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Precipitation and degeneration of grain-boundary Cr_7C_3 and M_4B_3 in Ni–Cr–Al–Ti nickel-base superalloys

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The precipitation of grain-boundary Cr_7C_3 and M_4B_3, and the degeneration from Cr_7C_3 to $Cr_{23}C_6$ and from M_4B_3 to $M_{23}C_6$ have been studied on the extraction carbon replicas of intercrystalline ruptures in two kinds of Ni–Cr–Al–Ti nickel-base superalloy using transmission electron microscopy. It has proved too difficult to obtain experiment results from the metallographic specimens or the thin foils as yet.

1. Introduction

Some research has suggested that the main grain-boundary phases existing in a Nimonic-80A superalloy are Cr_7C_3 and $Cr_{23}C_6$, and that Cr_7C_3 can transform into $Cr_{23}C_6$ [1]. However, because of the limitation of the metallographic method, only large blocky or granular carbides could be found, and detailed and distinct results about the fine lamellae of carbides have not yet been obtained. Moreover, the transformation from Cr_7C_3 to $Cr_{23}C_6$ has not been observed.

The degeneration of the MC phases, which occurs during ageing or use of some superalloys, has caught the attention of some researchers [2–6]; however, no observed results about the degeneration of Cr_7C_3 nor any study of whether or not borides could degenerate have been reported.

An Ni–Cr–Al–Ti superalloy (Alloy A), of which the chemical composition was close to that of Nimonic-80A, and another Ni–Cr–Al–Ti superalloy (Alloy B) were used in the experiment; extraction carbon replicas on intercrystalline fractures of the alloys were observed, the precipitation and the degeneration of grain boundary Cr_7C_3 and M_4B_3 were researched, and the results (not from the metallographic specimen or the thin foil) were obtained.

2. Experimental procedure

Specimens of Alloy A, which had been smelted in an electric furnace, were selected from rolled rods of 26 mm diameter. Specimens of Alloy B, which had been vacuum induction melted and electric slag remelted, were selected from rolled rods of 22 mm diameter. The main chemical compositions (wt %) of the superalloys are shown in Table I.

The heat-treatment procedures for the specimens are shown in Table II.

After keeping notched specimens in liquid nitrogen for about 30 min, they were impacted and then extraction carbon replicas of the intercrystalline fractures were prepared. The carbon replicas were observed with a transmission electron microscope (TEM), the precipitation phases in the carbon replicas were identified with TEM selected-area diffraction, and the composition (at %) of the M_4B_3 and $M_{23}C_6$ phases on the extraction carbon replicas of Alloy B were measured by means of energy dispersive X-ray spectrometry (EDAX).

3. Results

3.1. The precipitation and the degeneration of Cr_7C_3 phases

Only a small number of lamellar TiC were precipitated in some parts of the grain boundaries in Specimens A10, A11 and A12 after solid solution treatment. After normal heat treatment, a great number of grain-boundary Cr_7C_3 and $Cr_{23}C_6$ phases were precipitated over the whole surfaces of the grain boundaries in Specimen A2, i.e. smaller lamellae of Cr_7C_3, alternating with fine dentritic lamellae of $Cr_{23}C_6$, strung along the grain boundary surfaces (Fig. 1a), and a number of the large, thick or thin lamellae of Cr_7C_3 were precipitated in some parts of the grain boundaries (Fig. 1b).

TABLE I. Chemical composition (wt %) of the superalloys

Alloy	C	Cr	Al	Ti	Nb	Zr	B	Ni
A	< 0.06	19–22	0.55–1.0	2.2–2.8				bal.
B	0.052	20	0.91	0.90	1.50	0.021	0.008	bal.

