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TEMPERING OF MARTENSITE UNDER THE INFLUENCE OF AN EXTERNALLY APPLIED STRESS

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ABSTRACT

The influence of an externally applied stress on the precipitation of carbides during the tempering of martensite is examined using transmission electron microscopy. Whereas normal tempering leads to the formation of a Widmanstätten array of carbide particles, the imposition of a uniaxial compressive stress causes variant selection. Individual plates of martensite then contain just one carbide variant, or a variant which dominates. The results are utilised to interpret the nature of carbide precipitation in lower bainite.

INTRODUCTION

This paper is ostensibly about the tempering of martensite. However, the experiments were really designed to elucidate the nature of bainite. This broad interpretation of the scope of this conference, which is in honour of the late Professor Speich, seems wholly appropriate in view of his wide ranging contributions to the physical metallurgy of steels. One of the present authors (HB) has been lucky enough to acquire a carbon copy of Gill Speich's 1958 doctoral thesis entitled "The Growth of Bainite". The dissertation is probably the first ever on the subject of bainite. It is still frequently quoted and its contents are of sufficient value to have been included in Christian's "Theory of Transformations in Metals and Alloys"!

Lower bainite consists of a non-lamellar aggregate of ferrite and carbides. There are, however, two kinds of carbides. Like upper bainite, there is some precipitation of carbides from the carbon-enriched austenite between the bainite platelets. In addition, there is usually a fine dispersion of carbides within the lenticular ferrite plates. It is nature of these latter carbides which stimulated the experiments reported here. The striking feature of lower bainite is that the carbides which precipitate from the bainitic ferrite form in a single crystallographic variant, whereas the tempering of martensite leads to a Widmanstätten carbide precipitation pattern. When the carbide is cementite, examination of planar sections shows that the particles have their longest axes inclined at some 60° to the "growth direction" of the ferrite platelets [1-7].

These are general observations; detailed examination of published data show that many carbide variants can sometimes be found in individual platelets of lower bainitic ferrite [8-10]. Indeed, either a single variant of carbide or a dominant variant can sometimes be found in tempered martensite [see for example, Fig. 8.3, Ref. 11], in contrast to the Widmanstätten pattern that is normally assumed to exist in tempered martensite.

A variety of mechanisms have been proposed to explain the occurrence of a single carbide variant in lower bainite. These have been discussed elsewhere [12], but they include interphase precipitation [13], and precipitation on the plane of lattice-invariant shear in the ferrite. Neither of these fit the detailed experimental data that are now available [12]. An alternative explanation is that the strain associated with the displacive transformation mechanism during the formation of lower bainite stimulates the development of the particular variant which best complies with the strain [12].

Of course, the interaction of carbide precipitation with the shape change associated with the ferrite formation should be most effective if the carbide itself forms by a displacive mechanism. Such a mechanism must naturally involve the diffusion of carbon, but not of substitutional solutes; this is consistent with a large amount of data which show that the carbides associated with bainite do not partition substitutional solutes during transformation [14-16]. It is particularly interesting that the precipitation of cementite from martensite or lower bainite can occur under conditions where the diffusion rates of iron and substitutional atoms are very small compared with the rate of precipitation. The long-range diffusion of carbon atoms is of course, necessary, but, because of its interstitial character, substantial diffusion of carbon remains possible even at temperatures as low as -60 °C. Thus, the formation of cementite in these circumstances must differ from the normal reconstructive decomposition reactions, which become sluggish at low temperatures. It has been believed for some time that the cementite lattice may be generated by the deformation of the ferrite lattice, combined with the necessary diffusion of carbon into the appropriate sites. The Fe/X ratio thus remains constant everywhere and subject to that constraint, the carbon achieves equality of chemical potential; the cementite is then said to grow by *paraequilibrium* transformation [17,18]. The ways in which the ferrite lattice could be deformed to produce the right arrangement of iron atoms needed to generate the cementite has been considered by Andrews [19] and Hume-Rothery *et al.* [20], and the subject has been reviewed by Yakel [21]. Further high-resolution evidence supporting the idea that the carbide particles grow by displacive transformation (involving the diffusion of just carbon) has been published most recently by Sandvik [22], Nakamura and Nagakura [23] and Taylor *et al.* [24,25].

