Misorientation effect of grain boundary on the formation of discontinuous precipitation in second and third generation single crystal superalloys

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Abstract. [001] tilt artificial grain boundaries of Ni-based single crystal superalloys CMSX-4 and DD10 have been prepared by self-diffusion bonding. The microstructural stability of 0 ~ 30° artificial grain boundaries have been investigated after heat treatment at 1100 °C for 0 ~ 300 h. TCP phases and cellular colony developed on boundaries are related to misorientation angle of the bonded boundaries of DD10 and DD10 alloys as well as the bonded boundaries of CMSX-4 and DD10 alloys. The heterogeneous nucleation of TCP phase, enveloped by γ' film, occurred along 15° and 20° boundaries. Discontinuous Precipitation (DP) reaction occurred along high misorientation angle (20° ~ 30°) boundaries. However, no TCP phase formation existed along grain boundaries with different misorientation angles in CMSX-4/CMSX-4 bonded alloys as well as for a 0° boundary in DD10/DD10 and CMSX-4/DD10 bonded alloys. The current study clearly suggests that grain boundary precipitation and its morphology were influenced by the misorientation angle of grain boundary and the content of refractory elements in alloy.

1. Introduction

Ni-based single crystal superalloys are primary materials for high pressure turbine blades in advanced aircraft engines. The manufacture of multilateral component or hybrid component turbine blades has become attractive for industrial application, recently [1–3]. Fusion welding and diffusion welding techniques are used to produce these multi-component blades. The welding boundary with misorientation angle is similar to grain boundaries [4]. These boundaries are preferential heterogeneous nucleation sites for precipitates due to their high diffusion mobility, and the corresponding mechanical properties of materials and components would be affected [5–7]. To date, research on microstructure stability of boundaries with certain misorientation angle at service temperature is still limited.

Grain boundary precipitation has been classified as continuous precipitation (CP) and discontinuous precipitation (DP) by Geisler [8] and Newkirk [5]. In Ni-base superalloys, TCP phases preferentially precipitate at grain boundaries instead of the matrix due to high diffusion mobility of refractory alloying elements along the boundaries. DP transformation is one type of microstructural instability of a grain boundary, it transforms γ - γ' two-phase microstructure into γ - γ' + TCP lamellar structure in Ni-based superalloys. The occurrence of DP on grain boundaries in Re-containing single crystal superalloys were reported in several studies [9–14]. DP transformation depletes the strengthening elements Re

and W in the γ matrix, resulting in microstructural and property degradation. Limited studies indicated that DP initiation was linked to grain boundary misorientation as well as supersaturation of refractory alloying elements in an alloy [12,14]. Grain boundary misorientation had significant effects on grain boundary energy and migration [15]. It was reported that DP occurred at grain boundaries with high misorientation angles while only heterogeneous precipitation of TCP phase occurred along low angle grain boundaries [16]. These results are helpful to understand the misorientation effect on grain boundary precipitation. However, the pertinent research of alloy chemistry and misorientation effect of grain boundary on localized precipitation and DP transformation along grain boundary is still limited.

The present study is to investigate microstructural stability of diffusion bonded boundaries in 2nd and 3rd generation single crystal superalloys. The influence of alloy chemistry and misorientation angle of grain boundary has been focused on TCP phase precipitation and DP transformation along grain boundary. The current study will be helpful for understanding the microstructural stability of single crystal blades containing low angle boundary and the stability of boundary between multi-material blades.

2. Experimental

The two investigated alloys were a 2nd and 3rd generation Ni-based single crystal superalloys CMSX-4 and DD10, respectively. Their nominal compositions are given in

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Table 1. Nominal compositions of CMSX-4 and DD10 single crystal superalloys (wt.%).

Alloys	Cr	Co	Mo	W	Ta	Re	Al	Ti	Hf	C	Ni
CMSX-4	6.5	9.0	0.6	6.0	6.5	3.0	5.6	1.0	0.1	–	Bal.
DD10	4.0	12.0	2.0	6.0	7.0	5.0	5.0	–	0.15	0.02	Bal.

