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THE TEMPERING OF MARTENSITE IN AN IRON 1.5% NITROGEN ALLOY

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ABSTRACT

The tempering of iron 1.5% nitrogen martensite has been studied at temperatures up to 300°C using X-ray and electron microscope techniques. Stage 1 decomposition occurs below 270°C by the general precipitation, resembling spinodal morphology, of fine $\alpha''$ ($\text{Fe}_{16}\text{N}_2$) lamellae on {001} habit planes in both matrix and twin crystals of the partially {112} twinned martensite plates. Yet, gauged by changes in the X-ray spectrum, the reaction is discontinuous, the tetragonal martensite doublets decaying in intensity without change in their Bragg positions. The anomaly and the failure to detect by electron microscopy regions exhibiting fractional stages of the fine scale $\alpha' \rightarrow \alpha + \alpha''$ reaction is attributed to its occurrence at different times in different martensite (or parts of martensite) plates. It is believed that transformation occurs in this manner because the nucleation of coherent $\alpha''$ plates is controlled by the prevailing internal stress field. Thus the time exponent "n" for the reaction decays from a normal value between 1 and 0.67 to less than 0.3 as stress relief by recovery dominates the more protracted stages of the reaction.

Above 200°C the more stable nitride $\gamma'$ ($\text{Fe}_4\text{N}$) forms at an increasing rate as plates on {012} habit planes, accompanied by marked softening.

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INTRODUCTION:

Although there is a voluminous literature on the tempering of iron-carbon martensite, 1-7 comparatively little attention has been given to the behavior of the analogous iron-nitrogen alloys. This is surprising in view of the structural simplicity of both the transition and the equilibrium nitrides which form during the first and third stages respectively of the tempering of iron-nitrogen martensite. A tetragonal intermediate precipitate, Fe₄₆N₂ or α'' with a = 5.72Å, c = 6.29Å, was first identified by Jack 8,9 who detected its presence only on tempering below 200°C. Above this temperature, nitrogen martensite was presumed to decompose directly into ferrite and the face centered cubic nitride, Fe₄N or γ'.

The work reported here consists of a microstructural study of the precipitation processes during the tempering of a quenched (nominally) 1.5 wt.% nitrogen alloy. Such a nitrogen rich composition was chosen because the X-ray spectrum of the resulting martensite displays clearly separated tetragonal doublets ⁸,¹⁰ whose decay could be used to assess the progress of first stage decomposition. This composition also avoids the duplication of a recent study of the tempering of iron-nitrogen massive martensite. ¹¹ As the parent (α') and transition (α'') phases exhibit essentially the same type of tetragonal symmetry the system is of theoretical interest in that martensite containing approximately half the solute content of the precipitate may conceivably display spinodal characteristics during the initial stage of its decomposition.
EXPERIMENTAL PROCEDURE

Specimens of pure iron supplied by the National Physical Laboratory in the form of sheet 0.005 in. (0.125mm) thick were nitrided for >3 hr in ammonia/hydrogen gas mixtures at 730°C to give a homogeneous austenite structure before being directly quenched into water at room temperature. After treatment in liquid nitrogen to reduce the retained austenite content, the specimens were tempered in oil or salt baths as soon as possible after the nitriding treatment.

For optical metallography and micro-hardness measurements the specimens were mounted in cold setting resin. Those for X-ray or electron microscope examination were thinned chemically to ~0.002 in. (0.050 mm) thickness in HF/H$_2$O$_2$ solution before (a) mounting in an X-ray diffractometer equipped with a crystal monochromator or (b) thinning was continued by electropolishing in chromic/acetic acid mixtures using the standard window or disc jetting techniques. The foils obtained were examined in a number of electron microscopes including an A.E.I. EM6, a Siemens Elmiskop IA, both operated at 100 kV, and a Hitachi HU 650 operated at 650 kV.

RESULTS

Structure of the martensite as quenched

Optical examination of quenched specimens showed that the martensite was of the acicular variety$^{10}$ (Fig. 1), the larger first-formed plates displaying straight mid-ribs and distinctly irregular outlines. In some instances (as at A in Fig. 1) the mid-rib could be seen to consist of a band possessing a finite width (~1μm) with a tendency along part of its length to exhibit ragged, parallel off-shoots.
Electron microscopy proved that the martensite plates were partially twinned and dislocated, the mid-rib bands consisting of a parallel array of very fine (112) type twins (Fig. 2) which in foils of suitable orientation give rise to pronounced streaking in the selected area electron diffraction patterns. The streaking is a particle size effect arising from the small widths (< 15Å) of the twins which frequently were spaced no more than ~40Å apart. Other fainter linear markings also occurred in the large martensite plates either extending outward from the mid-ribs or inwards from the plate boundaries. Both types are visible in Fig. 2 which shows two twin related grains B and C in <111>T_P orientation separated by the twin boundary GH, which like the mid-rib EF of grain C lies along a <101> direction in the foil plane. The orientation of the neighboring grain A is such that individual dislocations can be resolved in its structure.