The purpose of the present work was to demonstrate the interaction of carbide precipitation during the tempering of martensite, with an externally applied stress.

EXPERIMENTAL PROCEDURE

The experiments were carried out using 300M steel, of chemical composition Fe– 0.44C – 1.74Si – 0.67Mn – 1.85Ni – 0.83Cr – 0.39Mo – 0.09V wt.%. Cylindrical samples 8 mm diameter and 12 mm length were sealed in quartz tubes containing pure argon, for homogenisation at 1200 °C for three days.

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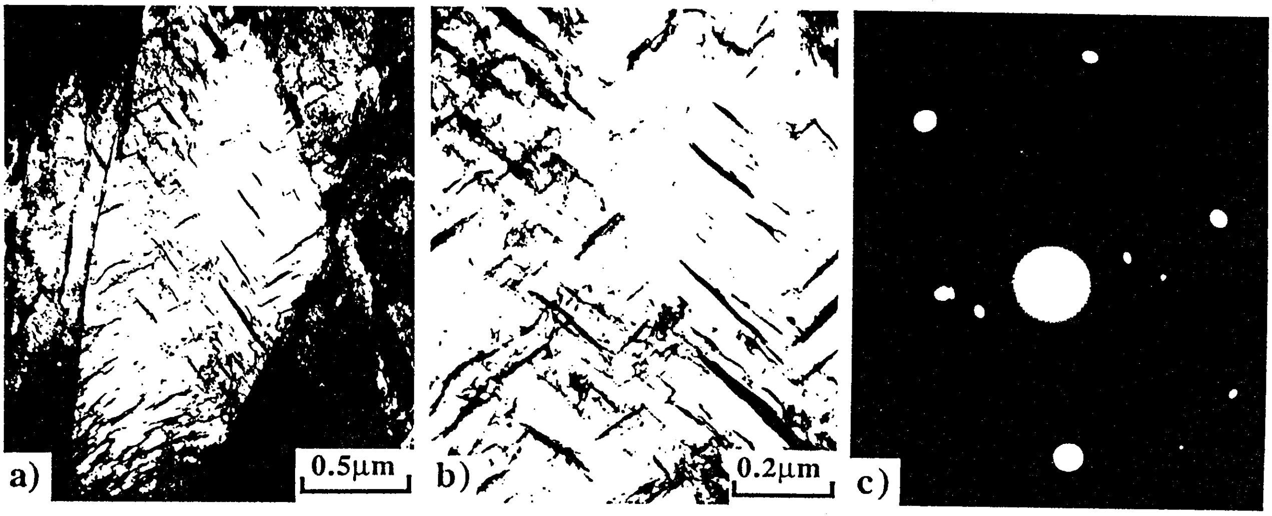
The subsequent heat treatments experiments involving transformation under the influence of stress were carried out in an adapted *Thermecmastor Z* thermomechanical simulator. The specimen is heated by induction, with a measured temperature variation along its length of only ±5 °C. The quench gas used was nitrogen. The uniaxial compressive load was applied via silicon nitride discs; for the samples used, this gave a stress of 700 MPa, which is lower than the yield strength of the martensite at the temperature concerned. Austenitisation was at 900 °C for 30 min, followed by rapid gas quenching to ambient temperature, and continued quenching in liquid nitrogen. They were then replaced into the simulator for tempering either at 300 or 400 °C for 30 min. The lower temperature gives ε–carbide whereas cementite is obtained during tempering at 400 °C [26].

Thin foil samples for transmission electron microscopy were cut perpendicular to the stress axis. They were electropolished in a Fischione twin-jet unit at -10 °C using an electrolyte consisting of 5% perchloric acid, 25% glycerol and 70% ethyl alcohol. The foils were examined in a Philips EM400T transmission electron microscope which was operated at 120 kV.

