A Study of the Early Stages of Tempering of Iron-Carbon Martensites by Atom Probe Field Ion Microscopy

M. K. MILLER, P. A. BEAVEN, AND G. D. W. SMITH

The redistribution of carbon atoms during the early stages of ageing and tempering of iron-carbon martensites has previously been studied only by indirect methods. The computer-controlled atom probe field ion microscope permits the direct, quantitative determination of carbon concentrations at the atomic level, and thus all the stages of the martensite decomposition process become amenable to direct study. Analyses of a low-carbon martensite, Fe-1.0 at. pct C, (Fe-0.21 wt pct C), water quenched and tempered for 10 min at 150 °C, showed a matrix carbon content of only 0.14 at. pct. Analysis of a 2 nm diam area centered on a lath boundary showed a local concentration of 2.01 at. pct C. There is some evidence that this carbon level is associated with the presence of a thin film of retained austenite at the boundary. In the case of a higher carbon martensite, Fe-0.64 at. pct Mn, 3.47 at. pct C, (Fe-0.65 wt pct Mn-0.78 wt pct C) water quenched and aged for approximately 24 h at room temperature, analysis of twinned regions showed a matrix carbon level of 2.7 at. pct and a concentration enrichment to 6.9 at. pct in a region 2 nm diam, centered on the coherent twin interface. Assuming the segregated carbon to be located in a single atomic layer at the twin interface, this result indicates that a carbon concentration of 24 at. pct exists locally at the boundary. These results appear to be the first direct demonstration of the segregation of carbon atoms to lattice defects in carbon martensites. Tempering of the higher carbon martensite for 1 h at 160 °C produced further segregation of carbon to the region of twin interfaces. The matrix carbon content fell to 1.5 at. pct and the average carbon content over a 2 nm diam region at the interface rose to 8.7 at. pct. The width of the carbon segregated regions also increased, which seems to imply that incipient carbide precipitation in the plane of the twin boundaries is occurring at this stage of the tempering process.

1. INTRODUCTION

THE nature of the carbon atom redistribution processes occurring during the early stages of ageing or tempering of ferrous martensites has long been a subject of scientific and technical interest. A large number of investigations have been carried out in recent years, using a wide range of physical techniques, but there is still no general agreement about the nature of some of the processes involved. A number of recent review articles[1–5] serve to illustrate the divergent views which are held.

Almost the only area where there is a reasonable degree of agreement is in the case of low carbon martensites, for which there is a considerable body of indirect evidence to indicate that the segregation of carbon atoms to lattice defects is the dominant process occurring in the temperature range up to about 200 °C.[6,7] In the case of higher carbon martensites, a number of additional effects arise. For certain freshly-formed martensites of very low M_s temperature, changes in lattice parameter and c/a ratio are observed in the temperature range below 0 °C.[8,9] These effects have been interpreted in terms of the ordering of carbon atoms into the z-sublattice from various other high energy, metastable sites.[10–12] In the temperature range between about −35 °C and 100 °C the concept of carbon atom clustering has been widely invoked to explain, for example, X-ray diffraction data,[13–14] dilatometry, electrical resistivity and hardness measurements,[15–19] electron diffraction and TEM observations,[20–27] and Mössbauer spectroscopy results,[28–31] from a wide range of martensites.

The most commonly proposed composition for the first stage carbon atom clusters is Fe_4C (see for example Refs. 19, 20, 26, 29), with a morphology, as deduced from TEM observations, which is thought to be plate-like with a $(102)_m$ habit plane.[20,23–26] However, there appears to be little direct evidence to support this stoichiometry and furthermore, the proposed structure involves a large degree of misfit with the parent martensite lattice. More complex cluster models have also been developed,[25,27] and calculations performed by Johnson,[32,33] based on an elastic relaxation model, suggested that a closer packing of carbon atoms may be more stable, but this has not been confirmed.

A rather different interpretation of the ageing data for high carbon martensites (particularly for the Mössbauer spectra) has been proposed by Fujita *et*

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al,[34–36] in terms of the redistribution of carbon atoms from octahedral sites to tetrahedral sites in the martensite lattice. However, this interpretation appears to be inadequate to explain the TEM observations, which indicate that a decomposition reaction of some kind is occurring. Khachaturyan *et al*[3,21] have suggested that this reaction may be spinodal-like in character, producing short-range ordered carbon-rich regions within the martensite lattice. Toyoshima and Nagakura[27] have also proposed that a modulated structure forms in the initial stage of clustering, with a wavelength of 0.8 to 1.0 nm normal to the $(102)_M$ plane. However, the exact nature of the process is still uncertain, and it may be that it takes place by classical nucleation and growth.

In the case of these high carbon martensites, almost no attention has been paid to the possible role of the segregation of carbon to lattice defects in the overall ageing process, although Tekin and Kelly[37] have pointed out that enlarged interstitial sites exist at the coherent twin interface, which might be expected to provide locations for the segregation of carbon atoms.

