Formation Mechanism of Lamellar $M_{23}C_6$ Carbide in a Cobalt-Base Superalloy During Thermal Exposure at 1000 °C

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Abstract The precipitation of the lamellar-shaped $M_{23}C_6$ carbide within the dendritic matrix of a cobalt-base superalloy during thermal exposure at 1000 °C has been investigated. Such a precipitation is not commonly observed in cobalt-base superalloys. It is found that $M_{23}C_6$ particles nucleate preferentially at stacking faults (SFs) in the dendritic matrix and grow along the SFs to develop a lamellar character. Additionally, a Cr depletion zone is observed in the vicinity of the lamellar $M_{23}C_6$ carbide, which strongly supports the presence of Suzuki segregation.

KEY WORDS: Cobalt-base superalloy; Carbide precipitation; Thermal exposure; Scanning/transmission electron microscopy

1 Introduction

Carbide precipitation is the primary strengthening mechanism in contemporary cobalt-base superalloys which are widely used for vanes and combustor sections in industrial and aircraft turbines. The common types of carbides in as-cast cobalt-base superalloys are MC , $M_{23}C_6$ and M_7C_3 [1–5]. Aging or service at high temperatures causes the precipitation of a large amount of secondary carbides, such as MC and $M_{23}C_6$ [6–8].

Secondary $M_{23}C_6$ carbide is a Cr-rich phase and has a cube-to-cube orientation relationship with the matrix in cobalt-base superalloys [9–11]. The precipitation of secondary $M_{23}C_6$ carbide occurs mainly around primary carbides or at grain boundaries [10–17]. The primary carbides may degenerate and serve as the C and Cr sources to facilitate the $M_{23}C_6$ formation at high temperatures. And grain boundaries can also act as sinks for solute atoms which increase element diffusion rates and therefore give rise to the precipitation of $M_{23}C_6$ carbide. As for the morphology of secondary $M_{23}C_6$ carbide in cobalt-base superalloys, it generally appears as particles, chains or rods, and the lamellar morphology of secondary $M_{23}C_6$ carbide is scarcely observed. The precipitation of lamellar $M_{23}C_6$ carbides was observed around primary carbides and grain boundaries by Jiang et al. [11] and by Taylor et al. [13], respectively.

In the present study, the precipitation of lamellar $M_{23}C_6$ carbides in a cobalt-base superalloy at high temperature is also observed, but these lamellar $M_{23}C_6$ carbides appear within the dendritic matrix. To the best of our knowledge, this is a novel phenomenon in cobalt-base superalloys and the purpose of this study is to investigate the formation mechanism of the lamellar $M_{23}C_6$ carbide.

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2 Experimental

The chemical composition of the test alloy is 0.42C–10.7Ni–25.5Cr–0.97Al–0.19Ti–0.23Mo–7.81W–0.34Ta–0.16Zr–balance Co (wt%). The test specimens were cut from the as-cast single crystal alloy bars and heat-treated at 1000 °C for 0.5, 1, 4, 50, 100 and 300 h, respectively, followed by air cooling. The specimens for metallographic observation were electrolytically etched for 10 s in a solution consisting of 42 pct H_3PO_4 + 34 pct H_2SO_4 + 24 pct H_2O . Microstructures of the alloy were observed by JEOL JSM-5800 scanning electron microscopy (SEM) with back-scattered electron (BSE) mode. Phase compositions were determined by energy-dispersive X-ray spectroscopy (EDS) equipped in SEM. Transmission electron microscopy (TEM) foils were prepared by traditional mechanical grinding and electrochemical twin jet thinning method with a solution of 10 vol.% perchloric acid in ethanol at 50 mA and –20 °C, followed by observing with a JEM 2100 TEM operating at 200 kV. Local chemical compositions around stacking faults (SFs) were analyzed by EDS using the scanning mode in a 300 kV transmission electron microscope (STEM) equipped with a field emission gun (FEI Titan G2 60–300).

