Defects and Their Elemental Distributions in a Crept Co-Al-W-Ti-Ta Single Crystal Superalloy

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Abstract: The structure of defects and their elemental distributions is the decisive factor to metal’s mechanical properties. The γ/γ’ structure Co-Al-W-based superalloy is a potential replicable alloy to Ni-based superalloys that have been used for a long time. Revealing the microstructure of a defect induced by high-temperature crept provides direct clues for the alloy development. Our work revealed the high-resolution, high-angle annular dark field images and corresponding elemental distributions on crept defects. Defects in the γ phase mainly contain dislocation networks, while the γ’ phase contains lots of stacking faults and anti-phase boundaries. The results indicate that dislocation networks and stacking faults contain more weight elements than the base γ’ phase, while anti-phase boundaries contain more light elements. Disclosing atomic structure and its elemental distributions gives direct evidence for alloy design and further high-temperature mechanical improvement.

Keywords: Co-Al-W-Ti-Ta; HAADF; Defects; EDS; TEM

1. Introduction

The Co-Al-W-based superalloy with coherent γ/γ’ matrix discovered in 2006 exhibits excellent mechanical properties and has been considered a promising candidate for high-temperature structural materials [1,2]. It opens new pathways for the development of high-temperature creep-resistant superalloys. These Co-base alloys exhibit a similar microstructure as the extensively studied and widely used Ni-base superalloys, where cubes of ordered γ’ phase, possessing the L12 crystal structure, are coherently (similar lattice parameters and same orientation) embedded in a solid-solution face-centered cubic γ phase matrix. Functional alloying elements such as Ti and Ta are conventionally added to improve the mechanical properties and high-temperature performance of these superalloys in applications [3–7]. It has been shown that the γ’ strengthened Co-Al-W-Ti-Ta superalloy displays improved structural stability and mechanical properties [7]. Tensile creep experiments performed at 900 °C on single crystalline Co-Al-W-Ti-Ta superalloys have demonstrated a creep resistance comparable to 1st-generation Ni-based superalloys [8].

Recently, the deformation mechanisms in crept Co-Al-W-based alloys have been investigated. Multiple slip modes were investigated to be activated within the γ’ phase, which include the slip of <110> dislocations below the peak and thermally activated slip of <112> dislocations [9], and the results indicate the shearing of the γ’ precipitates, leaving antiphase boundaries (APBs) in the wake of the dislocations. This is in contrast to Ni-base superalloys on a creep mechanism, which usually involve a stacking fault (SF) formed on a [111] plane by the glide of a 1/3<112> leading partial dislocation across multiple contiguous γ’ precipitates. A second 1/6<112> trailing partial dislocation
follows and transforms the SF into an APB [10]. Microstructure on the defect type, quantity, and
distribution of crept alloy is important for revealing the creep mechanism on this newly developed
Co-based single crystal superalloy. Research on defects mainly focused on their type and the amount
under the low-magnification scale. There are lots of kinds of defect, including dislocations and anti-
phase domains as reported in low magnified TEM images [11,12]; however, the study of their atomic-
scale structure is still limited. Recently, Titus reported that there are lots of stacking faults that
segregated weight elements in crept Co-based superalloys [10]. An atomic-scale study on the defect
structure and their relationships provides direct evidence for understanding the creep mechanism
under high temperatures.

A direct atomically resolved Spherical aberration corrected (Cs) TEM observation can provide
atomic-scale images on defect structure and give conclusive evidence for revealing creep
mechanisms. In this study, we systematically investigated the defects structure and elemental
segregation in a Co-Al-W-Ti-Ta alloy using high-resolution, high-angle annular dark field
(HRHAADF) and atomic super-EDX (Energy Dispersive X-Ray Spectroscopy) techniques. A three-
dimensional structure will be built based on atomic resolution data.

2. Experimental

The nominal composition of the experimental alloy is Co-7Al-8W-4Ti-1Ta (at.%) as reported
before [7]. The single crystal bars, 15 mm in diameter and 150 mm in length, are directionally
solidified using the conventional Bridgman method. After single-crystal bars were placed in quartz
tubes back-filled with Ar gas, they were solution heat treated at 1270 °C for 24 h and subsequently
aged at 900 °C for 50 h followed by air cooling. Creep tests occurred at 982 °C/248 MPa with an
interrupted deformation of 1% [7,8] with a loading direction of <001> direction based on the service
condition. The transmission electron microscopy (TEM) sample lamella preparation used the
conventional focused ion beam (FIB) cut-transfer method, and the lamella thickness was about 60
nm. The TEM and high-angle annular dark field (HAADF) experiments used an Thermo Fisher Titan
G2 60-300 KV equipped (Thermo Fisher Scientific, Waltham, MA, America) with a Super-X energy-
dispersive and X-ray spectroscopy (EDS) detector with a probe aberration-corrected. All the pictures
were acquired with a high tension of 300 KV. The quantification of the alloy element concentrations’
different regions (base and defects) was superimposed from a typical area discerned from elemental
difference with its base to obtain a sufficient signal. The K series peaks were chosen for Al, Ti and Co,
while the L series peaks were chosen for Ta and W for the EDS analysis.

