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Precipitation of vanadium carbides in 0.8% C–13% Mn–1% V austenitic steel

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The precipitation mechanism of vanadium carbides in 0.8% C–13% Mn–1% V austenitic steel was investigated by transmission electron microscopy and energy dispersive X-ray spectroscopy techniques. The precipitate size and nucleation sites were observed to differ with different heat-treatment cycles applied. Carbide particles were mainly seen to precipitate on grain boundaries, in the matrix and in association with stacking faults, depending on the ageing conditions. Characteristic stacking fault contrast was observed after ageing at low temperatures and stacking fault precipitation occurred in the samples that were water quenched and aged at high temperatures; whereas samples which were not water quenched showed only local matrix precipitation. Energy dispersive X-ray spectroscopy showed that the carbide particles are rich in vanadium. The observations suggest that the nucleation of these particles on stacking faults depends on the point defect concentration and dislocation density in the matrix, prior to ageing.

1. Introduction

To improve the wear resistance of austenitic 0.8% C–13% Mn–1% V steel without seriously reducing its toughness, a logical approach appears to lie in the production of properly dispersed hard carbides in the austenite matrix. In a research conducted previously, Atasoy [1] investigated the effects of heat-treatment procedures and alloying on the carbide dispersion of the austenitic manganese steel. The fine carbides homogeneously distributed throughout the austenitic matrix of Fe–0.8% C–13% Mn–1% V alloy have been produced by applying the so-called "step ageing process" [1].

Several observations have been made using transmission electron microscopy (TEM) to explain the morphology of carbide precipitates on dislocations and stacking faults that occurred in austenitic steels of 18% Cr/10% Ni/1% Nb [2–4], 24% Mn/0.7% V/0.4% C [5], 18% Cr/12% Ni/2% Ta [6, 7], 16% Cr/16% Ni/1.5% V/0.13% C [8], and 16% Cr/16% Ni/1.0–5.0% V/0.1–0.5% C [9].

In this study, the precipitation mechanism of vanadium carbides in 0.8% C–13% Mn–1% V austenitic steel was investigated by TEM and energy dispersive X-ray spectroscopy (EDS) techniques.

2. Experimental details

Details of the techniques used for melting, casting and the type of heat treatments are given elsewhere [1]. Prior to heat treatment, the samples were homogenized for several hours at 1350° C in evacuated silica tubes. After homogenizing, the samples were subjected to solution treatment for 2 h at 1150° C in evacuated silica tubes, and capsules were smashed on rapidly entering the water. Specimens were then re-encapsulated in evacuated silica tubes prior to ageing.

The structures produced by different heat treatments were studied using optical microscopy, TEM and EDS techniques. Thin foils for TEM were prepared from the heat-treated samples by electropolishing in 5% perchloric and 95% acetic acid solution at 15° C. Thin foils were then studied using a Hitachi-200F TEM operated at 200 kV.

3. Results

3.1. Optical microscopy

Fig. 1 shows the as-cast structure of Fe–0.8% C–13% Mn–1% V alloy. The structure consists of heavy

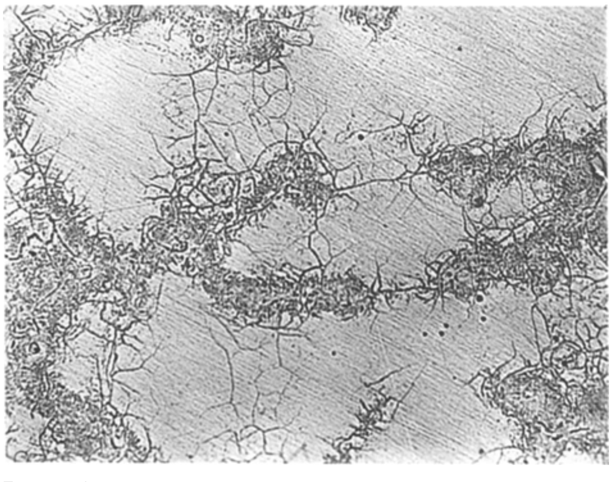


Figure 1 As-cast microstructure showing a coarse carbide dispersion on and around the grain boundaries.