The markings extending from the mid-rib in grain C (trace T_1, Fig. 2) coincide with the traces of the (112) twins constituting the mid-rib and as discussed by Shimizu, Oka and Wayman\textsuperscript{12} are believed to be due to slip. Those originating at the grain boundary (GH) between the twin related martensite grains (traces T_2, T_3 and T_4) represent planar defects on (101) planes in the relevant grains. They are likely to arise from (101) type twins now recognized to occur in tetragonal high carbon martensite.\textsuperscript{13,14} However, the very faint extension of the T_4 trace into grain C coincides with the trace of a (110) martensite plane and is considered to be due to slip which accommodates the (101) twinning in the neighboring grain B.

Twinning in the smaller martensite plates which form at later stages
in the transformation process was predominantly of the (112) type but in such plates the twins were more irregularly distributed and spaced. These microstructures are typical of partially twinned martensite plates as discussed fully in a recent review (Ref. 14).

An interesting feature of the nitrogen rich martensite was that in certain foil orientations (-<111>) the material was so magnetically hard that the field of the objective lens was insufficient to eliminate the magnetic domain boundaries. These became visible on defocussing the objective with the specimen mounted in the normal position using a standard holder, and examples of such domain contrast are visible at x in Fig. 6a. It should be noted that the widths of the domains could be altered by tilting slightly the specimen in the objective lens field. Discontinuities in the magnetic domain boundaries often delineated the profiles of the mid-ribs.

**The X-ray assessment of decomposition during tempering.**

The region of the X-ray spectrum containing the martensite doublets consisting of a combined (101)/(011)α' and the separate (110)α' reflections proved to be the most sensitive for observing the decomposition of the super-saturated solid solution during tempering. At 200°C (Fig. 3a) the (101)/(011)α' martensite peak quickly collapsed without change of its reflecting position, its decay being accompanied by the appearance of a weaker combined (202)/(022)α'' reflection from the tetragonal nitride phase (Fe₁₆N₂) at a slightly lower Bragg angle. Thus, in the manner of high carbon martensites, stage 1 tempering proceeds discontinuously in the sense that the (101)/(011)α' reflection does not move towards the (110) peak as might be expected for a homogeneous process in which
solute is drained progressively from the matrix. The change is more clearly visible in Fig. 4(a) which represents stage 1 decomposition at the lower temperature of 150°C.

With longer tempering at 200°C, the (202)/(022)α' peak attained a maximum after which its intensity declined as the (111)α' reflection from the stable Fe₄N nitride appeared at a still lower Bragg angle. The times for the respective (202)/(022)α" and (111)γ' peaks to attain maximum intensity on tempering in the range 150-300°C are plotted in Fig. 3b, which provides a crude time-temperature-transformation diagram. No great significance can be attached to the slopes of these lines since peak intensity is related to the particle size of the precipitate as well as its volume fraction. However, the results show that when small specimens are reheated rapidly, the intermediate α" precipitate persists in the structure to temperatures well above 200°C.

More precise data on the rate of decomposition during stage 1 tempering were obtained by studying the decline in intensity of the combined (101)/(011)α' martensite peak at temperatures of 150°C (Fig. 4(a)) and below. In these measurements, the line profiles were recorded by step scanning, the same specimen being successively tempered for longer times to construct an isothermal reaction curve. Results obtained in this way are presented in Fig. 4(b), the fraction transformed being given by the expression

$$f(t) = \frac{I_q - I_t}{I_q}$$ .......................... (1)

where \(I_q\) is the integrated intensity of the combined (101)/(011)α' martensite peak in the quenched condition and \(I_t\) the integrated intensity
after tempering for time \( t \). These quantities were obtained from the areas under the \((101)/(011)a'\) peaks after allowing for the overlapping tails of the neighboring \((202)/(022)a''\) and the combined \((110)a + (220)a'' + (110)a'\) peaks. In each case, this was done by subtracting a reflected profile of the interfering peaks. Minor variations arising from changes in the area irradiated on repositioning the specimen in the diffractometer were corrected by normalizing against the total intensity of all \(a, a''\) and \(a'\) peaks in this region of the spectrum. Both procedures may be criticized since the latter ignores loss of intensity through diffuse scattering whereas the former tends to overestimate the extent of the reaction in its later stages. Good agreement between the X-ray reaction curves and the change in resistivity observed by Brough\(^{16}\) in wires containing 1.45\% nitrogen suggests that the errors introduced are small.

A reciprocal rate plot of the data for a constant fraction of \(a'\) transformed, yielded an average activation energy, for stage 1 tempering of 28,600 cals/grm atom, a value in close agreement with that reported by King and Glover\(^{17}\) for the tempering of an iron 1.3 wt.% carbon alloy. For the reasons stated, the experimental precision does not merit a more detailed kinetic analysis, a conclusion supported fully by the electron microscope study.

