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Cementite precipitation during tempering of martensite under the influence of an externally applied stress

J. W. STEWART, R. C. THOMSON, H. K. D. H. BHADESHIA
Department of Materials Science and Metallurgy, University of Cambridge/JRDC, Pembroke Street, Cambridge CB2 3QZ, UK

The precipitation of cementite under the influence of an externally applied stress, during the tempering of martensite in steels, is investigated using transmission electron microscopy. The stress appears to favour the development of particular crystallographic variants of cementite in any given plate of martensite. Hence, a Widmanstätten array of cementite particles in a normally tempered sample changes to an array consisting of just one variant in stress-tempered samples. The results are discussed in the context of the mechanism of carbide precipitation during the lower bainite reaction.

1. Introduction

There is considerable accumulated evidence about the mechanism by which carbides precipitate during the tempering of martensite, or as a consequence of the bainite transformation. The evidence suggests that the carbides grow by a displacive transformation mechanism in which the carbide lattice is generated by a deformation of the supersaturated ferrite lattice. This process must naturally involve the diffusion of carbon, so that it is proper to describe it as a paraequilibrium* displacive transformation mechanism. Since the large atoms do not diffuse, the iron to substitutional solute atom ratio remains constant everywhere during this process.

The proposed mechanism is not unnatural – it has been established conclusively for the precipitation of vanadium hydride [2]. The supporting evidence for iron carbides can be summarized as follows. Many results show that the carbides associated with bainite and martensite have the same average substitutional solute concentration as the matrix when they first form [3–6]. These results are not conclusive because they refer to the bulk composition; there could exist very fine-scale variations in the vicinity of the transformation interface. However, Babu *et al.* [7] have demonstrated using an atomic resolution technique that the cementite that grows during the tempering of martensite forms without any diffusion of substitutional atoms, even on the finest conceivable scale.

It is relevant that the precipitation of cementite from martensite or bainite can occur under conditions where the diffusion rates of iron and substitutional atoms are incredibly small compared with the rate of precipitation [8]. The long-range interstitial diffusion of carbon atoms remains possible even at temperatures as low as − 60 °C. The way 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 [9] and Hume-Rothery *et al.* [8]. The subject has been reviewed by Yakel [10]. 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 several authors [11–14].

A displacive transformation is one in which the pattern in which the substitutional atoms are arranged is changed, without their diffusion. Therefore, associated with this change of pattern must be a macroscopic change in the shape of the transformed region. This shape change is, for the precipitation of plate-shaped carbides, likely to be an invariant-plane strain with a large shear component [13]. Because of the fine scale of the carbide precipitation, it has not been possible to observe the shape deformation experimentally. Nevertheless, the effect of the shape change has been revealed in some preliminary work in which virgin martensite was tempered under the influence of an externally applied stress [15]. Whereas normal tempering led to the formation of a Widmanstätten array of cementite particles in any given martensite plate, stress-tempered martensite plates contained only single variants. This response was as might be expected from a transformation which is accompanied by the shape deformation described above. The purpose of the work presented here was to verify this observation in greater detail, using a different steel so that the interpretations could be generalized.

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* The term *paraequilibrium* originates from the work of Hultgren [1]. It describes a transformation in which the substitutional solutes are unable to partition during the time-scale of the experiment. However, subject to this constraint, fast diffusing interstitial atoms such as carbon redistribute between the parent and product phases to an extent which allows their chemical potentials to be identical everywhere.

2. Experimental procedure

2.1. Materials and initial heat treatment

The chemical composition of the steel used, supplied by British Steel, is given in Table I. Part of the reason for choosing this steel is its low martensite reaction start temperature, M_s. This is in order to avoid autotempering on quenching, which would have resulted in the precipitation of carbides before the application of an external compressive stress. The M_s was estimated as 223 °C using a computer program described elsewhere [16]. M_s was also measured and found to be 256 °C by monitoring the relative length change of a cylindrical specimen in a thermomechanical simulator as a function of temperature, during gas-quenching. Although this measured temperature is somewhat higher than expected, it is considered to be sufficiently low to avoid autotempering.