Figure 1. (a) Schematic diagram of single crystal sector, one of the sectioning planes was (010); (b) schematic diagram of the contacted samples in a fixture.

Table 1. They represent low level and high level Re containing alloys. They were directionally solidified by using the Bridgman technique. The misorientation between the growth orientation and [001] orientation was less than 5° . CMSX-4 alloy was initially subjected to a solution heat treatment at $1300 \sim 1308^\circ\text{C}$ for 8 h, and DD10 alloy was processed by the standard heat treatment [17].

In this study, three types of have been prepared by using the self-diffusion bonding process and they were bonded by DD10 and CMSX-4 alloys. These artificial grain boundaries are termed as DD10/DD10 similar weldment, CMSX-4/CMSX-4 similar weldment and CMSX-4/DD10 dissimilar weldment. Figure 1a is the schematic diagram of single crystal sector. The (010) plane was set as the base plane of [001] tilt artificial grain boundaries in DD10/DD10 bonded alloys. The misorientation angle was assigned by rotating around [001] from (010) for a certain degree α , shown in Fig. 1a. CMSX-4/DD10 boundaries were [001] tilt boundary and (010) plane was the symmetrical plane in order to ensure the bonding surface in the same crystallography condition. The surfaces of bonding planes were polished with 400 through 2000 grit papers. Figure 1b is a schematic diagram of the contacted samples in a fixture. The sectioning planes of single crystal samples were held together tightly and were put in a superalloy fixture after ultrasonically cleaned in acetone for 15 mins, as shown in Fig. 1b. A superalloy wedge was inserted into the fixture to make these sectioning surfaces contact intimately. Al_2O_3 wafers were inserted into non-bonding surface to avoid bonding at high temperature.

The samples in the fixture were heated at 1290°C for 12 h in a vacuum furnace with 10^{-3}Pa and then furnace cooled. The X-ray back-scattering Laue method was used to measure the misorientation angle of boundaries. The error range for the target misorientation angle was less than 2° . The bonded samples were heat treated at 1100°C for $0 \sim 200\text{h}$, and air cooled. Samples were sliced along (001) surface and prepared by using standard metallographic techniques and etched by using a solution of 1 pct HF, 33 pct CH_3COOH , 33 pct HNO_3 , and 33 pct H_2O .

The microstructure of artificial grain boundaries were characterized by a Zeiss Supra 55 field-emission scanning electron microscope (FE-SEM). The growth direction and orientation change after DP transformation was verified by a TSL-OIM electron back-scattered diffraction (EBSD) analyzer attached to the SEM. The average width of a DP colony along an artificial grain boundary equals to the total area of DP colony divided by length of DP colony, which was measured using Adobe Photoshop CS5 software. To obtain statistically significant results of the average width of continuous DP colonies, 2 mm in length of DP colony were measured.

3. Results

3.1. Microstructure evolution of artificial grain boundaries

Figure 2a is the typical microstructure of 0° boundary just before heat treatment at 1100°C (0 h) in DD10/DD10 alloys. The fine and irregular γ' phase precipitated in the matrix during furnace cooling after heat treatment at 1290°C for 12 h in a vacuum furnace. The boundary can be hardly distinguished from the matrix of DD10 alloy. Figures 2b and 2c show the microstructure of 0° boundary after heat treatment for 50 h and 200 h, respectively. The γ' phase in the matrix changed to be cuboidal (Fig. 2b) and it showed coarsening, coalescence and rafting near the boundary with increasing heating time (Fig. 2c). A narrow zone of larger and irregular γ' precipitates indicates marks the 0° boundary.

Figures 2d to f show the microstructure of 15° boundaries in DD10/DD10 alloys after heat treatment at 1100°C for 0 h, 50 h and 200 h, respectively. A chain of relatively large γ' phase is the indication of boundary after the bonding process (Fig. 2d). It is interesting to note that an amount of granular TCP phase precipitated along 15° boundary, which was enveloped by a γ' film, after heat treatment for 50 h (Fig. 2e). Figure 2f illustrates the size of TCP phase. The average width of γ' film along 15° boundary was increased by increasing the heating time.

