Mechanism of $\alpha \rightarrow \alpha_2 + \gamma$ Phase Separation in Hypo-Eutectoid Ti-37 at%Al Alloy

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Features of the $\alpha \rightarrow \alpha_2 + \gamma$ phase separation in a hypo-eutectoid Ti-37 at%Al alloy were investigated by transmission electron microscopy. Note that the eutectoid reaction in the Ti-Al alloy system takes place at 1398 K in an Al concentration of 40 at%. The present data clearly show that in the hypo-eutectoid alloy the $\alpha_2 + \gamma$ lamellar structure is formed in an equilibrium state, just as in cases of the eutectoid and hyper-eutectoid alloys. A characteristic feature in the hypo-eutectoid alloy is the appearance of the amorphous state as an intermediate state. In other words, the sequence of the formation of the lamellar structure is the same as that in the eutectoid alloy, not in the hyper-eutectoid alloy. It can be therefore concluded that there are two types of the processes for the lamellar-structure formation in the phase separations of the Ti-Al alloy system.

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I. Introduction

According to the phase diagram of the Ti-Al alloy system⁽¹⁾, a Ti-40 at%Al alloy exhibits the $\alpha(\text{hcp}) \rightarrow \alpha_2(\text{D0}_{19}) + \gamma(\text{L1}_0)$ eutectoid reaction at 1398 K. Features of the eutectoid reaction are that it involves both the $\alpha \rightarrow \alpha_2$ ordering and the precipitation of the γ phase and the $\alpha_2 + \gamma$ lamellar structure is formed in an equilibrium state. Because the $\alpha_2 + \gamma$ lamellar structure has better ductility and toughness than the single α_2 or γ phase at room temperature, many studies are focused on the understanding of the lamellar structure for the purpose of the industrial application.

Features of the eutectoid reaction of the Ti-40 at%Al alloy had been examined by Yamabe *et al.*, mainly using optical microscopy⁽²⁾⁽³⁾. They showed that the lamellar structure is formed by the following two steps. The first step is the nucleation of the γ phase at a grain boundary of the ordered α_2 matrix and the second step is the growth of it in the matrix. Particularly, the growth of the γ phase has been so far explained in terms of the ledge mechanism⁽⁴⁾. As for the crystallographic relation between the α_2 and γ phases in the lamellar structure, further Blackburn already found the relation of $(00\cdot1)_{\alpha_2} // \{111\}_{\gamma}$ and $\langle 11\cdot0 \rangle_{\alpha_2} // \langle 110 \rangle_{\gamma}$ ⁽⁵⁾.

In addition to these previous works, we have examined the details of the formation of the lamellar structure in the Ti-40 at%Al alloy by transmission electron microscopy⁽⁶⁾⁻⁽⁸⁾. As a result, the lamellar structure was found to be formed via the appearance of the amorphous state as an intermediate state. This result is obviously inconsistent with the experimental data reported by Yamabe

et al., although the Blackburn's relation could be confirmed for the lamellar structure.

The formation of the $\alpha_2 + \gamma$ lamellar structure in the hyper-eutectoid Ti-Al alloys has been also examined by some groups⁽⁹⁾. Hono *et al.* revealed on the basis of experimental data obtained by atom probe field ion microscopy that the formation of the lamellar structure in a Ti-48 at%Al alloy is controlled by the long-range diffusion of atoms⁽¹⁰⁾. The formation is characterized by the nucleation and growth of the γ phase in the α matrix with the hcp structure. Very recently, we could basically get the same result for a Ti-44 at%Al alloy experimentally⁽¹¹⁾. In other words, the mechanism of the formation of the lamellar structure in the hyper-eutectoid alloy is essentially different from that in the eutectoid alloy. That is, the lamellar structure in the former alloy is formed by both the nucleation and growth of the γ phase in the α matrix and the subsequent $\alpha \rightarrow \alpha_2$ ordering, as mentioned above, while the appearance of the amorphous state plays an essential role in the formation of the lamellar structure in the latter.