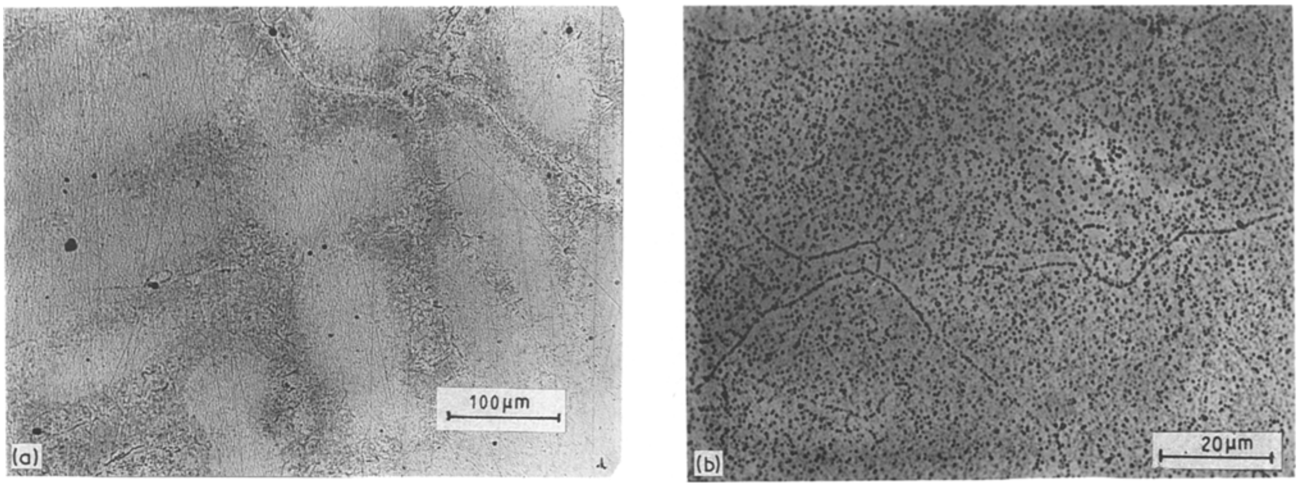


Figure 2 Microstructures (a) after solution treatment followed by ageing at 950° C for 6 h, and (b) after "step ageing".

carbide precipitation on and around the grain boundaries. After solution treatment at 1150° C followed by water quench, the structure shows evidence of undissolved fine carbide dispersion around the grain boundaries. This observation indicates that the solution treatment at 1150° C for 2 h was insufficient to take all the carbides into solution.

Figs 2a and b show the structures after solution treatment followed by ageing at 950° C for 6 h (heat treatment VII in [1]) and after solution treatment followed by ageing at 650° C for 1 h, then heating up to 950° C and ageing at this temperature for 6 h (heat treatment VI in [1]). The latter is called step ageing. Both heat treatment procedures prevented the formation of continuous carbide films at the grain boundaries. The step-aged samples showed an austenite matrix structure with fine vanadium carbides uniformly distributed therein (Fig. 2b). In the samples that were not subjected to a step-ageing treatment, only a zone containing fine precipitates was observed adjacent to the grain boundaries (Fig. 2b). However, the samples that were not subjected to a solution treatment did not show a continuous grain-boundary precipitation, as shown in Fig. 3. Instead, a fine precipitation of carbides around the grain boundaries occurred.

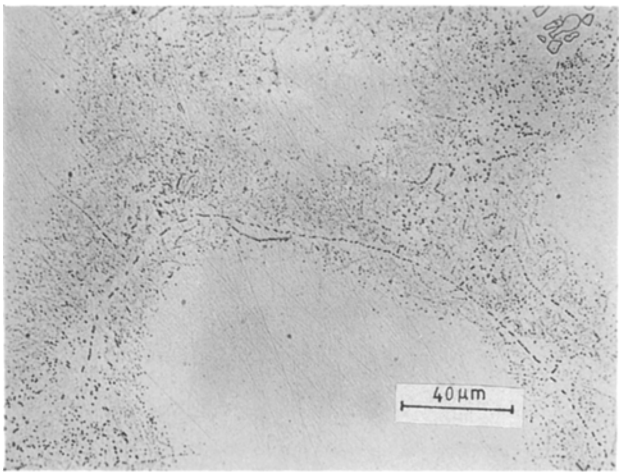


Figure 3 Microstructure after step ageing without solution treatment, showing the fine carbide dispersion on and around the grain boundaries.

