The Strengthening of an Fe-V-C Low-Alloy Steel by Carbide Precipitation During Continuous Cooling from the Austenitic Condition

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A simple Fe-1V-0.2C low-alloy steel has been cooled from the austenitic condition at rates between 0.1 and 500°C per min. Dilatometry, and optical and electron metallography have shown that the austenite undergoes decomposition in the range 800 to 700°C directly to ferrite containing a nonrandom distribution of vanadium carbide. The carbide precipitates are distributed in sheets, and although a range of intersheet spacings can be measured at each cooling rate, the mean intersheet spacing decreases with increasing cooling rate. The mechanical strength was also shown to increase as the cooling rate increased, but a ductile brittle transition occurred on increasing the cooling rate above approximately 20°C per min. The dispersion strengthening was found to obey an empirical relationship of the form $\sigma_p = k \cdot \lambda^{-1.1}$, where σ_p is the dispersion strengthening effect of the carbide distribution, and λ is the intersheet spacing. The brittle behavior of the alloy obtained at high cooling rates is thought to be possibly due to the carbide morphology and dispersion resulting from the mechanism of precipitation during the austenite-ferrite transformation.

THE effect of tempering a low-alloy vanadium steel in the quenched condition is well recorded, and a number of authors have discussed the precipitation sequences of carbides and the strengthening effects obtained.[1-3] However, recent electron microscope studies have shown that a dispersion of alloy carbide in ferrite can be obtained following direct isothermal decomposition of austenite.[4-6] It has been shown that precipitation occurs repeatedly at the austenite/ferrite transformation interface (termed interphase precipitation) and results in the alloy carbides being distributed in sheets. The carbide dispersion is representative of the isothermal transformation temperature, and controls the resulting strength of the alloy.[7,8] The present paper shows how similar distributions of alloy carbides can be obtained in an Fe-1V-0.2C alloy simply by continuously cooling the alloy from the austenitizing temperature, and relates the measured dispersions to the rates of cooling and the mechanical properties.

1. EXPERIMENTAL PROCEDURE

A 10 kg experimental alloy was prepared by vacuum induction techniques at the Corporate Laboratories of the British Steel Corporation (BISRA-Sheffield). The analysis of the alloy was 1.04 wt pct V, 0.20 wt pct C, and 0.023 wt pct Nb, with the total content of all other elements, including interstitials, less than 0.01 wt pct. The melt was homogenized and forged and then hot-rolled to ~12 mm diam rod. Laboratory homogenization was then carried out by annealing sections of the rod under a partial pressure of argon for 72 h at 1300°C. The cross-section was then reduced to ~6 mm diam by cold-swaging with intermediate softening anneals at 700°C. Round tensile specimens with a gage length of 16 mm and gage diam of 4.5 mm were machined from these rods and used to evaluate the tensile properties.

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Specimens for thin foil electron microscopy were cold-rolled to 0.5 mm thick sheet and heat-treated in this condition before further thinning.

All specimens were encapsulated in silica tubes under a partial pressure of argon prior to heat treatment. Each specimen was annealed for 30 min at 1200°C and quenched into water before beginning any experimental heat treatment. The experimental heat treatment consisted of annealing for 15 min at 1150°C, followed by rapid cooling to 850°C and then controlled furnace cooling at rates between 0.1°C per min and 200°C per min. Air cooling was found to give a cooling-rate as high as 500°C per min dependent on the specimen size.

Optical microscopy was carried out on specimens mechanically polished to 0.25 μm diamond and etched in 3 pct Nital. Standard techniques were used to obtain carbon extraction replicas of the etched surface. Specimens for transmission electron microscopy were first chemically thinned in a solution of 50 ml hydrogen peroxide, 50 ml water, and 7 ml hydrofluoric acid, and then electropolished using a potential of 50 V in methanol-1 pct perchloric acid held at −70°C. Tensile tests were carried out on an Instron machine at a testing speed of 0.05 cm per min.