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TABLE II. The heat-treatment procedures for the specimen

Specimen	Heat-treatment procedures[a]
A10, B1	1080 °C, 8 h, AC
A11	1020 °C, 8 h, AC
A12	980 °C, 8 h, AC
A10′	1080 °C, 8 h, FC
A2 (B2)	1080 °C, 8 h, AC + 700 °C (750 °C) 16 h, AC (normal heat treatment)
A3	Normal heat treatment + 700 °C, 50 h, AC
A4	Normal heat treatment + 700 °C, 100 h, AC
A5	Normal heat treatment + 700 °C, 730 h, AC
B3 (B6)	Normal heat treatment + 650 °C, (700 °C), 100 h, AC
B4 (B7)	Normal heat treatment + 650 °C, (700 °C), 300 h, AC
B5 (B8)	Normal heat treatment + 650 °C, (700 °C), 600 h, AC
B9	Normal heat treatment + 750 °C, 50 h, AC
B10	Normal heat treatment + 750 °C, 300 h, AC
B11	Normal heat treatment + 750 °C, 1000 h, AC

[a] AC and FC are air-cooled and furnace-cooled, respectively.

The Cr_7C_3 group or $Cr_{23}C_6$ group in Fig. 1a have the same orientation (Fig. 2a, b), and the diffraction pattern of lamellar Cr_7C_3 in Fig. 1b is shown in Fig. 2c. Fig. 2d and e are the indexes of Fig. 2a and c, respectively. The diffraction patterns show that the grain-boundary Cr_7C_3 were orthorhombic ($a = 0.4523$ nm, $b = 0.699$ nm, $c = 1.21$ nm) and were not the structure proposed by Westgren, and in Cr_7C_3, the $\{0\,1\,3\}$ (or $\{0\,1\,1\}$) growth twin was discovered from the electron diffraction patterns [7, 8].

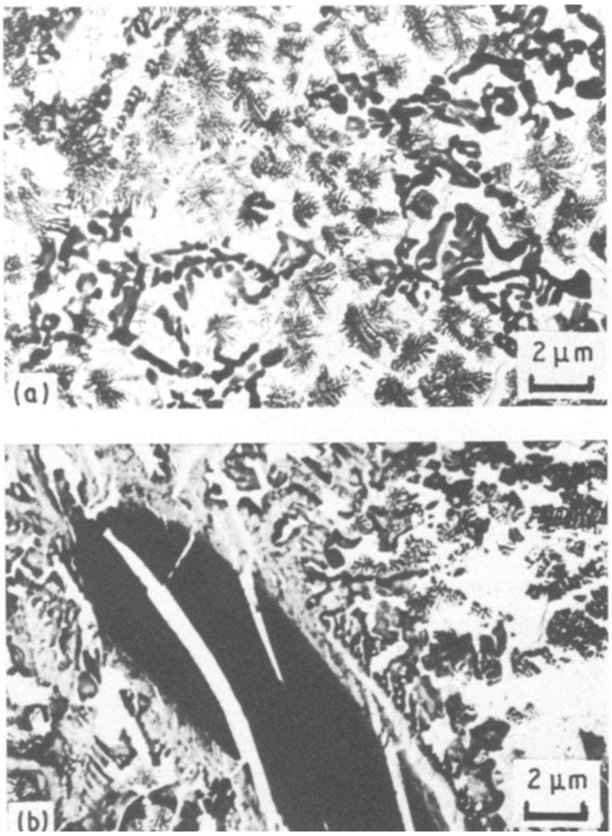

Figure 1 Cr_7C_3 and $Cr_{23}C_6$ phases (a) over the whole surfaces and (b) in some parts of the grain boundaries in Specimen A2.

After solid-solution treatment, a considerable number of the large Cr_7C_3 lamellae (Fig. 3a) and dentritic lamellae (Fig. 3b) were precipitated over the whole surfaces of the grain boundaries in Specimen A10′; it is evident that the large Cr_7C_3 lamellae were precipitated during slow cooling under a temperature below 980 °C.