A cylindrical rod of the steel, 10 mm in diameter, was sealed in a silica tube under a partial pressure of argon (150 mm Hg) to prevent decarburization and oxidation. The steel sample, sealed in the quartz tube, was placed on a ceramic boat in a furnace to preclude any contamination with the base of the furnace, and heat-treated at 1200 °C to homogenize for 3 days. The homogenized steel rod was machined down to 8 mm diameter to remove any decarburized layer and was cut into 12 mm lengths. These samples were resealed in silica tubes, again under a partial pressure of argon, and austenitized at 1000 °C for 10 min. The tubes were then removed from the furnace, broken and the samples quenched into an iced brine solution. A further quench in liquid nitrogen was found to be necessary to ensure complete transformation to martensite.

2.2. Thermomechanical simulator heat treatments

A computer-controlled thermomechanical simulator (Thermecmastor, manufactured by Fuji Electronic Industrial Co.) was used in order to control and monitor the initial heat treatments of the steel more accurately than could be achieved in a furnace. The Thermecmastor incorporates a sophisticated dilatometer, and can additionally be used for investigations of the effects of stress on transformation because the strains can be monitored in two orthogonal directions. It has a high-frequency induction heating system, allowing homogeneous heating of the specimen to within 5 °C. Rapid heating and cooling can be done at specified rates under vacuum or with a gas atmosphere (Ar, N_2, He).

In this work, heating was performed in a vacuum and quenching done with nitrogen gas. The temperature was measured using a Pt/Pt–13 wt % Rh thermocouple resistance welded to the surface. One specimen was kept as-quenched into the liquid nitrogen, and three others were tempered in the simulator at 400 °C for 30 min with no applied stress, and applied compressive uniaxial stresses of 500 and 950 MPa, respectively. The load was applied before any heating of the specimens to ensure that all the tempering was carried out under applied stress.

TABLE I Chemical composition of the steel investigated

Element	C	Si	Mn	Cr	P	S	N	Cu
Composition (wt%)	0.44	2.13	2.14	0.5	0.014	0.011	0.008	0.02

2.3. Hardness measurements

Macrohardness measurements were made using a Vickers pyramid hardness testing machine using a load of 20 kg.

2.4. Optical microscopy

Samples were prepared for microstructural characterization by hot mounting in acrylic moulding powder, followed by grinding on SiC paper to 1200 grit and polishing to 1 μm cloth coated with diamond paste. Specimens were mounted so that the surface examined was perpendicular to the applied stress during tempering. They were etched in 2% nitric acid in methanol.

2.5. Transmission electron microscopy

Thin slices of the steel samples were cut perpendicular to the direction of applied stress using a SiC slitting wheel and discs of 3 mm diameter mechanically punched out. The discs were then ground manually to 50 µm thickness and twin-jet electropolished to electron transparency at 50 V, with the solution cooled to − 10 °C using liquid nitrogen. The polishing solution used for the steel contained 5% perchloric acid, 25% glycerol and 70% methanol. The thinned samples were examined in a Philips 400T transmission electron microscope operated at 120 kV.

3. Results

A typical optical micrograph of the as-quenched microstructure is shown in Fig. 1. The microstructure is completely martensitic with no regions of any other phase large enough to be visible optically. Transmission electron micrographs of the as-quenched microstructure are presented in Fig. 2. Fig. 2a shows martensite platelets and Fig. 2b, at higher magnification, demonstrates that there has been no significant carbide precipitation on transformation, i.e. that no autotempering had occurred. There was no sign of retained austenite at the platelet boundaries, implying that the quench into the iced brine solution and then into liquid nitrogen was sufficient to ensure complete martensitic transformation.