3.2. EDS studies

Fig. 4 shows an electron micrograph of the grain-boundary carbides (a) and the vanadium (b) and manganese (c) X-ray maps of the same region. All the samples studied with EDS showed the same trend; i.e. carbides being rich in vanadium. Elemental distribution of manganese was random throughout the structure in all the samples investigated in this study.

3.3. TEM studies

3.3.1. Ageing at 350° C

After solution treatment followed by ageing at 350° C for 5 h, large numbers of stacking faults and undissociated dislocations were observed. The fringe contrast was visible, however no precipitation on faults was observed after ageing at this temperature, as shown in Fig. 5.

3.3.2. Ageing at 600° C

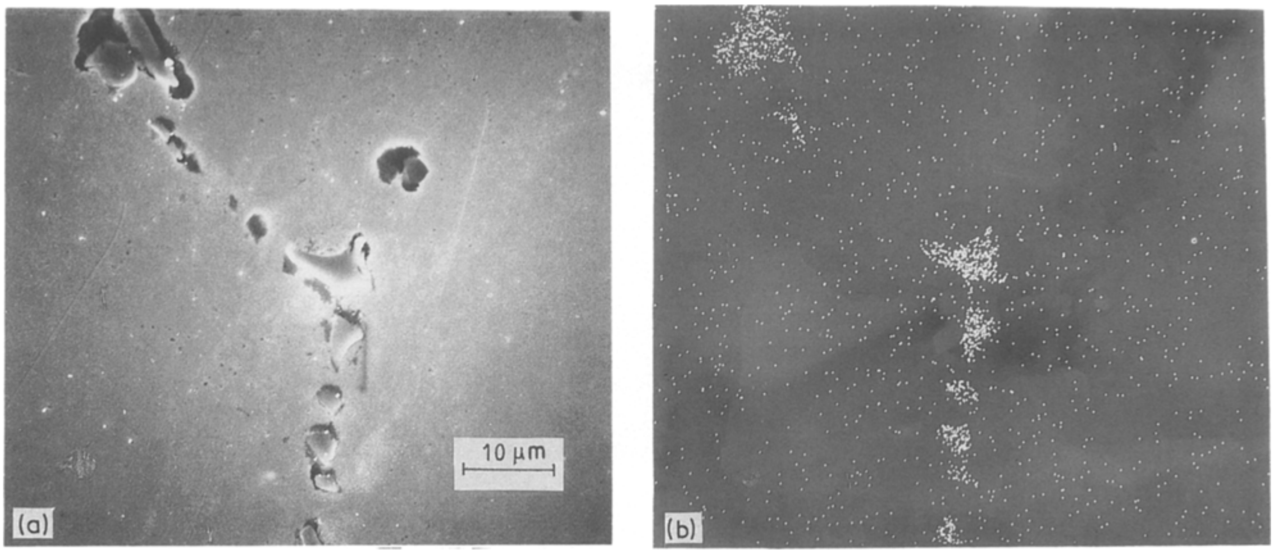
Fig. 6 shows the microstructure after solution treatment followed by ageing at 600° C for 96 h. This heat treatment resulted in partial matrix precipitation around the grain boundaries (Fig. 6a). The microstructure showed no indication of stacking fault precipitation. The diffraction patterns taken from the matrix region showed precipitate spots, as shown in Figs 6b and c. The vanadium carbide precipitates observed were grown to a large size at grain boundaries (Fig. 6d). The strain field contrast due to the lattice mismatch between the V_4C_3 and austenite was visible in the thin foils.

3.3.3. Ageing at 950° C

Figs 7a and b show the structure after solution treatment followed by ageing at 950° C for 6 h. The structure consisted of stacking faults and a fine dispersion of carbide particles within the faults, as well as matrix precipitates around the grain boundaries.