During long-term ageing at 700 °C, with an increase in ageing time, the thick or thin lamellae of the grain-boundary Cr_7C_3, which were precipitated during normal heat treatment, decreased continuously and their amount decreased gradually (Fig. 4a). The amount and size of the fine dentritic lamellae of $Cr_{23}C_6$ increased continuously and they became granular (Figs 1a and 4). From thicker external edges of the Cr_7C_3 (Fig. 1), we can see that the beginning of the degeneration from Cr_7C_3 to $Cr_{23}C_6$ might occur there.

3.2. The precipitation and degeneration of M_4B_3 phases

Only a small number of NbC blocks were precipitated in some parts of the grain boundaries in Specimen B1 after solid-solution treatment. After normal heat treatment, fine dentritic lamellae and particles were precipitated at the grain boundaries in Specimen B2.

During long-term ageing at 650 °C, the large dentritic lamellae and films were also precipitated at grain boundaries in Alloy B after normal heat treatment (Fig. 5a), and the size of the films was quite large in some parts of the grain boundaries.

The selected-area diffraction patterns (Fig. 5b and c) of the particle group (upper) and dentritic lamella (centre) showed that the former were $M_{23}C_6$ carbides and the latter were M_4B_3 boride, which is a face-centred tetragonal lattice with parameters $a = 0.771$ nm, $c = 1.016$ nm. A great many of the diffraction patterns showed that the dentritic lamellae and the films were all M_4B_3; the particles were all $M_{23}C_6$.

