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Growth of large single-grain decagonal quasicrystal by directional solidification of undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melt

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The growth of decagonal quasicrystals was investigated by the directional solidification of highly undercooled $Al_{72}Ni_{12}Co_{16}$ melts. The maximum single-grain decagonal quasicrystal contained in the grown crystals was about 0.5 mm in diameter and 6 mm in length. The quality of the grown crystals was examined by the X-ray powder diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM).

1. Introduction

The first discovery of quasicrystals was made at the end of 1984 [1] and it caused a great shock in all solid-state sciences, since they have no translation periodicity and display the so-called forbidden rotational symmetry, such as 5-, 8-, 10-, and 12-fold rotations. Subsequently, icosahedral and decagonal quasicrystals which are known to be stable were found in Al-Pd-TM (TM = Mn or Re) [2, 3] and Al–Cu–TM (TM = Fe, Ru or Os) [4, 5] systems and Al–Co–TM (TM = Cu or Ni) [6] systems, respectively. In order to investigate the mechanical and physical properties due to their quasiperiodic nature, the growth of large-sized single quasicrystals is essential. However, most of those systems are known to grow via a peritectic reaction, so preparing single quasicrystals of a large size is very difficult.

Unlike icosahedral quasicrystals, the decagonal quasicrystals possess both quasiperiodic and periodic directions in one grain [7–9]. Because of this particular structure, one can simultaneously compare the physical properties in the two directions. Thus it is clearly advantageous to perform experiments on the decagonal quasicrystals. Among all alloy systems in which decagonal quasicrystal was found, the Al–Ni–Co system is considered to be the easiest one for the formation of single-grain decagonal quasicrystals. Yokoyama *et al*. [10] constructed a partial isothermal phase diagram including the decagonal quasicrystal in an Al–Ni–Co system, determined the composition of the liquid which is in equilibrium with stoichiometric decagonal phase, and produced a single decagonal quasicrystal of $Al_{72}Ni_{12}Co_{16}$ by the Czochralski method. In addition, Sato *et al*. [11] studied the single–grain growth of decagonal quasicrystal with a nominal composition of $Al_{72}Ni_{12}Co_{16}$ alloy by the floating zone method.

In contrast to the conventional directional solidification, the directional solidification of the highly undercooled melt occurs under a negative temperature gradient at the solid/liquid interface. It has been found in the investigation of the solidification of undercooled alloys that, with the increase of undercooling, the macro solid/liquid interface changes from zigzag to planar [12], and at certain undercoolings the structure becomes columnar dendrites [13]. This implies that the undercooled melt can be directionally solidified under a certain condition. In this work, single-grain decagonal quasicrystals are grown by the directional solidification of

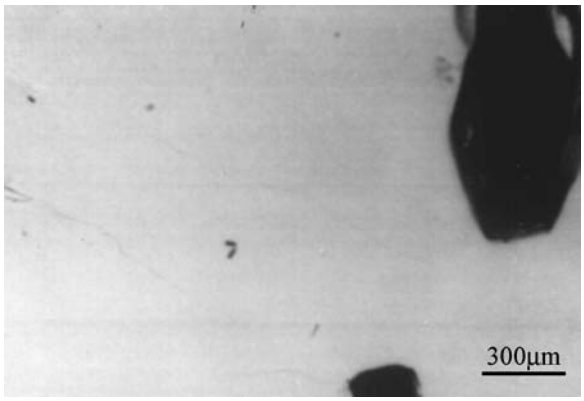

Figure 1 Back-scattering electron image of the arc-melted $Al_{72}Ni_{12}Co_{16}$ alloy.

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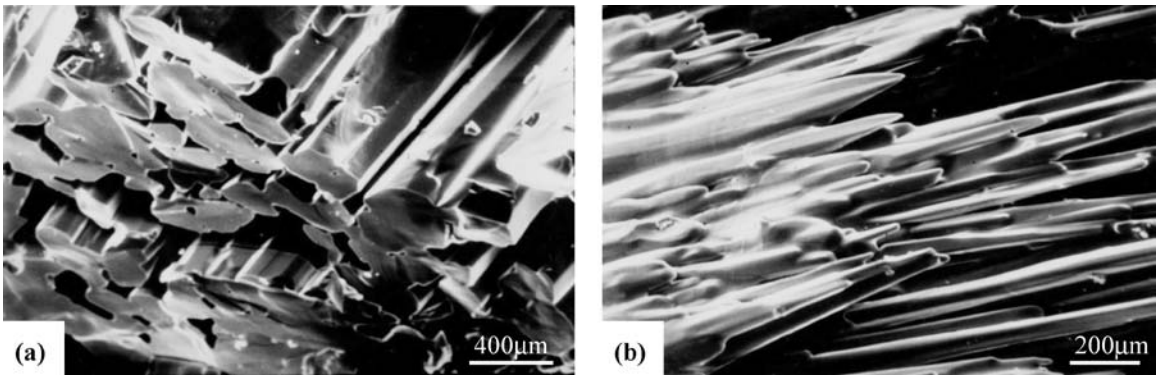

Figure 2 Scanning electron micrographs of the growth interface of the decagonal quasicrystal formed in the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melts with various undercoolings: (a) $\Delta T = 65$ K and (b) $\Delta T = 85$ K.

the undercooled $Al_{72}Ni_{12}Co_{16}$ melt at Ar atmosphere. The quality of the grown crystals is examined by X-ray powder diffraction, scanning electron microscope and transmission electron microscopy.