The hardnesses of the samples prepared for optical microscopy are given in Table II. The as-quenched steel is considerably harder than the samples which were tempered. This shows that significant microstructural rearrangement must have occurred during the 30 min temper. The hardnesses of the tempered samples were comparable, irrespective of the external stress applied. When the microstructures of the steels were examined optically after tempering heat treat-

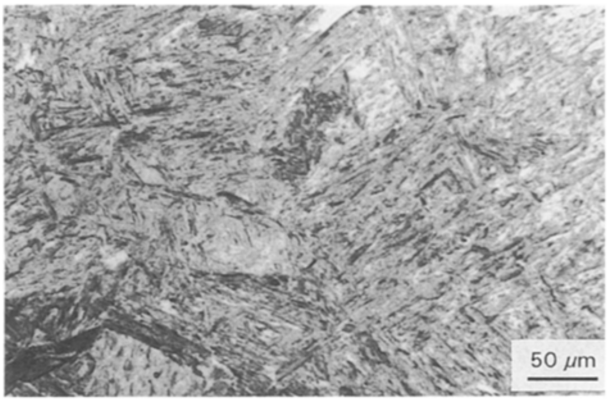

Figure 1 Optical micrograph of the as-quenched microstructure.

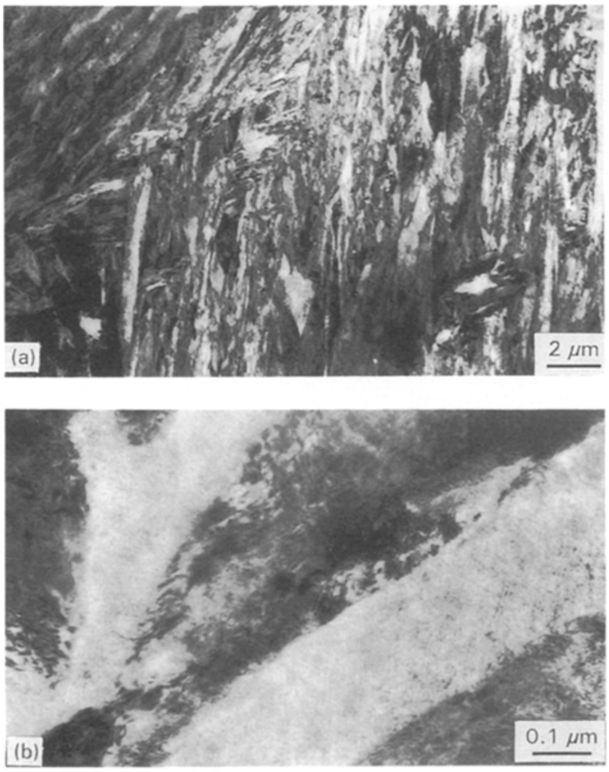

Figure 2 (a) Transmission electron micrograph of the as-quenched microstructure showing plates of martensite; (b) higher-magnification showing that there has been no significant carbide precipitation. Regions of high dislocation density can be seen.

TABLE II Vickers hardness of the prepared samples

	As-quenched	Tempered at 400 °C for 30 min		
		No stress	500 MPa	950 MPa
Hardness H_V	722 ± 9	587 ± 8	610 ± 8	601 ± 8