3.3.4. Step ageing

To increase the fine carbide dispersion by increasing the number of critical sized carbide clusters for nucleation, a step-ageing procedure was carried out at 650° C for 1 h and then at 950° C for 6 h, after solution treatment. The resultant structures are shown in Figs



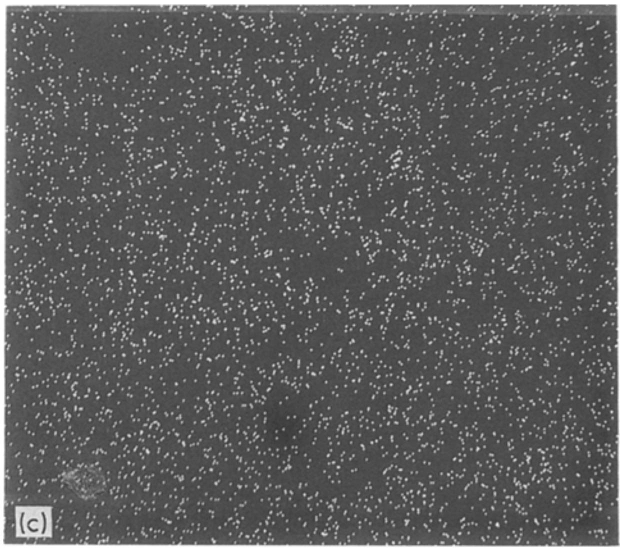


Figure 4 Electron micrograph of grain boundary carbides (a), their vanadium (b) and manganese (c) X-ray maps.

8 and 9. Holding at 650° C for 1 h then heating at 950° C gave a larger density of fine precipitates on the stacking faults and throughout the matrix, as evident in comparing these micrographs to that of Fig. 7. The carbide particles that precipitated on stacking faults are typically 5 to 10 nm diameter, whereas the carbides precipitated in the matrix are 20 to 25 nm diameter.

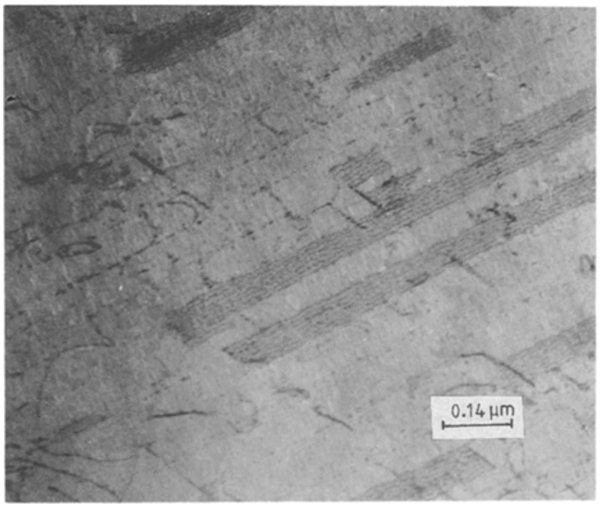


Figure 5 Transmission electron micrograph after solution treatment followed by ageing at 350° C for 5 h, showing the large numbers of stacking faults and undissociated dislocations.

3.3.5. Step ageing without solution treatment

To examine the effect of supersaturation of point defects on the precipitation of vanadium carbides, the step-ageing treatment at 650° C and heating up and ageing at 950° C for 6 h, without solution treatment, was carried out. Only the matrix precipitates around the grain boundaries were observed at this stage, as shown in Fig. 10.

3.3.6. Crystallographic relationship between the carbides and matrix

The selected-area diffraction patterns showed the presence of V_4C_3 precipitates with sodium chloride unit cell that exhibited a cube–cube orientation relationship with the fcc austenite, as shown in Figs 6, 7 and 9.

