Nanometer-Size Polycrystallization in bcc \rightarrow hcp + C15 Structural Change of a Ti–30 mol% Cr Alloy

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The crystallographic features of a bcc \rightarrow hcp + C15 structural change in a Ti–30 mol% Cr alloy have been examined by transmission electron microscopy. When the alloy was annealed at 873 K below the eutectoid temperature, the structural change occurred in the following five steps: bcc \rightarrow bcc + Zone I \rightarrow bcc + Zone II \rightarrow bcc + Zone II + hcp \rightarrow bcc + hcp + C15 \rightarrow hcp + C15. The interesting features of the change are that the diffuse \omega state is present in the metastable bcc matrix, and that in the fourth step the C15 grains with a size of about 2 nm appear in the bcc matrix around the hcp region. As a result of these extremely small C15 grains, the final microstructure, which was obtained from the 5-h-and 100-h-annealed samples, consists of the hcp and C15 grains with an average size of about 100 nm. On the basis of these results, the physical origin of the nm-size polycrystallization in the appearance of the C15 phase is discussed in relation to both the presence of diffuse \omega state in the metastable bcc matrix and the formation of the complex coordinated polyhedra in the C15 structure.

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1. Introduction

A phenomenon referred to as "inverse melting" was reported in Ti–(30–40) mol% Cr alloys by Blatter and von Allmen.$^{1-7}$ According to their studies, an amorphous state was found by annealing metastable bcc Ti–Cr alloys at 873 K, below the eutectoid temperature of about 940 K, which had been prepared by the laser quenching technique. They also showed that the amorphous state was converted into the high-temperature bcc phase by subsequent annealing at 1073 K above the eutectoid temperature. The crystal-to-amorphous change seems to be a reversible process.$^8$ A several works have been carried out since then to confirm the occurrence of inverse melting. The presence of the phenomenon was confirmed in metastable bcc Ti–Cr alloys prepared by mechanical alloying.$^9,10$ In bulk-quenched sample, on the other hand, the appearance of the amorphous state on annealing has not been established, although the structural change in bulk-quenched samples of the Ti–40 mol% Cr alloy have mainly been examined so far.$^{11-13}$ It is therefore left open whether inverse melting can be observed by bulk-quenching and annealing.

According to the reported phase diagram,$^{14}$ the Ti–12 mol% Cr alloy undergoes the eutectoid reaction from \beta–Ti to \alpha–Ti + \alpha–TiC$\gamma$ around 940 K. Crystal structures of the \beta–Ti, \alpha–Ti, and \alpha–TiC$\gamma$ phases were, respectively, reported to be the bcc, hcp, and C15 structures. It is worth noting that the C15 structure is characterized by an array of the complex coordinated polyhedra, the CN12 and CN16, which can be regarded as atomic clusters.$^{15}$ In addition to these equilibrium phases, the amorphous state was predicted as a metastable state of 55 mol% Cr by CALPHAD.$^9$ Inverse melting should be associated with the appearance of this amorphous state. To shed some more light on the presence of inverse melting in bulk-quenched samples, we have investigated the appearance of the metastable amorphous state during the bcc \rightarrow hcp + C15 structural change related to the eutectoid reaction. Concretely, a bulk-quenched Ti–30 mol% Cr alloy of the metastable bcc phase was annealed at 873 K, which is about 67 K lower than the eutectoid temperature. Features of the crystal structure and the microstructure were examined at various annealing times by transmission electron microscopy. This paper describes in detail the experimentally obtained data concerning the crystallographic features of the structural change in the Ti–30 mol% Cr alloy. The reason for using of the Ti–30 mol% Cr alloy is that, in the composition range where the inverse melting has been reported, the metastable bcc single phase is easily obtainable at room temperature with this alloy.

2. Experimental Procedure

A Ti–30 mol% Cr alloy ingot was made from Ti (purity: 99.5%) and Cr (99.6%) by the arc-melting technique in an Ar atmosphere. After the ingot was kept at 1523 K for 24 h for homogenization, it was cut into six sample pieces about 1 \times 10 \times 10 mm$^3$ in size. In order to induce the bcc \rightarrow hcp + C15 structural change, these pieces were, respectively, annealed at 873 K for 1, 3.5, 5 and 100 h as well as 0 and 3 min, followed by quenching in ice water. Observation of the samples was carried out at room temperature, by using H-8100 and JEM-3010 transmission electron microscopes with accelerating voltages of 200 and 300 kV, respectively. The crystallographic features of the sample at each annealing time were examined by taking electron diffraction patterns, and bright and dark field images. Specimens for observation were prepared by the Ar-ion thinning technique.