In order to obtain the full understanding of the formation of the $\alpha_2 + \gamma$ lamellar structure in the Ti-Al alloys, it is therefore necessary to investigate the details of the $\alpha \rightarrow \alpha_2 + \gamma$ phase separation in the hypo-eutectoid Ti-Al alloys. In this work, features of the phase separation in the Ti-37 at%Al alloy was actually examined by transmission electron microscopy. We then present experimental data obtained in the present work. The sequence of the lamellar-structure formation in the hypo-eutectoid Ti-Al alloy is also compared with those in the eutectoid and hyper-eutectoid alloys.

II. Experimental Procedure

An ingot of the Ti-37 at%Al alloy was made by an Ar-arc melting technique and annealed at 1473 K for 24 h for homogenization. From chemical analysis of the ingot, its average composition was determined to be 37.3 at%Al. Samples cut from the ingot were then aged to examine both crystal structures and microstructures during the $\alpha \rightarrow \alpha_2 + \gamma$ phase separation. Concretely three groups of samples were, respectively, aged at 1273 K for 0 min, 15 min, and 30 min, followed by quenching in ice water. Specimens for transmission electron microscopy observation were prepared by an Ar-ion mill equipped with both a rotating stage and a liquid N₂ cooling stage. The observation was performed by taking electron diffraction patterns, bright and dark field images of quenched samples at room temperature, using an H-800 transmission electron microscope.

III. Experimental Results

A microstructure in the sample aged for 0 min is, first of all, shown here. Figure 1(a) is a bright field image taken from a typical area of the sample. An electron incidence of the image is parallel to the $[11\cdot0]_{D0_{19}}$ direction, where the suffix $D0_{19}$ denotes the $D0_{19}$ structure. A feature of the image is that stripes are observed partially in the matrix along the $[\bar{1}1\cdot1]_{D0_{19}}$ direction, as is indicated by S. An average width of the stripes was determined to be about 0.2 μm . In order to check crystal structures of the stripe as well as the matrix, then an electron diffraction pattern was taken from each region. Two diffraction patterns obtained from the matrix and the stripe are shown in Figs. 1(b) and (c), respectively. In these figures, the pattern of the matrix is found to be different from that of the stripe. A simple analysis indicated that diffraction spots in the pattern of the matrix can be explained as both fundamental and superlattice spots due to the $D0_{19}$ ordered structure, while there are spots indexed in terms of the B_{19} structure in the pattern of the stripe. Thus the B_{19} structure appears in the hypo-eutectoid Ti-37 at%Al alloy, just as in the cases of the eutectoid Ti-40 at%Al and hyper-eutectoid 48 at%Al alloys⁽¹²⁾. In a dark field image taken by using the $011_{B_{19}}$ spot, actually the stripes are observed as the bright contrast, as is shown in Fig. 2. It is eventually understood that in the sample before aging at 1273 K there coexist the regions with the $D0_{19}$ and B_{19} ordered structures, instead of the single hcp phase. From the diffraction patterns, further both a crystallographic relation and an interface between the $D0_{19}$ and B_{19} regions were analyzed to be $(00\cdot1)_{D0_{19}} // (001)_{B_{19}}$ and $[11\cdot0]_{D0_{19}} // [010]_{B_{19}}$, and the $(11\cdot1)_{D0_{19}}$ plane, respectively. The lattice parameters of the $D0_{19}$ and B_{19} structures were also estimated to be $a=0.46$ nm and $c=0.58$ nm for the $D0_{19}$ structure and $a=0.45$ nm, $b=0.28$ nm and $c=0.47$ nm for the B_{19} structure.

In order to examine changes in both crystal structure and microstructure during aging at 1273 K below the

Fig. 1 Bright field image, (a), and two electron diffraction patterns taken from the sample aged at 1273 K for 0 min. Diffraction patterns of (b) and (c) were obtained from the matrix and a stripe region S, respectively. In the pattern (b), diffraction spots are indexed in terms of the $D0_{19}$ structure. On the other hand, there are diffraction spots due to the B_{19} structure in the pattern (c).

eutectoid line of 1398 K, their features were examined in the sample aged for 15 min. Figure 3(a) is a bright field image showing the microstructure in the aged sample. In this image, band-like regions about 50 nm in width are

Fig. 2 Dark field image taken from the area shown in Fig. 1(a). The electron incidence is parallel to the $[11\cdot0]_{D0_{19}}$ direction. The image was taken by using the 011 spot due to the B_{19} structure.

