Effects of magnesium and long-term ageing on intragranular precipitation in Fe–Cr–Ni–Mn–Mo–V–Nb superalloy

LI YUQING, GONG YUHAN
Research Institute of Daye Steel Works, Huangshi, Hubei Province 435001, People's Republic of China

Adding a suitable amount of magnesium to Fe–Cr–Ni–Mn–Mo–V–Nb alloy decreases large-sized intragranular lamellae and dentritic lamellae of $M_{23}C_6$, promotes the loss of the coherent relationship between intragranular small $M_{23}C_6$ block and mother phase and causes $M_{23}C_6$ lamellae to become spherical. During long-term ageing, intragranular fine VC precipitate as well as VC particles conglomerate. A mechanism by which some dislocations can cut across the VC particles is suggested. Increase in misfit between VC and austenite is about 1% at 160 p.p.m. magnesium content or after long-term ageing for 1000 h at 650 °C. The misfit between VC ribbon precipitated along dislocations and matrix is smaller than that between the VC particles near the ribbons and matrix.

1. Introduction

The size of intragranular VC particles have been measured by means of TEM, and the orientation relationships and the misfits between VC and austenite and between $M_{23}C_6$ and austenite in Fe–Cr–Ni–Mn–Mo–V–Nb alloy have been analysed [1, 2]. The stress–rupture life for notched specimens, the strengthening and weakening mechanism in grain boundaries and the effects of magnesium on grain boundaries in the alloy have also been studied [3]. In the present work, on the basis of above studies, the effects of magnesium and long-term ageing on the morphology, distribution of the intragranular VC and $M_{23}C_6$, and on the misfits between VC and mother phase and between $M_{23}C_6$ and mother phase were examined using thin foils of the alloy. A mechanism by which some dislocations can cut across the VC particles is discussed.

2. Experimental procedure

All the specimens were selected from 90 mm wrought square stock which had been electric arc melted and electric slag remelted, except Specimen B1 which was prepared from 20 mm wrought square stock which had been smelted in an electric furnace. The chemical composition (wt %) of the alloy is as follows: C 0.36, Mn 8.4, Cr 12.4, Ni 8.2, Mo 1.3, V 1.5, Nb 0.33, Ti 0.02, Al 0.12–0.30, Fe balance. Specimens A contain a negligible amount of magnesium and the magnesium contents of Specimens B are shown in Table I. The heat-treatment procedures and the stress-ageing state for the specimens are shown in Table II.

Sample slices, 250 μm thick, cut from the fractures of the above specimens were mechanically reduced to a thickness of 60 μm, and electrolytically reduced in a solution of 70% alcohol, 20% *n*-butyl alcohol and 10% perchloric acid to render them suitable for handling in the TEM. The appearance and distribution characterization of intragranular precipitates were investigated using a CM12 electron microscope on the foils. The coherent relationships between VC and the mother phase and between $M_{23}C_6$ and the mother phase, and the habits of $M_{23}C_6$ were analysed from the electron diffraction patterns. The misfits between VC and austenite and between $M_{23}C_6$ and austenite were determined, and a mechanism by which some dislocations could cut across the VC particles is discussed from the corresponding Moiré patterns.

3. Results and discussion

3.1. The effects of magnesium and long-term ageing on intragranular $M_{23}C_6$

3.1.1. Intragranular $M_{23}C_6$ after normal heat treatment

In Specimen A1 containing a negligible amount of magnesium, a large number of $M_{23}C_6$ appeared as long-flakes (Fig. 1a); and the rest appeared to be small stock. A simple coherent relationship existed between the $M_{23}C_6$ and austenite (Fig. 1b). It was determined that the habit of long-flaky $M_{23}C_6$ in (1 1 2) orientation (Fig. 1a) was (1 1 1) of austenite. The average spacing, *D*, was measured from the parallel Moiré pattern (Fig. 1a) of $(2\,2\,0)_\gamma$ and $(6\,6\,0)_{M_{23}C_6}$ diffractions, and the lattice parameter of austenite was known to be $a_\gamma = 0.3594$ nm [2], thus the misfit between the $M_{23}C_6$ and the mother phase was calculated to be 1.15%–1.68% according to the following equation [2, 4]

$$\delta = 2a_\gamma/(2D\,N^{1/2} + a_\gamma) \qquad (1)$$

TABLE I Magnesium contents (p.p.m.) of Specimens B

Specimen	Mg	Specimen number	Mg
B1	160	B2	68
B3, B4	66	B5	45

where $N = h^2 + k^2 + l^2$, h, k and l are 2, 2 and 0, respectively.