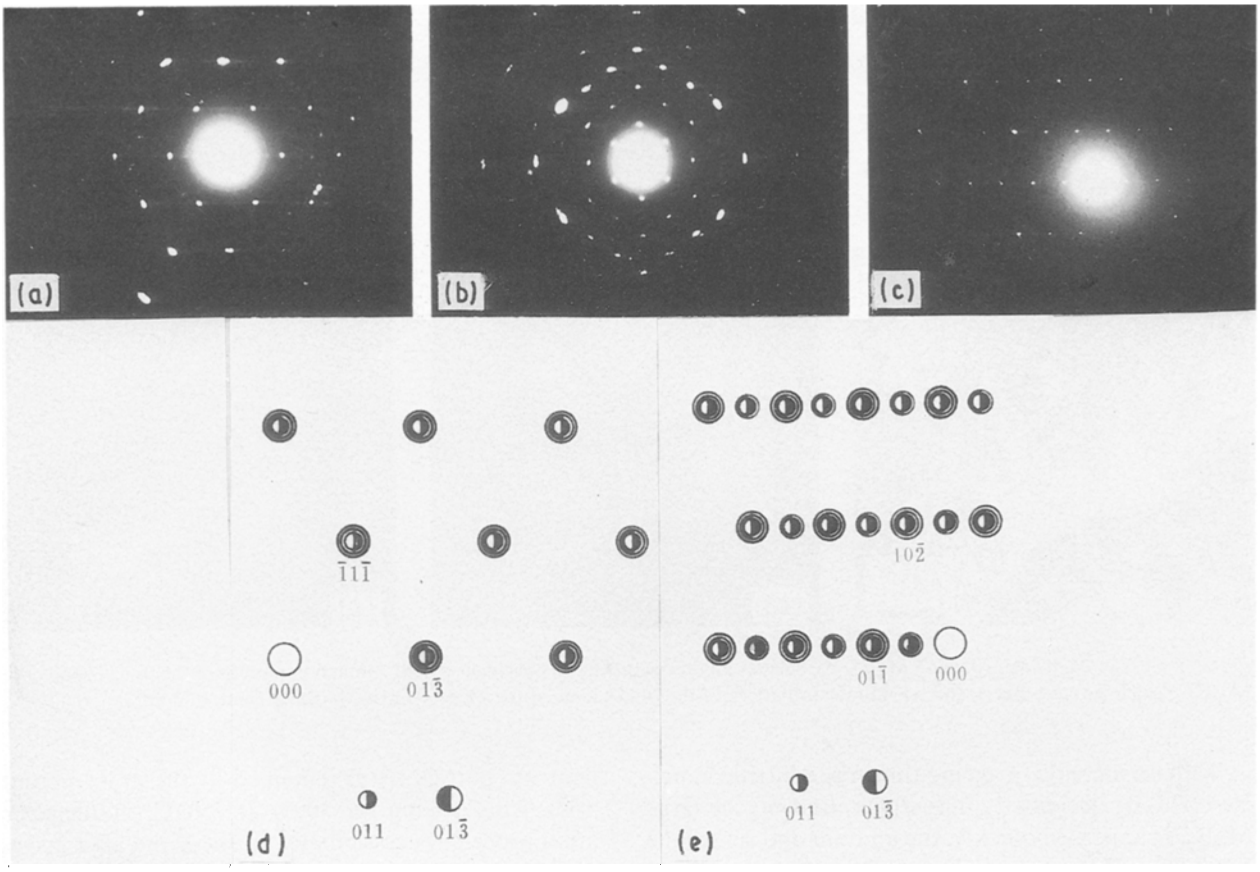

Figure 2 (a) Diffraction pattern of the $[2\,3\,1]$ zone of the Cr_7C_3 group and the $[\bar{2}\,3\,1]_T$ zone of the $(0\,1\,1)$ twin or the $[\bar{2}\,\bar{3}\,\bar{1}]_T$ zone of the $(0\,1\,\bar{3})$ twin of the Cr_7C_3; (b) diffraction pattern of the $[0\,1\,1]$ zone of the $Cr_{23}C_6$ group in Fig. 1a. (c) Diffraction pattern of the $[2\,1\,1]$ zone of lamellar Cr_7C_3 and the $[\bar{1}\,1\,0]_T$ zone of the $(0\,1\,1)$ twin or the $[\bar{1}\,\bar{1}\,0]_T$ zone of the $(0\,1\,\bar{3})$ twin of the lamella in Fig. 1b. (d, e) Indexing of (a) and (c), respectively.

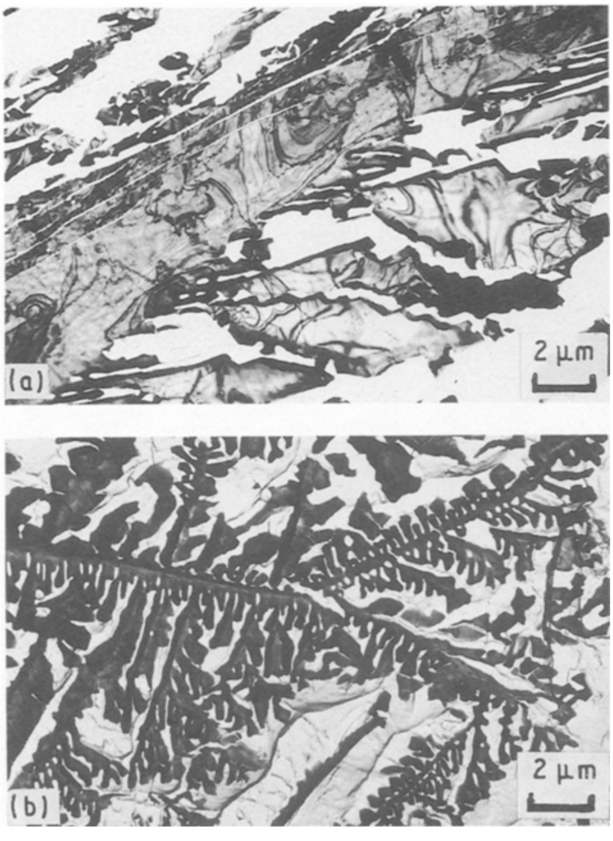

Figure 3 The large-sized (a) Cr_7C_3 lamellae in $(0\,1\,1)$ orientation, and (b) dentritic lamellae in $(4\,1\,1)$ orientation of Cr_7C_3 at grain boundaries in Specimen A10′.