The typical microstructure of 25° boundary in DD10/DD10 bonded alloys after heat treatment at 1100°C for 0 h, 50 h and 200 h are shown in Figs. 2g to i. Figure 2g exhibits that the 25° boundary was also distinguishable from the matrix due to relatively larger γ' phase on boundary just after bonding, similar to 15° boundary (Fig. 2d). However, unlike low angle boundaries, the cellular structure was observed along 25° boundary after heat treatment at 1100°C for 50 h, as shown in Fig. 2h. It is clearly suggested that the fine $\gamma + \gamma'$ microstructure transformed into $\gamma + \gamma' + \text{TCP}$ cellular structure as the DP reaction during heat treatment. Figure 2i indicates the size of TCP phase. Also, the average width of cellular colony

Figure 2. Typical microstructure near grain boundaries with different misorientation angles in DD10/DD10 bonded alloys after heat treatment at 1100 °C for 0 ~ 200 h. (a) 0°, 0 h; (b) 0°, 50 h; (c) 0°, 200 h; (d) 15°, 0 h; (e) 15°, 50 h; (f) 15°, 200 h; (g) 25°, 0 h; (h) 25°, 50 h; (i) 25°, 200 h.

Figure 3. Typical microstructure near 25° boundaries in CMSX-4/DD10 bonded alloys after heat treatment at 1100 °C for 0 ~ 200 h. (a) 0 h; (b) 100 h; (c) 200 h.

along 25° boundary increased with increasing the heating time. It should be noted that the granular TCP precipitates existed along the original boundary and the lamellar TCP phase grew with the curved moving reaction front away from the original boundary, which was nearly flat and normal to the [010] orientation (Figs. 2h and 2i). It is suggested that the cellular colony grew from the grain with the boundary normal to (010) plane into another grain, and

it was also a [001] tilt boundary, deviating from (010) plane for 25°.

The CMSX-4/CMSX-4 and CMSX-4/DD10 bonded alloys with 25° boundaries were also investigated after heat treatment at 1100 °C for 0 ~ 200 h. The typical microstructure along 25° boundaries in CMSX-4/CMSX-4 bonded alloys was $\gamma + \gamma'$ microstructure with neither TCP precipitates nor cellular colonies during the

Figure 4. Average widths of γ' film along 15° boundary and the cellular colony along 25° boundary as a function of time after heat treatment at 1100 °C in DD10/DD10 bonded alloys.

whole heat treatment (images not shown). Figure 3 shows that the typical microstructural features of 25° boundary in CMSX-4/DD10 bonded alloys were quite similar to those of DD10/DD10 bonded alloys during heat treatment (Figs. 3g–i). As expected, the formation of the cellular colony with $\gamma + \gamma' + \text{TCP}$ lamellar structure occurred along CMSX-4/DD10 boundary. It is noteworthy that the reaction front of the cellular structure was primarily migrated into the DD10 alloy.

Figure 4 shows the average widths of γ' film and cellular colony along 15 and 25° boundaries in DD10/DD10 bonded alloys after heating at 1100 °C as a function of time. The current results indicate that a linear relationship exists between the average width and the squared root of heating time, but the linear slopes were significantly different for two different boundaries.

3.2. Composition of phases in DP zone and matrix

Table 2 lists the compositions of TCP, γ and γ' phases within the cellular colony and the matrix in DD10/DD10 bonded alloys after heating at 1100 °C for 200 h. The cellular TCP phase was significantly enriched in W and Re. The Re contents of γ and γ' phases in the matrix were higher than those in the cellular colony. These results are consistent with previous studies [9, 16].

3.3. Orientation change of DP transformation

Figures 5a and 5c show the microstructure of 20° and 30° boundary in DD10/DD10 bonded alloys after heat treatment at 1100 °C for 300 h, which are similar to 15° and 25° boundary, respectively. Again, their typical microstructural features are γ' film along the boundary and $\gamma + \gamma' + \text{TCP}$ cellular colony, respectively. Figure 5b is the corresponding orientation map of Fig. 5a, illustrating that the original artificial grain boundary did not migrate at 20° boundary. The orientation map of 30° boundary shown in Fig. 5d indicates that the original artificial grain boundary migrated under the heat treatment process. The migration direction of cellular colony boundary primarily deviated from the original artificial grain boundary. Meanwhile, the

orientation of the cellular colony had the same orientation as the grain with the original artificial grain boundary normal to (010) plane.