3 Results and Discussion

As described in Ref. [18], the microstructure of the test alloy in the as-cast condition contains two types of primary carbides precipitated in the interdendritic area. Additionally, no secondary carbide is observed in the matrix since there is not sufficient time for its nucleation during solidification. After thermal exposure at 1000 °C for different durations, the microstructure of the alloy has undergone significant evolutions. Figure 1 shows the morphological evolutions of secondary $M_{23}\text{C}_6$ carbides with increasing exposure time from 0.5 to 300 h. After thermal exposure for 0.5 h as shown in Fig. 1a, it can be seen that a profusion of secondary $M_{23}\text{C}_6$ carbide mainly precipitates around primary $M_7\text{C}_3$ and MC carbides. Besides, random dot-type $M_{23}\text{C}_6$ carbides form in the central regions of the original dendrite (indicated by the arrows).

With thermal exposure time extension (1–4 h), new fine secondary $M_{23}\text{C}_6$ particles continue to precipitate and already precipitated secondary $M_{23}\text{C}_6$ particles gather and coarsen (Fig. 1b, c). Furthermore, it should be noted that the dash line feature formed by secondary $M_{23}\text{C}_6$ carbides distribution appears in the dendrite after thermal exposure for 4 h (Fig. 1c). This phenomenon is more pronounced after thermal exposure for 50 h (Fig. 1d). These dash lines are either parallel to or normal to each other. In addition, it

is also observed that these fine secondary $M_{23}\text{C}_6$ carbide particles have been coalesced into the lamellar structure. With exposure time further extended to 100 h and even 300 h (Fig. 1e, f), more dash lines formed by lamellar $M_{23}\text{C}_6$ carbides arise in dendrite matrix. In addition to these features, the chain-shaped $M_{23}\text{C}_6$ carbides around primary carbides are observed as well (Fig. 1f). Such a secondary $M_{23}\text{C}_6$ carbide chain was also observed in other alloys [11, 19]. These authors arrived at the same conclusion that its appearance is related to the morphology of dislocations, i.e., $M_{23}\text{C}_6$ particles nucleated on the dislocation and grew and coalesced into a chain along the dislocation. According to this interpretation, it is reasonable to infer that the formation of this dash line is likely to be caused by the precipitation of secondary $M_{23}\text{C}_6$ carbide at SFs.

Apart from the precipitation of secondary $M_{23}\text{C}_6$ carbide at 1000 °C, the degeneration of primary carbides also occurs as shown in Fig. 2. After thermal exposure for 0.5 h (Fig. 2a), it can be seen that some brighter particles are formed at the edge of MC and $M_7\text{C}_3$ carbides. The EDS (Fig. 2b) result indicates that these brighter particles are W-rich phases, which is similar to those in Refs. [11, 20] and thus can be determined as $M_6\text{C}$ carbides. The precipitation of $M_6\text{C}$ surrounding $M_7\text{C}_3$ [11, 20] and MC [18] has been reported in cobalt-base superalloys, and its formation is related to the W segregation in the vicinity of $M_7\text{C}_3$ carbide and the MC carbide degeneration, respectively. With increasing exposure time, primary carbides degenerate more severely. After thermal exposure for 100 h (Fig. 2c), no $M_6\text{C}$ carbide is observed around primary $M_7\text{C}_3$ and MC carbides (Fig. 2c). This indicates that the W atoms around these carbides diffuse out after a long time of thermal exposure, which leads to the disappearance of $M_6\text{C}$ carbide.

In order to investigate the inherent reason for the formation of lamellar secondary $M_{23}\text{C}_6$ carbides within the dendrite matrix in detail, the microstructures of the samples in different conditions were examined by TEM as shown in Fig. 3. Figure 3a shows that many SFs are observed in the matrix of the as-cast sample. Additionally, these overlapped SFs are vertical to each other. The SFs are common in cobalt-base superalloys, and their presence is related to an allotropic transformation from hexagonal close-packed structure to face-centered cubic at 417 °C in unalloyed cobalt [4]. After thermal exposure for 0.5 h, fine blocky $M_{23}\text{C}_6$ particles randomly nucleate at SFs as shown in Fig. 3b. As exposure time prolonged, these $M_{23}\text{C}_6$ particles at SFs are observed to grow and coalesce (Fig. 3c, d). After thermal exposure for 50 h, the lamellar $M_{23}\text{C}_6$ carbides, together with the SFs, can be seen in Fig. 3e. Thus, it can be confirmed that the formation of lamellar $M_{23}\text{C}_6$ carbide within the dendrite matrix is related to the morphology of