3. Results and Discussions

The γ' phase in original alloy exhibits a uniform brick-like contrast embedded in γ phase base,
as shown in the HAADF image in Figure 1a. The HAADF images, based on high-angle scattered
electrons of the Rutherford scattering, has an intensity roughly proportional to $Z^{1.6-1.7}$ [13]. It indicates
that the γ' phase contains more weight elements, while the γ phase contains more light elements. The
ordered L1_2-Co:(W,Al)-based structure of the γ' phase has been considered the alternation of two
distinct sublattices [1]. The corner positions of the cubic unit cell are mainly made of a W(Al)
sublattice, while the face-center positions are mainly made of a Co sublattice, as shown in Figure 1b.
In the case of our experimental alloy Co-7Al-8W-4Ti-1Ta, the γ' phase exhibits alternating dark Co-
rich and bright W-rich planes, presenting direct evidence of the L1_2 superlattice structure, as shown
in Figure 1c. The bright and dark dots in Figure 1c can be interpreted as W(Al) and Co sublattices
viewed along the [100] direction. The detailed x-ray spectroscopy (EDS) and its elemental
distributions in γ and γ’ phases can be seen in our early work [14].
Figure 1. (a) High-angle annular dark field (HAADF) image of Co-Al-W-Ti-Ta alloy; (b) atomic model of L1₂-γ’-Co₃(Al,W) structure; (c) high-resolution HAADF image on the γ’ phase.

Figure 2 is a typical low-magnification HAADF image on the crept alloy along the <110> direction. Two phases can be figured out by their contrast in HAADF images: bright contrast ribbons are rafted γ’ phase, while their surrounding dark contrast gaps are γ phase as indexed in Figure 2a. Three kinds of defects can be figured out along the <110> direction, as indexed in Figure 2a. Dislocation networks (DNs) usually appear in the γ phase adjacent to γ/γ’ boundary and they exhibit bright contrast in HAADF images. Stacking faults (SFs) usually appear in the γ phase as straight lines. Antiphase domains (APBs) are also a typical defect in Co-Al-W-based alloys and they appear as dark curved contrast in the γ phase in an HAADF image. More than 90% of the dislocations located in the γ phase and only 10% or less intersect into the γ’ phase. It is noted that an SF intersects the network dislocations, as the arrow indicates in Figure 2b. Both of the dislocation networks (DNs) and stacking faults (SFs) exhibit bright contrast that indicated their segregation of a high number atoms. Parts of the dislocations were enlarged as shown in Figure 2c and a bright contrast dislocation has a <112> direction, and obvious distortion can be seen across the dislocation. Two dashed lines were plot across the dislocation along the <112> direction in Figure 2c, and they cannot be connected into a line due to the kink across the dislocation index and the fact that there was a 1/2<112> shift of atomic planes across the dislocation.

Figure 2. (a) HAADF image on typical defect viewed along the <011> direction. (b) HAADF images on a dislocation network located in the γ phase adjacent to the γ/γ’ boundary and (c) its enlarged part of dislocation (square in b). Two yellow dashed lines were indexed on the shift of atomic planes across the dislocation.

Usually, the expansion/shrinking of the crystal in heat-treated samples can be attributed to the segregation of the weight/light number atoms or strains. We noticed that SFs exhibit bright contrast while APBs exhibit dark contrast in HAADF images and that it indicates the segregation of specific atoms. HAADF images and elemental mappings were acquired as shown in Figure 3a,b. It can be seen that SFs are rich in weight elements W and Ta. APBs are rich in Co atoms and deficient in W, Ti and Ta atoms. The quantification on the base γ phase has a composition of Co: 69.4 at%, Al: 10.5 at%,
W: 9.6 at%, Ti: 5.6 at%, Ta: 4.9 at%, the composition of SF contains Co: 70.2 at%, Al: 7.5 at%, W: 11.6 at%, Ti: 4.7 at%, Ta: 6.0 at%, and the APB has a composition of Co: 77.7 at%, Al: 9.8 at%, W: 5.7 at%, Ti: 3.2 at%, Ta: 3.6 at%. The elemental deviation degree to its base is often characterized by an elemental distribution coefficient ratio of precipitation or defect to the base they located [15]. $K_{\gamma'/\gamma}$ is defined as elemental distribution coefficients of SF (which only appears in $\gamma'$ phase) to the $\gamma'$ phase, while $K_{\gamma/\gamma'}$ is definite as elemental distribution coefficients of APB to the $\gamma'$ phase. The coefficient of distribution coefficient can be plotted in Figure 3c. It can be seen that W and Ta atoms have a tendency to aggregate in SFs and deficient in APBs, while Co has a tendency to aggregate in APBs.

