The Structure of an Al–Co–Ni Decagonal Quasicrystal in an $\text{Al}_{72}\text{Co}_8\text{Ni}_{20}$ Alloy Studied by Cs-Corrected Scanning Transmission Electron Microscopy

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The structure of an Al–Co–Ni decagonal quasicrystal in an $\text{Al}_{72}\text{Co}_8\text{Ni}_{20}$ alloy has been examined by Cs-corrected high-angle annular detector dark-field (HAADF)- and annular bright-field (ABF)-scanning transmission electron microscopy (STEM) observations with the incident beam parallel to the periodic axis. Observed ABF- and HAADF-STEM images clearly show the existence of large columnar clusters of a decagonal section with an about 3.2 nm in diameter and their arrangement with bond-orientational order (BOO) of a bond-length of 3.2 nm. Individual transition-metal (TM) atoms and mixed sites (MSs) of Al and TM atoms are represented as separated bright dots in observed HAADF-STEM images, and consequently arrangements of TM atoms and MSs on two quasiperiodic planes can be directly determined. The TM atoms and MSs are located at lattice points of a Penrose lattice with an edge-length of 0.25 nm, and so they are arranged with BOO on the two quasiperiodic planes. An atomic arrangement including Al atoms in the 3.2 nm cluster is speculated from observed HAADF- and ABF-STEM images. [doi:10.2320/matertrans.M2012333]

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1. Introduction

Six types of decagonal quasicrystals have been found in Al–Co–Ni alloys,^{1–5} and their structures have been interpreted by quasiperiodic arrangements of columnar atom clusters with bond-orientational order (BOO), which is one of important structural features in quasicrystals. The structures of five types of Al–Ni–Co decagonal quasicrystals except for one referred to as Ni-rich basic structure (hereafter called as Ni-rich decagonal quasicrystal) have been interpreted by BOO arrangements of columnar atom clusters with a decagonal section of 2 nm in diameter.^{6,7} On the other hand, the Ni-rich decagonal quasicrystal and Al–Ni–Fe one, which are known to be ones of highly ordered quasicrystals, were characterized by an arrangement of columnar atom clusters with 3.2 ($= 2 \times \tau$) nm in diameter.^{8,9} However, the recent investigation of the Ni-rich decagonal quasicrystal with Cs-corrected STEM, which has an enough resolution to represent individual TM atoms as separated bright dots in observed images of decagonal quasicrystals, has discussed the structure of only the 2 nm atom cluster, and has never touched on the 3.2 nm cluster.¹⁰ Therefore, in the present paper, we aim to reexamine the structure of the Ni-rich decagonal quasicrystal by full use of Cs-corrected STEM with HAADF and ABF techniques.

Before we started this study, we observed HAADF-STEM and ABF-STEM images of two crystalline phases of W-(AlCoNi)¹¹ and τ^2 - Al_3Co approximants,¹² the structures of which were determined by X-ray diffraction using single crystals,^{12,13} and we examined the correspondence between the observed HAADF-STEM and ABF-STEM images, and those structures. That result shows that arrangements of TM atoms and MSs in the structures can be directly determined from those of separated bright dots in the HAADF-STEM images, and also most of Al atoms in well-symmetric regions can be represented as separated dark dots in the ABF-STEM.

2. Experimental Procedures

An alloy of a nominal composition of $\text{Al}_{72}\text{Co}_8\text{Ni}_{20}$ was prepared by melting high-purity (99.99%) Al, Co and Ni metals in an arc furnace in an Ar atmosphere. A part of the ingot was sealed in an evacuated quartz tube, annealed at 900°C for 14 h and then quenched in water. HAADF- and ABF-STEM images were simultaneously taken with the incident beam parallel to the periodic axis by using of a Cs-corrected scanning electron microscope (JEM-ARM200F). HAADF- and ABF-STEM images were obtained with detectors of 90–370 and 12–24 mrd, respectively.