Since the tempering of iron-carbon martensite is characterized by anomalously low values of the exponent "\(n\)", \((-\frac{1}{3})\),\(^{15,18}\) in a reaction equation of the form

\[
f(t) = 1 - \exp(-kt^N)
\]

the X-ray results were replotted in a form in which \(n\) is obtainable directly from the slopes of the graphs as is shown in Fig. 5. It will
be seen that the lines are curved, the exponent tending to decrease from a value between $\frac{2}{3}$ and 1 in the initial stages to less than $\frac{1}{3}$ as decomposition proceeds.

**Electron microscope observations of stage I tempering**

Whilst no appreciable change could be detected in the appearance under the optical microscope of specimens tempered below ~200°C, examination under the electron microscope showed that those tempered to peak (202)/(022)\(\alpha''\) X-ray line intensity had developed a duplex structure of lamellae of the transition nitride, \(\text{Fe}_16\text{N}_2\), in a matrix of low nitrogen content (Figs. 6a and b). Both magnetic domain boundaries (X) and precipitate lamellae (Y) are visible in Fig. 6a whilst dark striae in the \(\alpha''\) phase shown in Fig. 6b suggests that the lamellae are subject to non-uniform strains. In this respect the indentation hardness (and presumably the magnetic hardness) remained high until \(\gamma'\) formation (stage 3) was underway (Fig. 7).

The occurrence of stage 1 tempering was easily detected in the electron diffraction patterns by the presence of faint extra spots at positions midway between those of the matrix and the central beam (Fig. 6c). These reflections arise because the \(\text{Fe}_16\text{N}_2\) unit cell is approximately twice as large as that of \(\alpha\) iron. In the \langle110\rangle directions of this pattern the (220) precipitate and (110) matrix spots coincide but along the "c" axial direction of the tetragonal precipitate there is clear separation between the (004) \(\alpha''\) and (002) matrix reflections. Only when doublets of this type could be resolved, were clear images of the \(\alpha''\) lamellae obtainable in the electron optical images. This is because there is lattice parallelism between the tetragonal structures of martensite and the precipitate which, as reported for martensite of lower nitrogen...
content,\textsuperscript{11} adopts (001) $\alpha''$ habit planes. In other foil orientations overlapping images of the $\alpha''$ plates are thus likely to occur at relatively small deviations of the plates from the vertical owing to the high volume fraction of the precipitate ($\sim 50\%$).

Clarity of the bright field images was also masked by complex strain field contrast arising from multiple beam diffraction. This was obviated by recourse to dark field techniques which facilitated the trace analysis of the precipitate. An example of the many carried out is shown in the bright field/dark field pair in Fig. 8a-d, which includes the relevant stereographic analysis.

The high magnification micrographs of the tempered condition presented thus far are from untwinned regions although it will be realized from Fig. 6a that the lengthwise growth of $\alpha''$ lamellae is restricted by twin bands (see region Y). A more detailed appreciation of the influence of \{112\} twins may be gained from Fig. 9a-d in which dark field micrographs using selected reflections reveal that $\alpha''$ plates form on the expected (001) $\alpha'$ habit planes in both the parent and twin lattices.

The fact that the morphology and habit of the $\alpha + \alpha''$ precipitation seems to be independent of martensite substructure suggests that the reaction \textit{in this sense} is homogeneous and is similar to the spinodal reaction. However, as is shown later, the reaction cannot proceed at the same time in all plates.

No examples of \{101\}$\alpha'$ twinning were found in specimens tempered to the completion of stage 1, an observation suggesting that defects of this type disappear early in the reheating process as tetragonality is lost due to precipitation of $\alpha''$.\textsuperscript{12}
Partial decomposition during stage 1 tempering

The previous micrographs of stage 1 tempering represent decomposition at or above 200°C for times when the \((202)/(022)\) reflection X-ray line attains maximum intensity. For the earlier stages a more sensitive measure of decomposition is provided by the decay of the \((101)/(011)\) reflections in the X-ray spectrum, as given in Fig. 4b. Use of these data permitted foils to be examined in various partially transformed states. As expected, reducing the tempering temperatures and times produced much finer precipitates which, however, remained lamellar in appearance whilst still adopting \((001)\) habit (Fig. 10). As before, these micrographs were taken from regions in which the \(\alpha''\) plates were normal to the plane of the foil, an orientation ensured by the presence of doublet \(\alpha''-\alpha\) reflections in the electron diffraction patterns (Fig. 10c).

An interesting feature of Figs. 10b and c is that despite the X-ray indication of only ~50% transformation at this time, no trace is visible in the selected area electron diffraction pattern of the \((002)\) reflection from the residual parent martensite. For partial decomposition, this would be expected to occur in an intermediate position between the \((004)\) and \((002)\) matrix spots. Numerous other foils were examined in various stages of decomposition but in no instance were triplet reflections of the type \((004)\) \(- (002)\) \(- (002)\) observed. This absence and the appearance of the electron optical images led us to conclude that in all regions characterized by precipitate/matrix doublets transformation was sensibly complete. However the X-ray data are obtained from considerably larger volumes than the electron diffraction patterns. Thus the X-ray results indicate that in some areas \(\alpha'\) has not yet transformed whereas
in others transformation is complete.