2. RESULTS

Fig. 1 shows the features of the transformation recorded by the usual form of continuous cooling transformation diagram, which has been obtained dilatometrically over the cooling rate range 5 to 50°C per min. The optical microstructure of a continuously cooled specimen is typically that shown in Fig. 2, and is ferritic although it is responsive to a Nital etch. It was found that 15 min at 1150°C conveniently dissolved all the vanadium carbide following the pretreatment at 1200°C, whilst keeping the austenite grain size to a minimum. The niobium addition to the alloy was designed to keep the niobium carbide out of solution at 1150°C and consequently aid austenite grain refinement. However, the change in cooling rate did cause a change

in ferrite grain size (mean linear intercept of grain boundaries), from approximately 0.10 mm at 2°C per min to 0.05 mm at 200°C per min.

Fig. 3 shows the alloy carbides dispersed in sheets, and also some coarse idiomorphic precipitation. The
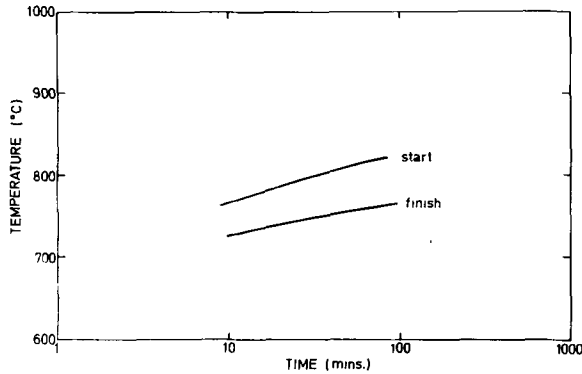

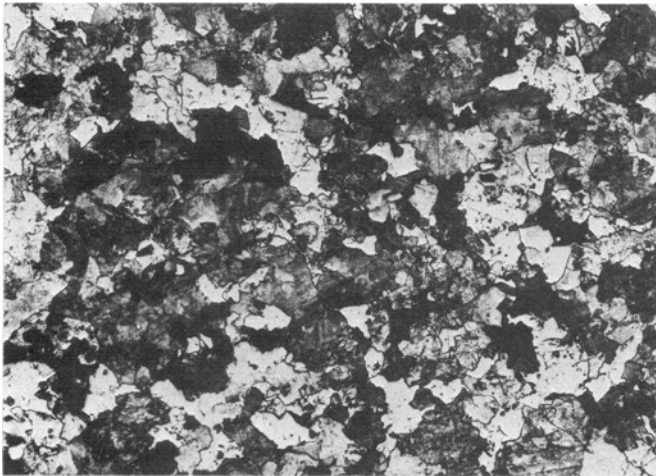Fig. 1—Continuous cooling transformation diagram for Fe-1 V-0.2 C.

Fig. 2—Fe-1 V-0.2 C alloy continuously cooled ~ 20°C per min; etched, magnification 75 times.

carbides were identified by electron diffraction as vanadium carbide. Interphase precipitation is readily recognized because not only are the precipitates distributed in sheets, but only one variant of the platelet precipitate habit is present.[5]

Fig. 4(a) shows the variation of the perpendicular intersheet spacing as a function of the cooling rate. Measurements were made from electron micrographs using both extraction replicas and thin foils. Extraction replicas were used for intersheet spacings down to ~500Å (corresponding to ~20°C per min cooling), where resolution of the sheets became difficult, and thin foils were used at the finer spacings. There is some overlap of the two methods, and in general it was found that thin foils give a narrower band of spacing measurements because whilst tilting the specimens in the electron microscope to bring the rows into the best contrast conditions, some of the error due to sectioning is reduced. Sectioning errors are apparent in the replica measurements, and magnify even further the spread of readings obtained because the transformation is occurring over a range of temperatures during cooling. It was not found possible to measure accurately the precipitate spacing within the sheets, but it was generally observed that this was much less than the intersheet spacing, and evidence of this is given by Fig. 3, and in electron micrographs published by other investigators.[6]

The variation of 0.2 pct proof strength, U.T.S., elongation and reduction in area with cooling rate is shown in Fig. 4(b). Greater scatter of the strength data points was obtained at 200 and 500°C per min, but extrapolation from the data obtained at lower cooling rates did delineate the mean values. To illustrate the influence of the intersheet spacing on the yield strength it was necessary to normalize the measured yield strength values to account for the change in grain size with cooling rate. It was decided to adopt the approach followed by Pickering and Gladman[9] who considered that all the strengthening effects in ferrite/pearlite structures were additive. The Hall-Petch equation was modified to account for each effect, and the yield strength (σ_y) expressed as