3. Experimental Result and Discussion

Figure 1 shows an HAADF-STEM image of the Ni-rich decagonal quasicrystal. Bright dots separately observed in the image correspond to TM and mixed sites (MSs) of TM and Al atoms, as will be mentioned later. In addition to clearly visible bright dots, one can recognize that clusters formed by ten bright dots encircling with decagonal symmetry, indicated by circled, are arrayed along lines parallel to the directions with tenfold rotational symmetry, showing a highly ordered decagonal quasicrystal. Also, one can see a variety of contrasts at centers of the clusters, e.g. a pentagonal arrangement of weak bright dots, decagonal arrangement of bright dots and asymmetric distribution of bright dots, indicated by white, blue and red circles, respectively, in Fig. 1. The clusters with a pentagonal arrangement of bright dots, which are rarely observed in this decagonal quasicrystal, are common ones in the other Al–Co–Ni decagonal quasicrystals,^{6,7} whereas the clusters with decagonal and asymmetric arrangements of bright dots are ones appearing in this decagonal quasicrystal.⁸

Figure 2(a) is an ABF-STEM image of the Ni-rich decagonal quasicrystal. In the image, TM and Al atoms are represented as dark dots, but it is not easy to distinguish

between TM and Al atoms from contrast of the dark dots without remarkable different darkness. However, an arrangement of TM atoms can be determined from HAADF-STEM images, as will be mentioned later. In the image of Fig. 2(a), one can see small rings formed by ten dark dots encircling with an interval of about 0.13 nm, and almost all of the ring contrasts are arranged with an interval of about 0.66 nm. By the close examination of an arrangement of the ring contrasts, one can recognize definite large clusters, indicated by circles, formed with ten small rings encircling with tenfold rotational symmetry, and that the large clusters are arranged with BOO in a pentagonal framework of an edge-length of 3.2 nm, as indicated by lines. It should be noticed that there are a variety of contrast distributions at the centers of the clusters, as exemplified by white, red and blue small circles.

Fig. 1 HAADF-STEM image of the Ni-rich decagonal quasicrystal. The clusters formed by ten bright dots encircling with tenfold rotational symmetry are arrayed along straight lines parallel to the directions of tenfold rotational symmetry, indicated by arrows. Also, one can see a variety of contrasts at centers of the clusters, e.g. a pentagonal arrangement of bright dots, decagonal arrangement of weak bright dots and asymmetric distribution of bright dots, indicated by white, blue and red circles, respectively.

Figure 2(b) is an HAADF-STEM image simultaneously taken with Fig. 2(a). From the close examination of the HAADF-STEM image and Fig. 2(a), one can recognize an arrangement of decagonal clusters of 3.2 nm in diameter with an edge-shearing linkage, and all bright dots in the decagonal cluster, except for its central part, are arranged with tenfold rotational symmetry. From the comparison of the central parts of the clusters between Figs. 2(a) and 2(b) images, a dark ring with a central dark dot and a bright spot without a central dot in the ABF-STEM image of Fig. 2(a), exemplified by white and red circles, correspond to ones with pentagonal and decagonal arrangements of bright dots, and ones with asymmetric arrangements of bright dots, respectively, in the HAADF-STEM image of Fig. 2(b).

Figure 3 shows an enlarged image of a part of Fig. 2(b). In Fig. 3(a), one can see clearly a distribution of bright dots on quadruplicate concentric circles with decagonal symmetry, except for the central part, in the 3.2 nm cluster. Also, it should be noted here that brightness of dots on the circle indicated by a dashed line in Fig. 3(a) is relatively weak, compared with the bright dots on the other concentric circles. Those weak bright dots can be considered to correspond to MSs, as will be mentioned later. Most of bright dots in the HAADF-STEM image can be connected by lines with an edge-length of 0.76 nm, as shown in Figs. 3(b) and 3(c). The structure of the Ni-rich decagonal quasicrystal is formed by two quasiperiodic planes of A and B stacking along the periodic axis,⁸⁾ and so the bright dots connected by the solid and dashed lines correspond to TM atoms on the A and B planes, respectively. In Figs. 3(b) and 3(c), one can see double pentagonal distributions of bright dots, which are composed with pairs of bright dots along the directions of fivefold rotational symmetry, in rightward pentagons in Fig. 3(b) and leftward ones in Fig. 3(c), whereas in leftward pentagons in Fig. 3(b) and rightward ones in Fig. 3(c), pentagonal and asymmetric distributions of bright dots are observed. The five dots of most outside of the double pentagonal distribution correspond to TM atoms and MSs on a different plane from the tiling plane, and the inner five dots

