The Structure of Type-II Al-Ni-Co Decagonal Quasicrystal Studied by Atomic-Scale Electron Microscopic Observations

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The structure of an Al-Ni-Co decagonal quasicrystal, showing electron diffraction patterns called “type-II”, in an $\text{Al}_{71.5}\text{Ni}_{12.5}\text{Co}_{16}$ alloy, has been examined by high-angle annular detector dark-field scanning transmission electron microscopy and high-resolution transmission electron microscopy. Its structure has a columnar cluster of atoms with a decagonal section of about 2 nm in diameter as a structural unit, and forms a heterogeneously aperiodic tiling of pentagonal and rhombic tiles in a two-dimensional arrangement of the columnar clusters. Translational arrangements of pentagons and rhombuses in the tiling can be observed locally. Also, the characteristic of a NaCl-type ordered arrangement of two kinds of columnar clusters of atoms, which have different orientations of pentagonal symmetry, is observed in the tiling.

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1. Introduction

A stable Al-Ni-Co decagonal phase has a wide composition range, in which several decagonal quasicrystals and crystalline approximants have been found by electron diffraction observations.¹⁻⁴⁾ Particularly, Ritsch *et al.* found eight different modifications of the Al-Ni-Co decagonal quasicrystals by electron diffraction analysis and proposed their stable regions in the Al-Ni-Co decagonal phase.³⁾ In these modifications, four ones called as type-I, type-II, S1 and 5F_{HT} states show diffraction patterns with so-called superlattice reflections. Recently, atomic-scale observations of high-angle annular detector dark-field scanning transmission electron microscopy (HAADF-STEM) clearly show that the diffraction patterns of the type-I, S1 and 5F_{HT} states can be interpreted by ordered arrangements of columnar clusters of atoms with pentagonal symmetry.⁵⁻⁷⁾ For examples, the type S1 state has an ordered arrangement of two kinds of atomic clusters with different orientations of pentagonal symmetry in a pentagonal tiling, and its ordered structure can be interpreted by the projection of a CsCl-type hypercubic lattice.^{5,8)} On the other hand, the structures of the type-I and 5F_{HT} states are characterized as rhombic tilings, and are formed with ordered arrangements of similar two kinds of atomic clusters and one kind of atomic clusters with the same orientation of pentagonal symmetry, respectively.^{6,7)} The ordered structure of the type I state can be interpreted by the projection of a NaCl-type hypercubic lattice.^{6,9)}

The purpose of the present work is to examine the structure of an Al-Ni-Co decagonal quasicrystal, showing peculiar electron diffraction patterns called “type-II”, in an $\text{Al}_{71.5}\text{Ni}_{12.5}\text{Co}_{16}$ alloy annealed at 900°C.¹⁰⁾

2. Experimental Procedures

An alloy ingot with a nominal composition of $\text{Al}_{71.5}\text{Ni}_{12.5}\text{Co}_{16}$ was prepared by melting high-purity (99.99%) Al, Ni and Co metals in an arc furnace in an Ar atmosphere. The ingot was sealed in an evacuated quartz tube and an-

nealed at 900°C for 72 h. Thin samples for electron microscopy were prepared by dispersing crushed materials on holey carbon films. HAADF-STEM observations were made on a 200 kV transmission electron microscopy (JEM-2010F) equipped with a scanning transmission mode (STEM). A beam probe with a half width of about 0.2 nm was scanned on the sample, and intensity of transmitted high-angle scattering beam was recorded with an annular detector of 60–160 mrad. High-resolution transmission electron microscopy (HREM) was made on a 400 kV transmission electron microscope (JEM-4000EX) with a resolution of 0.17 nm. HREM and HAADF-STEM images were taken with the incident beam parallel to the periodic axis of the decagonal quasicrystal.

3. Results and Discussion

Figure 1 shows an electron diffraction pattern of the type-II decagonal quasicrystal, taken with the incident beam parallel to the periodic axis. In the pattern, one can see peculiar diffuse scattering with small pentagonal arrangements, as indicated with arrows. These diffuse scattering is a characteristic of the type-II state.¹⁰⁾

An HAADF-STEM image taken from the diffraction pattern of Fig. 1 shows Fig. 2(a). The contrast of atomic-scale HAADF-STEM images is proportional to the square of atomic numbers of constituent atoms.¹¹⁾ Therefore, in Fig. 2(a), only the transition-metal atoms with large atomic numbers can be reproduced as bright contrast without disturbance from the majority Al atoms. The HAADF-TEM images are formed with intensity detected during scanning of the incident beam, and so sample drift during scanning of the incident beam makes the local deformation of image contrast. Therefore, one should take account of the image deformation to analyze observed HAADF images. Although there is the local deformation of alignment of bright rings and dots in Fig. 2(a), one can easily see from Fig. 2(a) that small bright rings, which have a pentagonal shape to be precise, are arrayed along five-fold directions indicated by arrows. Also, the small bright rings can be connected by bonds with a distance of about

Fig. 1 Electron diffraction pattern of the type-II Al-Ni-Co decagonal quasicrystal in an $\text{Al}_{71.5}\text{Ni}_{12.5}\text{Co}_{16}$ alloy annealed at 900°C for 72 h, taken with the incident beam parallel to the periodic axis. Arrows indicate diffuse scattering, which characterizes the type-II Al-Ni-Co decagonal quasicrystal.

