circle. This pole corresponds to the plane responsible for the trace of the planar feature.

Method 2

The habit of a planar feature can also be determined from the stereographic projection of the matrix and the angle of inclination, $(90-\beta)$, of the planar feature to the specimen axis. The angle of inclination (see Figure 23) can be determined⁸⁷ from the following equation

$$(90-\beta) = \tan^{-1} R\gamma/t,$$

where R is the local radius of curvature (see Appendix A), and γ is the angular shift of the planar feature due to the field evaporation of surface layers of thickness t .

APPENDIX C

DETERMINATION OF TRUE PARTICLE WIDTH FROM A CONTROLLED FIELD EVAPORATION
SEQUENCE

If the width of a particle in the specimen is represented by a straight line in space and if the coordinates of the end-points of the line are (x_1, y_1, z_1) and (x_2, y_2, z_2) , then the square of the true particle width 'w' is given by,

$$w^2 = (x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2.$$

In a spherical coordinate system the end-points are

$$x_1 = R_1 \sin\theta_1 \cos Q_1$$

$$y_1 = R_1 \sin\theta_1 \sin Q_1$$

$$z_1 = R_1 \cos\theta_1$$

and,

$$x_2 = R_2 \sin\theta_2 \cos Q_2$$

$$y_2 = R_2 \sin\theta_2 \sin Q_2$$

$$z_2 = R_2 \cos\theta_2 - (R_2 + L - R_1)$$

where, L , R_1 , R_2 , θ_1 , Q_1 , θ_2 , and Q_2 are as shown in Figure 24. The term $(R_2 + L - R_1)$ in z_2 accounts for the movement in the origin of the coordinate system caused by field evaporation of the specimen. Therefore,

Figure 24. Precipitate Movement Across the Image During Field Evaporation, A and B Represent the Initial and Final Positions of the Precipitate.

$$\begin{aligned}
w^2 &= (R_1 \sin\phi_1 \cos Q_1 - R_2 \sin\phi_2 \cos Q_2)^2 \\
&+ (R_1 \sin\phi_1 \sin Q_1 - R_2 \sin\phi_2 \sin Q_2)^2 \\
&+ (R_1 \cos\phi_1 - R_2 \cos\phi_2 + R_2 + L - R_1)^2.
\end{aligned}$$

The above equation is perfectly general and depends only on the two end coordinates (x_1, y_1, z_1) and (x_2, y_2, z_2) of the line in space. The applicability of this general equation is illustrated by the following examples.

Case 1. Particle Along Z-axis (see Figure 25(a)).

$$\begin{aligned}
\phi_1 &= 0 & \phi_2 &= 0 \\
Q_1 &= 0 & Q_2 &= 0
\end{aligned}$$

Therefore,

$$w^2 = (R_1 - R_2 + R_2 + L - R_1)^2 = L^2$$

Case 2. Particle in ZY-plane, Inclined to Z-axis, and with One End on Z-axis (see Figure 25(b)).

$$\begin{aligned}
\phi_1 &= \phi_1 & \phi_2 &= 0 \\
Q_1 &= 90 & Q_2 &= 0
\end{aligned}$$

Therefore,

$$w^2 = (R_1 \sin\phi_1)^2 + [R_1 \cos\phi_1 - (R_1 - L)]^2$$

Now, from Figure 25(b), it can be seen that

Figure 25. Particle Width Determination: (a) Particle Along Z -axis, (b) Particle in ZY -plane, Inclined to Z -axis, and with One End on Z -axis.

$$w^2 = (AB)^2 + (BD)^2$$

$$BD = R_1 \sin \phi_1$$

and,

$$AB = OB - OA$$

$$= OB - (OC - AC).$$

Since,

$$OB = R_1 \cos \phi_1$$

$$OC = R_1$$

and

$$AC = L$$

then,

$$AB = R_1 \cos \phi_1 - (R_1 - L).$$

Therefore,

$$w^2 = (R_1 \sin \phi_1)^2 + [R_1 \cos \phi_1 - (R_1 - L)]^2$$

Case 3. Particle Along the ZY-plane, Parallel to Y-axis, One End on Z-axis (see Figure 25(c)).

$$\phi_1 = \phi_1 \qquad \phi_2 = 0$$

$$Q_1 = 90 \qquad Q_2 = 0$$

Figure 25. (Continued) (c) Particle Along the ZY-plane, Parallel to Y-axis, One End on Z-axis, (d) Particle Along the XZ-plane, Parallel to X-axis, One End on Z-axis.