In Specimen B1 containing 160 p.p.m. Mg, a large number of $M_{23}C_6$ appeared as small stocks, the rest long-flakes. In general, the $M_{23}C_6$ small stocks were distributed along the direction parallel to the slip traces, thus, the habit plane of the $M_{23}C_6$ was determined to be $\{1\,1\,1\}$ of austenite. When a suitable amount of magnesium is added to the alloy, it can enter the grain boundaries of $M_{23}C_6$, thus magnesium can cause a large distortion of the $M_{23}C_6$ lattice and decrease or even almost eliminate the coherent $M_{23}C_6$ lamellae, and the $M_{23}C_6$ particles can substitute for the lamellae [3]. This result shows that the $M_{23}C_6$ small stocks in a specimen containing a suitable amount of magnesium substituted for the long-flaky $M_{23}C_6$ in the specimen containing a negligible amount of magnesium. Thus we can see that the effect of magnesium on intragranular $M_{23}C_6$ is similar to that of magnesium on intergranular $M_{23}C_6$.

3.1.2. *The effect of long-term ageing on intragranular $M_{23}C_6$*

In Specimen A2 containing a negligible amount of magnesium, the amount and size of intragranular $M_{23}C_6$ increased noticeably compared to that in specimen A1. Some $M_{23}C_6$ usually appeared as dentritic lamellae, in addition to a large number of long flakes and small stocks. The dentritic lamellae grow rapidly with increasing long-term ageing or long-term stress-ageing time (Fig. 2a).

In Specimen B2 containing 68 p.p.m. Mg, although the amount and size of intragranular $M_{23}C_6$ increased noticeably compared to that in Specimen B1, the $M_{23}C_6$ usually precipitated in the homogeneously dispersed small stock form and the amount and size of the dentritic lamellae decreased compared to that in Specimen A2. After long-term ageing for 1000 h at 650 °C, with increasing stress-ageing time, the $M_{23}C_6$ stocks in specimens with magnesium grew, the corners of the carbides were lost (Fig. 2b), and the electron diffraction patterns showed that the coherent relationship between the $M_{23}C_6$ and the mother phase was gradually lost. Similar to the grain-boundary $M_{23}C_6$ in the specimen containing a little magnesium, because the $M_{23}C_6$ grows gradually with increasing long-term ageing time, the lattice beside the coherent interface between the $M_{23}C_6$ and the austenite were mismatched, resulting in an increase in elastic energy in both $M_{23}C_6$ and austenite; hence, the interfaces will become unstable and become a semicoherent or even an incoherent interface, resulting in a decrease in total energy [3]. The intragranular $M_{23}C_6$, which lost its coherent relationship with the austenite, always tends to minimize its surface energy, and will gradually become stocky or granular (Fig. 2b).

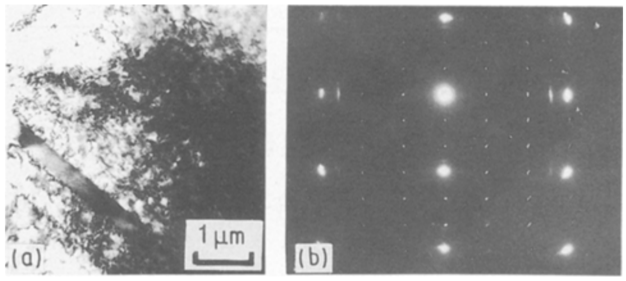

Figure 1 (a) Intragranular long-flaky and flaky $M_{23}C_6$ showing the Moiré pattern in Specimen A1, and (b) the composite electron diffraction pattern of $[1\,1\,2]_{M_{23}C_6}$, $[1\,1\,2]_\gamma$ and $[1\,1\,2]_{VC}$ zones.

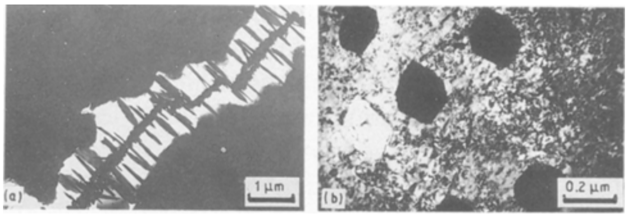

Figure 2 (a) Intragranular $M_{23}C_6$ dentritic lamellae in Specimen A3; (b) intragranular stocky $M_{23}C_6$ in Specimen B3.