observed in the $D0_{19}$ matrix, in addition to the B_{19} stripe. It seems that the region is nucleated at the B_{19} strip and grows along the $[11\cdot0]_{D0_{19}}$ direction. A microstructure composed of the band-like region and the matrix can be also identified as a lamellar structure. An important feature of the image is that the band-like regions give rise to an extremely uniform and featureless contrast like a liquid state. Then we tried to examine a crystal structure of each region in the hypo-eutectoid alloy by taking electron diffraction patterns. Figure 3(b) shows an electron diffraction pattern obtained from the area shown in Fig. 3(a), together with a corresponding schematic diagram, Fig. 3(c). The electron incidence is parallel to the $[11\cdot0]_{D0_{19}}$ direction. As is easily seen in the schematic diagram, diffraction spots in the pattern are composed of fundamental and superlattice spots due to both the $D0_{19}$ and B_{19} structures. Particularly the spots due to the B_{19} structure are very closely located at those due to the $D0_{19}$ one. In addition to these diffraction spots, a halo ring with very weak intensity can be detected, although the ring is not well reproduced in the diffraction pattern. This implies that the uniform and featureless contrast in the bright field image should be due to the amorphous state.

It is worth noticing that the uniform and featureless contrast was also obtained in the initial stage of the lamellar-structure formation in the eutectoid Ti-40 at%Al alloy. As was mentioned in our previous papers⁽⁶⁾⁻⁽⁸⁾, the contrast in the case of the eutectoid alloy was observed near the B_{19} precipitate in the $D0_{19}$ matrix, just like in the present alloy. We then analyzed it by taking electron diffraction patterns and high resolution electron micrographs. In addition to the presence of the halo rings in the patterns, a high resolution image revealed a unique contrast characterizing the amorphous state. Regions

Fig. 3 Bright field image, (a), and electron diffraction pattern, (b), taken from the sample aged at 1273 K for 15 min. The electron incidence is parallel to the $[11\cdot0]_{D0_{19}}$ direction and diffraction spots are indexed in terms of the $D0_{19}$ structure. The schematic diagram of the diffraction pattern is also depicted in (c). Fine circles indicated by OA-a, -b, and -c in the diagram are, respectively, locations of the objective aperture when the dark field images of Figs. 4(a), (b), and (c) were taken.

with a medium range order were also detected in the image.

Dark field images of the sample aged for 15 min were taken not only by the diffraction spots due to the $D0_{19}$ and B_{19} structures but also by the halo ring. Figures 4(a), (b), and (c) are, respectively, dark field images by using the $22\cdot2_{D0_{19}}$ and the $012_{B_{19}}$ spots, and a part of the halo ring, which are indicated by fine circles in Fig. 3(c). In the $22\cdot2_{D0_{19}}$ image of Fig. 4(a), the $D0_{19}$ region gives rise to the bright contrast, while the stripe and the band-like

Fig. 4 Dark field images, (a), (b), and (c), obtained from the area shown in Fig. 3(a). The dark field images of (a), (b), and (c) were, respectively, taken by using the $22 \cdot 2_{D0_{19}}$ spot (OA-a in Fig. 3(c)), $012_{B_{19}}$ (OA-b), and a part of the halo ring (OA-c).

region are observed as the dark contrast. The $D0_{19}$ matrix is then understood to be divided into small regions by the appearance of the band-like region. As for the B_{19} region, the stripes along the $[11 \cdot 0]_{D0_{19}}$ direction are clearly seen as a bright contrast in Fig. 4(b). There is no essential difference in the B_{19} stripe between the samples aged for 0 and 15 min. In addition to these images, the halo dark field image exhibits the bright contrast in the band-like region. It should be stressed that the region gives rise to the dark contrast in Figs. 4(a) and (b). These clearly imply that the amorphous state appears in the band-like region. The lamellar structure in the sample aged for 15 min is there-

Fig. 5 Bright field image taken from the sample aged at 1273 K for 30 min. The electron incidence is parallel to the $[11 \cdot 0]_{D0_{19}}$ direction.

fore understood to be composed of the $D0_{19}$ and amorphous regions. Eventually, the appearance of the amorphous state is a characteristic feature in the initial stage of the phase separation in the hypo-eutectoid Ti-37 at% Al alloy, just like the eutectoid Ti-40 at% Al alloy.