2 nm, as indicated with white lines, and produce an aperiodic tiling of Fig. 2(b). In the tiling of Fig. 2(b), which is formed by pentagonal tiles and two types of rhombic tiles, one can see a heterogeneous mixture of two-types of local regions, which are characterized as tilings formed mainly with fat rhombuses (the middle region indicated by an arrow), and with pentagons and thin rhombuses (the right and left regions). Also, translational arrangements of pentagons and thin rhombuses in the right and left regions can be seen, as indicated with dotted lines. This heterogeneous tiling can be considered to result in diffuse scattering in the diffraction pattern of Fig. 1. The characteristic of the heterogeneous tiling has already been observed in the HREM image,¹⁰⁾ but the HAADF-STEM image of Fig. 2(a) clearly shows the tiling with a bond length of 2 nm.

In order to see characteristics of bright dot distributions in the HAADF-STEM image, an HAADF-STM image with a higher magnification is shown in Fig. 3(a). In the image, one can see a common columnar cluster of atoms with a decagonal section of about 2 nm in diameter, which consists of a pentagonal arrangement of bright dots around its center and double concentric circles of bright dots surrounding the pentagonal arrangement, as indicated by a white circle. It should be noted here that the bright dots in the outer circle are elongated compared with those in the inner circle. This type of atomic clusters have also been found in some Al-Ni-Co⁵⁻⁷⁾ and Al-Ni-Ru¹²⁾ decagonal quasicrystals. In the image of Fig. 3(a), one can see two orientations for pentagonal arrangements at the centers of the atomic clusters. Figure 3(b) shows an arrangement of the two types of atomic clusters with different orientations of pentagonal symmetry. In Fig. 3(b), one can see the special feature that the two kinds of atomic clusters are orderly placed at lattice points by the definite manner, in which the two atomic clusters connected with the bond have

Fig. 2 (a) HAADF-STEM image taken with the diffraction pattern of Fig. 1, and (b) tiling obtained by connecting bright ring contrasts in (a) with lines.

different atomic clusters, although this manner is broken at pentagonal tiles. This ordered manner in a rhombic tiling can be explained from the projection of a NaCl-type hypercubic lattice.^{6,9)} Therefore, the structure of the type-II Al-Ni-Co decagonal quasicrystal has a disordered and heterogeneous tiling, but an arrangement of the atom clusters in the tiling has a characteristic feature of the NaCl-type hypercubic lattice.

Bright dots in the HAADF-STEM images can be considered to represent positions of transition-metal atoms, and no Al atoms contribute the image contrast of HAADF-STEM. Therefore, in order to examine an arrangement of Al atoms, HREM images are necessary. Figure 4 shows an HREM image taken with the incident beam parallel to the periodic axis. In Fig. 4, the atomic cluster of 2 nm in diameter consists of a wheel-like contrast at the center and ten ring contrasts sur-

Fig. 3 (a) HAADF-STEM image taken with a higher magnification than that of Figs. 2(a), and (b) tiling obtained by distinguishing two kinds of atom clusters with different orientations of pentagonal symmetry. A circle in (a) indicates an atomic cluster with a decagonal section of about 2 nm in diameter. In (b), open and closed circles indicate two kinds of atom clusters with different orientations of pentagonal symmetry, and solid and dotted lines show bonds connecting different and the same kinds of atom clusters, respectively.

rounding the wheel-like contrast, as indicated by a large circle. From the HAADF-STEM and HREM images of Figs. 3(a) and 4, a structural model of the atomic cluster with 2 nm in diameter can be derived, as shown in Fig. 5. From the comparison between the HAADF-STEM image of Fig. 3(a) and the projected model of Fig. 5(c), one can notice that the bright dots forming pentagonal and decagonal arrangements around the center correspond to individual atom columns of transition-metal atoms, and each extended spot at the outer decagonal arrangement to two transition-metal atoms separated with a small distance of 0.15 nm. Figure 5(d) shows a HREM image calculated from the structure mode of Fig.

Fig. 4 HREM images of the type-II Al-Ni-Co decagonal quasicrystal in an $\text{Al}_{71.5}\text{Ni}_{12.5}\text{Co}_{16}$, annealed at 900°C for 72 h, taken with the incident beam parallel to the periodic axis. A large circle shows an atom cluster with a decagonal section of about 2 nm in diameter, and small circles indicate arrangements of small ring contrasts in rhombic tiles.

Fig. 5 Structure model of the atomic cluster with a decagonal section of about 2 nm in diameter, which is a structural unit in the type-II Al-Ni-Co decagonal quasicrystal. (a) and (b) atomic arrangements in two layers separated by an interval of about 0.2 nm along the periodic axis. (c) the projection of the two layers in (a) and (b), and (d) a HREM image calculated from the model of (c), using the multislice method with a sample thickness of 2 nm and defocus value of 45 nm.

5(c). One can see a good correspondence between the observed contrast of the atomic cluster in Fig. 4 and calculated one of Fig. 5(d). Also, in Fig. 4, one can see the contrast of deformed atomic clusters, particularly in arrangements of ten bright rings, in rhombic tiles, as indicated by small circles in Fig. 4. The structures of the deformed atomic clusters were

Fig. 6 Frameworks explaining the structures of the rhombic tiles, which are characterized by small white circles in Fig. 4. Atomic arrangements in the frameworks can be obtained by putting an atomic arrangement of Fig. 5.

described by the framework with a bond length of 0.47 nm in Fig. 6. The atomic arrangements in the rhombic tiles can be obtained from putting the atomic arrangement of Fig. 5 in the frameworks of Fig. 6.

The present structure model of the atom cluster with pentagonal symmetry is the same as that proposed in our previous papers.⁵⁻⁷⁾ That is to say, it can be concluded that the structures of four types of Al-Ni-Co decagonal quasicrystals, the type-I, type-II, S1 and 5f_{HT} states, are characterized as different tilings formed with the same atom clusters.

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