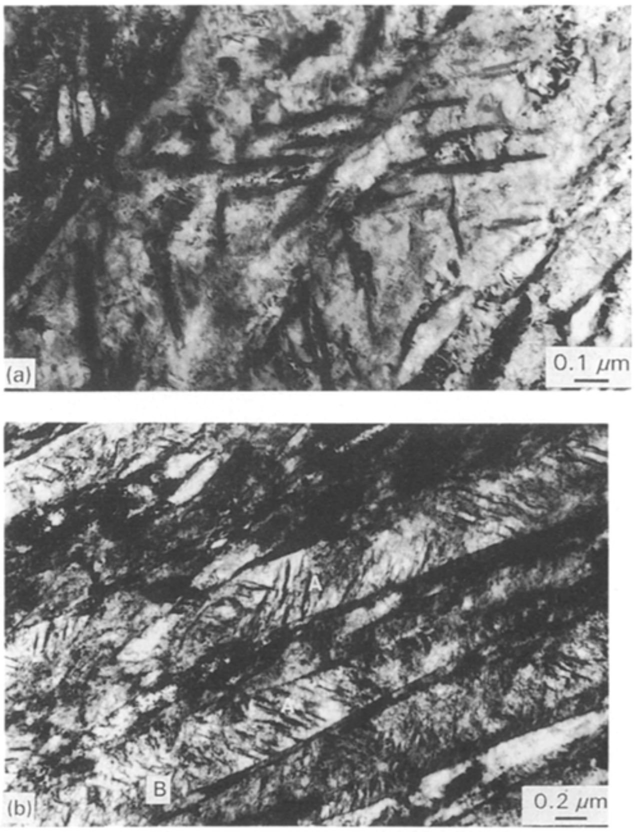

Figure 3 (a) Transmission electron micrograph of the microstructure of sample tempered at 400 °C for 30 min with no applied stress, showing a Widmanstätten array of carbides; (b) as (a), showing regions with only one variant (marked A) and regions with a Widmanstätten array of carbides (marked B).

ment, no apparent change in microstructure could be discerned, as expected.

Examination of the tempered specimens in the transmission electron microscope revealed that extensive carbide precipitation had occurred within the martensite platelets. Fig. 3a and b illustrate the microstructure obtained after tempering the quenched steel at 400 °C for 30 min. without any externally imposed stress. Most of the martensite plates were found to contain more than one crystallographic variant of carbide particles. However, only a single variant of carbide could be found in some of the tempered martensite plates. These observations confirm the general opinion that a Widmanstätten array of carbides is obtained when carbon-supersaturated martensite is tempered. The number of carbide variants observed is surprisingly small, usually only two or three clear variants being discernible. Recent work by Taylor *et al.* [13] has shown that the precipitation of carbides may be influenced by a variety of precursor events. A further factor which could limit the number of variants is, of course, the internal stresses arising due to the shape change of the martensitic plates themselves.

Fig. 4 shows the striking change in carbide precipitation behaviour caused by tempering the martensite at 400 °C for 30 min under the influence of a uniaxial compressive stress of 950 MPa. The vast majority of plates revealed only a single variant of carbide, although rare instances were observed where two variants were found (Fig. 4d). Even in this case the different variants of carbide particles were not intimately mixed, but each carbide variant appeared to occupy a particular region of the plate in isolation. The carbides were identified as cementite by electron diffraction, as shown in the inset in Fig. 4d.

The sample tempered at 400 °C for 30 min with an applied compressive stress of 500 MPa was also found