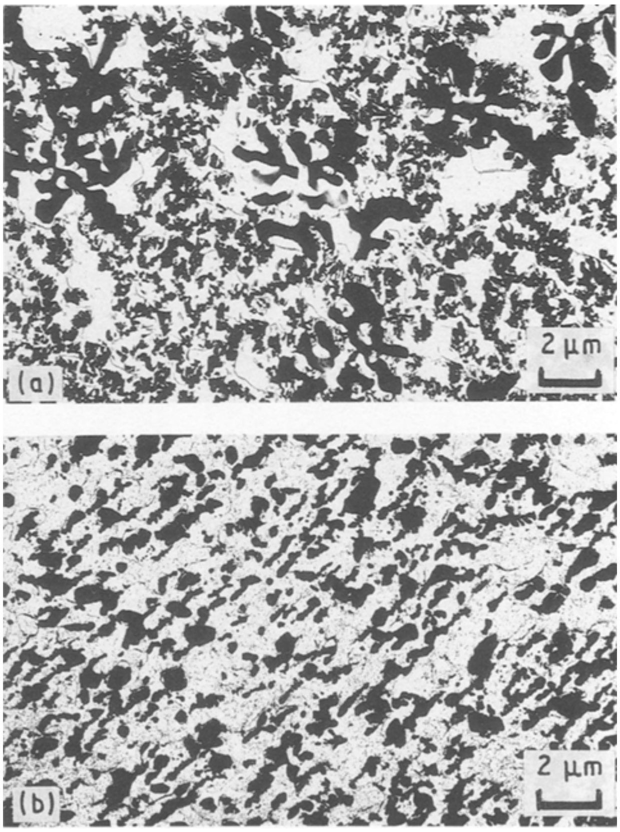

Figure 4 (a) Grain-boundary Cr_7C_3 and $Cr_{23}C_6$ in Specimen A3, (b) grain-boundary $Cr_{23}C_6$ in Specimen A5.