Fig. 3—Fe-1 V-0.2 C alloy continuously cooled ~ 10°C per min; thin foil, magnification 23,000 times.

$$\sigma_y = \sigma_o + \sigma_s + \sigma_p + k_y d^{-1/2}$$

where σ_o represents the inherent matrix friction stress, σ_s the solid solution hardening, σ_p the precipitation hardening, and $k_y d^{-1/2}$ the contribution due to grain size. For comparative purposes we can ignore the friction stress, and can also assume that under the continuous cooling conditions used in the present experiments the solid solution hardening term will be a constant. By setting σ_y equal to the measured 0.2 pct proof stress $(\sigma_{y(0.2)})$ we have

$$\sigma' = (\sigma_{y(0.2)} - k_y d^{-1/2}) = \sigma_p + \text{constant},$$

and the variation in σ' reflects a variation in the precipitation hardening term (σ_p) over the values of λ considered, even if the constant $(\sigma_0 + \sigma_s)$ is given a maximum value. A logarithmic plot of strength (σ') against the minimum values of the intersheet spacing over the range 2 to 50°C per min is illustrated in Fig. 5. A linear relationship was expected over the range of λ values used and because of the experimental scatter was found to fit the equation

$$\sigma' = k \cdot \lambda^{-1.1}.$$

The computed values of $k_y d^{-1/2}$ used, where k_y is set equal to 1.8 kg/mm$^{3/2}$.[10] are plotted as a function of cooling rate in Fig. 4(b). It was also assumed that the minimum intersheet spacings recorded were the true intersheet spacings for the finest structures formed at the lowest temperatures and would be proportional to any mean spacing controlling the dispersion strengthening at any absolute cooling rate.

Evidence of dislocation/precipitate interactions was obtained from thin foil electron microscopy of strained specimens. As the strain rate increased it was found more and more difficult to image sharply the precipitates. Fig. 6(a) shows dislocations tangled into the precipitate sheets after ~5 pct tensile strain. By comparison with Fig. 3 it will be seen that even the larger idiomorphic vanadium carbide is difficult to image, let alone the smaller precipitates in the sheets. After 80 pct strain by rolling it was still possible to observe rows of precipitates (Fig. 6(b)) although following such severe deformation the sheets have rotated towards the rolling plane, thus making it more difficult to obtain them parallel to the electron beam when examining thin foils in the electron microscope. Fig. 6(b) also shows some evidence of a dense dislocation cell structure which is dependent on the precipitate sheet spacing.

Fig. 6(c) is similar to Fig. 6(a) except that the specimen was strained ~2.5 pct in tension at 272°C and then held under load for 30 min at this temperature. The area shown in Fig. 6(c) was a thick part of the foil observed in a JEOL 200 kV electron microscope. The stress:strain curve following yield was noticeably steep and serrated and the specimen acquired a blue tinge, indicating that straining was taking place in the blue-brittleness range for the alloy. It was intended that interstitial atoms would diffuse to the dislocations and prevent them from relaxing to equilibrium positions when the load was removed. Consequently, it is thought that some of the dislocations in Fig. 6(c) illustrate configurations representative of their behavior during straining.