In the present work, we have attempted to shed light on some of these problems by means of a direct study of the carbon redistribution process, using the technique of atom probe field ion microscopy.[38,39] The atomic resolution of the field ion microscope, combined with the single atom chemical analysis capability of the atom probe, and the sensitivity of the latter technique to light elements such as carbon, provides a uniquely-powerful method of investigating these complex phenomena. A preliminary account of this work was presented at the International Conference on Martensitic Transformations, Cambridge, Mass., USA.[40]

2. EXPERIMENTAL

Two alloys were selected for this initial investigation, a low carbon steel Fe-1.0 at. pct C (Fe-0.21 wt pct C) with a lath-type martensitic structure, and a high carbon steel Fe-0.64 at. pct Mn-3.47 at. pct C (Fe-0.65 wt pct Mn-0.78 wt pct C) with a predominantly twinned microstructure. The compositions and heat treatments of these alloys are summarized in Table I. All specimen materials were water quenched after austenization; the low carbon steel was then immediately aged at 150 °C, whilst the high carbon steel specimens were further quenched into liquid nitrogen, and were stored at 80 °K until required for examination. During specimen preparation, insertion into the microscope, and pump down to ultra-high vacuum, exposure to room temperature (~20 °C) occurred for approximately 24 h. The specimens were then cooled to liquid nitrogen temperatures for analysis.

Field-ion tips were prepared from the heat treated wire using a two-stage polishing technique. The first stage consisted of a standard double layer polish with an electrolyte of 25 pct perchloric acid in acetic acid floated on carbon tetrachloride, and was used to produce a neck in the wire. For the second stage a single electrolyte of 2 pct perchloric acid in 2-butoxy-ethanol was used. This stage was continued briefly after the lower half of the wire separated, in order to slightly back-polish the specimen. Both stages were carried out at 25 v DC. Particular care was taken during electropolishing to ensure that the temperature of the electrolyte did not exceed 20 °C. It is unlikely that the temperature of the specimen deviated significantly from that of the polishing bath.

The atom probe used for this investigation was a conventional time of flight instrument with an overall flight path of 1.2385 m. The flight times were measured using a fast digital timing system which operated at a frequency of 159.6 MHz. The timer was interfaced into a PDP 11/10 computer which controlled the experimental cycle, recorded the data, provided on-line output of the mass to charge ratio (m/n) of every ion analyzed, and accumulated spectra during the experiment. A full description of the instrument can be found in Ref. 41.

Atom probe analyses were carried out under the following experimental conditions:

a) a system base pressure of $<3 \times 10^{-10}$ torr
b) a background pressure during analysis of $<1 \times 10^{-9}$ torr, *i.e.* with the image gas removed from the system
c) the specimen cryostat cooled with liquid nitrogen
d) an effective probe aperture diam of 2 nm
e) a pulse fraction of 15 pct
f) a pulse repetition rate of 50 Hz
g) ion collection rates of $10^{-2} - 10^{-1}$ per pulse
h) a neon image gas pressure of 1×10^{-4} torr.

The form of the data obtained from atom probe experiments and the procedures adopted for presentation and interpretation of the results are described elsewhere.[41,42] It is sufficient to note here that spectra are plotted using a semilogarithmic scale in order to emphasize the minor peaks. We also note the necessary assumptions for defining the absolute level of solute segregation at an interface. For the specific case of a boundary which is centrally positioned within a 2 nm diam aperture hole and lies parallel to the axis of the specimen (for other cases, see Ref. 41), only ~20 pct of the ions detected may be regarded as originating from the atomic plane of the boundary; the re-

Table I. Compositions and Heat Treatments of Steels

A. Low-carbon martensite

Fe-1.0 at. pct C (Fe-0.21 wt pct C) (high purity alloy) austenitized 1 h at 1000 °C, water quenched, tempered 10 min at 150 °C.

B. High-carbon martensite

	At. pct	wt. pct
Carbon	3.47	0.78
Manganese	0.64	0.65
Silicon	0.44	0.23
Sulphur	0.037	0.022
Phosphorous	0.019	0.011
Nickel	0.018	0.02
Chromium	0.072	0.07

Austenitized 2 h at 1200 °C, water quenched, further quenched into liquid nitrogen. Then aged at 20°C for 24 h. Some material was additionally tempered for 1 h at 160 °C after the liquid nitrogen quench.

maining ~80 pct originate from the matrix regions abutting the boundary which also lie within the area covered by the aperture hole. If it is assumed that the segregation of solute atoms is confined to the plane of the boundary, then, following Mills,[43] the grain boundary enrichment factor (β) may be defined as:

$$\beta = \frac{C_B}{C_M} = \frac{5C_D - C_M}{C_M}$$

where

C_B = true solute concentration in the plane of the boundary

C_D = solute concentration determined experimentally when the boundary is positioned centrally in the probe aperture hole

C_M = solute concentration determined experimentally from the matrix region of the specimen.

This definition of enrichment factor is used except where there are indications that the carbon-rich region may extend to several atom layers in width.