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3. Experimental Result

Changes in the crystallographic features during the bcc $\rightarrow$ hcp + C15 structural change were examined by transmission electron microscopy. It was found that two types of zone formation, denoted here as Zones I and II, occurred in the initial stage of the structural change, and that C15 regions with a grain size of about 2 nm appeared just after the annihilation of Zone II. In addition, the final microstructure was found to consist of equilibrium hcp and C15 grains with an average size of about 100 nm. The details of the experimental data will be described here.

A bright field image of the as-quenched sample is shown in Fig. 1, together with two corresponding electron diffraction patterns. A difference between these two patterns is just the exposure time. That is, the exposure time of about 60 s for the pattern in Fig. 1(c) is much longer than 4 s for the pattern in Fig. 1(b). The electron incidence in the image and the patterns is parallel to the $[001]_{\text{bcc}}$ direction. Note that the subscript bcc denotes the bcc structure. No conspicuous contrast is detected in the image in Fig. 1(a), corresponding to the bcc diffraction pattern in Fig. 1(b). In the pattern with the long exposure time in Fig. 1(c), on the other hand, diffuse scattering characterized by a ring shape is observed with fourfold symmetry. A width of the ring-shaped diffuse scattering was estimated to be an inverse of about 2 nm. The ring-shape scattering was already reported to be due to the diffuse $\omega$ state.\(^{16,17}\)

Figures 2(a), (b), and (c) are, respectively, a bright field image and two corresponding electron diffraction patterns of the sample annealed for 3 min. The pattern in Fig. 2(c) is an enlarged pattern around the 020 spot in Fig. 2(b). The electron incidence is parallel to the $[001]_{\text{bcc}}$ direction. There exists diffuse scattering elongated along the $[010]_{\text{bcc}}$ direction around the bcc diffraction spot, as indicated by the arrow in Fig. 2(c). The ring-shape diffuse scattering due to the diffuse $\omega$ state can be detected in the pattern, although it is hard to reproduce the $\omega$ diffuse scattering because of its very weak intensity. Note that diffuse scattering elongated along the $[010]_{\text{bcc}}$ direction is obviously distinct from the $\omega$ scattering with the ring shape, which is clearly seen in Fig. 1(c). In the image of the 3-min-annealed sample in Fig. 2(a), further line contrasts along one of the $(100)_{\text{bcc}}$ directions are observed. It is easily understood that the elongated diffuse scattering is directly related to the line contrasts in the image. One feature of the line contrast is that some are observed as dark-bright-dark contrasts, as indicated by the arrows. That is, the contrast originates from a strain field produced by the zone formation. This indicates that a zone like the G.P. zone in Cu–Al alloys is formed in the initial stage of annealing.\(^{18}\) That zone is referred to as Zone I here.

Microstructures of the sample annealed for 1 h were found to be divided into two groups, major and minor ones. A bright field image in the major group is first shown in Fig. 3(a), together with a corresponding electron diffraction pattern in Fig. 3(b). The electron incidence in the image and the pattern is parallel to the $[001]_{\text{bcc}}$ direction. Plate-like regions with about 500 nm in length and about 15 nm in width are observed in the image. These regions are referred to as Zone II.

Fig. 1 (a) Bright field image taken from the as-quenched sample, together with two corresponding $[001]_{\text{bcc}}$ electron diffraction pattern in (b) and (c). In order to clearly see diffuse scattering, the pattern in (c) was taken with the exposure time of about 60 s.

Fig. 2 (a) Bright field image and (b) corresponding $[001]_{\text{bcc}}$ electron diffraction pattern of the sample annealed for 3 min. An enlarged pattern in the vicinity of the 020 diffraction spot is also shown in (c).
Fig. 3 (a) Bright field image obtained from the sample annealed for 1 h, together with a corresponding [001]_{bcc} electron diffraction pattern in (b).

Fig. 4 (a) Bright field image indicating the analyzed area containing Zone II, and (b) the determined Ti composition at each numbering location in the image. The electron incidence is parallel to the [001]_{bcc} direction.

Fig. 5 (a) Bright field image and (b) corresponding electron diffraction pattern taken from the sample annealed for 1 h. The image was obtained from an area different from that in Fig. 3(a). The electron incidence is inclined by about 5 degree from the [001]_{bcc} incidence along the [110]_{bcc} direction.