Alternatively, it is possible that during electron microscope observations, tempering is accelerated in thin foil specimens subject to bombardment in the electron beam. This possibility was investigated by examining specimens aged for various periods at room temperature where the reaction proceeds very slowly (Fig. 4b). No extra $\alpha''$ reflections were detected in foils prepared soon after water quenching despite prolonged exposure to 100 kV electrons. However, in specimens aged to -30% transformation (6 months at 25°C) both matrix/$\alpha''$ doublets and faint $\alpha''$ reflections in the mid-positions arising from the doubly large Fe$_{16}$N$_2$ cell were detectable in a proportion of the grains in the foil. Both the precipitate and matrix reflections at this stage were diffuse but not sufficiently to mask the fact that the doublet intensity maxima occurred at the positions expected for an (004)$_{\alpha''}$/002$_{\alpha}$ pair (e.g. as in Fig. 10c). We deduce from these observations that the tempering reaction proceeds at different times in different grains, a finding which largely accounts for the apparently discontinuous character of the reaction as judged by the behavior of the Debye-Scherrer X-ray spectra. Doubts concerning the heating effect of the electron beam were finally dispelled when it was found that $\alpha''$ reflections could be present or absent in patterns taken from relatively small neighboring martensite plates.

Generally, in room temperature aged specimens the lowest order $\alpha''$ reflections were too weak and diffuse to give satisfactory dark field images. However, the fine, lamellar nature of the precipitate on (001)$_{\alpha'}$ habit planes was confirmed by imaging with the (004)$_{\alpha''}$/002$_{\alpha}$ doublet reflections, as in Fig. 10d. Here it will be seen that $\alpha''$ plates formed
at room temperature are ~30-50Å in width and that some of the martensite grains exhibit two sets of intersecting \{101\}_a twins.

Two points require final comment concerning the initiation of stage 1 decomposition. Despite intensive search, not only were no examples of partially transformed martensite plates detected but no evidence was found in the electron diffraction patterns of \{001\}_a' streaking, as might be anticipated in the early stages of \(\alpha''\) growth when the plates are very thin. In our view, this is because a metastable condition is imposed on the untransformed regions by a constraint on nucleation which, once lifted, results in a rapid particle growth over a small time interval. The fine platelet stage associated with streaking is thus too short lived to be easily detected. In this sense the reaction is morphologically similar to the spinodal reaction.

Secondly, exposure of a foil to 650 kV electrons undoubtedly accelerates stage 1 decomposition because of accelerated diffusion associated with knock-on damage (the threshold for iron is ~430 kV). This can be seen from the bright field/dark field micrographs in Fig. 11 which is from a specimen aged for 6 months at room temperature. The sequence was taken in a 100 kV microscope from a foil examined previously at 650 kV. The relative coarseness of the \(\alpha''\) lamellae, which are 100/150Å wide, may be gauged by comparison with Fig. 10d. The (002)_\(\alpha\) type reflections from the wider lamellae were also sufficiently strong to give an acceptable dark field image (Fig. 11b), which shows a curious intersection of the \(\alpha''\) plates by dark lines not visible in the (101)_\(\alpha\) image (Fig. 11c). The lines are thought to be antiphase domain boundaries in Fe_{16}N_2 caused by a shift in the regular interstitial sites occupied
by the nitrogen atoms by \( \frac{1}{4}[111] \) to the next near neighbor interstice positions. Such a displacement would be invisible in the \( (101) \) image since the vector lies in this plane but not in that formed by the \( (002) \) reflection.

**Stage 3 tempering**

The final stages of tempering involving the formation of the cubic nitride, Fe₄N or \( \gamma' \) (stage 3), occur at an increasing rate above 200°C (Fig. 3b). Under the optical microscope, the change is accompanied by a tendency for the martensite to become rapid etching, although the conversion to \( \gamma' \) in the larger martensite plates proceeds in a heterogeneous manner (Fig. 12). Thus, transformed regions spread inwards from the plate boundaries or outwards from the mid-ribs in those martensite plates displaying the latter feature.

