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Secondary M6C Precipitation in Ni-20Cr-18W-1Mo Superalloy

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Abstract—The carbide precipitation behavior in Ni-20Cr-18W-1Mo superalloy solution treated at 1280 °C and then aged at 800 and 1000 °C has been investigated using SEM, EDS and TEM in the present work. Since the content of W and Mo is high enough (>6-8 wt.%) and the value of proportion (Cr at.% /(Cr+Mo+0.7W) at.%) is 0.8206, satisfying the condition for the formation of secondary M6C, it is granular and W-rich M6C as secondary phase instead of lamellar and Cr-rich M23C6 that precipitates at grain boundaries when the aging temperature is not lower than 1000 °C. The precipitation of secondary M6C is suggested through a direct reaction between the metal elements and carbon atoms mechanism, in which the decomposition of primary M6C carbide provides the necessary elements. M is mainly W element with modest level of Ni, Cr and Mo. The result provides a foundation for improving the mechanical property of the alloy.

Index Terms—Ni-20Cr-18W-1Mo superalloy, carbide, secondary M6C, grain boundary

I. INTRODUCTION

The evolution of intergranular and intragranular precipitates in a wide range of alloy systems has drawn intense interest owing to their proudly influence on the mechanical properties, corrosion resistance and other properties [1]-[10]. These precipitates include Cr-rich M23C6, W or Mo-rich M6C, discontinuous precipitates and intermetallic compounds in different kinds of alloys, such as austenitic stainless steels, Ni or Co-based superalloys and Pb−Sn alloys [1], [4]-[6], [11]-[17].

It is found that the type and morphology of secondary carbides have a close relationship with both chemical composition and heat-treated condition of alloys. Quanyan et al find that Cr23C6, Mo-rich M6C and Ti(C,N) constitute the major primary precipitates with fine Cr23C6 as the main secondary carbides [12]. Fine eta-M6C carbides are observed at temperatures from low to intermediate, whereas the coarse eta-M6C carbides increase in extent at 871°C [12]. Additionally, the research about DZ40M alloy shows that M7C3 and MC precipitate as primary carbides, while Cr-rich M23C6 acts as secondary carbide [11]. Sudin et al report that the type of secondary phases, including superstructures and carbide precipitates, are formed as a function of temperature in alloy 230 [17]. In austenitic stainless steels and some nickel-based superalloys, only M23C6 can be found as secondary carbide [1], [16], [18].

It is claimed that secondary M6C carbide is presented only when the molybdenum or tungsten content exceeds about 6 to 8 wt.% in nickel or cobalt- based superalloys [11]. It is also reported that the type of secondary carbide in nickel-based superalloy has a close relationship with the relative content of several elements, such as Cr, W, and Mo in austenitic matrix [19]. When the value of proportion (Cr at.% /(Cr+Mo+0.7W) at.%) is more than 0.82, only Cr-rich M23C6 can precipitate, when the value above is less than 0.72, only W or Mo-rich M6C as secondary carbide appears. Otherwise, both M23C6 and M6C can present according to the exposure temperatures.

Ni-20Cr-18W-1Mo is a newly developed wrought superalloy gaining its strength from solid-solution and dispersed carbides. It can be used at temperature as high as 1100 °C and employed widely in aerospace, chemical process industries and nuclear reactor because of its superior properties, such as excellent mechanical strength at high temperatures, long-term creep rupture strength as well as the oxidation or corrosion resistance. These special properties are seriously affected by the secondary precipitates, especially the carbides at grain boundaries (GBs). Hence, the investigation of evolution behaviors for secondary carbides is of significant importance. According to the chemical composition of Ni-20Cr-18W-1Mo alloy [5], [6], it can be deduced that both Cr-rich M23C6 and W-rich M6C can be precipitated as secondary phase. Some work focusing on the decomposition of primary M6C and precipitation of secondary M23C6 at GBs have been carried out in our group [5], [6], [20], [21]. However, the precipitation behavior of secondary M6C in the alloy has not been investigated.