Features of Zone II are that the major direction of Zone II is parallel to the [100]_{bcc} direction, and that fine vertical stripes along the [010]_{bcc} direction can be observed, as indicated by the arrow. In the pattern, on the other hand, there exist diffraction spots with weak intensities and streaks, in addition to the spots due to the bcc structure. Zone II has its own crystal structure, unlike Zone I. The simple analysis of diffraction patterns with various electron incidences showed that the crystal system is orthorhombic. An important feature is that streaks run along the [010]_{bcc} direction through the 0 k/2 0-type position. In addition, we determined a chemical composition of Zone II by an EDX measurement. Figure 4 shows chemical compositions at three locations denoted by 1, 2, and 3 in a corresponding bright field image. In the image, Zone II drawn a black region is present in the middle of the bcc matrix by a gray region. From the determined compositions in Fig. 4(b), Zone II is understood to have 76.3 mol%Ti while the composition of the bcc matrix is still about 70 mol%Ti. The composition of Ti : Cr = 3 : 1 in Zone II is obviously one of the crucial feature to construct its structural model.

Figure 5 shows a bright field image and a corresponding electron diffraction pattern in the minor group for the 1-h-annealed sample. The image was taken by rotating the specimen about the [110]_{bcc} direction from the [001]_{bcc} incidence by about 5 degrees. As is seen in the image, a region with the hcp structure is observed at the middle of Zone II about 50 nm in size, as indicated by the arrow. We actually see diffraction spots due to the hcp structure as well as the bcc and Zone II spots in the pattern. That is, the difference
between these two microstructures in the 1-h-annealed sample is only the appearance of the hcp region. This implies that the hcp region is nucleated after the formation of Zone II. Zone II plays the role of a nucleation site for the hcp phase.

Bright and dark field images and a corresponding electron diffraction pattern from the sample annealed for 3.5h are shown in Fig. 6. The electron incidence in the images and the pattern is inclined by about 10 degrees from the [001]_bcc incidence along the [110]_bcc direction. There are the bcc and hcp diffraction spots, diffuse ω scattering, and partial Debye rings due to the C15 structure in the pattern. No Zone II spot can be detected. The most important feature is that the intensity distribution of the partial 311 Debye ring due to the C15 structure is very similar to that of the diffuse ω scattering, as indicated by the large arrow. In fact, the partial 311 ring is obtained with fourfold symmetry like the ω diffuse scattering. This clearly suggests that the appearance of the C15 phase is strongly influenced by the presence of the diffuse ω state. From other diffraction patterns, further the orientation relationship between the bcc and hcp structures in the 3.5-h-annealed sample was found to be the Burger’s relation of (101)_bcc || (00 · -1)_hcp and [111]_bcc || [12 · 0]_hcp, where the subscript hcp denotes the hcp structure. In the bright field image in Fig. 6(b), on the other hand, we see a complex contrast. It is hard to understand the details of the microstructure on the basis of the bright field image. We then took dark field images by using the bcc and hcp spots, and a part of the partial C15 ring, respectively. Figure 6(c) is an example of the dark field images taken by a part of the 311 Debye ring of the C15 structure, which is indicated by the open square in Fig. 6(a). An enlarged image of the area surrounded by black lines in Fig. 6(c) is also shown in Fig. 6(d). From the dark field images obtained, the hcp and C15 regions were understood to be observed as the bright-contrast and less-contrast regions in the bright field image in Fig. 6(b), respectively. Particularly, the C15 region is clearly observed as a bright dot in Fig. 6(d). Features of the C15 region are that its size was estimated to be just about 2 nm, and that the overlapping of such regions forms relatively large areas, as indicated by the arrows. Note that a size of the hcp region was, on the other hand, found to have a size of about 50 nm, which is the same as that in the 1-h-annealed sample.

Figure 7 shows a bright field image and a corresponding electron diffraction pattern taken from the sample annealed for 5h. The diffraction pattern in Fig. 7(a) is found to consist of partial Debye rings due to only the equilibrium hcp and C15 phases. An interesting feature is that the hcp spots in the 3.5-h-annealing are changed into the partial Debye rings in the 5-h-annealing. The sharpness of the rings indicated that the C15 grains became larger, compared with those of the 3.5-h-annealed sample. Another important feature of the pattern is that the partial Debye rings due to both the hcp and C15 structures exhibit rough fourfold symmetry. This indicates that there is some texture in the microstructure of the 5-h-annealed sample. As for the microstructure, the C15 grains are obtained as a less-contrast region in the image, as indicated by the letter A. An average size of the C15 grain was determined to be about 100 nm, which is much larger than about 2 nm in the 3.5-h-annealed sample. The hcp grain also has the size of about 100 nm in an average. In addition, the

Fig. 6  (a) Electron diffraction pattern, (b) bright field image, and (c) dark field image of the sample annealed for 3.5h. The electron incidence is inclined by about 10 degree from the [001]_bcc incidence along the [110]_bcc direction. The dark field image in (c) was taken by using a part of the 311 Debye ring due to the C15 phase, which is indicated by the open square in (a). An enlarged image of the area indicated by the black square in (c) is shown in (d).
boundary between the C15 and hcp grains is very obscure. Anyhow, it is understood that the grain growth of the C15 grain takes place in the later stage, together with both the annihilation of the bcc phase and polycrystallization of the hcp phase. A similar microstructure was found in the sample annealed for 100 h. It should be concluded that the polycrystalline microstructure shown in Fig. 7(b) is the microstructure of the equilibrium state in this structural change.