Under the electron microscope, \( \gamma' \) was found to be platelike in form in fully tempered specimens (Fig. 13a), the boundaries of the \( \gamma' \) plates being much straighter than those of the \( \alpha'' \) phase. An approximate orientation relationship of the Kurdjumow and Sachs type was found to exist between the lattices of \( \gamma' \) and the ferritic matrix, (Fig. 13b), while use of the dark field technique revealed that defects are present in the \( \gamma' \) lattice along traces of \( \{111\} \), planes (Figs. 13c and d). The frequent streaking of \( \gamma' \) reflections in <111>\( \gamma' \) directions suggests that these defects may be stacking faults, or twins. A similar striated substructure in Fe₄N precipitated from ferrite has been reported by Pitsch.¹⁹

Trace analysis of the \( \gamma' \) plates to establish their habit planes presented difficulties once it became clear that the solution did not correspond to a simple pole at the corners of the stereographic unit
triangle. Within the limitations of a single surface analysis, the data were most satisfactorily accounted for by a solution of the form \( \{012\}_\alpha \), which is the habit plane reported to exist for the precipitation of plates in ferrite.\(^{19,20}\) A typical analysis is presented in Fig. 14, chosen because it shows the intersection of two separate colonies of \( \gamma' \) plates. Despite a superficial resemblance to cellular precipitation revealed by this micrograph (and also by the light optical micrograph of Fig. 12), the mechanism of precipitation involved is clearly different as the orientation of the matrix is common to both colonies. Such behavior appears to be conditioned by preferential \( \gamma' \) nucleation which was observed to occur at martensite grain boundaries and mid-ribs with the subsequent growth into the \( \alpha + \alpha'' \) matrix of parallel arrays of Widmanstatten sideplates from these sites.

**DISCUSSION**

**Stage 1. Tempering of iron-carbon martensites**

Theoretical understanding of the kinetics of the stage 1 tempering of iron-carbon martensites has been hampered by the conflicting requirements of (1) the discontinuous nature of the changes in the X-ray spectra\(^{15,21}\) and (2) the relatively low value of the time exponent \( n' \), \((-\frac{1}{3})\), when the reaction is analyzed by means of a reaction equation of the Johnson-Mehl type.\(^{15,22}\) A discontinuous change in the X-ray spectra is normally associated with a cellular or two-phase type precipitation process for which the corresponding values of the time exponent tend to be high \((3-4)\).\(^{23}\) On the other hand, for fine scale, continuous precipitation, an \( n' \) value of \( \frac{3}{2} \) has been predicted theoretically for spheroids of any shape (plates, needles, spheres) provided that all nuclei are present at the start of
the reaction when \( t = 0 \).

Various hypotheses have been presented to overcome these difficulties as improved techniques have become available for (a) assessing quantitatively the degree of martensite decomposition and (b) observing the fine structure of both the precipitate and parent phases. The original reports that \( n = 0.30 \) during stage I tempering based on dilatometric measurements\(^{15}\) of alloys varying from 0.6 to 1.4% in carbon content, prompted the suggestion of a physical model in which it was postulated that the \( \epsilon \) transition carbide and low carbon martensite grow as an aggregate behind a planar front. Carbide nuclei were considered to be present from the moment of quenching, at interfaces formed by the second, inhomogeneous shear of the martensite transformation. With the reaction controlled by the diffusion of carbon down the steep concentration gradients which form each side of these planes, a theoretical equation was deduced containing a time exponent of \( n = \frac{1}{2} \). A reaction of a discontinuous nature with a low exponent thus became possible provided that the preferential precipitation sites are well separated, a contention seemingly supported by the later observation using replica techniques of carbide precipitation at sub-boundaries in the martensite.\(^{18}\)

However, despite a reassessment of the experimental data\(^{22}\) the discrepancy between the experimental \( \frac{1}{3} \) and the theoretical \( \frac{1}{2} \) values of '\( n \)' persisted which led to the formulation of a new theory for the reaction based on the attraction of solute atoms by the stress fields of a planar array of edge dislocations.\(^{22}\) Whilst yielding the required \((\text{time})^{1/3}\) law, denudation of solute atoms by this means may be expected to predominate at the initial stages of decomposition which were not covered
by the dilatometric tests since there was a delay of 30 minutes before
the first measurements were made.

More recently, electrical resistance has been employed\(^{17,5}\) to
observe decomposition, enabling changes to be recorded within a short
time of the start of tempering. Although there are problems in correlating
this parameter with the fraction transformed, it is now clear that 'n'
values larger than \(\frac{1}{3}\) may characterize the initial stages of the reaction.\(^5\)
This finding led to the affirmation of a diffusion controlled model in terms
of \(e\) carbide precipitation on transformation twin interfaces spaced
\(\sim 500\) Å apart. Choice of the latter dimension was justified by reference
to transmission electron microscope studies in which \(Fe_3C\) precipitation
at twin interfaces in martensite had been observed. However, the
possibility of smaller spacings was admitted rendering it increasingly
difficult to justify the explanation advanced previously for the
discontinuous character of the change in X-ray spectrum, a problem tacitly
ignored by Wilson and Owen in the discussion of their paper.\(^5\)

With the greater precision obtainable by resistivity methods, it
was also established that the activation energy for stage 1 tempering is
dependent on the carbon content of the steel,\(^{17}\) the observed increase
over that for the diffusion of carbon in ferrite being attributed by
Hillert\(^{24}\) to the tetragonal lattice distortion. This conclusion, however,
disregards possible short-circuiting effects arising from the high defect
density in martensite and conflicts with the known decrease in activation
energy with carbon content for the diffusion of that element in austenite.\(^{25}\)

Variation in activation energy \((Q)\) with the extent of stage 1
decomposition is another complication,\(^{24}\) changes of this nature being
reported both in plain carbon and chromium bearing low alloy steels.\textsuperscript{5,26,27} Whereas $Q$ appears to increase during the initial stages of the reaction at low temperatures ($<120^\circ$C), lower and decreasing values are claimed for more advanced transformation (10-30\%) at higher temperatures.\textsuperscript{5} These observations are difficult to understand and make dubious any simple correlation with the activation energy for interstitial diffusion in martensite.