4. Discussions

Instead of the formation of precipitates at random within the alloy matrix, nuclei of new phases form preferentially at grain boundaries due to interfacial nucleation sites as well as their high diffusion mobility. Localized precipitation occurs at the grain boundary in earlier stage of CP, and then the precipitates grow along the grain boundary during the extended heat treatment [18]. DP transformation is the combination of heterogeneous precipitation and grain boundary migration. Across the reaction front, there is a discontinuous change in both orientation and solute concentration [19]. DP initiation is linked to grain boundary energy and supersaturation of refractory elements in the alloy [9, 16].

It is well known that the formation of TCP phases and DP reaction is closely associated with the content of refractory alloying elements. TCP phases are composed principally of the elements Cr, Mo, Co, W and Re, and these elements are most effective at conferring resistance to creep [20]. In order to improve the creep resistance, 5 ~ 6 wt.% Re is usually added to 3rd generation single crystal superalloys compared with 2nd generation single crystal superalloys containing about 3 wt.% Re [20]. In this study, no TCP precipitates existed on different boundaries in the 2nd generation single crystal alloy CMSX-4 after heat treatment at 1100 °C for 0 ~ 200 h (images not shown). However, both CP and DP transformation were observed on boundaries in DD10/DD10 and CMSX-4/DD10 bonded alloys (Figs. 2e–2i, 3b and 3c). It should be noted that the DP reaction front of CMSX-4/DD10 boundary primarily migrated into the DD10 alloy (Figs. 3b and 3c). The current results indicate that Re content plays an important role in CP and DP transformation. Supersaturation of Re in the matrix is the driving force for heterogeneous nucleation of TCP phases and DP transformation in boundary precipitation [5]. High Re content in DD10 alloy is closely related to the migration direction of DP reaction front along CMSX-4/DD10 boundaries.

Misorientation of grain boundary is another important factor to influence the precipitate formation and grain boundary migration [19]. Both grain boundary energy and migration rate are associated with the misorientation angle of grain boundary [6]. In the fcc Al, the relative grain boundary energy of [100] tilt boundaries with 15 ~ 30° misorientation angles were approximately equal [15, 21]. However, there was a rapid increase in the migration rate of grain boundary at about 15 ~ 20° misorientation angles [15]. Heterogeneous nucleation of TCP phases was observed at 8° grain boundary in a 3rd generation single crystal superalloy containing 6.3 wt.% Re in a previous study [14], while the growth of cellular colony was detected on grain boundaries that were misoriented by 14°. Walston [8] suggested higher misorientation angle of grain boundaries were required for DP transformation in more stable alloys. In the current investigation, granular TCP phases enveloped

Table 2. Composition of γ , γ' and TCP phases within the cellular colony (CC) and matrix at 25° boundaries in DD10/DD10 bonded alloy after heat treatment at 1100 °C for 100 h (wt. %).

phase	Al	Cr	Co	Ni	Mo	Ta	W	Re
TCP in CC	0.00	5.06	10.15	9.63	6.59	3.55	24.01	41.02
γ' in CC	8.48	1.73	9.38	57.59	1.34	12.67	7.14	1.69
γ in CC	6.10	5.48	17.24	54.54	3.24	1.40	5.39	5.34
γ' in matrix	10.09	2.49	11.64	58.11	1.43	9.15	2.86	4.24
γ in matrix	5.96	4.78	14.59	49.45	2.95	4.85	8.18	9.25

Figure 5. SEM and EBSD images (x direction IPF) of two different boundaries in DD10/DD10 bonded alloys after heat treatment at 1100 °C for 300 h. (a) 20°, SEM image; (b) 20°, EBSD image; (c) 30°, SEM image; (d) 30°, EBSD image.

