New Chemical Layered Structure in Ti–Cr Alloys

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The new chemical layered structure, referred to as a chemical stripe structure, was found as a metastable state in the (bcc → hcp + C15) metastable phase separation in the Ti–Cr alloys. Note that a metastable separation is here defined as a separation characterized by a positive value of the second derivative of Gibbs free energy with respect to chemical composition. The experimental data showed that the layered structure had periodicity of $4 \times d_{002}$, about 0.72 nm, and chemical ordering of Ti : Cr = 3 : 1, and that a lot of antiphase boundaries with phase shifts of $\pi/2$ and $\pi$ were involved in the structure. The coherent length of the layered structure was estimated to be about 15 nm along the modulated direction. In addition to these features, it was found that the layered structure was formed from the local bct state as another metastable state, not directly from the zone structure consisting of one Cr layer. On the basis of these data, the physical origin of the formation of the chemical layered structure is also discussed.

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1. Introduction

It is known that chemical phase separation occurs when an alloy of a single phase is kept into a two-phase region in a phase diagram. Recent electronic phase separation characterized by the spatial separation of electrons or holes has also been suggested in highly correlated electronic systems.1,2) In the case of chemical phase separation, its behavior is classified into two groups on the basis of a sign of the second derivative of Gibbs free energy with respect to chemical composition. One is an unstable separation for a negative sign; that is, spinodal decomposition, in which a chemical modulated structure is initially formed. The other separation for a positive sign is a metastable separation characterized by the nucleation and growth mechanism. In the metastable separation in Ti–Cr alloys, we found a new layered structure (LS), which consists of three Ti and one Cr layers.3) It should be remarked that in our previous work the LS in the Ti–Cr alloys was referred to as Zone II. However, the LS state was observed as a plate-like precipitate with about 15 nm in width and about 300 nm in length, as will be clearly shown later. That is, the LS has a coherent length of about 15 nm along the modulated direction, which is much longer than that of a zone structure. It is then understood that the LS state in the Ti–Cr alloys is one of metastable states, not a zone structure. Another notable thing is that the LS has some similarity to electronic stripe structures, which appear when electronic phase separation is suppressed by the Coulomb interaction. In the case of the La-cuprates, the electronic stripe structure is characterized by a four-layer structure, in which one of the four layers is occupied by holes, instead of solute atoms in chemical LS’s.4,5) Based on this similarity, we thus refer to a chemical LS in the metastable separation as a chemical stripe structure (CSS). The details of the CSS state in the Ti–Cr alloy will be described below.

A Ti–12 mol%Cr alloy undergoes the eutectoid reaction from the $\beta$-Ti phase to the $\alpha$-Ti and $\alpha$-TiCr2 phases around 940 K, which have the bcc, hcp, and C15 structures, respectively.6) We have so far investigated the crystallographic features of the related bcc → hcp + C15 phase separation in a Ti–30 mol%Cr alloy by transmission electron microscopy. In our previous work, the metastable separation was reported to consist of the five steps, bcc → bcc + Zone → bcc + CSS → bcc + CSS + hcp → bcc + hcp + C15 → hcp + C15.3) In this sequence, Zone I and Zone II in the previous paper are, respectively, replaced by Zone and CSS on the basis of the reason mentioned above. One of noteworthy features in the separation is that the CSS state characterized by the chemical LS is formed as a plate-like precipitate with about 15 nm in width and about 300 nm in length. The CSS state was also found to act as a nucleation site for the hcp phase. In other words, the CSS state is not a transitional state to the equilibrium C15 phase, but just a metastable state appearing after the annihilation of Zone. It can then be said that the presence of the CSS state is a unique feature in the metastable separation of the Ti–Cr alloys. It should be remarked that a preliminary transmission-electron-microscopy examination of the plate-like precipitate was already made for a Ti–40 mol%Cr alloy by Sinkler and Luzzi.7) They pointed out that the precipitate has a body-centered tetragonal structure involving chemical ordering with periodicity of $4 \times d_{002}$, where $d_{002}$ is the interplanar spacing of the (002) plane.

In order to establish the CSS state, we have reexamined the detailed features of both Zone and the CSS state in a Ti–30 mol%Cr alloy by transmission electron microscopy, mainly by taking high resolution electron micrographs and determining its chemical composition. The Ti–30 mol%Cr alloy, not the Ti–40 mol%Cr alloy, was used because it allowed each step in the phase separation to be observed independently. Such observation is possible because the progress of the phase separation in the former alloy is relatively slow, compared with that of the latter. In this paper, we describe the crystallographic features of Zone and the CSS state in the Ti–30 mol%Cr alloy, which have been obtained in the present

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work. A physical origin of the CSS state is also discussed, together with a proposal of a modulation model of the CSS state.