Fig. 4(b) shows a distinct change in tensile ductility over the cooling rate range considered and this is also reflected by the fracture appearance of the specimens, two examples of which are shown in Fig. 7.
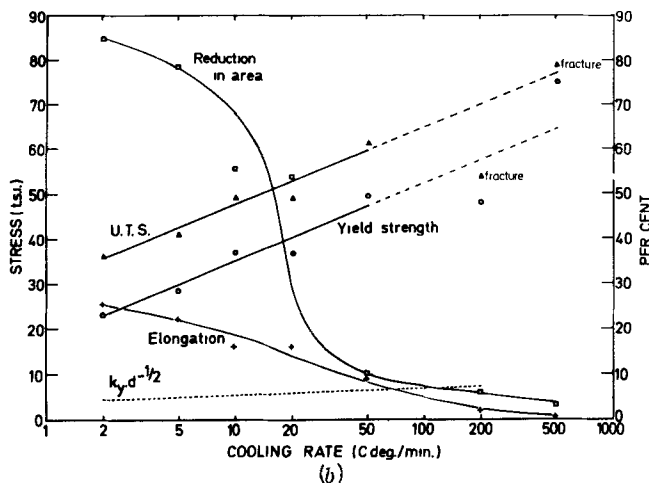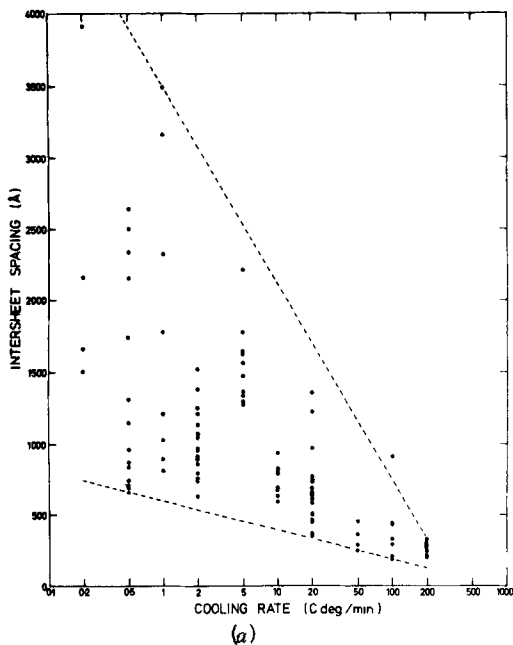
3. DISCUSSION

The present results show that transformation of an Fe-V-C low-alloy steel during continuous cooling gives a much larger spectrum of precipitate sheet spacings (Fig. 4(a)) than has been observed over a range of isothermal transformation temperatures by Batte.[7] Inevitably, at the slower cooling rates a wide scatter occurs, of the order of more than 1000Å between 0.2 and 20°C per min, because the ferrite/carbide aggregates form slowly over the largest temperature range. At a cooling rate of 200°C per min the scatter observed, even with sectioning errors, was only of the order of 100Å, indicating a much faster low temperature reaction over a smaller temperature range.

However, if the general strength levels are related to the intersheet spacings through the cooling rate, then the values correspond favorably with the results of Batte *et al.*[8] for the same alloy in the isothermally

Fig. 4 —(a) Intersheet spacing measurements, and (b) mechanical properties and the parameter $k_y d^{-1/2}$, plotted as a function of the cooling rate.
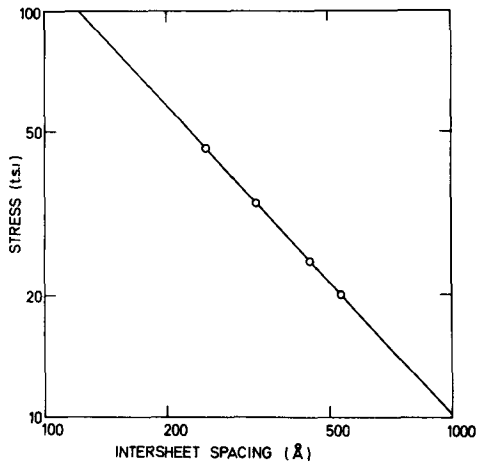
Fig. 5—The dispersion strengthening parameter σ' plotted as a function of the intersheet spacing.

transformed condition. The present results showed that the precipitate dispersion influenced the yield strength, and that the intersheet spacing (λ) can be related to the dispersion strengthening (σ_p) by an empirical relationship of the form