3.2. The effects of magnesium and long-term ageing on intragranular VC

3.2.1. *Intragranular VC after normal heat treatment*

The morphology and distribution of intragranular VC in Specimen A1 with a negligible magnesium content were similar to those of Specimen B1 containing 160 p.p.m. Mg. The VC has a simple coherent relationship with austenite (Fig. 1b) and a transformation matrix from the plane index of γ to that of VC has

TABLE II The heat-treatment procedures and stress-ageing state for the specimens

Specimen	Heat-treatment procedure[a]	Stress-ageing state
A1, B1	1140 °C, 2 h, WC + 660 °C, 16 h + 770 °C, 16 h, AC (normal heat treatment)	
A2, B2	Normal heat treatment + 650 °C, 1000 h, AC	
A3	Normal heat treatment + 650 °C, 1000 h, AC	650 °C, 373 MPa, 113 h
B3	Normal heat treatment + 650 °C, 1000 h, AC	650 °C, 373 MPa, 703 h
B4	Normal heat treatment + 650 °C, 600 h, AC	650 °C, 373 MPa, 645 h
B5	Normal heat treatment + 650 °C, 1000 h, AC	800 °C, 147 MPa, 206 h

[a] WC and AC are water-cooled and air-cooled, respectively.

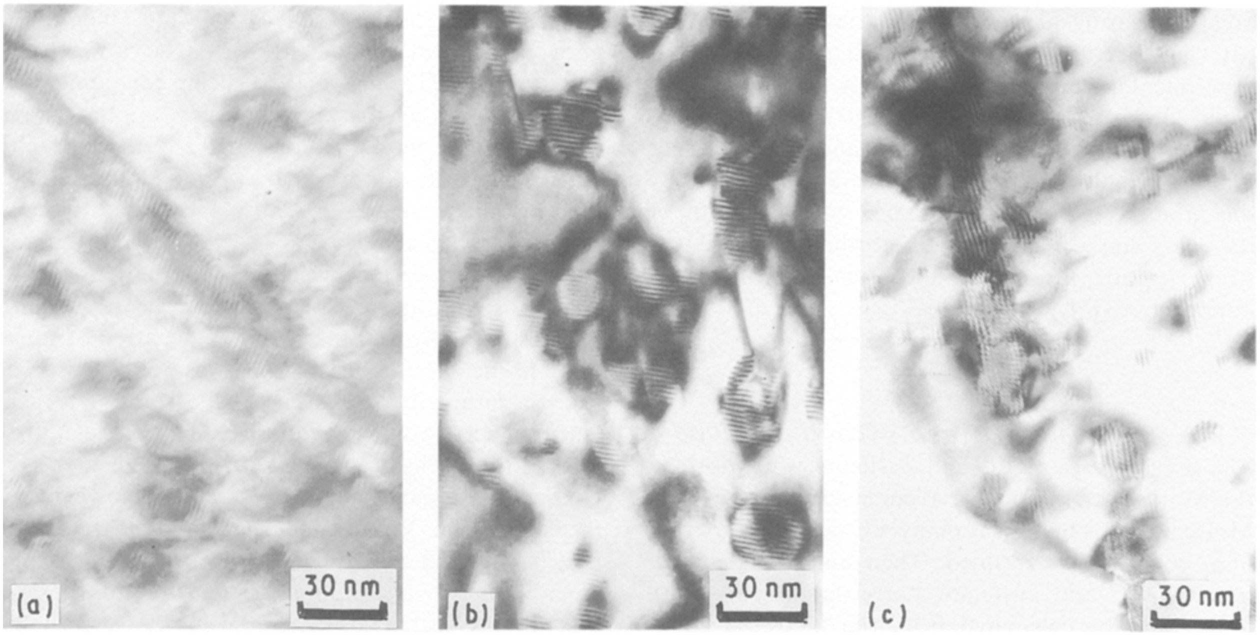

Figure 3 The precipitation features of intragranular VC in Specimens (a) B1 and (b, c) B2.

been obtained as follows

$$[_{VC}S_{\gamma}] = 1.16\,[I] \quad (2)$$

where $[I]$ is the unit matrix.