RESULTS

The metallographic results presented here are representative of a large number of micrographs taken during the course of the investigation. Fig. 1 shows the microstructure obtained after tempering the quenched steel at 300 °C for 30 min, without any externally imposed stress. Most of the martensite plates were found to contain more than one crystallographic variant of ε–carbide particles. Only a single variant of carbide could be found in some of the tempered martensite plates (Fig. 2). These observations confirm the general feeling that a Widmanstätten array of carbides is obtained when carbon–supersaturated martensite is tempered. However, the number of carbide variants observed is surprisingly small, given that the orientation relationship between ε–carbide and the matrix is, as expected, found here to be consistent with the Jack [27] relationship. Similarly, given that the ferrite/cementite orientation was always found to be consistent with the Bagaryatski relationship, the number of possible variants should be larger than has been observed. Recent work by Taylor *et al.* [24] shows that the precipitation of transition carbides is influenced by a variety of precursor events. Thus, it is found that the number of carbide variants that form is less than that expected from an examination of just the crystallography, because precipitation is preceded by spinodal decomposition which causes carbon concentration waves along the elastically soft directions of the matrix. The number of these soft directions is limited by the tetragonal symmetry of the martensite lattice. The carbides then nucleate and grow by a displacive paraequilibrium mechanism along the carbon–enriched bands. They therefore observed only two carbide variants in any given martensite plate, even though the plane of precipitation $\{0\ 1\ 2\}_\alpha$ has a higher crystallographic multiplicity. A further factor which could limit the number of variants is of course the internal stresses arising due to the shape change of the martensite plates themselves.



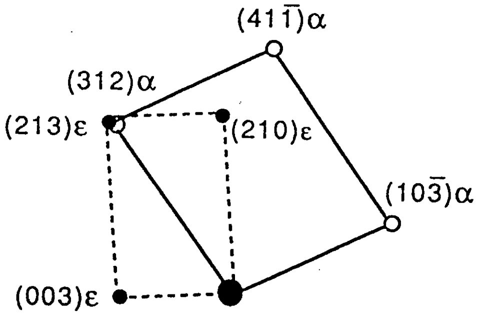


Fig.1 Electron micrograph of specimen tempered at 300°C with null stress.
a,b) Bright field image
c) Corresponding diffraction pattern

Figure 3 shows the striking change in carbide precipitation behaviour, caused by tempering the martensite at 300 °C under the influence of a compressive stress of 700 MPa. The vast majority of plates revealed only a single variant of ϵ-carbide, although rare instances were observed where two variants were found (Fig. 3b). Even in the latter case, the different variants of carbide particles were not intimately mixed as in Fig. 1b, but each carbide variant appeared to occupy a particular region of the plate in isolation.

An increase in the tempering temperature to 400 °C for 30 min revealed that even in the absence of an applied stress, the cementite tended to form in just one orientation within a given martensite plate, although minute quantities of another variant could be observed occasionally (Fig. 4). When tempered under the compressive stress, only one variant could ever be found.

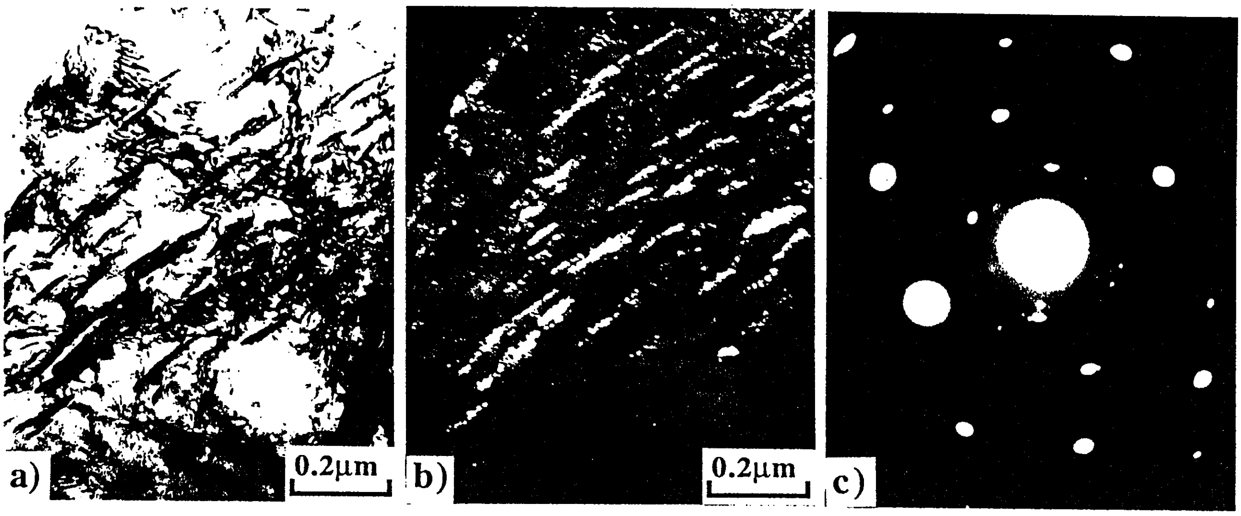
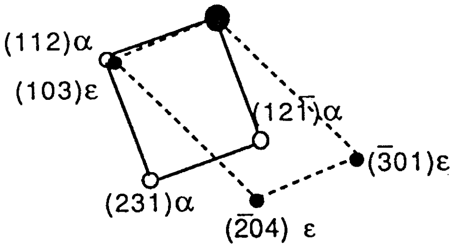