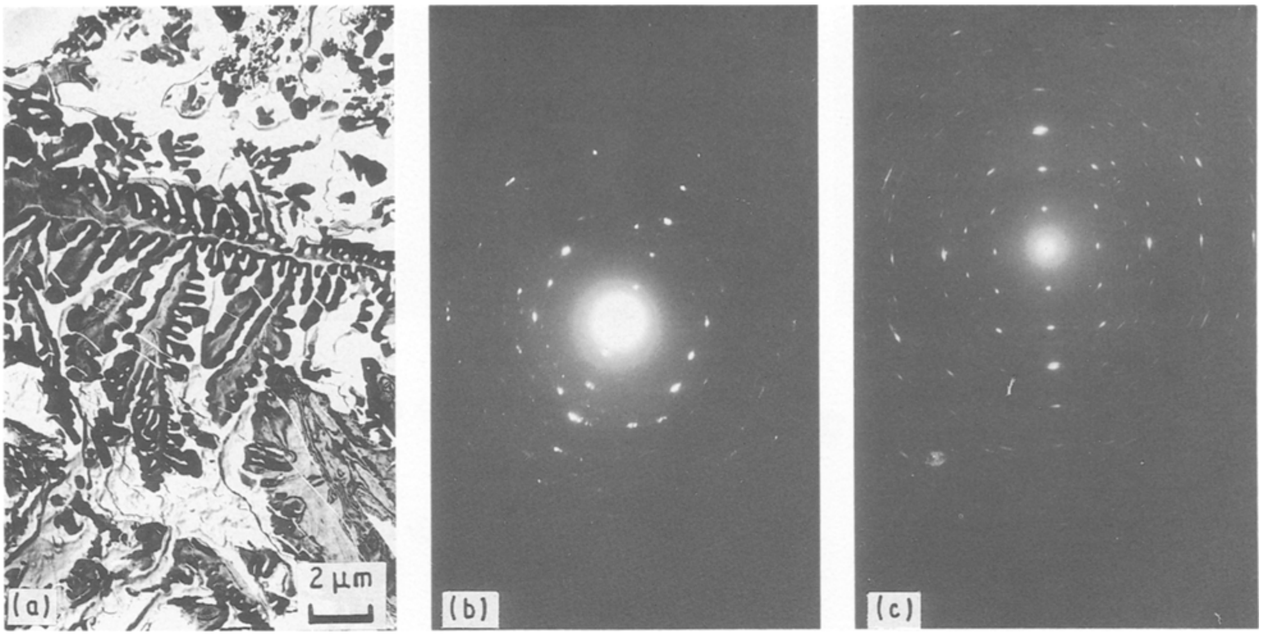

Figure 5 (a) The M_4B_3 dentritic and $M_{23}C_6$ particles at a grain boundary in Specimen B3; (b) diffraction pattern of the [0 1 2] zone of the $M_{23}C_6$ particle group (upper), and (c) diffraction pattern of the [0 1 0] zone of the M_4B_3 dentritic lamellae (centre) in (a).

With an increase in ageing time, the dentritic lamellae of M_4B_3 decreased gradually; moreover, the large M_4B_3 disappeared quickly, the amount and size of the $M_{23}C_6$ particles increased gradually (Fig. 6a, b) and the degeneration process from dentritic M_4B_3 to granular $M_{23}C_6$ was observed: the early transformation from the lamellae to the particles might occur at the external edges of the "branch" or "trunk" of M_4B_3 (Fig. 5a), and then whole "branches" or "trunks" of M_4B_3 were transformed into the particles.

With an increase in ageing temperature, the degeneration process from the dentritic M_4B_3 to granular $M_{23}C_6$ was obviously accelerated. After ageing for 600 h at 700 °C, only a small number of smaller M_4B_3 dentritic particles still remained at the grain boundaries. After ageing for 300 h at 750 °C, the degeneration process was essentially finished, and after ageing for 1000 h at 750 °C, the granular $M_{23}C_6$ had grown to about 2 μm in size (Fig. 6c).

By means of EDAX, the chemical composition (at %) of the larger M_4B_3, which were dentritic with a thinner centre and thicker edge, smaller M_4B_3 dentritic and $M_{23}C_6$ particles were measured on extraction carbon replicas of Specimens B3 and B10, respectively (see Table III). The analysis showed that the type of metal elements in M_4B_3 was similar to that in $M_{23}C_6$, but smaller M′(Cr, Ni) atoms in the $M_{23}C_6$ were more numerous than those in M_4B_3, and the