The bright field image of intragranular VC which retained a coherent relation with austenite reveals a parallel Moiré pattern with a spacing D. The precipitation features of intragranular VC are fully revealed by the Moiré patterns at high magnification. The VC normally precipitated in the homogeneously dispersed granular form, but some VC precipitated along dislocations and formed continuous ribbons (Fig. 3a) in both Specimens A1 and B1. The enlarged Moiré pattern of the (1 1 1) lattice of VC in Fig. 3a resulted from (1 1 1) spots of austenite and VC [4].

3.2.2. *Intragranular VC after long-term ageing*

After long-term ageing for 1000 h at 650 °C, in both Specimen A2 with a negligible magnesium content and Specimen B2 containing 68 p.p.m. Mg, intragranular VC particles conglomerated, small VC particles were precipitated (Fig. 3b), and the density of VC increased. VC conglomerates were found along dislocations in both these specimens (Fig. 3c). Fig. 3b shows the enlarged $(\bar{1}\,\bar{1}\,1)$ lattice of VC and Fig. 3c shows the enlarged $(\bar{1}\,\bar{1}\,1)$ and $(0\,\bar{2}\,2)$ lattices of VC.

During long-term ageing and long-term stress-ageing, the density of VC increases and the VC usually retains its coherent relation, described by Equation 2, with austenite, hence, the interactions between dislocations and VC particles under fracture force or stress were similar to those between dislocations and γ' phases in some superalloys: the dislocations could not only by-pass the VC particles but also cut up and pass through them. Fig. 4a shows the enlarged $(\bar{1}\,\bar{1}\,1)$ and $(0\,\bar{2}\,2)$ lattices of VC in (0 1 1) orientation (Fig. 4b); the dislocations cut some VC particles in two. From Fig. 4b, the slip plane of the dislocations cutting VC particles was the $(1\,\bar{1}\,1)$.

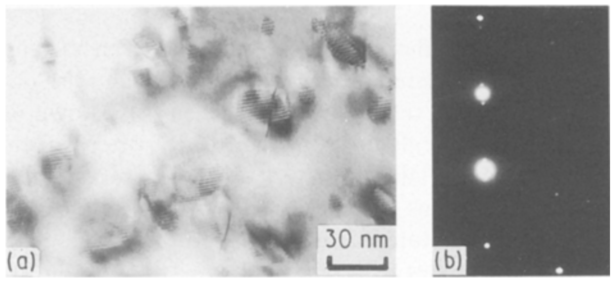

Figure 4 (a) Dislocations cutting and passing through the VC particles in Specimen B2; (b) selected-area electron diffraction pattern of [0 1 1] zone, corresponding to (a).

If the alloy is properly heat treated, it is possible to form large-sized intergranular filmy VC. In addition, dislocation pile-ups in the intergranular filmy VC extracted have also been observed [5, 6]. Once the dislocation pile-ups in VC of the alloy have been observed and the VC particles maintained the simple coherent relationship with austenite, it is possible for the dislocations to cut up and pass through VC particles under fracture force or stress.

The dislocations cutting γ' particles have to overcome antiphase boundary energy in the γ' phase. Although there was no domain boundary in the VC particle, due to the greater misfit between VC and the mother phase, the dislocations had to overcome a bigger stress field around the VC particles and the carbon atoms in VC could check dislocation movement [5, 6]. Thus a higher grain strength in the alloy was obtained. After long-term ageing, larger $M_{23}C_6$ lamellae-accumulated areas appeared at grain boundaries of the alloy, resulting in decreased grain-boundary strength [3]. Therefore, the grain-boundary strength and grain strength of the alloy do not have enough coordination and the stress–rupture life of the alloy containing negligible magnesium is lower [3].

Adding a suitable amount of magnesium to the alloy could decrease the $M_{23}C_6$ lamellae-accumulated areas appearing at grain boundaries and cause the MC lamellae to become spherical [3]. The above experimental results showed that the magnesium could decrease the large-sized intragranular long-flaky and dentritic lamellar $M_{23}C_6$ and retain a higher grain strength during long-term ageing. Thereby the grain-boundary strength and grain strength of the alloy have a favourable coordination, and the stress–rupture life of the alloy has been increased noticeably [3].