Fig. 2 ABF- (a) and HAADF-STEM (b) images of the Ni-rich decagonal quasicrystal. Note large clusters, indicated by circles, formed by ten small rings encircling with tenfold rotational symmetry in (a), and a BOO arrangement of the clusters by an edge-sharing linkage of a decagonal section in a pentagonal framework of an edge-length of 3.2 nm in (b). It should be noticed that there are a variety of contrast distributions at centers of the clusters, as exemplified by white, red and blue small circles in (a) and (b).

Fig. 3 Enlarged images of a part of Fig. 2(b). In (a), one can see that the bright dots on quadruplicate concentric circles except for the central part are arranged with decagonal symmetry in the 3.2 nm cluster, and that brightness of dots on the circle indicated by a dashed line is relatively weak, compared with the bright dots on the other concentric circles. Most of bright dots in the image can be connected by lines with a length of 0.76 nm, as shown in (b) and (c). Note double pentagonal distributions of bright dots, which are composed with pairs of bright dots along the directions of fivefold rotational symmetry, in the rightward pentagons in (b) and leftward ones in (c), exemplified by red pentagons, and pentagonal and asymmetric distributions of bright dots in the leftward pentagons in (b) and rightward ones in (c), exemplified by blue pentagons.

Fig. 4 Arrangements of TM atoms and MSs in pentagonal and rhombic frames with an edge-length of 3.2 nm on the A (a) and B (b) planes, derived from Fig. 3. The TM atoms connected by red lines correspond to bright dots with asymmetric arrangements indicated by a blue circle in Fig. 3(d) and ones connected by solid and dashed red lines in Fig. 5. The tiling indicated by dashed lines is a Penrose lattice with an edge-length of 0.25 nm.

and central dot inside of the double pentagonal distribution correspond to MSs on the tiling plane, as can be seen in Fig. 3(d). The feature can be seen in the structures of the W-(AlCoNi) and τ^2 -Al₃Co approximants.^{12,13)}

Figure 4 shows arrangements of TM atoms and MSs on the A and B planes, derived from the HAADF-STEM image of Fig. 3. All of TM atoms and MSs are located at lattice points of a Penrose lattice with an edge-length of 0.25 nm, and consequently arranged with BOO. The distribution of MSs, which are always located in downward pentagons in Fig. 4(a) and upward ones in Fig. 4(b), can be seen in the B plane of the W-(AlCoNi) approximant.¹³⁾ In the structure model, bright dots of asymmetric arrangements, indicated by a blue circle in Fig. 3(d), are located at corners of pentagons with an edge-length of 0.47 (= 0.76/ τ) nm, as shown by red solid and dashed lines in Fig. 5. It should be noticed that one edge of the pentagons corresponds to a short distance in the pentagonal lattice with an edge-length of 0.76 nm, and the pentagonal lattice with an edge-length of 0.47 nm can be seen on the A plane of the W-(AlCoNi) approximant.¹³⁾ In Fig. 4, the TM atoms corresponding to the bright dots connected by red lines in Fig. 5 are drawn as ones connected by red lines.