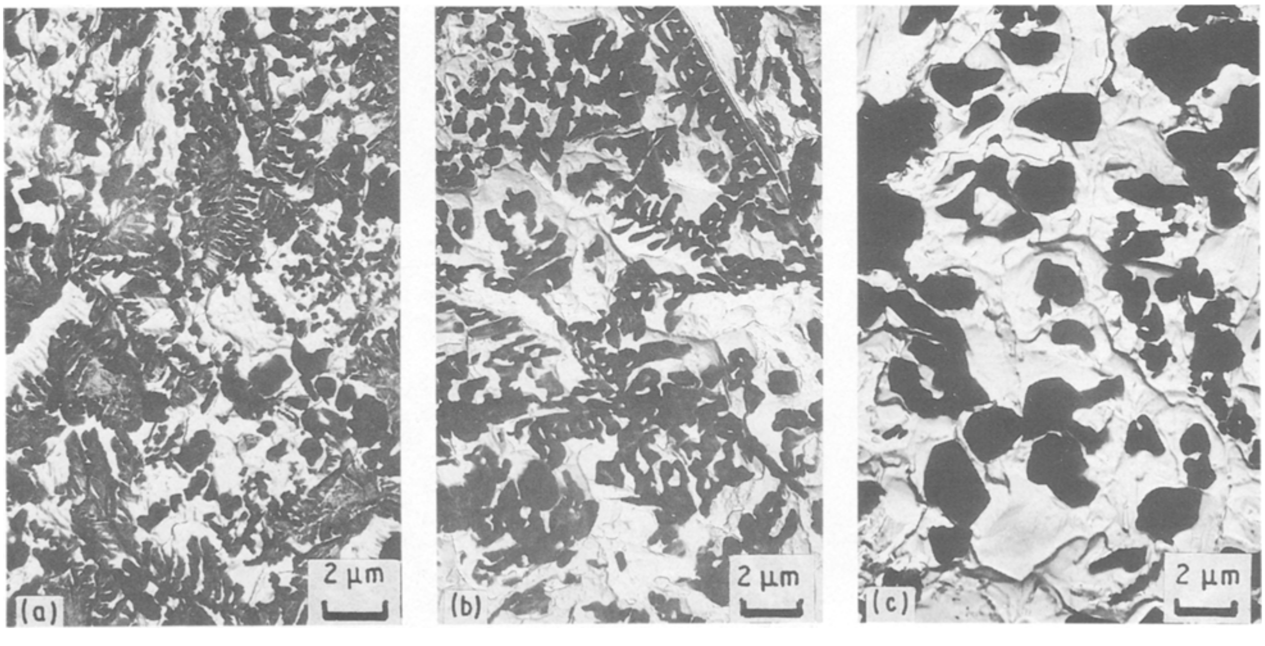

Figure 6 The M_4B_3 dentritic and $M_{23}C_6$ particles at grain boundaries in (a) Specimen B4 and (b) Specimen B5; (c) the granular $M_{23}C_6$ at grain boundaries in Specimen B11.

TABLE III. Compositions (at %) of metal atoms in the M_4B_3 and $M_{23}C_6$

Phase	Composition				Number of M′ atoms/number of M atoms
	Nb	Ti	Cr	Ni	
Centre of the larger dentritic	19.3	13.5	67.2		2.05
Edge of the larger dentritic	2.10	4.00	93.9		15.4
Fine dentritic	6.42	5.88	87.7		7.13
Particle 1	5.26	3.47	86.9	4.39	10.5
Particle 2	4.45	4.06	87.5	4.02	10.8
Particle 3	5.80	3.30	86.2	4.73	10.0

larger M (Nb, Ti) atoms in the $M_{23}C_6$ were fewer than those in M_4B_3.

4. Discussion

Alloy A is similar in compositions to Nimonic-80A. Some researchers have observed precipitation phases in Nimonic-80 and Nimonic-80A [1]. They believed that the Cr_7C_3 phases were precipitated in the superalloys during slow cooling at temperatures from 1150–1000 °C, and Cr_7C_3, which was precipitated at higher temperature, became $Cr_{23}C_6$ during the heat under lower temperature; however, the transformation has not yet been observed.

Experimental results mentioned above showed that there were two ways of Cr_7C_3 precipitation in Alloy A. First, the precipitation of the Cr_7C_3 competes against $Cr_{23}C_6$ at lower temperature (700 °C) (Fig. 1). At higher C/Cr ratio parts of grain boundaries, Cr_7C_3 would be precipitated first, and they grow into large, thick or thin lamellae. The fine dentritic $Cr_{23}C_6$ were precipitated at the lower C/Cr parts of grain boundaries and they were also precipitated around Cr_7C_3; this was due to the precipitation of Cr_7C_3 which resulted in a decrease of the C/Cr ratio. Second, Cr_7C_3 was not precipitated during slow cooling at temperatures from 1080–1000 °C, and during slow cooling at temperatures below 980 °C, the large Cr_7C_3 lamellae and dentritic lamellae were precipitated over the whole grain boundaries (Fig. 3). It was also shown that carbon has a stronger tendency to segregate to the grain boundaries of the alloy compared with chromium, during slow cooling, resulting in higher C/Cr ratios at whole grain-boundary surfaces.