3. RESULTS

3.1 Low-Carbon Steel, Fe-1.0 at. pct C (Fe-0.21 wt pct C)

A neon field ion micrograph of a specimen of the low carbon martensite, tempered for 10 min at 150 °C, and containing a boundary is shown in Fig. 1. The angular misorientation across the boundary was found to be approximately 60 deg about an axis close to [011], which is of the form found by Rao and Thomas[44] for the orientation relationship between adjacent laths in a martensite packet. This, together with the high incidence of such boundaries in the microstructure, leads us to conclude that the boundary in Fig. 1 separates adjacent martensite laths. Complementary TEM images of the same specimen, (Fig. 2), show that the boundary contained a periodic array of dislocations with a spacing of approximately 8 nm, with no evidence for any carbide precipitation.

A striking feature of the FIM micrograph (Fig. 1) is the presence of a continuous dark-imaging band at the boundary, approximately 3 nm in width. We originally interpreted this feature as a contrast effect arising simply from the presence of a high angle boundary.[40] However, more recent work in our laboratory by Barnard,[45] on the FIM imaging characteristics of retained austenite films in alloyed martensite-austenite "dual phase steels", shows that the austenite films have precisely the same dark-imaging characteristics as observed here, whereas martensite-martensite interfaces which do not have films of retained austenite give images which consist of a single, very narrow, dark line. Further, in certain parts of the FIM micrograph of Fig. 1, it is just possible to discern two separate interfaces, on either side of the dark imaging band. We therefore take the view that a film of retained austenite is almost certainly present at the boundary in the present case. Attempts were made to confirm this using electron diffraction, but within the limitations imposed by the use of a single tilt stage and the small volume of electron transparent material in the apex region of the specimen, it was not possible to make a positive identification, although some reflections could be indexed according to the fcc unit cell of austenite.

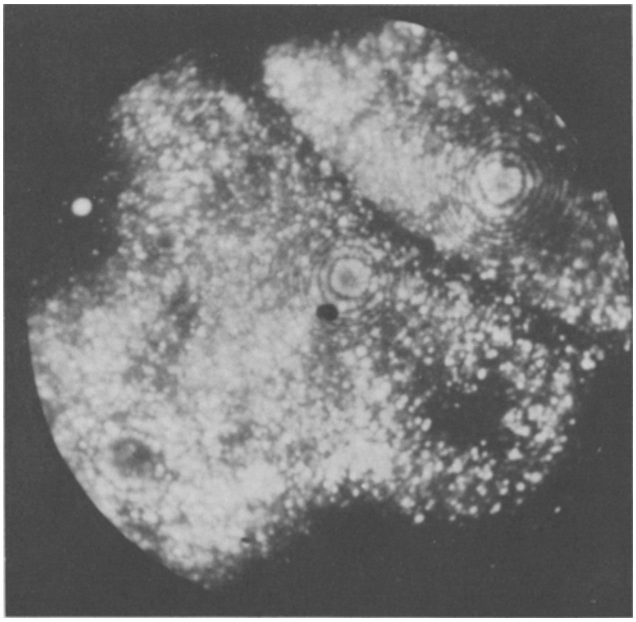

Fig. 1—Neon field ion micrograph of Fe-1.0 at. pct C (Fe-0.21 wt pct C) martensitic steel showing a lath boundary. Imaging voltage 15 kV.

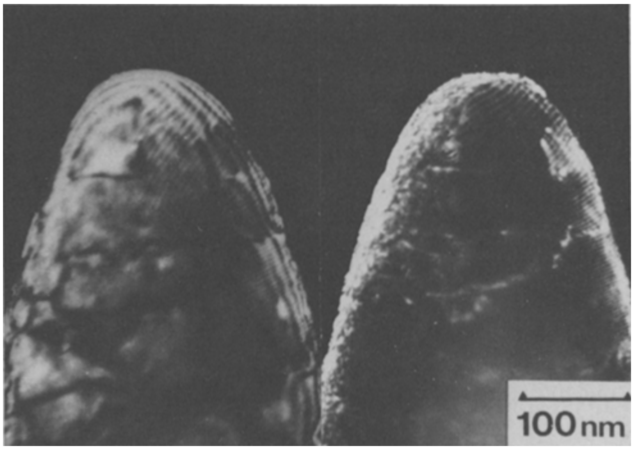

Fig. 2—Complementary transmission electron microscope images of the specimen of Fig. 1, showing periodic array of dislocations in the lath boundary. Some matrix dislocations are also visible.

Some matrix dislocations can also be observed in the TEM micrographs, and spiral-type image contrast characteristic of dislocations was also observed in matrix regions in the FIM; however, the density of matrix dislocations may have been reduced, or their configuration altered, by the action of the field stress applied during FIM imaging.

Atom probe analyses taken from the matrix and boundary regions of this specimen are summarized in Table II. The carbon content of the martensitic matrix, 0.14 at. pct, is lower by a factor of 7 than the nominal carbon content of the steel. This figure could underestimate the extent of carbon depletion in the

Table II. Summary of Atom Probe Analyses of Low Carbon Martensite Tempered for 10 Min at 150 °C

Matrix composition:	0.14 ± 0.04 at. pct C
2 nm diam region centered on lath boundary:	2.01 ± 0.2 pct C

matrix for two reasons: (i) if a dislocation with segregated carbon atoms were to have intersected the volume analyzed, and (ii) if some background signals were to have arisen from the dissociative adsorption of residual carbon monoxide on the specimen surface. Although both of these factors could increase the number of carbon signals recorded, their influence is thought to be small in this particular case. The boundary region shows substantial enrichment of carbon, with the overall analysis of the 2 nm diam area centered on the dark bank at the interface giving a carbon content of 2.01 at. pct, a factor of more than 14 higher than the matrix analysis. This value appears to be typical of a retained austenite film.[45]