Fig. 1 BSE micrographs of the test alloy heated at 1000 °C for: **a** 0.5 h, **b** 1 h, **c** 4 h, **d** 50 h, **e** 100 h **f** 300 h

Fig. 2 Evolution of primary carbides with various heat treatment time at 1000 °C: **a** BSE image of carbide morphology for 0.5 h, **b** EDS pattern of M_6C carbide, **c** BSE image of carbides morphology

the SFs. Specifically, the lamellar carbides vertical to each other can be observed after thermal exposure for 100 h as shown in Fig. 3f, which is in good agreement with SEM result (Fig. 1e). This consistence further proves the view just previously mentioned that the formation of lamellar $M_{23}C_6$ carbides within the dendrite matrix is associated with the SFs. Furthermore, the increase in the SFs density with increasing aging time was observed by Vander Sande et al. [21] in the Co–Cr–Mo–C alloy as well as by Koizumi et al. [22] in a Co–Ni-based superalloy. In the alloy of this study, since the distribution of SFs in the matrix is random, it is very difficult to accurately determine the density

change during thermal exposure. However, it is assured that the increase in SFs density will promote the precipitation of $M_{23}C_6$ carbides.

As is well known, the presence of secondary $M_{23}C_6$ carbide is attributed to the reaction of metal atoms with carbon atoms at high temperatures [9–11]. The carbon source is provided by the decomposition of primary carbides since the carbon content in the solid solution matrix of the as-cast condition is negligible and almost all carbon atoms have been consumed in the formation of primary carbides [11]. Metal atoms derive from both the decomposition of primary carbides and the solid solution matrix.

Fig. 3 TEM micrographs of the test alloy **a** in the as-cast condition and after heated at 1000 °C for: **b** 0.5 h, **c** 1 h, **d** 4 h, **e** 50 h **f** 100 h

Therefore, it is observed that a profusion of secondary $M_{23}C_6$ carbides precipitates around primary MC and M_7C_3 carbides. However, some dot-like or lamellar $M_{23}C_6$ carbides distribute within the dendrite matrix. Logically, the precipitation of $M_{23}C_6$ carbide hardly takes place in the dendrite matrix which is far away from the primary carbides. Then, a question should be put forward: What causes the formation of secondary $M_{23}C_6$ carbide in the dendrite matrix? As previously described, a large number of SFs distribute in the matrix in the as-cast condition. It is well known that the solute atoms have a tendency to be attracted to SFs and form segregation zones [23], namely, “Suzuki segregation.” Sims [4] and Jiang et al. [11] suggested that the precipitation of secondary $M_{23}C_6$ carbide was controlled by the amount of carbon. Thus, it is presumed that the carbon atoms released by primary carbide degeneration diffuse and segregate to the SFs in the dendrite matrix at 1000 °C. And these SFs could act as nucleation sites to promote the formation of the lamellar structure. However, the carbon diffusion rate is so high that it does not limit the precipitation process of secondary $M_{23}C_6$ carbide. So for the Cr-rich $M_{23}C_6$ carbide, the amount of Cr may become an important controlling factor of $M_{23}C_6$ carbide precipitation. Koizumi et al. [22] reported a strong segregation of

Cr atoms at the SFs in a Co–Ni-based superalloy at 973 K obtained by the phase-field simulation. Thus, it can be another presumed that Cr atoms originated from both the decomposition of primary M_7C_3 carbides and the solid solution matrix diffuse and segregate to SFs at 1000 °C, resulting in the formation of the lamellar $M_{23}C_6$ carbide.

In order to determine whether the solute atoms (C or Cr) segregate at SFs, the quantitative analysis using STEM-EDS is performed and the result is shown in Fig. 4. Figure 4a is a STEM image of the 1000 °C/300 h heat-treated alloy, and the beam direction is set parallel to [110] SFs. Figure 4b shows the EDS measurements of the composition profile across two different SFs and the lamellar $M_{23}C_6$ carbide along the green line in Fig. 4a. Neither segregation nor depletion of any elements is detected around the SFs in the profiles. Similar results are obtained by Koizumi et al. [20] in Co–Ni-based superalloy after aging at 973 K for 1 h by STEM-EDS. They pointed out that it may be due to the interference of constituent elements (Co, Ni, Cr, Mo) because of their similarities in the energies of the characteristic X-rays. In our study, these elements that need to be analyzed are similar to their study. Therefore, no segregation or depletion of any elements is found near SFs in this work. Meanwhile, it is difficult to obtain the accurate