2. Experimental Procedure

Samples of the Ti–30 mol% Cr alloy were prepared according to the procedure described in our previous paper.\(^5\) In order to obtain Zone and the CSS state, as-quenched samples of a metastable bcc phase were aged at 873 K for 3 min, 10 min, 1 h, and 3.5 h in vacuum, followed by quenching into ice water. Observation of the samples was made at room temperature by using H-8100, H-9000UHR, and JEM-3010 transmission electron microscopes operating at accelerating voltages of 200, 300, and 300 kV, respectively. The crystallographic features of the samples were examined by taking high resolution electron micrographs as well as electron diffraction patterns, and bright and dark field images. A local chemical analysis of the samples was also performed by the HF-2000 transmission electron microscope equipped with an energy-dispersive X-ray (EDX) spectroscope (Kevex Sigma). An EDX analysis was carried out with an electron probe about 2 nm in diameter. Specimens for observation were prepared by an Ar-ion thinning technique.

3. Experimental Results

As found in our previous work, Zone and the CSS state were formed in the initial stage of the bcc $\rightarrow$ hcp + C15 metastable phase separation. A bright field image taken from the sample aged at 873 K for 3 min is first shown in Fig. 1, together with a corresponding electron diffraction pattern. The inset in Fig. 1(a) shows the enlarged pattern around the 002 reflection. The electron incidence is parallel to the [100] direction. As can be clearly seen in the inset, diffuse scattering extends in the (001) directions around diffraction spots due to the metastable bcc phase. This diffuse scattering is obviously indicative of the presence of the coherent precipitate, which is referred to as Zone here. In the bright field image in Fig. 1(b), a sharp line contrast showing the coherent precipitate can be observed with strain contrast surrounding it, as indicated by the arrows. From these features, Zone is basically characterized as a one-layer Cr zone in the Ti matrix, just like the G.P. I. zone in Cu–Al alloys.\(^8\)–\(^12\)

In addition to Zone and the CSS state, a new metastable state between them was found in the present work. Figure 2 shows a bright field image and a high resolution electron micrograph of a 10 min-aged sample, together with a corresponding electron diffraction pattern with the incidence in the [100] direction. An intensity maximum can be detected in the pattern, as indicated in the inset, in addition to the bcc fundamental spots. That is, the diffuse scattering in Fig. 1(a) produces the intensity maximum in the 10-min aging. Corresponding to the presence of the intensity maximum in the pattern, local regions elongated along the [010] direction are observed with an arc-shaped contrast in the bright field image in Fig. 2(b). The arc-shaped contrast is due to a strain field induced by the appearance of the local region. An average size of the local region was determined to be about 5 nm in width and about 100 nm in length. In order to understand the crystallographic features of these local regions, we took high resolution electron micrographs, an example of which is shown in Fig. 2(c). Lattice fringes with a spacing of about 0.18 nm are seen in the center part of the micrograph. It is obvious that the spacing is identical to that derived from the location of the intensity maximum in the pattern. This indicates that these local regions with a lattice spacing of about 0.18 nm were formed by 10-min aging. The local regions had a bct symmetry with an axial ratio of $c/b = 1.12$ and are referred to as the local bct state. Aging after the appearance of Zone therefore resulted in the formation of the local bct state with $c/b = 1.12$.

Aging for 1 h and 3.5 h produced the CSS state with periodicity of $4 \times d_{002}$. Figure 3 shows three electron diffraction patterns as well as a corresponding bright field image, which were taken from a sample aged for 1 h. The electron incidences of the patterns in Figs. 3(a), (b), and (c) are parallel to the [100], [101], and [110] directions, respectively. The image in Fig. 3(d) was obtained in the [100] incidence. In addition to the bcc spots, there exist new diffraction spots with relatively weak intensities and streaks along the [010] direction in the patterns, as indicated by the arrows A, B, and C. Particularly the location of the spot A is identical to that of the intensity maximum in Fig. 2(a). These new spots and streaks are indicative of the CSS state. In the bright field image in Fig. 3(d), on the other hand, the CSS state is seen as a plate-like precipitate about 300 nm in length and about 15 nm in width, as was reported previously. Fine vertical stripes are also seen in the interior of the precipitate. A simple analysis of the
patterns obtained from the precipitate indicates that there is no extinction rule for the new spots, and that the streaks run along the [010] direction through the 001 1/2-type positions. Because the spot C is slightly shifted toward the [110] direction and is not on the line connecting the 220 and 222 bcc spots, the crystal system of the CSS state is understood to be orthorhombic with c/b = 1.12 and b/a = 1.01. Note that the value of c/b is the same as that of the local bct state.