Therefore, the primary objectives of this work concentrate on the investigation of precipitation behavior and formation mechanism of secondary M6C in Ni-20Cr-18W-1Mo superalloy.

II. EXPERIMENTAL METHODS

The chemical composition (wt-%) of Ni-20Cr-18W-1Mo superalloy is: Cr, 19.82; W, 18.48; Mo, 1.24; Al, 0.46; C, 0.11; B, 0.0028; La, 0.026; P, S<0.004, Bal. Ni. The process for fabrication of the alloy is as follows. Initially, the cast material was vacuum induction melted (VIM) and vacuum arc remelted (VAR). Then, the ingot was homogenized for 24h at 1200 °C and furnace cooled. Finally, it was hot forged and rolled at 1050 °C to 1150 °C into a sheet with a 9mm thickness. The samples were cut from the sheet and solution treated at 1280 °C for 0.5h, water quenched (WQ). The microstructure of the alloy in annealed condition is shown in Fig.1.

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It can be seen that the average grain size is about 100μm, primary M6C particles are randomly dispersed throughout the grain structure and a number of twin grain boundaries are present. Subsequently, the samples were aged at 800 ºC for 10h and 1000 ºC for durations up to 100h, followed by water quenching. Standard metallographic techniques were used to prepare the metallographic samples and the polished samples were etched with aqua regia (HCl: HNO3=3:1) to reveal the microstructures. The microstructures were observed by scanning electron microscope (SEM, TESCAN VEGA3 LMU) with energy dispersive spectroscopy (EDS) for composition identification. Transmission electron microscopy (TEM, tecnai G2 F30) was used to identify the carbide phase. TEM samples were prepared by the twin-jet method in 8% perchloric acid carbinol solution at -30 ºC.

III. RESULTS AND DISCUSSION

Fig.2 shows the morphologies and EDS analysis of secondary carbides at grain boundary for the samples aged at 800 and 1000 ºC for 10h, respectively. It is noted that lamellar carbide precipitates at 800 ºC (Fig.2a) and directionally grows into one side of matrix. EDS analysis (spectrum 1 in Fig.2c) shows that the lamellar carbide is rich in Cr and identified as M23C6 which has been studied detailedly in the prior work [5], [6], [20]. The decrease of Cr concentration in matrix resulted from the precipitation of Cr-rich M23C6 at GBs will reduce the strength of alloy [5]. Besides, the M23C6 will be firstly broken and cracks generate at GBs due to both the brittle of M23C6 and the low bong strength at the M23C6/matrix interface during the tensile deformation process [5]. The obvious reduction in strength for thed aged alloy with lamellar M23C6 as secondary phase at GBs reveals that the lamellar M23C6 is not favorable in this alloy. The carbide becomes granular with aging temperature reaching to 1000 ºC, as shown in Fig.2b, which attracts the researchers a lot of interest. Compared with the Cr content in the lamellar M23C6, granular carbide is rich in W and low in Cr, which can be seen from the EDS analysis (spectrum 2 in Fig.2c).

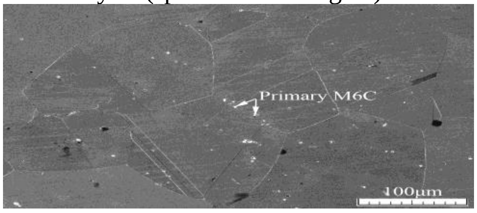

Fig.1 Microstructure of Ni-20Cr-18W-1Mo in annealed condition

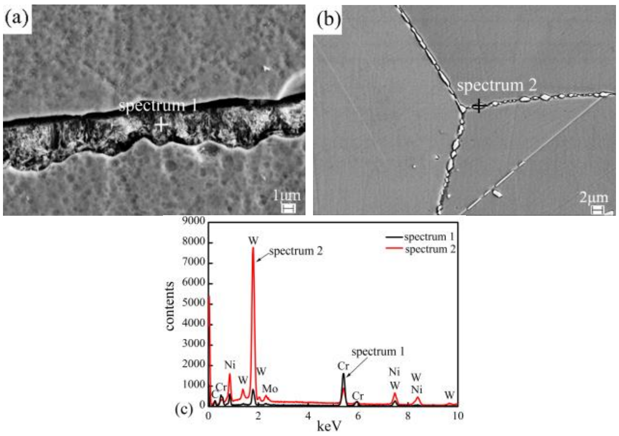

Fig.2 SEM micrographs and EDS analysis for carbides in Ni-20Cr-18W-1Mo superalloy aged at different temperatures for 10h: (a) 800 ºC; (b) 1000 ºC; (c) EDS analysis of carbides in (a) and (b).