by γ' film precipitated along 15° and 20° boundaries (Figs. 2e, 2f and Fig. 5a) after heat treatment at 1100 °C for 200 ~ 300 h, while the cellular colony developed on 25° and 30° boundaries of DD10/DD10 alloys (Figs. 2h, 2i and Fig. 5c) at the same heat treatment condition. No boundary migration and no orientation change occurred at 20° boundaries after TCP phase formation, while the DP transformation and the orientation change happened at 30° boundaries of DD10/DD10 alloys, illustrated by the EBSD maps (Fig. 5). The current results clearly suggest that localized precipitation of TCP phases occurred along grain boundaries with a misorientation angle less than 20°, but the DP transformation existed along boundaries with the misorientation angle larger than 20° after heat treatment at 1100 °C for 200 ~ 300 h. One of the driving forces for TCP phase formation along grain boundary in both CP and DP transformation is grain boundary energy associated with misorientation angle. However the growth of cellular colony required high grain boundary migration after the TCP phases nucleated on boundaries. The high grain boundary migration merely supplied by 25 and 30° boundaries. Therefore, the misorientation angle of grain boundary for DP transformation in the current DD10 alloy was clearly higher than 14° as shown in the previous study [16]. The lower Re content in the DD10 alloy (5.0 wt.%) may be the main reason of higher threshold of misorientation value for DP reaction.

The DP growth rate in Ni-based superalloys was considered to be controlled by volume diffusion of high refractory elements [12, 22, 23]. Walston [12] and Matsuoka [24] investigated secondary reaction zones and determined their diffusion coefficients from the slope of $d-t^{1/2}$ (d : the average width of SRZ zone; t : heat treatment time). The calculated diffusion coefficients had the same order as Al diffusion in Ni [25, 26]. They suggested that

the SRZ growth was controlled by Al diffusion from coating to substrate. In this study, the diffusion coefficient at 25° boundary of DD10/DD10 alloys which calculated from the slope of the $d-t^{1/2}$ plot in Fig. 4 is $3.02 \times 10^{-16} \text{ m}^2/\text{s}$. The diffusion coefficients of W and Re in Ni at 1100 °C were reported by Karunaratne and Reed [27] to be $6.67 \times 10^{-16} \text{ m}^2/\text{s}$ and $1.40 \times 10^{-16} \text{ m}^2/\text{s}$, respectively. The diffusion coefficient in the current study is in between them. The results illustrated that the growth rate of the cellular colony was controlled by the diffusion of Re and W.

Grain boundary migration was affected by crystal anisotropy [28]. Anisotropy of SRZ formation in aluminized Ni-based single crystal superalloys has been investigated by Murakami [29]. SRZ was not formed along the {001} <100> directions in TMS-75 alloy, and greatly enhanced SRZ was formed along the {001} <110> directions. In the current study, the growth of cellular colony significantly deviated from (010) plane into another grained as shown in Fig. 5d. The results indicate the tendency of DP formation on (010) was lower than for another orientation. The preference of DP formation was similar to previous research [29], and suggested that DP formation on DD10/DD10 boundaries was anisotropic.

5. Conclusions

A series of artificial grain boundaries in Re-containing CMSX-4 (2nd generation single crystal superalloys) and DD10 (3rd generation single crystal superalloys) alloys with certain misorientation angles were investigated for microstructural stability of boundaries after heat treatment at 1100 °C for 0 ~ 300 h. No TCP phase formation existed along grain boundaries with different misorientation angles in CMSX-4/CMSX-4 bonded alloys as well as

for 0° boundary in DD10/DD10 and CMSX-4/DD10 bonded alloys. The TCP phase, enveloped by γ' film, precipitated along 15° and 20° boundary in DD10/DD10 bonded alloys without the migration of original artificial grain boundaries; while the DP reaction occurred on 25° and 30° boundary in DD10/DD10 and CMSX-4/DD10 bonded alloys, and the cellular colony grew from the grain with the boundary normal to (010) plane into another grain in DD10 alloy. The current study clearly suggests that grain boundary precipitation and its morphology was influenced by the misorientation angle and refractory alloying elements, especially for Re content.

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