$$\sigma_p \propto \lambda^{-1.1}.$$

Owing to the range of spacings occurring during continuous cooling and the assumptions made, no great significance can be attached to this equation. However, preliminary studies by Batte et al.[8] first showed a tentative relationship of the form $\sigma_p \propto \lambda^{-0.5}$ for this same Fe-1 V-0.2 C alloy in the isothermally transformed condition where more accurate control of spacing is achieved. This is identical to that obtained for lamellar pearlite in plain carbon steels where λ would be the interlamellar spacing.[11] Batte[7] subsequently showed that a relationship of the form $\sigma_p \propto \lambda^{-0.7}$ best fitted the
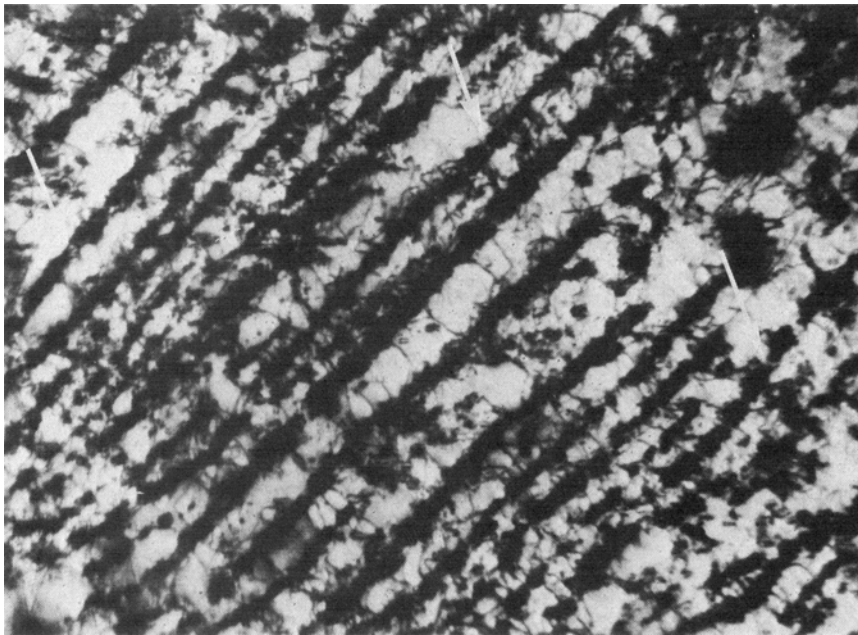

(a)
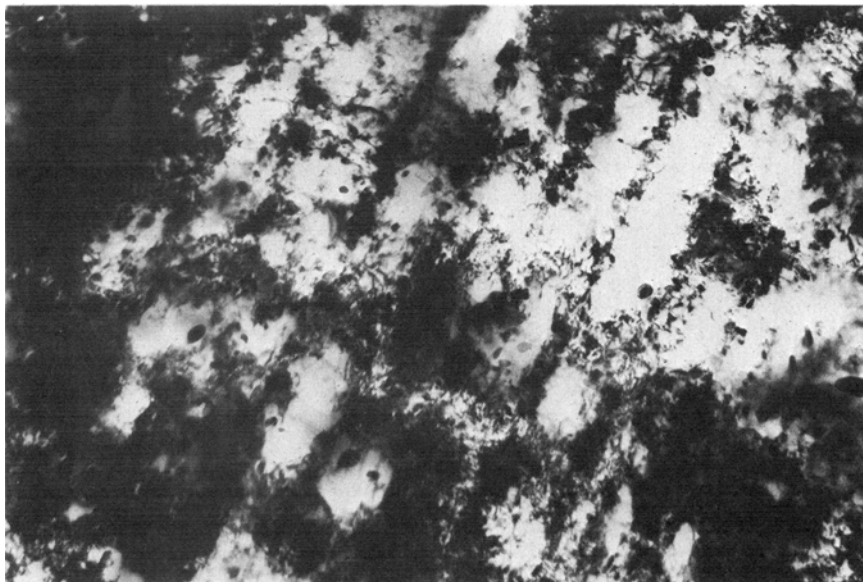
(b)

Fig. 6—Fe-1 V-0.2 C alloy (a) continuously cooled ~ 10°C per min and strained ~ 5 pct; thin foil, magnification about 19,000 times, (b) continuously cooled ~ 10°C per min and rolled ~ 80 pct; thin foil, magnification about 17,000 times, and (c) continuously cooled ~ 4°C per min and strained ~ 2.5 pct at 272°C and then annealed under stress for 30 min; thin foil, magnification about 25,000 times.