4. Discussion

The as-quenched samples after solution treatment at 1150° C for 2 h did not exhibit any precipitates associated with stacking faults. Marked formation of stacking faults did not occur until the steel was aged at 350° C for 5 h. At this stage, the structure consisted of both undissociated dislocations and stacking faults, but no evidence of carbide precipitation on stacking faults was visible, as seen in Fig. 5. Ageing at a higher temperature, i.e. at 600° C for 96 h gave partial matrix precipitates (Fig. 6a). Matrix precipitates were small in size; however, larger precipitates were observed on grain boundaries (Fig. 6d). The increase in ageing temperature from 350 to 950° C resulted in an increase in the diffusivity of vanadium in the austenite with the result that the growth of precipitate particles became very fast. Fig 7 shows the extent of precipitation following ageing at 950° C for 6 h, which gave evidence of stacking fault formation, and precipitation on both stacking faults and partially in the matrix. Extensive stacking fault precipitation occurred along with those present throughout the matrix, when step ageing was carried out, as can be seen in Fig. 8.

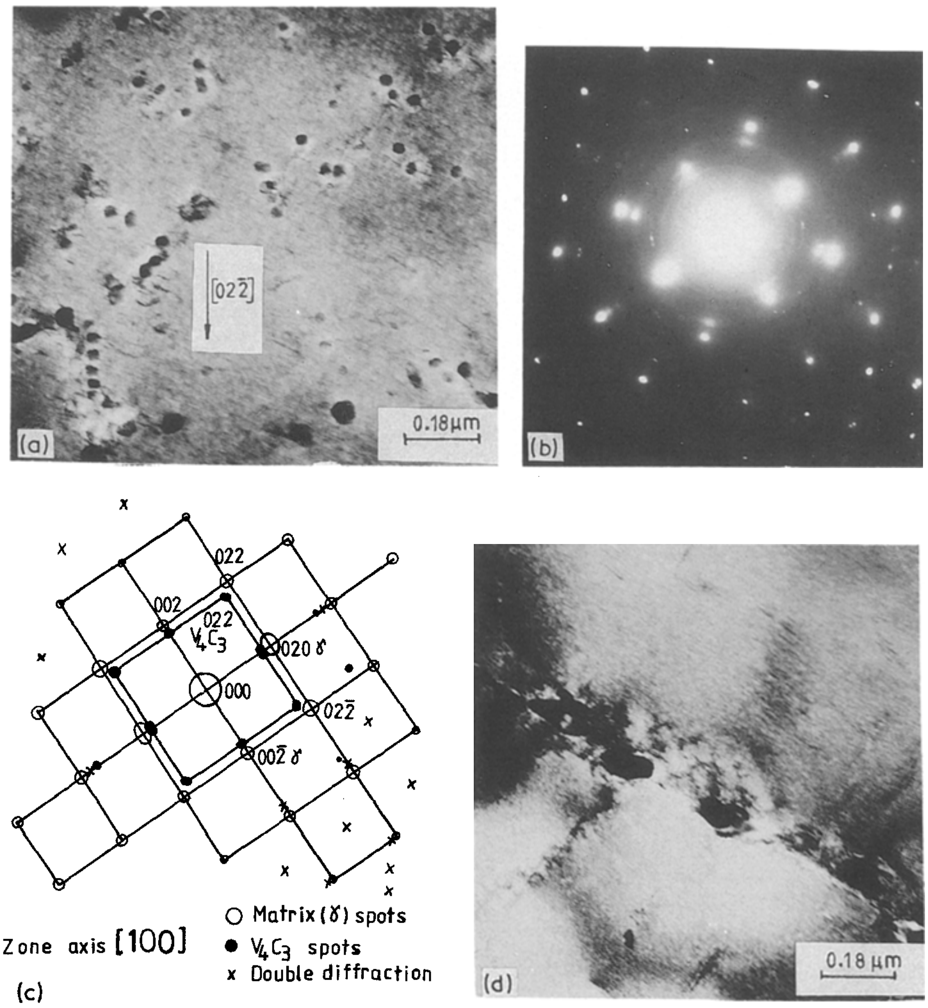
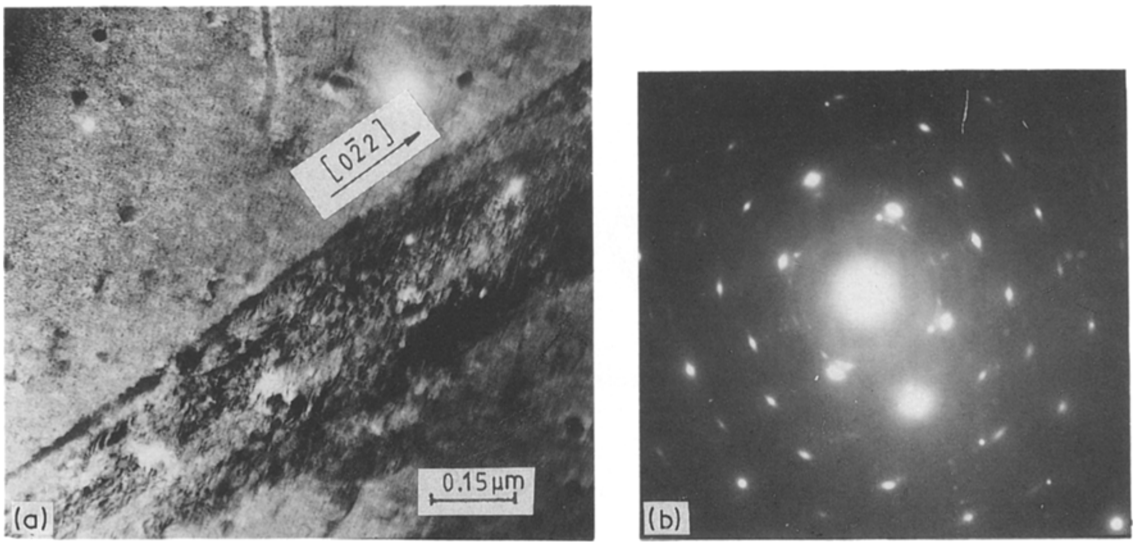