\textbf{Stage 1 tempering of iron-nitrogen martensite.}

It is against this background of prior work on iron-carbon martensite that the results of the present investigation must be interpreted. The mode of $\alpha''$ precipitation observed at all temperatures in nitrogen rich martensite is on a relatively fine scale, with the spacings between the lamellae formed at room temperature $<50\AA$. Yet the changes in X-ray spectra are clearly discontinuous, with the slope of the reaction curve in its later stages tending to the low 'n' values that characterize the stage 1 tempering of iron-carbon martensite. Evidently none of the theoretical models proposed previously will satisfy the conflicting requirements of the relatively macroscopic X-ray results and the micro-structural changes revealed under the electron microscope.

The solution to this dilemma is to be found in the observation that the reaction does not proceed at the same time in all martensite crystals (and possibly also in parent and twinned regions of a given crystal). With the acceptance of this new concept of a heterogeneous reaction the difficulty of associating a discontinuous change in the X-ray spectra with a fine precipitate structure immediately disappears. Thus the decay in the (101)/(011)$\alpha'$ X-ray line intensity is simply an
indication of the number of martensite plates (or portions of a plate) in which decomposition has not been triggered. Once initiated it is probable that the reaction proceeds relatively rapidly, which would account for the inability to detect partially transformed grains in the electron diffraction patterns. At room temperature, random walk of nitrogen in ferrite over a distance of $50\text{A}$ occurs in $\sim 10^3$ seconds.

The explanation for this unexpected behavior — all theoretical treatments presume that individual martensite grains transform at the same rate from the start of tempering — is to be found in the effect of stress on the nucleation of coherent $\alpha''$ precipitates. The inhibiting and accelerating effects of compressive and tensile stress fields respectively on the precipitation of $\alpha''$ from ferrite has recently been demonstrated and a theory postulated in which an elastic strain energy term adds to or subtracts from the normal activation energy for homogeneous nucleation. In these tests, the stresses applied were relatively low ($\sim 13,000$ psi) and well below both the macro and micro internal stresses found in quenched steels. Those in the latter category, which may fluctuate between one martensite plate and the next, have been reported to be as high as $200,000$ psi, generally exceeding the long range internal stresses by a factor of 2-5.31

Since the nucleation frequency is a logarithmic function of the stress, the internal stresses in quenched martensite may be expected to have a much more intense effect than those applied to ferrite of low yield stress. We thus envisage that internal stresses of a compressive character exceeding some critical value will effectively prevent $\alpha''$ formation until such time as the stress has relaxed to below this point. In ferrite, a stress of 13,000 psi is predicted to change the nucleation
The stress concerned is that which acts parallel to the "c" axis of a martensite crystal, grains subject to a tensile component along this axis being free from the restraint on α'' nucleation. In its early stages, therefore, the overall transformation curve may be expected to conform with that of a conventional precipitation process (n = 3/2, or lower if the precipitates nucleate at and grow along interfaces when it is predicted that n = 1 for rods or n = 1/2 for films or large plates,) with the reaction becoming prolonged in its later stages owing to the control on transformation by stress relaxation in unfavorably oriented grains. Activated mechanisms other than the diffusion of nitrogen in martensite will be involved in the latter process.

The concept that internal stress controls martensite decomposition is not new but whereas Averbach and Cohen predicted that it would stimulate transformation our observations suggest the reverse, compressive stresses having a specific inhibiting effect on nucleation. Unfortunately adoption of this view renders intractable the derivation of a quantitative analytical solution since the bulk reaction curve will depend on the distribution of local stresses from grain to grain in a martensite of variable internal structure and orientation. Whilst these stresses may be expected to show a statistical distribution about a mean, the magnitude of the latter will be affected by super-posed macro-stresses whose occurrence and intensity are determined by such factors as specimen size, shape and quenching conditions.