Fig. 4 EDS analysis intended to detect Suzuki segregation around the SFs in the test alloy: **a** STEM image of the alloy heated for 300 h, **b** profile of EDS analyses from each solute element along the green line in **a**. The red circles in the EDS profile of Cr show that a Cr depletion zone exists around the lamellar $M_{23}C_6$ carbide

composition profile of carbon element with EDS measurement because carbon is considered to be a pollution element. In addition, when the EDS measurements were across the matrix and lamellar $M_{23}C_6$, it can be seen that the contents of Co and Ni decrease and the Cr content increases, but the W content changes little. Besides, the Co content decreases more significantly than the Ni content. From the EDS results of $M_{23}C_6$ and matrix (Table 1), the contents of Co and Ni of the matrix are higher than that of $M_{23}C_6$, and the difference of Co content between matrix and $M_{23}C_6$ is larger than those of Ni. As a result, a more remarkable decrease in the Co content occurred in the site where the lamellar $M_{23}C_6$ is formed as compared to Ni. Similarly, it also can explain the changes in the content of W and Cr. However, it is worthy to note that a Cr depletion zone appears in the vicinity of lamellar $M_{23}C_6$ carbide (marked by the red circles in Fig. 4b). In general, the Cr depletion zone appears near grain boundaries [24]. The grain boundaries act as the sinks for Cr atoms with increasing diffusion rate. Accordingly, secondary $M_{23}C_6$ carbides preferentially nucleate and grow on the grain boundaries. These particles need to draw Cr atoms from the vicinity of grain boundaries and thus contribute to the formation of the Cr depletion zone. Moreover, Taylor et al. [10, 13] believed that the interaction between the grain boundary and solute atoms resulted in the formation of lamellar $M_{23}C_6$ carbides near the grain boundary.

Table 1 EDS compositions of $M_{23}C_6$ and the matrix (wt%)

	Cr	Ni	W	Al	Co
Matrix	25.41	10.97	3.93	0.44	59.24
$M_{23}C_6$	77.11	2.02	5.2	–	15.67

Similarly, the presence of a Cr-depleted zone near the lamellar $M_{23}C_6$ carbide in this work can be explained in this way. During thermal exposure at 1000 °C, Cr atoms originated from both the decomposition of primary M_7C_3 carbides and the solid solution matrix diffuse and segregate to SFs since SFs as a crystal defect, forming the Cr segregation. The presence of the Cr segregation at the SFs provides the chemical condition for the $M_{23}C_6$ formation. Thus, this leads to an earlier nucleation of $M_{23}C_6$ at SFs. Additionally, these overlapped SFs in the dendritic matrix are vertical to each other, which provide the structure condition for lamellar $M_{23}C_6$. Consequently, $M_{23}C_6$ carbides grow along the SFs and coalesce into the lamellar structure. Meanwhile, the growth of $M_{23}C_6$ carbides requires the absorption of Cr atoms from around SFs, leading to the appearance of Cr-depleted zone (Fig. 4). This result strongly supports the presence of Suzuki segregation. The lamellar $M_{23}C_6$ may be detrimental to the mechanical properties since the crack will propagate along the lamellar structure and thus accelerates the failure [25]. Therefore, the appropriate heat treatment should be selected to avoid the occurrence of such lamellar $M_{23}C_6$ carbide.

4 Conclusion

The degeneration of primary M_7C_3 and MC carbides induces the precipitation of secondary $M_{23}C_6$ during thermal exposure at 1000 °C in a cobalt-base superalloy. The secondary $M_{23}C_6$ carbide exhibits the lamellar-shaped morphology within the dendritic matrix. The precipitation behavior of the lamellar $M_{23}C_6$ carbide is related to the SFs. It is found that $M_{23}C_6$ particles nucleate and grow preferentially at SFs in the dendritic and develop a lamellar

character. Furthermore, a Cr depletion zone is observed near the lamellar $M_{23}C_6$ carbide, which strongly supports the presence of Suzuki segregation.

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