The $\alpha_2 + \gamma$ lamellar structure is formed in the hypo-eutectoid Ti-37 at% Al alloy. A bright field image obtained from the sample aged for 30 min is shown in Fig. 5. The electron incidence is parallel to the $[11 \cdot 0]_{D0_{19}}$ direction. The lamellar structure is clearly observed in the image, as is denoted by L1, and a width of one stripe in the lamellar structure was determined to be about 50 nm. We then took an electron diffraction pattern of the lamellar structure in Fig. 5, although we do not show the pattern here. The pattern indicated that the lamellar structure is composed of the $D0_{19}$ and $L1_0$ structures, instead of the $D0_{19}$ and amorphous ones. In other words, the $\alpha_2 + \gamma$ lamellar structure is formed by the crystallization of the amorphous state to the $L1_0$ structure. In the image, an area denoted by L2 also exists between the areas labeled by L1. Although a faint lamellar structure could be detected in the area, a corresponding electron diffraction pattern never exhibited a simple array of diffraction spots, which are expected from some single crystals with severe lattice distortion. That is, the crystal lattice in the L2 area is severely distorted. In spite of the severe distortion, we could confirm that there is no region with the B_{19} structure in the area. Therefore the formation of the lamellar structure is characterized by the annihilation of the B_{19} structure as well as the crystallization of the amorphous state. Features of the $\alpha_2 + \gamma$ lamellar structure in Fig. 5 are entirely the same as those in the eutectoid Ti-40 at% Al alloy.

IV. Discussion

The present experimental data show that the $\alpha \rightarrow \alpha_2 + \gamma$ phase separation in the Ti-37 at% Al alloy is character-

ized by the formation of the $\alpha_2 + \gamma$ lamellar structure and proceeds via the appearance of the amorphous state as the intermediate state. On the basis of these experimental data, we can propose a scenario of the lamellar-structure formation in the hypo-eutectoid alloy. We first focus on the fact that there exist both the $D0_{19}$ matrix and the B_{19} stripes in the sample before aging at 1273 K. This obviously implies that even in the sample quenched from 1473 K the hcp $\rightarrow D0_{19}$ ordering takes place, together with the structural change from hcp structure to the B_{19} one. When the sample is aged at 1273 K, the band-like region with the amorphous state is nucleated at the $B_{19}/D0_{19}$ boundary and grows at the expense of the $D0_{19}$ matrix, as is shown in Fig. 3(a). As a result of the growth of the amorphous region, the lamellar structure composed of the amorphous and $D0_{19}$ regions appears as the intermediate state. Both the crystallization of the amorphous state to the $L1_0$ structure and the annihilation of the B_{19} stripe then result in the $\alpha_2 + \gamma$ lamellar structure as the equilibrium state. Eventually, this scenario is basically consistent with that proposed for the formation of the $\alpha_2 + \gamma$ lamellar structure in the eutectoid Ti-40 at%Al alloy⁽⁶⁾⁽⁷⁾.

It is made clear that the process of the lamellar-structure formation in the hypo-eutectoid alloy is quite different from that in the hyper-eutectoid alloy. This should be due to the crystal structure of the matrix during the precipitation of the γ phase. In the hypo-eutectoid alloy, the matrix has the $D0_{19}$ ordered structure. The precipitation of the γ phase must then take place in the ordered matrix. As is known, it is much difficult for atoms to diffuse in the ordered lattice rather than in a disordered one. Therefore, the appearance of the amorphous state as the intermediate state is understood to be an effort of the alloy to the precipitation of the γ phase with the Al concentration of about 50 at%Al. On the other hand, the γ phase in the hyper-eutectoid alloy precipitates in the disordered lattice with the hcp structure. Because the diffusion takes place easily in the disordered lattice, it is obvious that the amorphous state is not needed for the precipitation of the γ phase in the hcp structure.

In conclusion, the formation of the $\alpha_2 + \gamma$ lamellar

structure in the hypo-eutectoid Ti-37 at%Al alloy was found to be formed in the equilibrium state. The sequence of the formation is characterized by the appearance of the amorphous state, just as in the case of the eutectoid Ti-40 at%Al alloy. The simple discussion suggests that the intermediate amorphous state is the effort of the alloy for the precipitation of the γ phase with the $L1_0$ structure in the matrix with the $D0_{19}$ ordered structure.

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