Figure 3. (a) HAADF image containing a typical stacking fault (SF) and an antiphase boundary (APB) and (b) its elemental mapping viewed along the $<110>$ direction; (c) elemental distribution coefficient defect to the $\gamma'$ phase.

Figure 4 is a high-resolution HAADF image including $\gamma'$, SFs and APBs viewed along the [110] direction. The SF has bright linear contrast with an "L" shape, while APB displays two adjacent dumbbell-like dark contrast compared with its background $\gamma'$ phase. The atomic-scale image of Figure 4 is then analysed by geometric phase analysis (GPA). HAADF images give the nuclear sites of atoms based on Rutherford scattering and the dots in the image are irrelative with sample thickness. Different colours in GPA analysis represent different lattice parameter deviation from the standard part (green colour), and red colour part represent lattice expansion part while dark blue part indicates lattice shrink. The core principal of GPA is based on the difference of local lattice parameters and locations compared with base parameters and it is a basic method to analyse lattice distortions on a nanometre scale [16]. The GPA colour analysis of Figure 4a is shown in Figure 4b and we can clearly determine two typical kinds of distortions compared with their base $\gamma'$ phase. The bright yellow coloured cores exhibit lattice expansion and they usually appear in the SF region. The lattice shrinking with a dark blue colour part appears in the APB. Part of the SF indexed in square 1 is enlarge and analysed in Figure 4c. Bright contrast dots which represent the W(Al) rich rows were plot out by red circles and yellow dashed lines circled out the SF boundary. It indicates that there was a $<112>$ atomic plane ($2\times2\times2$) shift along the SF line. Part of the APB indexed in square 2 is enlarge and analysed in Figure 4d. Bright contrast dots which represent the W(Al) rich rows were plot out by red circles and yellow dashed lines circled out boundaries of the APB, and it indicates that there was no atomic plane shift across the APB.
Figure 4. (a) High-resolution, high-angle annular dark field (HRHAADF) image including SF and APB and its corresponding (b) geometric phase analysis (GPA) analysis of Figure 3a, and different colors represent different lattice parameter deviations from the standard part (green color). (c) Part enlarged SF and its atomic skeleton of rectangle “1” in (a). (d) Part enlarged SF and its atomic skeleton of rectangle “2” in (a).

Both of the stacking faults (SFs) and the antiphase domain have typical planner defect characters as tilting experiments as shown in Figure 5a viewed along the [100] direction and 5b viewed along the [110] direction. Shape of SF and APB is thus deduced in schematic demonstration in Figure 5c,d along different view directions. The stacking faults exhibit a narrow band-like structure along the [100] direction while it displayed a wide fan-like structure after tilting to the [110] direction. The antiphase domain (APB) is another typical planar defect appearing in Co-base superalloys, and its tilting experiments are shown in Figure 5a,b as indexed. The APB is only visible when viewed along the [100] direction and intersects with SFs in the $\gamma'$ phase, as shown in Figure 6a. The APB, however, loses its contrast in HAADF image and only displayed two blurred dashed borders after tilting to the [110] direction. It thus can be concluded that SF and APB are both planar defects and tilting makes their contrast become weak due to overlapping to their base.
From the above data and analysis, elemental segregation on defects is obvious and usually SFs are rich in W and Ta atoms while they are deficient in APB. The widths of SF and APB, however, are different viewed along [100] and [110], which can be explained by the atomic schematic illustrations in Figure 6. An SF plane has 2-3 atomic layers’ segregation as emphases by yellow shadowed atoms. When viewed along the [110] direction, it is vertical or parallel to the viewing direction as shown in Figure 6a. The SFs, however, have a width about 50-100 nm in the HAADF image due to the incline of the segregation plane as shown in Figure 6b. The different HAADF contrast of APB after tilting can also be explained by their elemental segregation on specific atomic planes with that of SFs.

4. Conclusions

Atomic-scale, high-angle annular dark field images and corresponding elemental distributions on different kinds of defects on the high-temperature crept of the Ni-based superalloys were systematically characterized and analyzed. Defects in the γ phase contains dislocation networks, while the γ’ phase contains lots of stacking faults and anti-phase boundaries. There is a 1/2<112> shift of atomic planes across the dislocation, while there is no shift across an anti-phase boundary from atomic-scale images. Dislocation networks and stacking faults contain more weight elements, W and Ta, while they are deficient in Ti and Al atoms. Anti-phase boundaries contain more Co atoms than...
the base phase. The series tilting experiment and elemental segregations disclosed the HAADF contrast difference between different viewing directions on different kinds of defects. Atomic structure and its elemental distributions give direct evidence for alloy design and further high-temperature mechanical improvement.

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