3.2 High-Carbon Steel, Fe-0.64 at. pct Mn-3.47 at. pct C (Fe-0.65 wt pct Mn-0.78 wt pct C)

A neon field ion micrograph of a quenched and room-temperature aged, high carbon steel specimen having a twinned microstructure is shown in Fig. 3. The image reveals a series of parallel interfaces (arrowed), the traces of which correspond unambiguously to the $\{211\}_m$ twin habit plane. The distance between the twin interfaces, as measured from the micrograph, varies between 4 and 12 nm which corresponds well with the expected range of values for this microstructure. Our micrograph of the room-temperature aged martensite shows substantially more uniform contrast than those published previously by Sekhar and Richman[46] and Ranganathan and Grenga.[47] These previous observations were made using hydrogen as the imaging species, and it seems likely that the chemically active nature of this gas has resulted in some degree of preferential chemical reaction at the twin interfaces, thus altering the contrast locally.

A neon field-ion micrograph of a similar high carbon steel specimen tempered for 1 h at 160 °C is shown in Fig. 4. The twin interface regions appear much broader and darker than in the case of the specimens aged at room temperature. There are also traces of dark striations within some of the twins. This micrograph may also be compared with the hydrogen ion observations of Sekhar, Schreiner, and Richman[48] and Ranganathan and Grenga.[49,50] Sekhar *et al*[48] observed long, parallel, dark bands, generally similar to those reported here, whereas Ranganathan and Grenga[49,50] observed a rather different structure consisting of discrete, dark-imaging platelets lying on $\{001\}$ planes. This difference may be interpreted in terms of the nature of the martensitic substructure present before tempering. Thus the imaging regions of the specimens studied by Ranganathan and Grenga appear to have consisted predominantly of untwinned martensite, from which fine, matrix, carbides precipitated on tempering, whereas the majority of the specimens studied in the present work, and by Sekhar *et al*,[48] were initially finely-twinned. In this latter case, carbide precipitation at twin interfaces appears to be a major process during tempering, as noted previously in the TEM work of Kelly and Nutting,[51] and Tekin and Kelly.[37] The faint dark striations observed within the matrix of some of the twins in the micrograph of Fig. 4 probably correspond to the smaller matrix car-

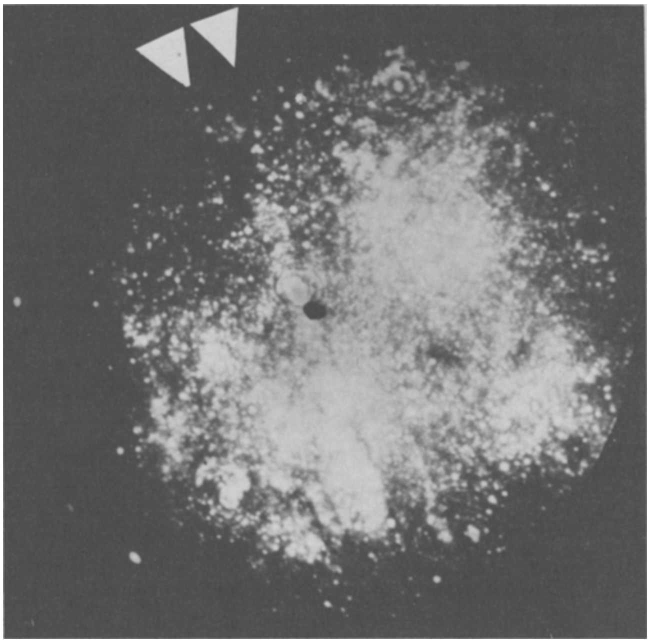

Fig. 3—Neon field ion micrograph of Fe-0.64 at. pct Mn-3.47 at. pct C (Fe-0.65 wt. pct Mn-0.78 wt. pct C) steel, quenched and aged at room temperature. The parallel lines in the image represent coherent twin interfaces. Imaging voltage 15.9 kV.

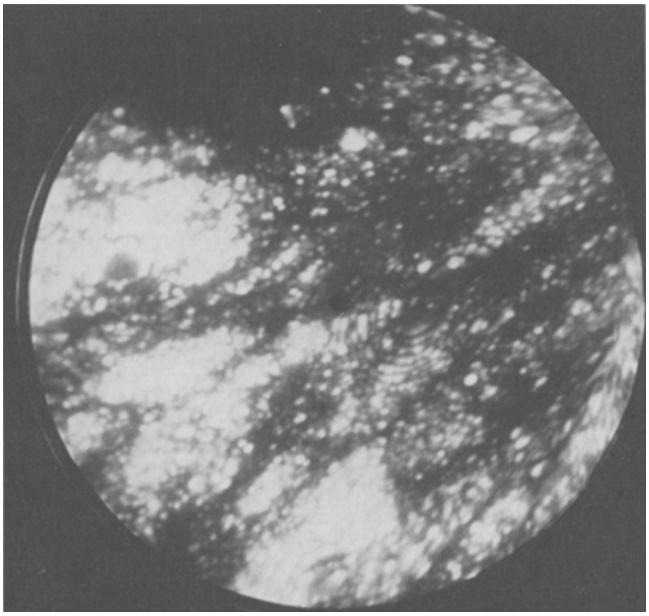

Fig. 4—Neon field ion micrograph of the steel of Fig. 3, quenched and tempered 1 h at 160 °C. The dark striations correspond to carbon-enriched regions at twin interfaces. Imaging voltage 10.4 kV.