One of high resolution electron micrographs taken from the CSS state in the sample aged for 3.5 h is shown in Fig. 4, together with a corresponding [001] electron diffraction pattern in the inset. The plate-like precipitate denoted by the letter B is located between the bcc regions by A in the micrograph. In the bcc regions, we can see the (011)bcc and (011)bcc lattice fringes with a spacing of about 0.21 nm. On the other hand, there are some lattice fringes as well as the [011] fringes in the CSS state. One notable feature is that in the CSS state we can detect fringes with a spacing of d_{001}, as indicated by two parallel white lines, where d_{001} represents the (001) lattice spacing of about 0.36 nm. Vertical dark lines along the [010] direction are also arranged irregularly, as marked by the arrows α and β. Another important feature is that the [011] fringes in the CSS state are coherently connected with those in the surrounding bcc regions, as seen in the inset.

In order to understand the details of the crystallographic features of the CSS state, we produced a diffraction pattern from the obtained micrograph in Fig. 4 and reproduced an image for each diffraction spot and streak in the pattern by computer calculation. The calculated diffraction pattern produced from the area indicated by the black square in Fig. 4 is shown in Fig. 5(a). The images in Fig. 5(b), (c), and (d) were, respectively, reproduced by using the 001 and 010 spots, and the streak through the 0 0 1/2 position in Fig. 5(a). In the pattern, the very strong streaks running along the [010] direction through the 001 1/2-type position are well reproduced, in addition to the 001, 011, 01, 011, and 011 spots. It is hard to detect the 010 and 010 spots because of their weak intensities. As for the reproduced images, further coherent fringes with a spacing of 0.36 nm are seen over the whole area in the 001-spot image in Fig. 5(b). On the other hand, only the local regions with a size of 3 nm are reproduced in the 010-spot image in Fig. 5(c). This indicates that the 010 diffraction spot basically originated from an additional atomic displacement. For that reason, we did not take into account the 010 and 010 spots in constructing the LS model for the CSS state. The most interesting features to be noted here are that the image for the strong streak in Fig. 5(d) shows black and zigzag stripes with a spacing of 2 × d_{001}, and that there exist a lot of antiphase boundaries, as indicated by the arrow. The zigzag stripes then come from the presence of antiphase boundaries. Careful analysis indicated that there are two kinds of antiphase boundaries with phase shifts of π/2 and π. Based on these features, the CSS state could be identified as a LS with periodicity of 4 × d_{002} and containing a lot of antiphase boundaries, where d_{002} is the (002) lattice spacing of about 0.18 nm.

In order to determine the chemical composition of the CSS state, an EDX measurement was performed for the 3.5-h-aged sample in an area containing the plate-like precipitate. Figures 6(a) and (b) are, respectively, a bright field image showing the area analyzed in the present work and the Ti composition at the location 5 which represents that of the precipitate. The precipitate is located at the center of the image. Note that the locations 1–4 and 6–9 are in the bcc area and that the composition at the location 5 represents that of the precipitate. From the lower diagram, the Ti composition at the location 5 is found to be about 76 mol%, while the bcc area basically has the initial composition of about 70 mol%, except for the location 6 near the CSS state. The composition of about 76 mol%Ti indicates that chemical ordering of Ti : Cr = 3 : 1 characterizes the CSS state in the phase separation of the Ti–30 mol%Cr alloy.
4. Discussion

When being kept at 873 K, the Ti–30 mol%Cr alloy of the bcc single phase exhibited the metastable separation into the (hcp + C15) equilibrium phases. In the separation, the CSS state observed as the plate-like precipitate was formed in the early stage. The precipitate had the average size of about 15 nm in width and about 300 nm in length. The important feature of the separation are that the CSS state is not directly produced from Zone, but that between Zone and the CSS state there is the local bct state with about 5 nm in width and about 100 nm in length. This state must be a clue for the formation of the CSS state. Based on these experimentally obtained data, we first propose the LS model for the CSS state and then discuss the physical origin of its formation.