TEM micrographs and typical [011], [001] and [$\bar{1}12$] SAED (selected area electron diffraction) patterns of the granular carbide are shown in Fig.3. The SAED patterns (Fig.3b-d) demonstrate that the granular precipitates possess the same crystal structure and their characteristic reflections are present at near every third position of the FCC matrix reflection. Hence, the precipitates have an FCC structure with a lattice constant that is nearly three times that of the matrix, and the orientation relationship between the carbide and matrix is ascertained to be <011>carbide//<011>matrix and {$\bar{1}\bar{1}1$}carbide // {$\bar{1}\bar{1}1$} matrix. The lattice parameter of the carbide is calculated to be approximately 1.133nm. Furthermore, it can be seen from the [001] SAD pattern (Fig.3b) that the {200} type reflections are absent, indicating that these carbides have an FCC lattice type belonging to Fd3m space group. It is reported that M6C is more thermodynamically stable than M23C6 at lower Cr concentration owing to the lower Cr/C ratio in M6C than in M23C6. The lattice type of both M23C6 and M6C are FCC, and their lattice parameters are close, a_0 of M23C6 is from 1.048 to 1.080 nm and that of M6C is from 1.085 to 1.175 nm. In addition, the structure of M23C6 belongs to Fm3m space group, whereas that of M6C belongs to Fd3m, thus, unlike M23C6, all hk0 reflections where h+k≠4n, such as 420, 200, 600, etc., have a zero structure factor and will not appear in beam reflections, such as [001] [12], [22]. The above analysis got from the granular carbide precipitated at 1000 ºC in Ni-20Cr-18W-1Mo is in accordance with the characterization of M6C. As a result, the secondary intergranular carbide is identified as M6C at 1000 ºC, which is different from the lamellar carbide identified as M23C6 at 800 ºC.

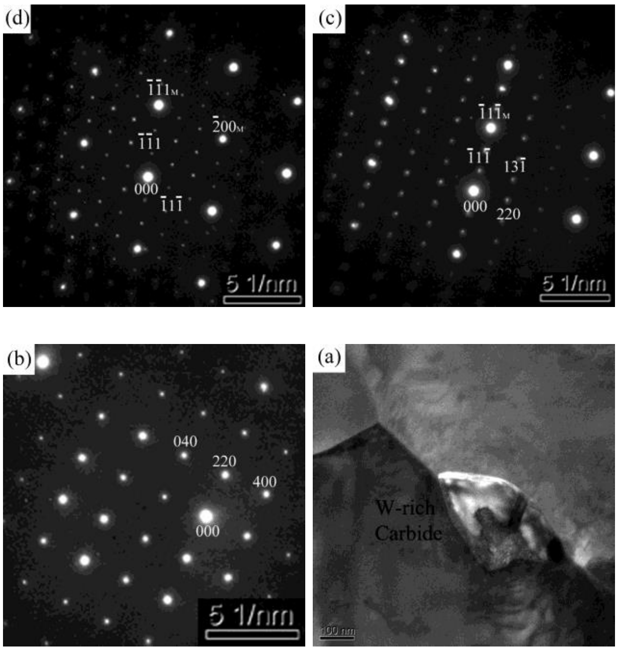

Fig.3 TEM analysis for carbide in the sample aged at 1000 ºC for 10h: (a) BF micrograph for carbide precipitated at 1000 ºC; (b) [001]; (c) [$\bar{1}12$]; (d) [011] SAED pattern.