Fig. 6—Continued
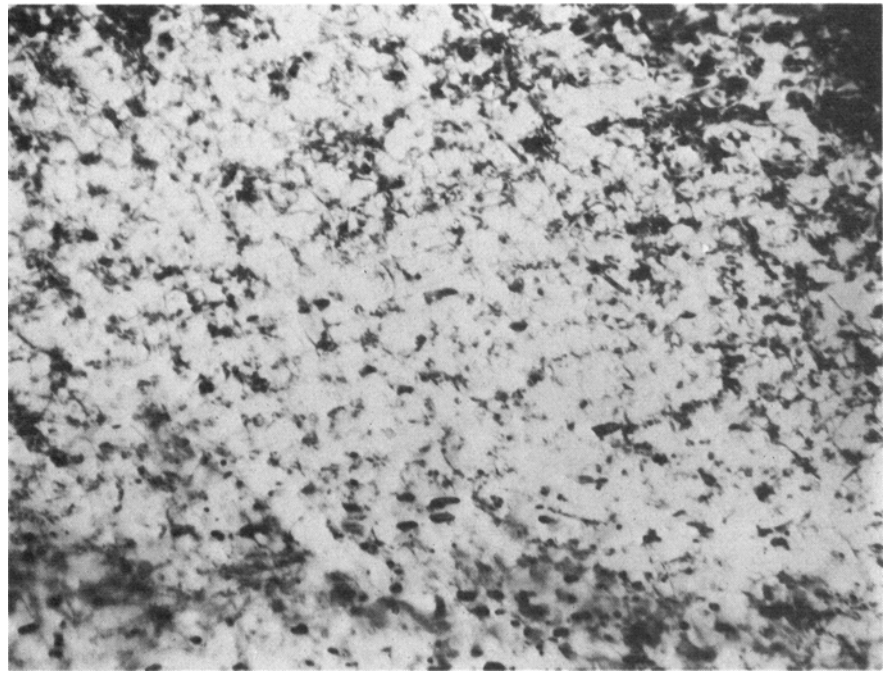
(c)

experimental data, and that this indicates behavior intermediate between an interlamellar and a random dispersion hardened structure. Furthermore, Freeman,[12] working on similar carbide dispersions in isothermally transformed Fe-Ti-C alloys has shown that an empirical relationship of the form $\sigma_p \propto \lambda^{-0.9}$ best fits his experimental data. It is worthwhile noting that the strengthening structure in these directly transformed low-alloy steels can be obtained with finer spacings than in pearlitic steels, and can also be achieved at much lower carbon concentrations.

The electron microscope observations would support the argument that the carbides could be instrumental in nucleating dislocations in the early stages of yielding, and also act as effective barriers to dislocation movement. Indirect evidence for their action as nucleation centers follows from the difficulty experienced in sharply imaging them following straining, whilst both Figs. 6(a) and 6(c) show examples of dislocations bowing between vanadium carbide particles due to pinning. A simple yielding model envisaged would be that shown schematically in Fig. 8(a) where dislocation loops expanding from precipitates A and B interact with other precipitates in the sheets. It can be seen that as the spacing of precipitates in the sheets is much less than the intersheet spacing, then impenetrable lamellae of precipitate/dislocation tangles would soon be built up, making the free path for dislocation movement necessarily between the precipitate sheets. This idea of continuous lamellae is reinforced by Fig. 6(b) which indicates sheets of precipitate which are not apparently dislocated even after very high strains. Areas similar to that dotted in Fig. 8(a) can be seen in Fig. 6(a) (arrowed), where dislocations can be resolved between precipitates in the sheets. However, in general, at the strain illustrated by Fig. 6(a) the dislocation content is high enough to make the sheets virtually continuous lines of dark contrast from the precipitate/dislocation tangles.

It is thus apparent that the precipitation reaction that occurs during the continuous cooling transformation of

alloyed austenite to ferrite can lead to a controlled dispersion of alloy carbide which can impart very high strengths to the ferrite. This suggests a potential new and simple route in the heat-treatment of low-alloy steels requiring high strengths. No longer would it be necessary to add alloying elements to improve the hardenability of low-carbon steels so as to be able to achieve a bainitic or martensitic structure that can subsequently be tempered to secondary hardening: instead, direct high-temperature decomposition at a controlled cooling rate to a uniformly dispersion-strengthened ferrite could be employed. In fact, it is likely that the Nb-containing controlled-rolled carbon-manganese steels in commercial use can attribute a substantial proportion of their strength to the fact that the ferrite contains a fine distribution of aligned NbC[9,13] formed during cooling in the way already discussed. Furthermore, the creep-resistant Cr-Mo-V steels widely used in the power generating industry, are often heat-treated nonuniformly owing to their large section size, and consequently contain large volume fractions of ferrite rather than bainite, and there is evidence that this ferrite is also strengthened by an aligned dispersion of V_4C_3 formed during cooling.[14,15]