In constructing the LS model for the CSS state, attention was paid to certain experimental data; specifically, the presence of Zone, periodicity of $4 \times d_{002}$, chemical ordering of Ti : Cr = 3 : 1, and the presence of the antiphase boundaries. In view of the presence of Zone, the CSS state should be a layered structure consisting of the Ti and Cr layers. It is obvious that a four-layered structure with respect to the (002) plane is the most appropriate because of the $4 \times d_{002}$ periodicity. The chemical ordering of Ti : Cr = 3 : 1 indicates that Cr atoms occupy every four (002) layers. The basic layered unit of the CSS state constructed on the basis of these features is a chemical LS with periodicity of about 0.72 nm, as shown in Fig. 7(a). The presence of both the 001-type spot and the streaks through the 0 0 1/2-type positions also indicates that a longitudinal atomic displacement should be involved in the CSS state. Because the Cr atom is smaller in size than the Ti atom, the two Ti layers surrounding the Cr layer move toward the latter, as indicated by the arrows. Furthermore, when the antiphase boundaries with the phase shifts of $\pi/2$ and $\pi$ are taken into account, we can propose one of the possible models for the CSS state, as shown in Fig. 7(b). In addition, the coherent length of the LS can be estimated to be about 15 nm on the basis of the width of the plate-like precipitate.

It is now time to discuss the origin of the formation of the CSS state in the metastable separation. As was mentioned earlier, the CSS state with periodicity of $4 \times d_{002}$ was already found in the Ti–40 mol%Cr alloy. The periodicity of the state is therefore independent of both aging time and chemical composition. In addition, the CSS state has a composition of about 25 mol%Cr, which is smaller than the initial composition of 30 mol%Cr. It is obvious that the composition of 25 mol%Cr corresponds to periodicity of $4 \times d_{002}$. This indicates that the formation of the CSS state is not related to that...
of the equilibrium C15 phase with a composition of about 63 mol% Cr. A systematic change in the diffraction patterns shown in Figs. 1, 2, and 3 suggests that the CSS state is associated with Zone. Because no CSS state has been reported in any alloys, the local bct state should also be crucial for the formation of the CSS state.

Our scenario for the formation of the CSS state is as follows. We start with the situation that each Cr layer dressed by a strain field exists independently, as was seen in Fig. 1. When some Cr layers are newly formed in the vicinity of the layer present originally on aging, strain fields dressing these layers are overlapped one another. The alloy should make an effort for the accommodation of the overlapping strain fields locally. From our experimental data shown in Fig. 2, it is understood that the accommodation leads to the local bct state with $c/b = 1.12$; that is, the longer $c$ axis. This local bct state is thus a unique feature in the metastable separation of the Ti–Cr alloys, as mentioned above. Then, we think what happens in the local bct state with the longer $c$ axis in it. We believe that the bct state produced by the accommodation of the overlapping strain fields forces the rearrangement of the Cr layers along the $c$ axis in it. As a result of the rearrangement, the CSS state with periodicity of $4 \times d_{002}$ is then formed. We are sure that this scenario is one of physical origins for the formation of a chemical LS in a metastable separation. That is, we conclude that the CSS state is produced by an indirect interaction between the Cr layers via a strain field dressing each Cr layer.

5. Conclusion

When a CSS state is defined as a chemical LS in a metastable phase separation, such a state was formed as a plate-like precipitate with about 15 nm in width and about 300 nm in length in the (bcc $\rightarrow$ hcp + C15) separation of the Ti–Cr alloys. The CSS state in the Ti–Cr alloys has periodicity of $4 \times d_{002}$, 0.72 nm, and consists of three Ti and one Cr layers. Because the CSS state is formed from the local bct state with $c/b = 1.12$, we proposed that the CSS state originated from the indirect elastic interaction between the Cr layers via the strain field dressing each Cr layer.
Fig. 5 (a) Electron diffraction pattern of the region surrounded by black lines in Fig. 4, obtained by Fourier transformation. The images in (b), (c), and (d) were respectively reproduced for the 001 and 010 spots, and the streak through the 0 0 1/2 position by computer calculation.

Fig. 6 (a) Bright field image indicating the analyzed area of the 3.5 h-aged sample containing CSS state, and (b) the determined Ti composition at each numbering location in the image (a). The electron incidence is parallel to the [100] direction.

Fig. 7 (a) Schematic diagram of the basic layered unit, and (b) one possible model for the CSS state.
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