Fig.2 Electron micrograph of specimen tempered
at 300°C with null stress.
a) Bright field image
b) Corresponding dark field image
c) Corresponding diffraction pattern



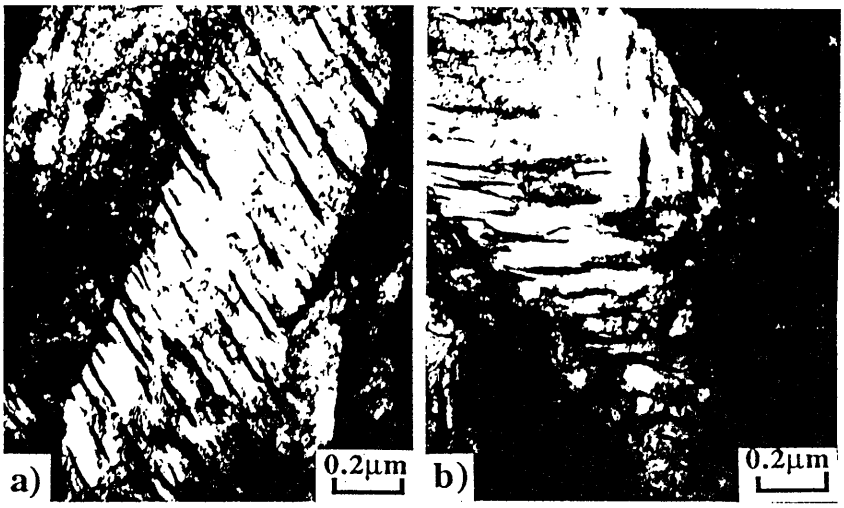


Fig.3 Electron micrograph of specimen tempered at 300°C
with 700MPa of applied stress.

Fig.4 Electron micrograph of specimen tempered at 400°C with null stress.
a) Bright field image
b) Corresponding diffreaction pattern

Fig.5 Electron micrograph of specimen tempered at 400°C with 700MPa of applied stress.

DISCUSSION

It is evident that an externally applied stress can reduce the number of variants of carbide particles that precipitate in any given martensite plate. It follows that any internal stresses, due for example to the invariant–plane strain (IPS) shape change accompanying the growth of martensite can have a similar effect. Furthermore, it is now generally accepted that the carbide particles formed during the tempering of martensite probably themselves grow by a displacive transformation mechanism which may involve the diffusion of carbon [19–25]. This makes it even more probable that the precipitation of carbides should be influenced when it occurs in a stress field.

It is worth commenting on two particular observations: (i) the rather large effect observed in the present experiments, of the applied stress on variant selection; (ii) why the tendency for variant selection is largest at higher transformation temperatures.

A displacive transformation can justifiably be regarded as a mode of deformation of the parent phase [28–34]. The additional characteristic of the deformation is that the crystallographic structure of that phase is altered in the deformed region. A phase transformation like this can therefore be triggered either by cooling below a certain transformation–start temperature (*i.e.* by a chemical driving force), or by the application of a stress in appropriate circumstances (*i.e.* by a mechanical driving force), or by a combination of these factors.

A thermodynamic calculation, carried out using the MT-DATA package [35], of the chemical driving force for the precipitation of equilibrium cementite from supersaturated ferrite is presented in Fig. 6. The calculation accounts for all the alloying additions present in 300M steel. Given that we have not been able to do the relevant calculations for the metastable ϵ–carbide, the data presented in Fig. 6 represent the upper limit of the free energy change accompanying the precipitation of any carbide.