3.2.3. The misfit between VC and austenite

The $(h\,k\,l)$ planes of VC and austenite which formed the Moiré pattern and the average spacing, D, of the Moiré patterns of a great many VC particles on every film, could be determined. Then an average misfit between VC and austenite, corresponding to every film, could be calculated from the following equation [2]

$$\delta = 2a_\gamma/(2D\,N^{1/2} - a_\gamma) \quad (3)$$

Fig. 5 shows the average misfits, δ, between VC and austenite calculated from every film which was obtained from all the specimens. The misfits shown as circles were calculated from the Moiré patterns from the different $h\,k\,l$ diffractions of austenite and VC. The circles with poles indicate the average misfits of VC ribbons precipitated along dislocations, and circles connecting circles with poles indicate those of the VC particles near the ribbons.

It is seen that the misfit of intragranular VC with austenite in Specimen A1 was generally 11%–12%, 12%–13%, in Specimen B1, and the misfit in Specimen A2 was similar to that in Specimen B2. Magnesium added to the superalloy can enter MC at the grain boundaries [3]. As mentioned above, the average misfit of intragranular VC increases slightly at 160 p.p.m. Mg content, so we see that magnesium can also enter intragranular MC; no effect of magnesium on the misfit of VC particles has been detected at 68 p.p.m. Mg. Fig. 5 shows that the misfit of intragranular VC with the matrix increased slightly after long-term ageing and long-term stress-ageing, and the misfit increased obviously at higher ageing temperature. The experimental results mentioned above show that small-sized VC particles were precipitated, as well as granular VC being conglomerated after long-term ageing; the increasing amount of VC could decrease the lattice parameter of the austenite matrix, and thus the misfit between VC and mother phase would increase. Fig. 5 also shows that the misfits between austenite and VC ribbons precipitated along the dislocations were smaller than those between austenite and the VC particles near the ribbons. The results show that the strong segregation of vanadium in the alloy to dislocations was not only beneficial to form ribbons along dislocations, but also perhaps increased the vanadium content of the mother phase around dislocations, which resulted in the increased lattice parameter of austenite and lowered the misfit between VC and the austenite. Because the matrix supplied the ribbons with an amount of the vanadium, the vanadium content in the matrix near the ribbons decreased, hence the misfit between the matrix and VC particles increased.

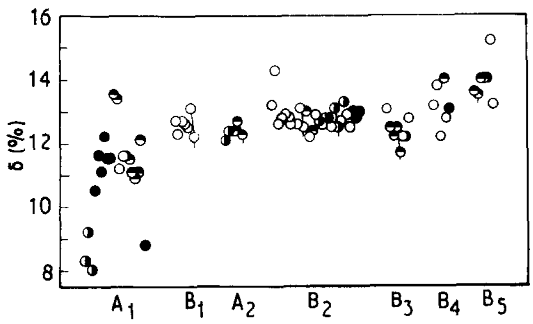

Figure 5 The misfits between intragranular VC and the mother phase determined from Moiré patterns of VC on every film obtained from all the specimens: (○) 1 1 1, (◓) 2 0 0, (◑) 2 2 0, (●) 3 1 1.

4. Conclusions

1. Adding a suitable amount of magnesium to the superalloy can result in small $M_{23}C_6$ stock instead of large-sized long-flaky and dentritic lamellar $M_{23}C_6$ precipitated along {1 1 1} of austenite. During long-term ageing, the amount and size of $M_{23}C_6$ increase gradually, the long-flaky and dentritic lamellar $M_{23}C_6$ in a specimen with a negligible amount of magnesium grow rapidly with increasing ageing time, and the addition of a suitable amount of magnesium causes the small $M_{23}C_6$ stock to become spherical because the coherent relation between $M_{23}C_6$ and mother phase is lost.

2. The VC normally precipitated in the homogeneously dispersed granular form, but some VC precipitated along dislocations and formed ribbons in specimens both without and with magnesium. During long-term ageing, the VC small particles precipitated together with conglomeration of the dispersed granular VC during normal heat treatment, and the dislocations could cut some VC particles in two.

3. Adding 160 p.p.m. Mg to the superalloy could increase the misfit slightly (about 1%) between VC and austenite. The misfit between VC precipitated along dislocations, and the matrix was smaller than that between granular VC near the ribbons and the matrix. The misfit of VC with austenite increased slightly during long-term ageing and long-term stress-ageing.

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