Figure 6 Transmission electron micrographs after solution treatment followed by ageing at 600° C for 96 h, showing (a) partial matrix precipitation and strain field contrast around the carbides, (b) SADP from same area (the image-pattern rotation has not been corrected), (c) indexed pattern and (d) coarse carbide precipitation on the grain boundary.



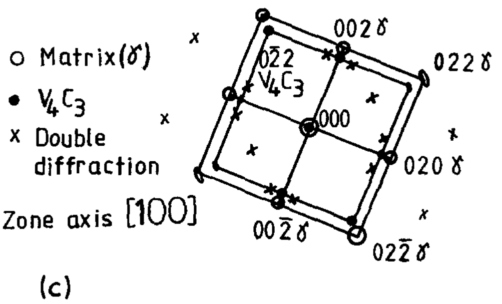


Figure 7 Transmission electron micrographs after solution treatment followed by ageing at 950° C for 6 h, showing (a) fine carbide precipitation within the stacking faults, (b) SADP from same area (the image-pattern rotation has not been corrected), and (c) indexed pattern.

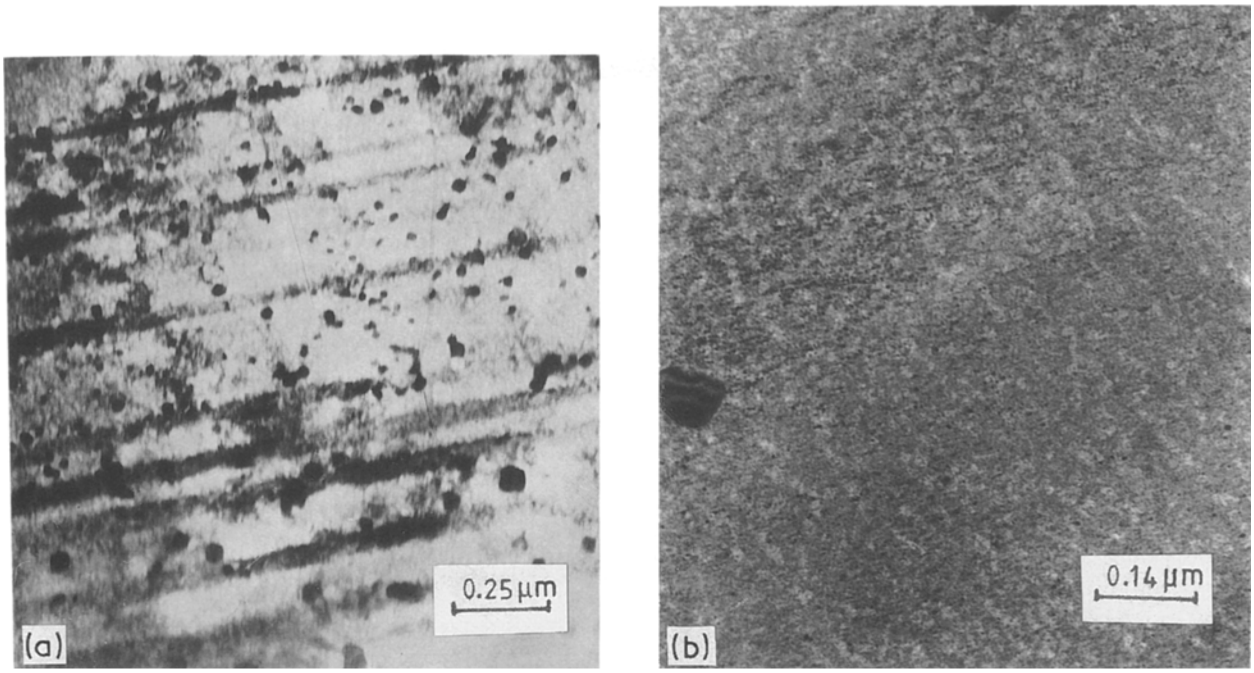


Figure 8 Transmission electron micrographs after solution treatment followed by step ageing. Stacking fault fringe contrast disappears due to the fine carbide precipitation.

4.1. Effect of quenched-in vacancies

The stacking fault formation is considered to be the result of supersaturation of solute (vanadium) atoms, dislocation density and the concentration of vacancies [2, 6]. The nucleation of stacking faults requires vacancies to condense on dislocations. The suitable stacking fault sites are formed by the climb of dislocations induced by quenched-in vacancies [8]. Once the fault growth begins then the production of vacancies by climb of Frank partials helps to accommodate more carbide precipitates at least when they are in the nucleation and early growth stages.

Fig. 10 shows only local matrix precipitation around the grain boundaries of the alloy that is step aged without solution treatment. There was no evidence of stacking fault formation, in contrast to the samples that were solution treated and water quenched prior to step ageing, as shown in Fig. 8. This suggests that quenching after solution treatment causes supersaturation of vacancies as well as vanadium.