The results show that the transformation from substable Cr_7C_3 to $Cr_{23}C_6$ was observed; moreover, it was not the transformation from the Cr_7C_3 which was precipitated at higher temperature, to the $Cr_{23}C_6$ during heating at lower temperature, but the transformation from Cr_7C_3 which was precipitated at lower temperature (700 °C), to the $Cr_{23}C_6$ with an increase in heating time at the same temperature (Figs 1a and 4).

$$23Cr_7C_3 \rightarrow 7Cr_{23}C_6 + 27C \qquad (1)$$

$$6C + 23Cr \rightarrow Cr_{23}C_6 \qquad (2)$$

In Alloy B, lamellae of grain-boundary M_4B_3, which were precipitated easily at lower temperature (e.g. 650 °C), were similar to Cr_7C_3 in Alloy A, i.e. the lamellae were substable, and they degenerated gradually to $M_{23}C_6$ particles during long-term ageing at 650–750 °C (Figs 5a and 6). Moreover, from the thicker external edges of M_4B_3 and Cr_7C_3, we can see that the beginning of the transformation from the lamellae to the particles occurred easily at these edges.

From Table III, we can see that the ratios of M′ atom number to M atom number are much higher at the edge of the large dentritic M_4B_3 than that in the centre of the large dentritic phase, and the ratio in the fine dentritic M_4B_3 lies between the ratios at the edge and centre of the large dentritic phase's it may be that the result measured in the fine dentritic was obtained simultaneously from the edge and centre of the dentritic. The ratio of M′ atom number to M atom number in the $M_{23}C_6$ particles is also higher. Therefore, the EDAX results EDAX coincide with those observed by TEM (see Fig. 5a), i.e. the onset of M_4B_3 degeneration occurred at the external edges of the "branches" and "trunks", and then whole dentritic phase degenerated into the $M_{23}C_6$ particles

$$(M', M)_4B_3 + (M', C) \rightarrow (M', M)_{23}C_6 + (M, B) \quad (3)$$

This showed that the M (metal) and B (boron) atoms have a stronger tendency to segregate to the grain boundaries compared with M′ (metal) and C (carbon) atoms, respectively, due to smaller solubility and larger mismatch of the former in the alloy matrix during ageing at lower temperatures [9, 10], and grain-boundary M_4B_3 were precipitated easily; with an increase in ageing time, substable M_4B_3 was degenerated gradually, some M and B atoms returned to the grain boundaries, while some M′ and C atoms leave the grain boundaries; thus the stable $M_{23}C_6$ or $M_{23}(C, B)_6$ were precipitated.

5. Conclusions

1. During ageing at 700 °C in Ni–Cr–Al–Ti (A) alloy the smaller lamellae of the Cr_7C_3 and the fine dentritic lamellae of the $Cr_{23}C_6$, alternating with the former, were precipitated in strings on whole grain boundaries, and a number of the large, thick or thin lamellae of Cr_7C_3 were precipitated on some parts of the grain-boundary surfaces. A considerable number of large Cr_7C_3 films and dentritic lamellae were precipitated on the whole grain boundaries during slow cooling at temperatures below 980 °C. During ageing at 750 °C in Ni–Cr–Al–Ti (B) alloy, dentritic lamellae of M_4B_3 and particular $M_{23}C_6$ were precipitated at

whole grain-boundary surfaces and, during the early period of long-term ageing at lower temperature, the large M_4B_3 dentritic lamellae and films were also precipitated at grain boundaries.

2. With an increase in ageing time, substable Cr_7C_3, which was precipitated at grain boundaries in Alloy A during ageing at 700 °C, degenerated gradually into $Cr_{23}C_6$ particles, and substable M_4B_3, which was precipitated at grain boundaries in Alloy B during ageing at 650–750 °C, was also degenerated gradually into $M_{23}C_6$ particles. The degeneration from Cr_7C_3 or M_4B_3 to $Cr_{23}C_6$ or $M_{23}C_6$ particles, respectively, begin at the external edges of the lamellae, and with an increase at ageing temperature, the degeneration of M_4B_3 was accelerated.

3. The clear details about the precipitation and degeneration of Cr_7C_3 and M_4B_3, which have proved too difficult to obtain as yet from metallographic specimens or thin foils, can be obtained from the extraction carbon replicas of the intercrystalline fractures in both alloys.

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