Concerning stress distribution, it is of interest to note that when the tempering of a given specimen is assessed using the decay of tetragonal X-ray reflections other than (101)/(011)α'', different rates of decomposition
are observed (Fig. 15). The more rapid decay of the $(002)_{a'}$ and $(112)_{a'}$ reflections conform with the proposals made since in conventional diffractometer measurements it is only those grains with the appropriate planes parallel to the surface of the specimen which contribute to a reflection. Thus the $(002)_{a'}$, $(112)_{a'}$ and $(101)_{a'}$ reflections provide a measure of decomposition in martensite crystals whose "c" axes are respectively $90^\circ$, $55^\circ$ and $45^\circ$ to the specimen surface. Since most of the reflected intensity comes from the layer close to the surface (the infinite thickness of an iron specimen to Co $K_\alpha$ radiation is 0.0013 in.) where the normal stress vanishes, the decay of the $(002)_{a'}$ peak provides a measure of $\alpha''$ precipitation in grains free from a "c" axis stress. In contrast the stresses are highest along the c axis of those grains contributing to the $(101)_{a'}$ reflection.

Although stress controlled nucleation may be important in the advanced stage 1 tempering of alloys of high nitrogen content, there are difficulties in extending this concept to low nitrogen martensites. In these, if the behavior of iron-carbon alloys is paralleled, the internal stresses should be lower with a correspondingly more extended range of transformation exhibiting a normal time exponent for diffusion controlled growth. The results of Bell and Brough $^{11}$ in which they report $n = \frac{1}{3}$ over a wide transformation range in alloys containing 0.51% nitrogen are contrary to this expectation. They ascribe the low exponent to stress assisted diffusion of nitrogen atoms to dislocations at the $\alpha''$ plate interfaces once coherency is lost. The criticism of this is that the chemical driving force for the reaction is discounted at a late stage in the reaction when a $t^{1/2}$ law should produce more rapid decomposition than
a $t^{1/3}$ law and not vice-versa as they suggest. It may be that the internal stress level of freshly quenched martensite is abnormally high as a result of nitriding or that the extent of stress controlled nucleation is greater than envisaged.

Clearly, the findings in the present paper do little towards the realization of a quantitative kinetic theory. We have emphasized the complexities of the precipitation process e.g. the martensite plates themselves contain mixtures of substructure (twins and dislocations) so that the nucleating conditions cannot be everywhere the same. Furthermore, the difficulties in allowing for overlapping stages such as solute attraction to dislocations and twins, coherent precipitation and impingement have been increased by the introduction of a stress controlled nucleation factor. Also as Christian\textsuperscript{23} points out, close precipitate spacings (<100A) will invalidate almost all treatments of overall kinetics concerned only with diffusion limited precipitation. In this respect the initial $a''$ precipitates in the 1.5% nitrogen alloy were so fine that no indication was given in the micrographs of nucleation on either twin interfaces or dislocations. Superficially the precipitates at low temperatures resembled the structures displayed by alloys which decompose spinodally, except that the $a''$ lamellae formed during tempering adopt a single habit plane.

**Stage 3 tempering**

In contrast to the ambiguity concerning $a''$ nucleation, the more stable nitride $\gamma'$ nucleates predominantly at martensite plate boundaries and mid-ribs, the growth of parallel arrays of Widmanstatten side plates giving stage 3 decomposition a heterogeneous character, superficially
resembling cellular precipitation. That the reaction is not of this
type is proved by the unchanged orientation of the matrix in adjoining
arrays, whose dark appearance under the optical microscope is due to
localized chemical attack during etching.

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REFERENCES


ILLUSTRATION CAPTIONS

Fig. 1. Light micrograph showing acicular plate martensite in a water quenched iron 1.5% nitrogen alloy. The larger plates contain well defined mid-ribs consisting of bands of finite thickness, e.g. at A. x 700

Fig. 2. Electron micrograph encompassing three plates of 1.5% nitrogen martensite (A-C). Grains Band C are in <111>_{T_P} orientation, the latter containing a mid-rib along line EF which consists of a stack of fine (112) twins (trace T1). Traces T2, T3 and T4 are thought to represent (101)twins in plates C and B. Grain A displaying dislocation contrast is of <133> orientation. (650 kV).

Fig. 3. (a) Changes in the X-ray spectrum in the region of the (101)-(011)_{\alpha}' martensite doublets on tempering an iron 1.5% nitrogen alloy at 200°C for the times indicated. Cobalt K_{\alpha} radiation

(b) An Arrhenius plot of the times for the (202)_{\alpha}'' and (111)_{\gamma}' reflections to attain maximum intensity on tempering iron 1.5% nitrogen martensite.

Fig. 4. (a) Changes in the X-ray spectrum in the region of the (101)-(011)_{\alpha}' martensite doublets on tempering an iron 1.5% nitrogen alloy at 150°C for the times indicated. Cobalt K_{\alpha} radiation

(b) Isothermal transformation curves for the stage 1 tempering of iron 1.5% nitrogen martensite based on the decay in intensity of the (101)/(011)_{\alpha}' martensite peak.

Fig. 5. A log/log plot of ln(1-f) against time, where f is the fraction transformed, to determine the time exponent 'n' of the stage 1 tempering reaction assuming it obeys an equation of the form f = 1 - exp(-kt^n).
Fig. 6. Electron micrographs of iron 1.5% nitrogen martensite tempered to the completion of the stage 1, \( \alpha' \rightarrow \alpha + \alpha'' \) reaction.