Note that the conditions are same as case 2.

$$w^2 = (R_1 \sin \phi_1)^2 + [L - (R_1 - R_1 \cos \phi_1)]^2$$

Now,

$$R_1 - R_1 \cos \phi_1 = L,$$

Therefore,

$$w^2 = (R_1 \sin \phi_1)^2$$

which can be verified from the Figure 25(c).

Case 4. Particle Along the XZ-plane, Parallel to X-axis, One End on Z-axis (see Figure 25(d)).

$$\begin{array}{ll} \phi_1 = \phi_1 & \phi_2 = 0 \\ Q_1 = 0 & Q_2 = 0 \end{array}$$

Therefore,

$$w^2 = (R_1 \sin \phi_1)^2 + (R_1 \cos \phi_1 + L - R_1)^2.$$

Since,

$$R_1 - R_1 \cos \phi_1 = L,$$

$$w^2 = (R_1 \sin \phi_1)^2$$

which can be verified from Figure 25(d).

APPENDIX D

DETERMINATION OF PARTICLE DENSITY

The particle density (number/cm³) can be determined by counting the number of particles in a known volume of material field evaporated. This volume can be determined by either of the following two methods.

Method 1

It is assumed here that equal amounts of material are removed over the entire specimen surface during field evaporation as illustrated in Figure 26. ABC and FED are the specimen surfaces before and after field evaporation with the centers at O_1 and O_2 , respectively. The thickness of material field evaporated is Nd_{hkl} , where N is the number and d_{hkl} is the d-spacing of hkl planes. R is the average radius of curvature of the specimen surface given by the arithmetic mean of the initial and final radii of curvature and ϕ_p is as shown in Figure 26.

The volume of material field evaporated is represented by the spherical cap which when flattened out gives rise to the disc GBIJEH. The thickness and radius of the disc are Nd_{hkl} and $R\phi_p$, respectively. Then the volume of the disc, V , is simply given by

$$V = \pi (R \phi_p)^2 N d_{hkl}$$

Method 2

Assume that the field-ion tip is a spherical cap on a truncated cone as shown in Figure 27 and let ABC and DEF be the surfaces of the specimen before and after field evaporation, respectively, of a number,

N, of (hkl) planes. The field evaporated thickness is given by Nd_{hkl} , where d_{hkl} is the interplanar distance of these planes; R_1 and R_2 are the radii of curvature and O_1 and O_2 are the centers of the surfaces ABC and DEF, respectively, and ϕ_p is as shown in Figure 27.

The volume of material field evaporated,

$$\begin{aligned} V_{ABCFEDA} = & \text{Volume of the truncated cone DGFCHAD} \\ & + \text{Volume of the spherical segment AHCBA} \\ & - \text{Volume of the spherical segment DGFED} \end{aligned}$$

The terms on the right hand side of the above equation can be obtained from mensuration tables; therefore,

$$\begin{aligned} V_{ABCFED} = & \pi/3 [(R_2 - R_1) (1 - \cos \phi_p) + Nd_{hkl}] \times (R_1^2 + R_1 R_2 + R_2^2) \sin^2 \phi_p \\ & + (\pi/3) R_1^3 (1 - \cos \phi_p)^2 (2 + \cos \phi_p) \\ & - (\pi/3) R_2^3 (1 - \cos \phi_p)^2 (2 + \cos \phi_p) \end{aligned}$$

or,

$$\begin{aligned} V_{ABCFED} = & \pi/3 [(R_2 - R_1) (1 - \cos \phi_p) + Nd_{hkl}] \times (R_1^2 + R_1 R_2 + R_2^2) \sin^2 \phi_p \\ & - \pi/3 (1 - \cos \phi_p)^2 (2 + \cos \phi_p) (R_2^3 - R_1^3) \end{aligned}$$

The radius of curvature of the specimen can be determined by the method given in Appendix A, by knowing the applied voltage to the specimen. The angular width of the image ' ϕ_p ' can be obtained by measuring the angle between the center of the image and its outer periphery.

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