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The temperature range for the secondary M6C formation is reported from 850 °C to 1210 °C, and the best temperature range is from 950 °C to 1100 °C [19]. In generally, the content of W is highest in M6C. In addition, the stable temperature for the formation of M6C is higher than that for M23C6. Hence, if the composition of alloy satisfies the condition shown in introduction, M23C6 will not precipitate at GBs when the alloy is aged at high temperatures. For Ni-20Cr-18W-1Mo superalloy, the content of W and Mo is high enough (>6-8 wt.%) and the value of proportion (Cr at.% /(Cr+Mo+0.7W) at.%) is 0.8206, satisfying the condition for the formation of M6C. It is furthers confirmed that the granular carbide precipitated at 1000 °C is M6C. According to the experiments we have done, it can be speculated that the starting temperature for secondary M6C to precipitate in Ni-20Cr-18W-1Mo is at about 950 °C, and the ending temperature is at about 1200 °C. As for the starting time to precipitate, it is believed to be very short for the M6C to nucleate and precipitate at so high aging temperature. The evolution of M6C morphologies during aging treatment at 1000 °C is shown in Fig.4. It can be seen from Fig.4 (a) that the secondary M6C has appeared when the aging time reaches 0.5h.

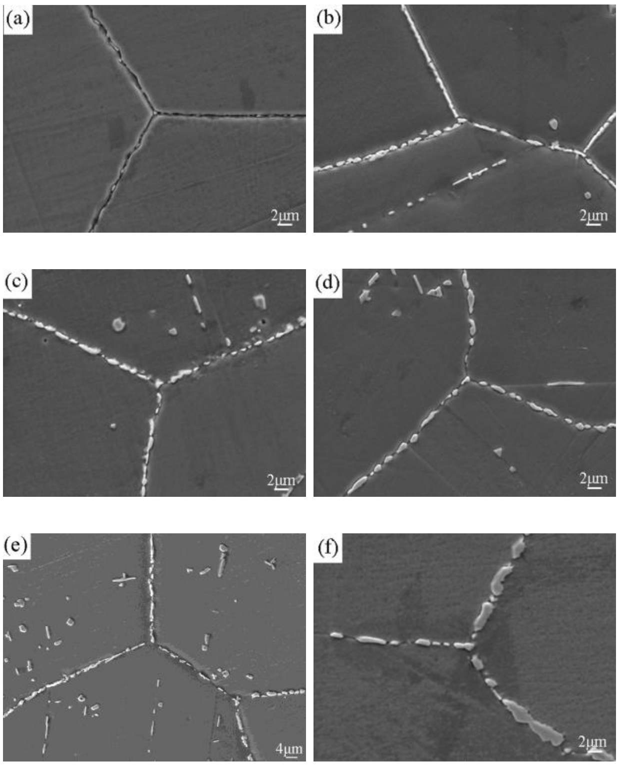

Fig.4 Microstructures of Ni-20Cr-18W-1Mo superalloy aged at 1000 oC for different time: (a) 0.5h; (b) 1h; (c) 2h; (d) 5h; (e) and (f) 100h.

Based on some superalloys, some mechanisms of secondary M6C precipitation have been proposed. In Mar-M200 nickel-base alloy [23], it is proposed that the secondary M6C is formed owing to the decomposition of M23C6

$$M23C6 \rightarrow M6C \quad (1)$$

M6C may also be attributed to the reaction between the decomposition product of MC carbide and the alloy matrix [23]:

$$MC+\gamma \rightarrow M6C \quad (2)$$

The research on DZ40M alloy proves that the presence of tungsten rich M6C is attributed to the addition of minor alloying elements [11], such as Ta, Ti, Zr, inducing the formation of primary MC carbides with high tungsten content. Local tungsten segregation is formed through subsequent decomposition of primary MC during the aging treatment, which satisfies the chemistry condition for the precipitation of secondary M6C and the surface of the neighboring M7C3 carbide acts as an effective nucleating site for the good lattice match between M7C3 and M6C, promoting secondary M6C precipitation. The study on K40S cobalt-based alloy proposes that M6C can be formed by a direct element reaction mechanism [24]. During the aging treatment, primary M7C3 partly degenerates to provide the main M6C forming elements, which will diffuse locally into the W-rich zone inherited from the as-cast condition in the matrix and react with C to form M6C.