bide precipitates, which were also observed by Kelly and Nutting.[51] The nature of the interface phase is not clear from the micrograph of Fig. 4, but the atom probe analyses, described below, clearly show an extensive build-up of carbon concentration at the twin interfaces during this stage of tempering.

A mass spectrum of the quenched and room temperature aged martensite is shown in Fig. 5. The peaks at mass to charge ratios (m/n) 6, 12, 18, 24 and 36 are all due to carbon, and correspond to the species C^{2+}, C^+ or C_2^{2+}, C_3^{2+}, C_2^+ and C_3^+, respectively. The iron peaks (Fe^{2+}) are located at m/n = 27, 28, 28.5 and 29. There are also minor peaks due to Si^{2+} at m/n = 14, 14.5 and 15, Cr^{2+} at m/n 25, 26, 26.5 and 27, and Mn^{2+} at m/n = 27.5. A summary of selected area chemical analyses of matrix and twin interface regions in fully twinned areas of room temperature aged specimens is given in Table III. These results show that the interfaces are strongly enriched in carbon. Assuming that all the carbon is located in the precise atomic plane of the interface, then the boundary enrichment factor (β) is 9 in this case, and the average carbon atom concentration in the plane of the interface is 24 at. pct. The matrix carbon concentration is depleted from the original level of 3.47 at. pct to 2.7 at. pct at this stage of ageing.

Mass spectra of the high carbon martensite tempered for 1 h at 160 °C show the same general features that are present in spectra of the room temperature aged material, including the multiple carbon peaks at m/n 6, 12, 18, 24 and 36. A summary of selective analyses of the twin interface and matrix regions is presented in Table IV. Comparison with the data for room temperature aged material shows that the segregation of carbon to the interface is substantially enhanced during this tempering to an average level of 8.7 at. pct within the area covered by the probe hole aperture. The matrix concentration of carbon is depleted by a further 45 pct compared to the concentration after room temperature ageing, giving an average level of 1.47 at. pct. This is in good agreement with the value calculated on the basis of X-ray lattice parameter measurements.[15]

Table III. Summary of Atom Probe Analyses of High Carbon Martensite Aged ~24 H at 20 °C

Matrix composition	2.7 ± 0.2 pct C
2 nm diam region centered on twin interface:	6.9 ± 0.4 pct C

Table IV. Summary of Atom Probe Analyses of High Carbon Martensite Tempered 1 H at 160 °C

Matrix composition	1.5 ± 0.3 pct C
2 nm diam area centered on twin interface:	8.7 ± 0.5 pct C

From the FIM micrograph of Fig. 4 it appears that the carbon-rich region at the twin interface extends to a thickness of 1 to 2 nm. This, together with the observation that fine precipitation has already commenced within the matrix suggests that carbide formation at the twin interfaces is occurring during this stage of tempering. However, the data are insufficient to identify the specific carbide phase (or phases) involved.

3.3 Carbon Atom Clustering (Fe-0.65 wt pct Mn-0.78 wt pct C)

The atomic-scale distribution of carbon within the microstructure can also be examined in terms of the grouping of carbon atoms in the evaporation sequence. Unfortunately, successive ions collected during the atom probe analyses do not necessarily originate from adjacent atomic sites, but may arise from any position covered by the probe hole aperture. A further difficulty exists concerning the shape and

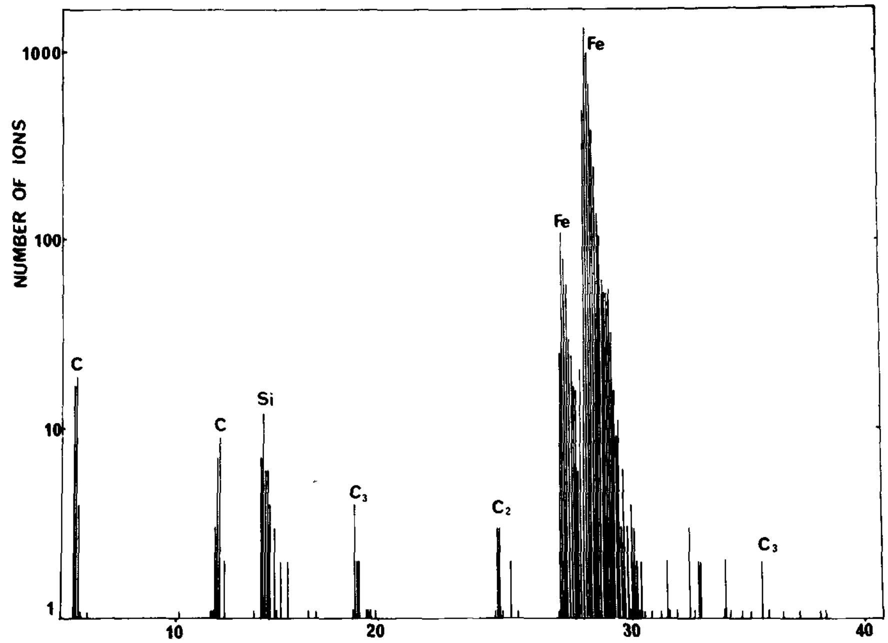

Fig. 5—Atom Probe mass spectrum of the high carbon steel of Fig. 3. The spectrum is plotted on a semi-logarithmic scale, to emphasize minor peaks.