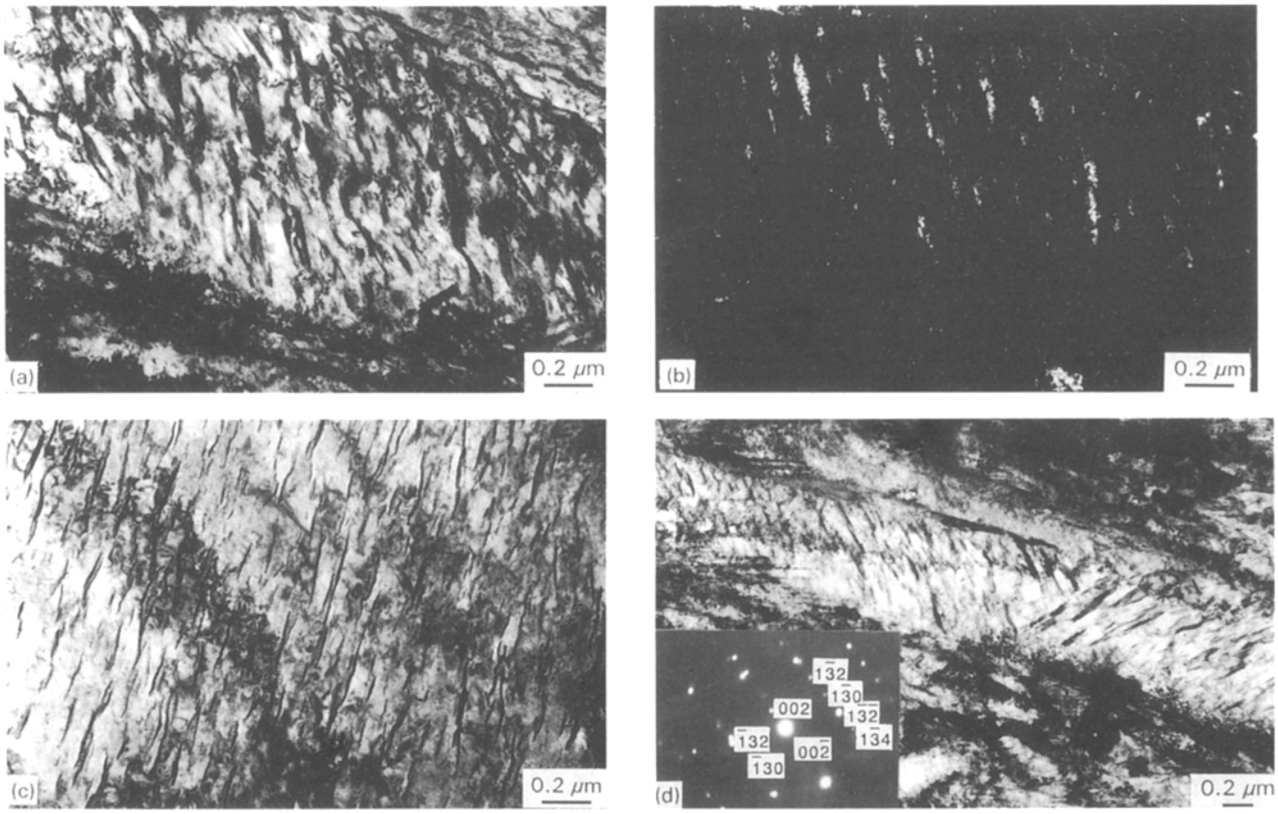

Figure 4 (a) Bright-field transmission electron micrograph of specimen tempered at 400 °C for 30 min with a uniaxial compressive stress of 950 MPa applied, showing a single variant of carbide; (b) corresponding dark-field image; (c) as (a), again showing a single variant of cementite; (d) as (a), showing different variants dominant in different regions of the plate. The inset is a selected-area electron diffraction pattern identifying the carbides as cementite.

to have highly aligned carbides (Fig. 5), although some regions could be found with two variants of carbide together (Fig. 6), suggesting that the preference for one particular variant over the others was weaker than for the sample tempered under the 950 MPa compressive stress.

4. Discussion

Consistent with previous preliminary results on a different alloy, it has been demonstrated that the tempering of martensite under the influence of an externally applied stress reduces the number of variants of carbide precipitated. This is consistent with the displacive transformation mechanism, discussed earlier, for the growth of carbides during the tempering of martensite.

A displacive transformation can be regarded as a mode of deformation of the parent phase, with the additional characteristic that the crystallographic structure of that parent phase is altered in the deformed region. Such a phase transformation can be triggered by cooling below a certain transformation 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.

It is possible to calculate the chemical driving force for the precipitation of cementite using MTDATA [17], a computer package allowing the calculation of multicomponent phase equilibria. Fig. 7 shows the results of the thermodynamic calculations. The calculations take into account the major components of the steel (Fe, C, Si, Mn, Cr) and the phases ferrite and cementite.

Figure 5 Transmission electron micrograph of specimen tempered at 400 °C for 30 min with an applied compressive stress of 500 MPa, showing a single variant of carbide.