In contrast with the TM atoms and MSs exactly located at lattice points of a Penrose lattice with an edge-length of

0.25 nm, Al atoms are considered to shift from the lattice points, from the structures of the crystalline approximants of W-(AlCoNi) and τ^2 -Al₃Co,^{12,13)} and it is difficult to

Fig. 5 An enlarged image of the central area of the pentagonal frame in Fig. 3(a). Note that bright dots with asymmetric arrangements in pentagonal frames are connected by pentagonal tiling with an edge-length of 0.47 nm.

determine exact positions of Al atoms from the ABF-STEM image. However, it is worthwhile to discuss the structure of the 3.2 nm cluster, including an arrangement of Al atoms, from the observed HAADF- and ABF-STEM images. Figure 6 shows observed HAADF- and ABF-STEM images of the 3.2 nm cluster having a central part of approximate decagonal symmetry, and its structure model. The arrangement of TM and MSs in Fig. 6(c) can be directly derived from Fig. 6(a), and the structure of Fig. 6(d) including an arrangement of Al atoms is derived from the ABF-image of Fig. 6(b), assuming that all of Al atoms are located at lattice points in a Penrose lattice with an edge-length of 0.25 nm. As can be seen in Fig. 6(d), the ring contrasts formed with ten bright dots in the ABF-STEM image of Fig. 6(b) correspond to the projection of five MSs and five Al atoms, which are located on different planes, as indicated by circles in Fig. 6(d). All of dark dots in the ABF-STEM image of Fig. 6(b) reproduce TM atoms, MSs and Al atoms. It should be mentioned here that the present structure model of the 3.2 nm cluster is nearly the same as that in a previous paper except for the existence of MSs.⁸⁾

4. Summary

The structure of the Al–Co–Ni decagonal quasicrystal in an Al₇₂Co₈Ni₂₀ alloy has been examined by Cs-corrected

Fig. 6 HAADF (a)- and ABF (b)-STEM images, an arrangement of TM atoms and MSs (c), and a structure model (d) including Al atoms for the 3.2 nm cluster. Note that the ring contrasts formed with ten bright dots in (b) correspond to the projection of five MSs and five Al atoms, which are located on different planes, as indicated by circles in (d). The tiling of dashed lines in (b) and (d) is a Penrose lattice with an edge-length of 0.25 nm.

HAADF- and ABF-STEM. Observed ABF- and HAADF-STEM images taken with the incident beam parallel to the periodic axis clearly show the existence of large columnar clusters with a decagonal section of 3.2 nm in diameter, and their arrangement with bond orientational order (BOO) of a bond-length of 3.2 nm. Individual TM atoms and MSs are separately represented as bright dots in observed HAADF-STEM images, and consequently arrangements of TM atoms and MSs on the two quasiperiodic planes can be determined in pentagonal and rhombic frames with an edge-length of 3.2 nm. The TM atoms and MSs are located at lattice points of a Penrose lattice with an edge-length of 0.25 nm, and consequently the TM atoms and MSs are arranged with BOO on the two quasiperiodic planes. The structure of the 3.2 nm cluster, including an arrangement of Al atoms, is discussed from the observed HAADF- and ABF-STEM images. More detailed and quantitative analysis of the structure should be performed by computer simulation of HAADF- and ABF-STEM images.

Although the structure of the 3.2 nm cluster is nearly the same as that derived from the structure of the W-(AlCoNi) approximant and ordinary HAADF-STEM observations in the previous paper,⁸⁾ more detailed and definite structure can be determined directly from Cs-corrected HAADF- and ABF-STEM observations. Also, the present work shows that the arrangement of TM atoms in a full region including the 3.2 nm clusters and glue regions between the clusters can be expressed as pentagonal tiling with an edge-length of 0.76 nm, and also indicates that all of TM atoms and MSs

are located at lattice points of a Penrose lattice with an edge-length of 0.25 nm. That result shows that the structure of the $\text{Al}_{72}\text{Co}_8\text{Ni}_{20}$ decagonal quasicrystal should be characterized as the tiling of TM atoms and MSs with BOO, and consequently the 3.2 nm clusters are formed at well-symmetric positions of the tiling.

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