orientation of any clusters which may be present. Clusters lying in the plane of the surface will be detected more readily than those lying normal to the surface, since in the latter case the atoms will be most unlikely to desorb in immediate succession. On balance, it appears that analyses of the field evaporation sequence will tend to underestimate the extent of any clustering phenomena, although a full statistical treatment of the situation has yet to be carried out. In the present paper, therefore, we restrict ourselves to a consideration of the desorption of molecular carbon species from the room-temperature aged high carbon martensite. Inspection of the mass spectrum of Fig. 5, shows that a large portion of the carbon evaporates in the form of molecular ions of the type C_2^{n+} and C_3^{n+}. The peak at m/n = 12 is ambiguous, as it can arise from either C_2^{2+} or C^+ species, or a mixture of both, but even assuming this peak to be composed entirely of C^+ ions, the overall proportion of carbon desorbing as molecular ions is approximately 50 pct from matrix regions, and in excess of 60 pct from twin interface regions. By comparison, the proportion of molecular ions evaporating from the cementite phase in pearlite, studied under identical experimental conditions, was found to be ~37 pct.[52] For the formation of molecular ions to occur, it would seem to be necessary for the atoms concerned to be in close proximity on the specimen surface. Hence, these results lend support to the view that carbon atoms form clusters during the room temperature ageing of high carbon martensites, although the possibility that surface diffusion processes may influence the observations cannot be totally ruled out (see below).

4. DISCUSSION

The atom probe results from the low carbon steel tempered for 10 min at 150 °C provide direct and convincing evidence for (a) a marked depletion in the carbon content of the martensite matrix, by about 85 pct with respect to the nominal concentration of carbon in the steel, and (b) a substantial enrichment of the carbon content in the region of a martensite lath boundary, by a factor of two with respect to the nominal content of the steel. The first of these observations clearly provides strong support for the interpretation of resistivity data in low carbon martensites given by Speich,[6] in terms of the removal of carbon atoms from solid solution by a process of segregation to lattice defects. The second observation shows that the interlath boundary regions form one of the possible areas to which carbon can segregate. A number of TEM investigations have established the presence of retained austenite films at such interfaces in quenched martensitic steels, with the stabilization of the austenite being attributed to either mechanical or composition effects, or a combination of both.[53,54] Attempts have been made[44] using the lattice imaging method to estimate the degree of carbon enrichment in retained austenite films, and these suggest that levels of 2.0 to 5.0 pct may be present. The atom probe results presented here indicate a carbon concentration at the lower end of this range, and imply that both carbon enrichment and mechanical stabilization are necessary for the preservation of stable austenite at and below ambient temperatures. This suggestion is made on the basis of very limited observations; further work is being carried out to substantiate these conclusions, and to determine at what stage the carbon segregation process occurs. Plain carbon steels of low carbon content have high M_s temperatures, and it is quite likely that at least part of the observed segregation takes place during the initial quench to room temperature. Further changes may occur during holding at room temperature, as well as during tempering. A series of parallel experiments is being carried out on iron-nickel-carbon martensites, to help resolve some of these issues.

In the case of the high carbon martensite, an extremely complex series of processes is evidently occurring and many of the details are still far from clear. Nevertheless, the present results demonstrate that twin interfaces play a significant role as segregation sites for carbon atoms after low temperature ageing (in agreement with the prediction of Tekin and Kelly[37]), and also that such interfaces provide suitable sites for carbide precipitation during tempering at temperatures as low as 160 °C. Thus the importance of microstructural features in determining the course of tempering reaction is considerable, even in steels of high carbon content.

A question which arises in the case of the high carbon steel, as for the low carbon material, concerns the extent to which the effects found may have taken place during the quenching process. The calculated M_s temperature for this particular high-carbon steel is 230 °C, and the transformation is 90 pct complete at a temperature of 130 °C. Reliable data for the diffusion of carbon in the body centered tetragonal structure of martensite are not available; however, figures obtained from internal friction studies of body centered cubic iron in the temperature range 50 to 150 °C give some indication of the magnitudes involved.[55] With $D_o = 0.394\ \text{mm}^2\text{s}^{-1}$ and $Q = 80.15$ kJ mole^{-1}, at a temperature of 230 °C, carbon atoms are able to move an average distance of 0.2 nm in 20 μs. The time required for this movement is increased to 2.5 ms at 130 °C. It is therefore clearly possible for some carbon atom migration to occur during the water quenching process. However, similar calculations show that at 20 °C the carbon atoms are still able to move through an average distance of 0.2 nm in a period of 20 s. Since the specimens were aged at room temperature for approximately 24 h before examination, it is likely that the majority of the redistribution process has occurred at room temperature. Studies of the kinetics of the room temperature ageing process in similar steels, for example by Roberts *et al*,[16] substantiate these conclusions, and further show that the rate of change in the microstructure becomes slower during the longer-term ageing at room temperature, indicating a gradual increase in the activation energy of the processes occurring.