(a) tempered 1 min. at 270°C. Magnetic domain walls are visible at X in grains of \(<111>\) orientation and \(\alpha''\) nitride lamellae at Y.

(b) tempered 1 hr. at 200°C. An enlarged area of \(\alpha\) and \(\alpha''\) lamellae in which the \(\alpha''\) phase is clearly visible because the 'c' axis of its tetragonal lattice lies in the plane of the foil.

(c) selected area diffraction pattern from treatment (b) showing reflections from the larger \(\alpha''\) unit cell and the tetragonal doublets in the 'c' axis direction. (all at 100 kV).

Fig. 7. The variation in micro-hardness on tempering iron 1.5% nitrogen martensite at 200°C.

Fig. 8. A bright field (a) - dark field (b) pair of electron micrographs from iron 1.5% nitrogen martensite tempered 1 hr. at 200°C using the \((130)_{\alpha''}\) reflection to produce (b). The foil orientation given by the selected area diffraction pattern (c) is \([931]_{\alpha/\alpha''}\) and the trace analysis in (d) establishes the average habit of the \(\alpha''\) lamellae as \((001)_{\alpha''}/(001)_{\alpha''}\). (100 kV).

Fig. 9. Dark field electron micrographs of \{112\} type twinned iron - 1.5% nitrogen martensite tempered 1 hr. at 200°C showing \(\alpha''\) lamellae on \((001)_{\alpha''}\), habit planes in both parent (a) and twin (b) lattices. In (a) the operating reflections are the combined \((110)_{\alpha} + (220)_{\alpha''}\) parent spots and in (b) the \((002)_{\alpha''}\) in the twin. The \(\alpha''\) lamellae in the parent crystal are less distinct in (a) because of their smaller inclination to the foil plane (650 kV). The diffraction pattern (schematic) is shown in (c) whilst (d)
is a stereographic analysis of the twin and $a''$ lamellae traces.

(650 kV)

Fig. 10. Electron micrographs of iron 1.5% nitrogen martensite in foil of (100) $a'_{1}$ orientation tempered for
a) 1 hr at 150°C, bright field
b) 2 mins at 150°C, dark field using the $(004)_{a''}$ reflection.
c) selected area diffraction pattern of (b) suggesting that stage 1 tempering is complete in this region.
d) 6 months at 25°C, dark field using the combined $(002)_{a'}/(004)_{a''}$ reflections. Fine $a''$ lamellae are resolvable between the intersecting traces of (101)$a'$ twins. (all at 100 kV).

Fig. 11. Electron micrographs at 100 kV of iron 1.5% nitrogen martensite aged 6 months at 25°C. The foil was examined previously at 650 kV, a treatment thought to be responsible for the coarsening of the $a''$ lamellae visible both in bright field (a) and dark field (b) and (c). The dark lines intersecting the $a''$ lamellae in (b) may be antiphase domain boundaries caused by an $\frac{a}{4}\langle 111\rangle_{a}$ shift in the interstices occupied by the nitrogen atoms.

Fig. 12. Light micrograph showing the heterogeneous character of the stage three, $a' \rightarrow a + \gamma'$, tempering reaction in iron 1.5% nitrogen martensite tempered 4 hr at 200°C. $x$ 1000

Fig. 13. Electron micrographs showing the completion of stage three, $a' \rightarrow a + \gamma'$, tempering in iron 1.5% nitrogen martensite tempered for 1 hr at 300°C. Parallel sided $\gamma'$ plates on several habit plane variants are shown in (a), the selected area diffraction pattern from which (b) proves the existence of a Kurdjumow and
Sachs type orientation relationship between the $\alpha$ and $\gamma'$ lattice. The electron beam is parallel to $[111]_\alpha$ and $[0\bar{1}1]_\gamma$, zone axes. Bright field and dark field images are shown in (c) and (d), using a $(100)_\gamma$, reflection for the latter. The lines in the $\gamma'$ crystals are structural defects which could be stacking faults, twins or antiphase domain boundaries. (all at 100 kV)

Fig. 14. A trace analysis of the $\gamma'$ plates in two intersecting colonies in one martensite plate (a) tempered for 1 hr at $300^\circ$C. Each colony displays the same matrix orientation and both trace normals from the $\gamma'$ plates pass through $\{012\}_\alpha$ poles (b). (100 kV)

Fig. 15. Isothermal reaction curves for the stage 1 tempering at $100^\circ$C of iron 1.5% nitrogen martensite based on the decay of the tetragonal martensite X-ray reflections indicated. The data suggest that the kinetics of the reaction are orientation dependent.
Fig. 1
Fig. 6
Fig. 7
Fig. 8
Trace normal α'' lamellae in twins

Trace of α'' lamellae in twins

Trace normal α'' lamellae in parent matrix

Trace of twins in matrix

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Fig. 9
proj 112
proj 001
110

Fig. 10a
Fig. 10b and c
Fig. 10d
Fig. 13
Fig. 14
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