However, all the mechanisms above cannot correctly explain the formation of secondary M6C at GBs in Ni-20Cr-18W-1Mo. As shown in Fig.4, the size of secondary M6C particles increases all through with increasing aging time. And the particles are largely coarsened when the time reaches to 100h (Fig.4f). The formation of secondary M6C cannot be explained by the mechanism shown in Eq.(1). According to this mechanism, Cr rich and lamellar M23C6 should present at the first stage of aging treatment in this alloy and secondary M6C precipitates on the surface of M23C6. Besides, the size of secondary M6C particles should be limited according to that of prior M23C6, but the lamellar M23C6 cannot be found at GBs. There are no MC in this alloy because of the lack of the strongest MC-forming elements, such as Ta, Ti, Zr, as a result, the mechanism of secondary M6C precipitation in this alloy cannot be explained by the MC carbide degeneration mechanism. In Ni-20Cr-18W-1Mo, the primary carbide is W-rich M6C instead of Cr-rich M7C3 and the secondary M6C precipitates at grain boundaries, not in the matrix, which is different from the K40S cobalt-base alloy. Hence, the mechanism for the M6C formation in K40S is not suitable for the present work.

Based on the present metallographic observations, the mechanism for the precipitation of secondary M6C at GBs is suggested to be also through a direct reaction:

$$6M + C \rightarrow M6C \quad (3)$$

During the annealing treatment at 1280 °C for 30min, the primary M6C carbide is metastable and partly decomposes. The main M6C forming elements are released. The fast cooling rate caused by water quenching, following the annealing treatment, suppresses M6C formation and leads the matrix to be saturated with W and C. As a result, the content of W increases in matrix, which will in turn limit Cr-rich M23C6 to precipitate and lead W instead of Cr to diffuse to GB and form carbides with C during aging treatment at high temperatures. Besides, the solid solubility of Cr increases with increasing temperature, which will be unfavorable for the precipitation of Cr-rich M23C6 at high temperature aging treatment. As is well known, carbon atoms is easily attracted to dislocations, stacking faults and grain boundaries [18]. During the high-temperature aging treatment suitable for the precipitation of secondary M6C, the M6C forming elements will diffuse to GBs and react with C to form M6C.

The formation of secondary M6C leads to the further decomposition of primary M6C in matrix. It can be observed from Fig.4c-e that the morphology of primary M6C in matrix has changed from spheroidal to irregular, including polygonal or tricorn shape, and the size becomes smaller, which confirms the decomposition of primary M6C.

As for the morphology of the secondary M6C in Ni-20Cr-18W-1Mo superalloy, it is found that the secondary M6C is granular (Fig.2b), which is different from that of secondary M23C6 with lamellar morphology (Fig.2a). It is proved that the spheroidization of lamellar carbide occurs due to the assembling, coarsening and fusing of carbide lamellas at high temperatures [25], [26]. Hence, the lamellar morphology cannot present at high temperatures. This gives a good explanation for the morphology of secondary M6C.

IV. CONCLUSION

The precipitation of secondary W-rich M6C at grain boundaries is studied in Ni-20Cr-18W-1Mo superalloy. When the aging temperature is not lower than 1000 °C, it is secondary W-rich M6C carbide with a granular morphology instead of lamellar Cr-rich M23C6 that will precipitate at grain boundaries. The formation of secondary M6C is through a direct reaction mechanism: 6M + C → M6C, where M is mainly W element with modest level of Ni, Mo and Cr. The necessary elements for the precipitation of secondary M6C come from the decomposition of primary M6C carbide during the solid solution process and aging heat treatment. Since the spheroidization of lamellar carbide occurs due to the assembling, coarsening and fusing of carbide lamellas, the lamellar morphology cannot present at high temperatures. This is the reason that the secondary M6C has a granular morphology.

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