Another migration process which could in principle contribute to the observed effects (particularly with regard to clustering and molecular ion formation) would be the diffusion of carbon on the surface of the specimen during analysis in the atom probe. It is difficult to quantify the possible extent of this process, but Klein[56] and Radon[57] have both shown by field emission microscopy that carbon is a very immobile adsorbate on another bcc metal (tungsten), even at the relatively high temperature of 800 K. The migration effect on iron is thus expected to be minimal at the cryogenic temperatures used in atom probe investigations. Also, the fact that we are able to observe large, stable concentration gradients of carbon over distances of a few nanometres, in the region of twin interfaces, implies that the extent of any diffusion processes on the specimen surface must be very small indeed. However, we cannot completely exclude the possibility that at least some of the carbon atoms may execute at least one jump on the specimen surface prior to evaporation, and thus it is necessary to be cautious at this stage in drawing detailed conclusions about the nature and extent of the carbon atom clustering processes occurring in the matrix. Since we observe between 50 and 60 pct of all the carbon atoms from the room-temperature aged material to desorb in the form of molecular ions—a proportion which is much higher than we observe during the field evaporation of cementite plates,[51] we conclude that qualitatively, at least, the atom probe results seem to indicate that significant clustering of carbon atoms has occurred in the matrix, and that the carbon atoms are probably in very close proximity to one another within these clusters. Further experiments are planned, involving the use of helium cooling of the specimens during analysis, and employing alloy martensites of lower M_s temperatures, in an effort to obtain some more detailed information about this process.