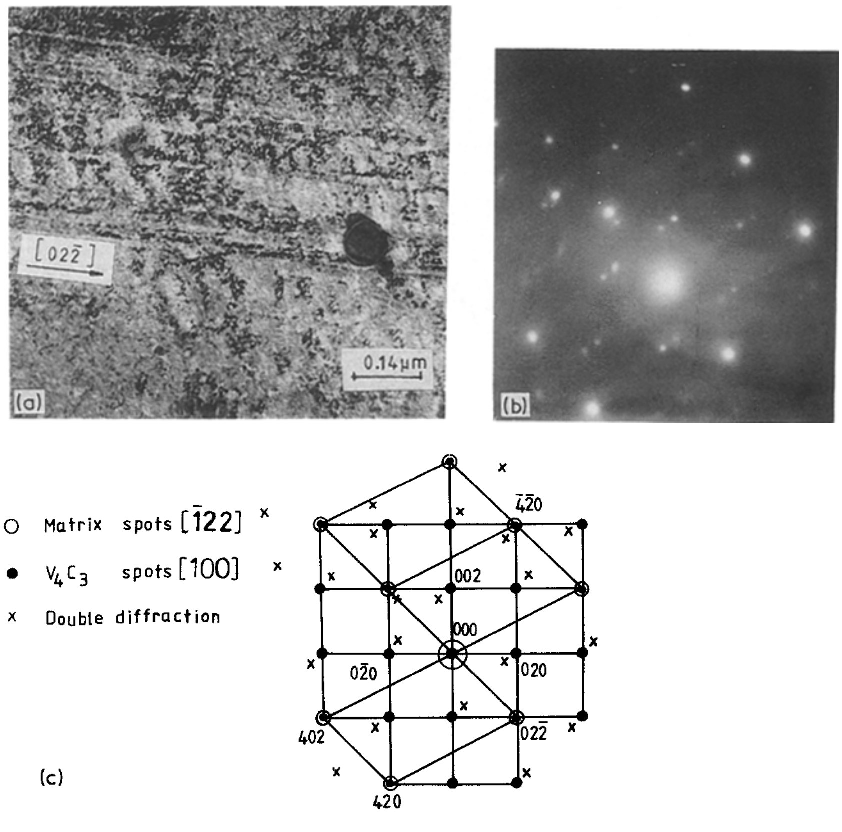


Figure 9 Transmission electron micrograph after solution treatment followed by step ageing, showing (a) fine carbide precipitation within the stacking faults, (b) SADP from same area (the image pattern rotation has not been corrected), and (c) indexed pattern.

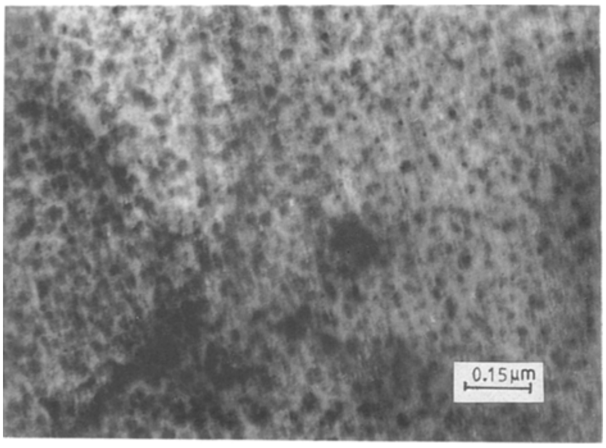


Figure 10 Transmission electron micrograph after step ageing without solution treatment, showing local matrix precipitation of carbides around the grain boundaries.

4.2. Matrix precipitation

The vacancies are thought to be associated with vanadium atoms at the early stages of ageing. The resultant "vanadium–vacancy pairs" can be sufficiently mobile to form clusters slowly on a local basis [5]. The growth of clusters into stable nuclei takes place by local migration of vanadium-vacancy groupings. A significant local vacancy concentration may be required before effective stable carbides are formed in the matrix. The formation of stacking faults appears to permit the formation of a finer dispersion than that resulting from "vanadium-vacancy groupings" in the matrix. The coarse carbides precipitated in the matrix generate dislocations as a result of local lattice distortions [3].

4.3. Step ageing

The comparison of the microstructures of the samples with and without step-ageing treatment indicates that there is a critical ageing temperature above which the clusters will reach a critical size before any further growth occurs. The carbides grow after ageing at 950° C for 6 h on carbide particles that have grown after pre-ageing at 650° C for 1 h to the critical size required for nucleation at 950° C. The pre-treatment at 650° C effectively controls the number of stable nuclei at 950° C ageing temperature [10]. During the isothermal heating period at 950° C the precipitation of carbide-forming vanadium atoms occurs to both critical-sized clusters and dislocations already slightly dissociated due to the low stacking fault energy (10 to 20 mJ m^{-2}) [11], of the austenite matrix, with a consequent further lowering of stacking fault energy, which causes the dislocations to dissociate. After a few hours of residence at 950° C, the extension of the stacking fault bands continues but the fringes become spotted and gradually disappear, due to the formation of a very fine uniform precipitation, as shown in Fig. 8.

5. Conclusions

1. The so-called "step-ageing" process produces fine carbides homogeneously distributed throughout the austenite matrix of Fe–0.8% C–13% Mn–1% V alloy.
2. The stacking fault formation is connected with the concentration of the quenched-in vacancies. The formation of stacking faults appears to permit the formation of a finer dispersion than that resulting from a random nucleation in the matrix.
3. The vanadium-vacancy groupings produce stable nuclei of carbides in the matrix.
4. The carbides grow after ageing at 950° C for 6 h on carbide particles that have grown after preageing at 650° C for 1 h to the critical size required for nucleation at 950° C.

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