The mechanical driving force can be estimated using the Patel and Cohen model for the interaction of the applied stress with the shape strain of the carbide [28–30]:

$$U = \frac{\sigma}{2}[s \sin 2\theta \cos\phi + \delta(1 + \cos 2\theta)] \qquad (1)$$

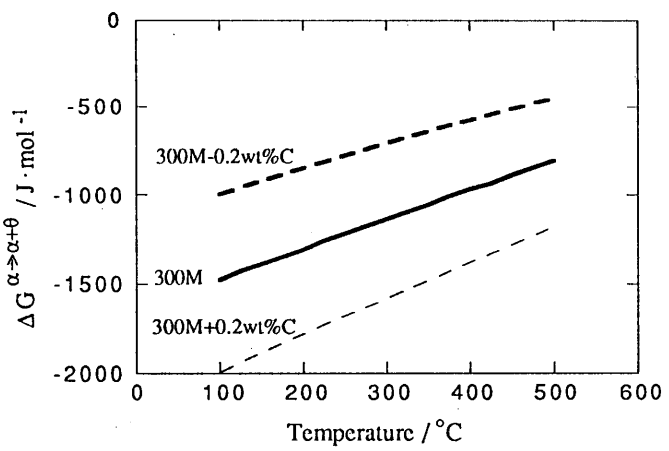


Fig.6 The free energy change accompanying the precipitation of equilibrium cementite from supersaturated ferrite in 300M steel.

where ϕ is the angle between the shear direction and the direction of the shear component of the applied stress (σ) as resolved on the habit plane, θ is the angle between the habit plane normal and the stress axis. s and δ are the shear and dilatational components respectively of the IPS shape deformation of the carbide phase, assumed here to be 0.211 and 0.157 respectively from the data given by Taylor *et al.* [24]. In these circumstances, the maximum value of the mechanical driving force amounts to about 1020 J mol^{-1} for an applied stress of 700 MPa.

Referring again to Fig. 6, it is evident that the mechanical driving force is quite large or comparable with the chemical driving force. It is therefore not surprising that the applied stress has a large effect on carbide precipitation behaviour. Furthermore, the influence of stress should increase as the tempering temperature is raised, since the magnitude of the mechanical driving force becomes even larger when compared with the chemical driving force. This explains why the tempering at 400 °C led to fewer variants of carbide, even in the absence of the applied stress, since internal stresses could themselves be sufficient to stimulate variant selection.

These results have significant implications on the interpretation of carbide precipitation in lower bainite. The lower bainite grows at relatively high temperatures where the driving force for carbide precipitation from supersaturated ferrite is likely to be smaller than that associated with martensite in the same steel. The chemical driving force will be further reduced since some of the excess carbon can escape into the residual austenite. This is illustrated in Fig. 6 by calculations where the carbon concentration of the 300M steel was altered by ±0.2 wt.%. It is not therefore surprising that there is a tendency to find just one crystallographic variant of carbide in platelets of lower bainitic ferrite.

FUTURE WORK

The work presented above suggests some further experiments. For example, it would be instructive to vary the carbon concentration of martensite without changing its M_S temperature, and then to temper the alloys under the influence of an applied stress. The higher carbon variants should show a larger number of carbide variants per martensite plate since the chemical driving force for carbide precipitation will be relatively large. A variation in the applied stress could also lead to a similar effect, with an increase in stress leading to a decrease in the number of carbide variants. It would also be instructive to study the role of applied stress on the tempering kinetics of martensite.

It has been suggested [36] that a more controlled experiment might first grow selected variants of virgin martensite by imposing an external stress, and then temper this martensite under stress. The relationship between the applied stress, the martensite plate and the carbide variant could then be systematically studied.

CONCLUSIONS

It appears that an externally applied stress can influence the precipitation of carbides in martensite. The number of carbide variants which grow in any given plate of martensite decreases when the virgin martensite is tempered under the influence of the stress. The effect becomes more prominent as the magnitude of the mechanical driving force increases relative to the chemical driving force for carbide precipitation. The results can be interpreted to explain why lower bainite is usually associated with a single variant of carbide within any individual plate of bainitic ferrite.

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