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REFERENCES

1. G. R. Speich and W. C. Leslie: *Met. Trans.*, 1972, vol. 3, p. 1043.
2. Y. Imai: *Trans. Japan Inst. Metals*, 1975, vol. 16, p. 721.
3. G. V. Kurdjumov and A. G. Khachaturyan: *Met. Trans.*, 1972, vol. 3, p. 1069.
4. G. V. Kurdjumov: *Met. Trans. A*, 1976, vol. 7A, p. 999.
5. P. G. Winchell: *Proc. Intl. Conf. on Martensitic Transformations (ICOMAT 79)*, Cambridge, Mass., 1979, p. 547 (publ. M. I. T.).
6. G. R. Speich: *Trans. TMS-AIME*, 1969, vol. 245, p. 2553.
7. V. I. Sarrak and S. O. Suvorova: *Phys. Met. Metallogr.*, 1968, vol. 26, no. 1, p. 143.
8. L. I. Lysak and Ya. N. Vovik: *Phys. Met. Metallogr.*, 1965, vol. 19, no. 5, p. 52.
9. G. V. Kurdjumov and L. K. Mikhaylova: *Phys. Met. Metallogr.*, 1966, vol. 22, no. 6, p. 129.
10. L. I. Lysak and L. O. Andrishchuk: *Phys. Met. Metallogr.*, 1969, vol. 28, no. 2, p. 166.
11. L. I. Lysak, N. A. Storchak, and A. G. Drachinskaya: *Phys. Met. Metallogr.*, 1977, vol. 43, no. 3, p. 138.
12. L. I. Lysak, V. Ye. Danil'chenko, Yu. M. Polischuk, and A. I. Ustinov: *Phys. Met. Metallogr.*, 1976, vol. 41, no. 2, p. 108.
13. G. V. Kurdjumov and L. Lysak: *J. Tech. Phys. USSR*, 1949, vol. 19, p. 525 and *J. Iron & Steel Inst.*, 1947, vol. 156, p. 29.
14. P. C. Chen: Ph. D. Thesis, Purdue University, May 1979.
15. C. S. Roberts, B. L. Averbach, and M. Cohen: *Trans. ASM*, 1953, vol. 45, p. 576.
16. P. G. Winchell and M. Cohen: *Trans. ASM*, 1962, vol. 55, p. 347.
17. H. Gerdien: *Arch. Eisenhuttenw.*, 1959, vol. 30, p. 673.
18. G. Eldis: Ph. D. Thesis, Massachusetts Institute of Technology, 1971.
19. A. M. Sherman: Ph. D. Thesis, Massachusetts Institute of Technology, 1972.
20. V. I. Izotov and L. M. Utevskiy: *Phys. Met. Metallogr.*, 1968, vol. 25, no. 1, p. 86.
21. A. G. Khachaturyan: *Fiz. Tverd. Tela.*, 1967, vol. 9, p. 2861.
22. A. G. Khachaturyan and T. A. Onisimova: *Phys. Met. Metallogr.*, 1968, vol. 26, no. 6, p. 12.
23. S. Nagakura, K. Shiraishi, Y. Hirotzu, A. Ono, and H. Yotsumoto: *Electron Microscopy 1974*, vol. 1, p. 664 (*Proc. 8th Intl. Congr. Electron Microscopy*, Canberra, Aug.–Sept. 1974). Publ. Australian Academy of Science, Canberra, Australia.
24. S. Nagakura, K. Shiraishi, and Y. Hirotsu: *Trans. Japan Inst. Metals*, 1975, vol. 16, p. 601.
25. S. Nagakura and M. Toyoshima: *Trans. Japan Inst. Metals*, 1979, vol. 20, p. 100.
26. A. K. Sachdev: Ph. D. Thesis, Massachusetts Institute of Technology, 1977.
27. M. Toyoshima and S. Nagakura: *Proc. Intl. Conf. on Modulated Structures*, Hawaii 1979, p. 263 (publ. Amer. Inst. of Physics).
28. J. R. Genin and P. R. Flinn: *Trans. TMS-AIME*, 1968, vol. 242, p. 1419.
29. W. K. Choo and R. Kaplow: *Acta Met.*, 1973, vol. 21, p. 725.
30. N. DeCristofaro and R. Kaplow: *Met. Trans. A*, 1978, vol. 8A, p. 35.
31. N. DeCristofaro, R. Kaplow, and W. S. Owen: *Met. Trans. A*, 1978, vol. 9A, p. 821.
32. R. A. Johnson: *Acta Met.*, 1965, vol. 13, p. 1259.
33. R. A. Johnson: *Acta Met.*, 1967, vol. 15, p. 513.
34. F. E. Fujita, C. Shiga, T. Moriya, and H. Ino: *J. Japan Inst. Metals*, 1974, vol. 38, p. 1030.
35. C. Shiga, M. Kimura, and F. E. Fujita: *J. Japan Inst. Metals*, 1974, vol. 38, p. 1037.
36. C. Shiga, F. E. Fujita, and M. Kimura: *J. Japan Inst. Metals*, 1975, vol. 39, p. 1205.
37. E. Tekin and P. M. Kelly: "Precipitation from Iron Based Alloys", G. R. Speich and J. B. Clark, eds., 1963, p. 173. AIME Metallurgical Society Conference Series, vol. 28.
38. E. W. Muller, J. A. Panitz and S. B. McLane: *Rev. Scient. Instrum.*, 1968, vol. 39, p. 83.
39. M. K. Miller, P. A. Beaven, R. J. Lewis, and G. D. W. Smith: *Surface Sci.*, 1978, vol. 70, p. 470.
40. P. A. Beaven, M. K. Miller, and G. D. W. Smith: *Proc. Intl. Conf. on Martensitic Transformations, ICOMAT 79*, Cambridge, Mass, 1979, p. 559 (publ. M. I. T.).
41. (a) M. K. Miller: D. Phil. Thesis, Oxford University 1977; (b) M. K. Miller, P. A. Beaven, and G. D. W. Smith: *Surface and Interface Analysis*, 1979, vol. 1, p. 149.
42. P. A. Beaven, M. K. Miller, and G. D. W. Smith: Proc. "Phase Transformations" York, 1979, vol. 2, pp. 1, 12–14. Inst. of Metallargists, Conf. Series 3, No. 11, London 1979.
43. P. F. Mills: D. Phil. Thesis, Cambridge University, 1980.
44. B. V. N. Rao and G. Thomas: *Proc. Intl. Conf. on Martensitic Transformations, ICOMAT 79*, Cambridge, Mass., 1979, p. 12 (publ. M. I. T.).
45. S. Barnard, G. D. W. Smith, M. Sarkara, and G. Thomas: *Scri. Met.*, 1981, no. 4, in press.
46. P. C. Sekhar and M. H. Richman: *Metallography*, 1971, vol. 4, p. 133.
47. B. N. Ranganathan and H. E. Grenga: *Phil. Mag.*, 1972, vol. 26, p. 265.

48. P. C. Sekhar, M. R. Schreiner and M. H. Richman: *Metallography*, 1971, vol. 4, p. 147.
49. B. N. Ranganathan and H. E. Grenga: *J. Microscopy* (London), 1973, vol. 98, p. 49.
50. B. N. Ranganathan and H. E. Grenga: *Phil. Mag.*, 1974, vol. 30, p. 161.
51. P. M. Kelly and J. Nutting: *J. Iron and Steel Inst.*, 1961, vol. 197, p. 199.
52. M. K. Miller and G. D. W. Smith: *Metal Science*, 1977, vol. 11, p. 249.
53. B. V. N. Rao, R. W. Miller and G. Thomas: *Proc. Intl. Conf. Heat Treatment*, 1976, The Metals Society, London, p. 75.
54. H. K. H. D. Bhadeshia and D. V. Edmonds: *Proc. Intl. Conf. on Martensitic Transformations, ICOMAT 79*, Cambridge, Mass., 1979, p. 28.
55. A. E. Lord and D. N. Beshers: *Acta Met.*, 1966, vol. 14, p. 1659.
56. R. Klein: *J. Chem. Phys.*, 1953, vol. 21, p. 1177.
57. T. Radon: *Acta Phys. Polonica*, 1976, vol. A50, p. 3.