4. Discussion

The present experimental data showed that the sequence of the bcc → hcp + C15 structural change in the Ti–30 mol%Cr alloy involves five steps: bcc → bcc + Zone I → bcc + Zone II → bcc + Zone II + hcp → bcc + hcp + C15 → hcp + C15. It should be remarked that the appearance of a platelet precipitate like Zone II had been reported in previous works.15,20 The interesting features of this structural change, which are described in this paper, are that Zone II plays the role of a nucleation site for the hcp phase and that the appearance of the C15 phase results in polycrystallization. In other words, we could not find any amorphous state in this work that should be related to inverse melting. The result obviously rules out the possibility that inverse melting can be obtained in bulk-quenched sample. It was also found that polycrystallization is characterized by the appearance of the C15 grains with the average size of about 2 nm and can thus be referred to as nm-size polycrystallization. Therefore, the following discussion concerns the origin of the nm-size polycrystallization induced by the appearance of the C15 phase.

As was mentioned earlier, the C15 structure is characterized by an array of the CN12 and CN16 polyhedra as atomic clusters. The formation of the C15 phase thus requires that of these polyhedra. This poses the question of how these polyhedra are formed in a Ti–Cr alloy. In this discussion, it is first assumed that the development of the polyhedra needs some extent destruction of the bcc matrix. When asking where the destruction occurs in the bcc matrix, we paid attention to the following experimental results; that is, the presence of the diffuse ω state in the bcc matrix and the similarity between the intensity distributions of the partial 311 Debye ring due to the nucleated C15 regions and the ω diffuse scattering. Both the distributions exhibit fourfold symmetry. In addition, since the width of the ω diffuse scattering is an inverse of about 2 nm, a coherent length of the diffuse ω state is understood to be about 2 nm. This length is identical to the size of the C15 grain just after it appears. Based on these results, it is suggested that polyhedra must be formed in the diffuse ω region. As a matter of fact, a large number of atomic vacancies are expected in the diffuse ω region. The fluctuation in the coordinate number, which is induced by the presence of many vacancies, should result in some extent destruction of the lattice. In other words, the diffuse ω region can play the role of a nucleation site of the C15 phase. It is therefore understood that the nm-size polycrystallization induced by the appearance of the C15 phase would be caused by the presence of the diffuse ω state in the metastable bcc matrix, not by the metastable amorphous state around 55 mol%Cr. It seems to us that the phenomenon reported as inverse melting in bulk-quenched samples is not inverse melting itself but the nm-size polycrystallization occurring in the appearance of the C15 phase.

We finally construct the structural model of Zone II on the basis of the present experimental data. There are two important data, which were taken into account for the model. One is that the streaks are present along the [010]bcc direction through the 0 k/2 0-type position. The other is the chemical composition of Ti : Cr = 3 : 1 in Zone II. The model of Zone II, which was obtained based on these two features, is schematically depicted in Fig. 8. As is seen in Fig. 8, the structure is identified as a chemical modulated structure involving a lot of antiphase boundaries with phase shifts of π/4 and π/2. The modulated structure has the periodicity of 4 × d_{020} and consists of three Ti layers and one Cr layer, where d_{020} is the interplanar spacing of the modified (020) plane in Zone II. However, a physical origin of the formation of Zone II is still open and should be a feature task.19

5. Conclusion

From the present experimental data, the bcc → hcp + C15 structural change in the Ti–30 mol%Cr alloy is characterized by the following five steps: bcc → bcc + Zone I → bcc + Zone II → bcc + Zone II + hcp → bcc + hcp + C15 → hcp + C15. One interesting feature in this change is that in the fourth step the C15 grains about 2 nm in size are formed in the bcc matrix in the vicinity of the hcp region. In this work, this development of the C15 phase is called the nm-size polycrystallization, which is directly related to the formation of the
polyhedra involved in the C15 structure. Because the polyhedra were suggested to be first formed in the diffuse ω region in the metastable bcc phase, the nm-size polycrystallization was understood to be directly caused by the presence of the diffuse ω state. It was also pointed out that the phenomenon reported as inverse melting in bulk-quenched samples must be associated with the nm-size polycrystallization in the appearance of the C15 phase.

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