The general levels of tensile ductility are illustrated by Fig. 4(b). These levels were not expected to be high owing to the large grain size achieved by the austenitizing temperature used in this series of experiments. However, vanadium has an advantage over Ti and Nb additions, which also give similar precipitation dispersions,[12,16] in that the solubility of vanadium carbide is greater[17] and hence generally lower austenitizing temperatures can be employed. However, Fig. 4(b) also shows that there is a catastrophic reduction in ductility, which is accompanied by a transition from fibrous to cleavage fracture (Fig. 7) at cooling rates in excess of 20°C per min. This corresponds to intersheet spacings of < 300Å, which have been achieved by Batte et al.[8] by isothermal transformation at < 775°C, and it is interesting that at about this dispersion the tensile ductility of the same alloy tested by Batte et al.[8] also showed an
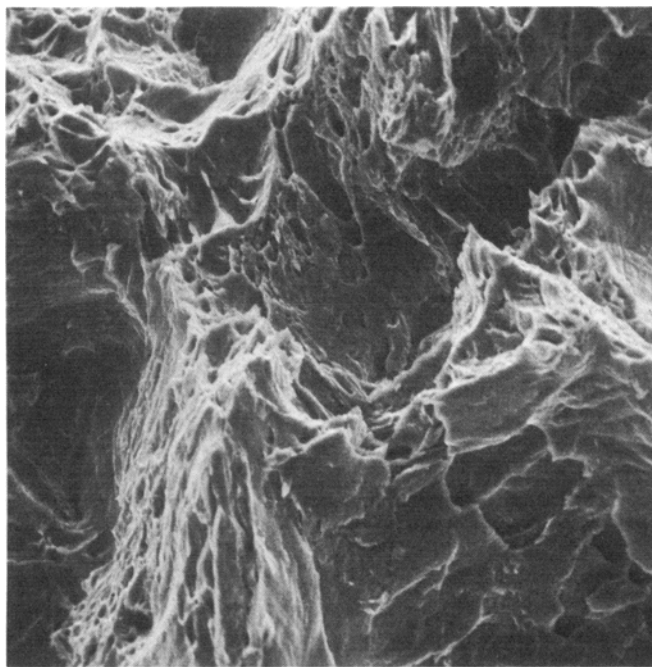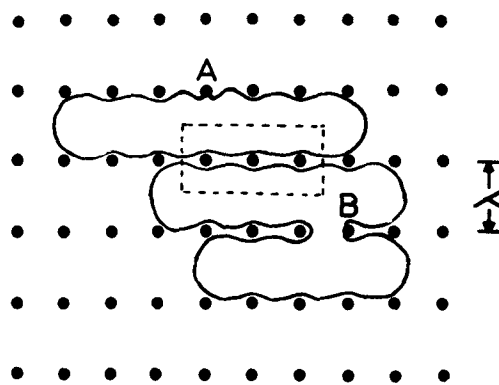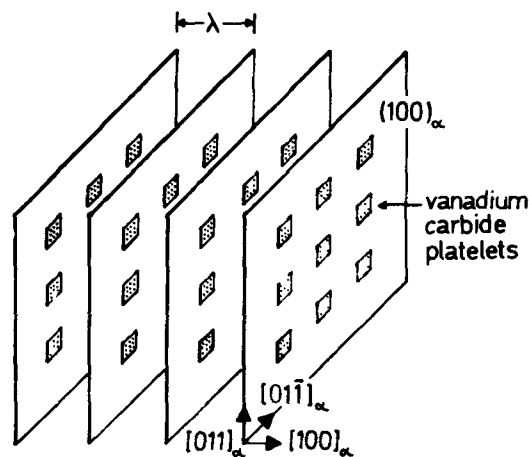
(a)
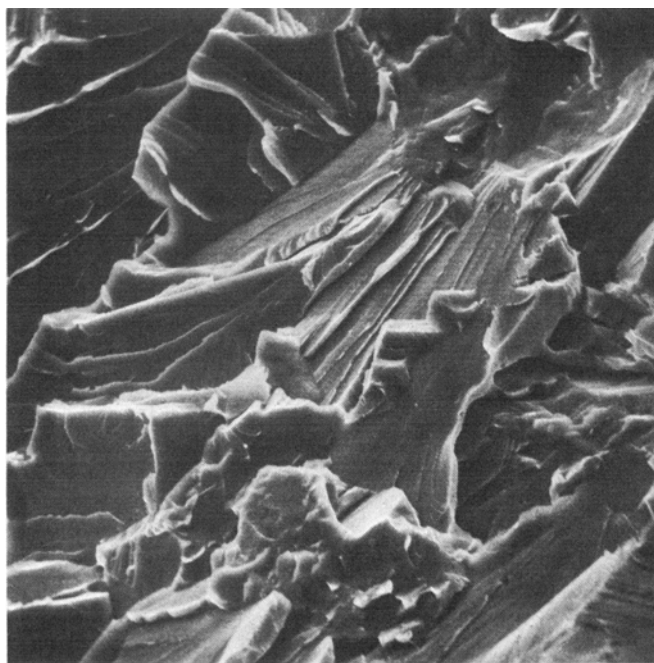
(b)