It is also possible to estimate the mechanical driving force for the precipitation of carbide using the Patel and Cohen model for the interaction of the applied stress with the shape strain of the carbide [18]:

$$U = 0.5\sigma[s \sin 2\theta \cos\phi + \delta(1 + \cos 2\theta)]$$

where ϕ is the angle between the shear direction and

Figure 6 Transmission electron micrograph of specimen tempered at 400 °C for 30 min with an applied compressive stress of 500 MPa, showing some plates containing more than one variant.

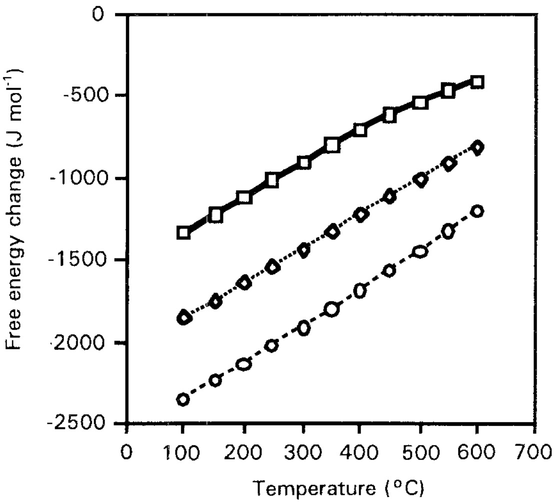

Figure 7 Calculated free energy change accompanying the precipitation of cementite from supersaturated ferrite in steel 226, allowing for ± 0.2 wt % C additions: (◇, · · ·) unmodified; (o, - - -) − 0.2 wt% C; (□, ——) + 0.2 wt % C.

the direction of the shear component of the applied stress (σ) as resolved on the habit plane, and θ is the angle between the habit plane normal and the stress axis. The constants s and δ are the shear and dilatational components, respectively, of the invariant plane-strain shape deformation of the carbide phase, assumed here to be 0.211 and 0.157, respectively, from the data for a transition iron carbide given by Taylor *et al.* [13]. In these circumstances, the maximum value of the mechanical driving force is approximately 730 J mol^{-1} for an applied stress of 500 MPa, and 1380 J mol^{-1} for an applied stress of 950 MPa.

It can be seen that the magnitudes of the chemical and mechanical driving forces are comparable. It is therefore not surprising that the applied stress has a large effect on carbide precipitation behaviour, and that this effect is more pronounced for the larger applied stress, because it has a larger mechanical driving force associated with it. The thermodynamic calculations imply that the influence of a fixed stress on carbide precipitation should increase with tempering temperature, because the chemical driving force decreases whilst the mechanical driving force remains constant. This has been shown for a steel of different composition, although with ε-carbide rather than cementite precipitation, in an earlier investigation [15].

Lower bainite forms at higher temperatures than martensite, and therefore the chemical driving force for carbide precipitation is likely to be lower than for martensite in the same steel. Additionally the chemical driving force will be further reduced because of the high probability of some carbon escaping into the surrounding austenite. This effect can be seen from the curves in Fig. 7, which represent a calculation of the free energy change accompanying the carbide precipitation reaction in a steel with ± 0.2 wt % C. This was done to give an indication of the effect of local changes in carbon concentration on the chemical driving force. It can be seen that a decrease in the carbon concentration reduces the magnitude of the chemical driving force, and vice versa. It can be concluded that lower bainitic plates are therefore much more likely to contain only a single carbide variant than martensite, and it is perhaps not surprising that this is a characteristic feature of the lower bainite transformation.

5. Conclusions

The application of an external stress during the tempering of martensite influences the precipitation of carbides, resulting in a decrease in the number of variants. As the magnitude of the stress is increased, so the effect becomes more noticeable and only one variant may be observed in each plate for large applied stresses. These results are consistent with cementite growth by a paraequilibrium displacive transformation mechanism.

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