Fig. 7—Fe-1 V-0.2 C fracture surfaces: (a) continuously cooled ~ 5°C per min, magnification about 500 times, and (b) continuously cooled ~ 200°C per min, magnification about 1000 times.

(a)

(b)

Fig. 8—Schematic diagram of (a) model dislocation movement through the precipitate dispersion, and (b) the unique habit plane orientation of the vanadium carbide platelets.

abrupt ductile-brittle transition. It is a feature of the interphase precipitation reaction in Fe-V-C alloys that only one variant of the vanadium carbide platelet habit is present. At low temperatures where diffusion considerations are important this tends to be the habit plane which lies nearest to the plane of the interface.[5,18] This means that at the lower temperatures of transformation there is likely to be a predominance of precipitate sheets containing the habit plane of the vanadium carbide as illustrated in Fig. 8(b). As the habit planes of the platelets are of the form $\{100\}_\alpha$, and as this is

the cleavage plane of the bcc ferrite, it is possible that such a configuration of precipitates may reduce the effective fracture surface energy on the cleavage plane and thus reduce the ductility of the alloy. Consequently, if this is a true influence on the fracture resistance of the matrix by the precipitate dispersion, steps must be taken to compensate for this behavior, firstly by refining the grain size, and secondly by transforming at the higher transformation temperatures, before the full benefit of achieving very high strengths by simple heat treatments can be obtained. However, some advantages in ductility would be expected because of the deformability of the precipitate/dislocation lamellae which would avoid any brittle phase cracking such as occurs in more conventional pearlitic steels.[19]

4. CONCLUSIONS

1) Sheets of vanadium carbide precipitates in ferrite may be obtained by simple cooling of an Fe-1V-0.2C alloy from the austenitic condition.

2) The intersheet spacing decreases as the cooling rate is increased.

3) As the cooling rate increases the strength of the alloy increases, but the tensile ductility is reduced.

4) The dispersion strengthening due to precipitation varied with the intersheet spacing as

$$\sigma_p = k \cdot \lambda^{-1.1}$$

where σ_p is the dispersion strengthening component of

the yield strength, and λ is the intersheet spacing.

5) Electron microscopy shows evidence of both dislocation nucleation and dislocation pinning by the vanadium carbide precipitates, and also that the sheets of precipitate develop into lamellae of precipitate/dislocation tangles in the early stages of straining.

6) An abrupt reduction in tensile ductility observed in the experimental alloy at a cooling rate >20°C per min could be attributable to the orientation and distribution of the vanadium carbide precipitates resulting from the interphase precipitation mechanism, and highlights the importance of grain size control if both high strengths and high ductilities are to be obtained by this simple heat treatment process.

ACKNOWLEDGMENTS

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