2. Experimental procedure

High purity aluminum, nickel and cobalt (purity better than 99.98%) were taken to form an alloy with a stoichiometry of $Al_{72}Ni_{12}Co_{16}$ (at.%). The melting process was carried out in a vacuum arc-melting furnace under an Ar atmosphere. The button ingots approximately 3 cm in diameter were remelted three times to get a completely homogeneous composition.

The experiments on samples were carried out in an electromagnetic melting apparatus manufactured by Edmund Buhler Co, Germany. The working chamber was initially evacuated to about 10^{-6} mbar, then back-filled with high-purity Ar gas (purity higher than 99.999%). For the purpose of deactivating heterogeneous nucleation sites in melt, each sample was cyclically superheated to a superheat of 300 K for 5 min. At the predetermined undercooling, nucleation was stimulated at one end of the specimen, and solidification went toward the other end spontaneously. The thermal behavior of the samples was monitored by an infrared pyrometer with a relative accuracy of 3 K, and response time of 5 ms, respectively [14]. Before the experiments the pyrometer was calibrated with a standard $PtRh_{30}$-$PtRh_6$ thermocouple.

The crystallographic features were examined by a Rigaku X-ray powder diffractometor (XRD) with a Cu-K_α radiation. The solidified samples were comminuted into powders prior to XRD. For metallographic examinations we used a JXA-840 scanning electron microscope (SEM) and a JEM-200cx transmission electron microscopy (TEM). The composition was examined by backing-scattering the electron image (BEI) of the SEM.

3. Results and discussion

In order to check the compositional homogeneity of the arc-melted $Al_{72}Ni_{12}Co_{16}$ alloy, the back-scattering electron image (BEI) was taken. As shown in Fig. 1, except for the black holes, the image contrast is almost the same for all surface regions, suggesting that a homogeneous composition was obtained.

Fig. 2 shows SEM micrographs of the decagonal quasicrystal with various undercoolings, ΔT, obtained by the directional solidification of the highly undercooled $Al_{72}Ni_{12}Co_{16}$ melts. In contrast with the conventional solidification [6], a significant improvement in the quasicrystal size, growth orientation and growth morphology was achieved using the directional solidification of the highly undercooled melt, as shown by the parallel growth quasicrystal prism about the maximum 0.5 mm in diameter and 6 mm in length under the undercooling of 65 K (see in Fig. 3). From Figs 2 and 3, it is

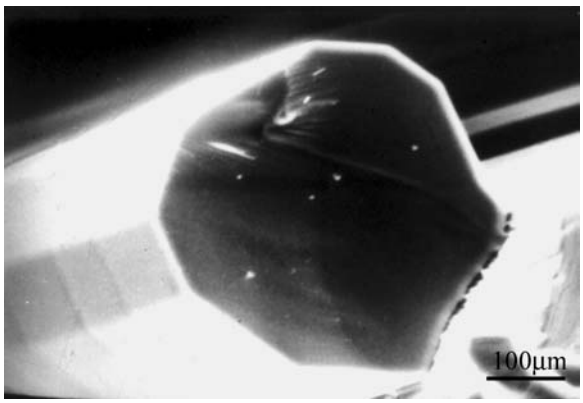

Figure 3 Scanning electro-micrograph of a maximum single-grain decagonal quasicrystal formed in the sample pictured in Fig. 1a.

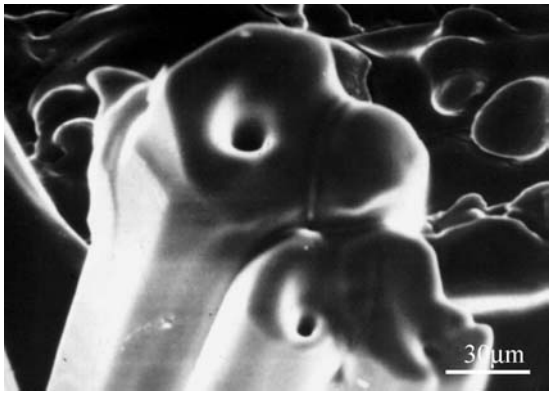

Figure 4 Scanning electro-micrograph of a decagonal hollow prism which is a part of the interface pictured in Fig. 1b.

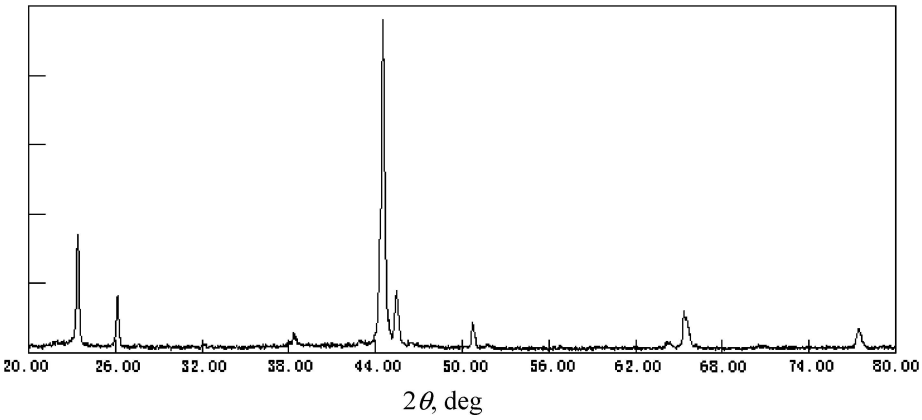

Figure 5 X-ray powder diffraction pattern of the grown crystal formed in the $Al_{72}Ni_{12}Co_{16}$ alloy melt undercooled by 65 K.

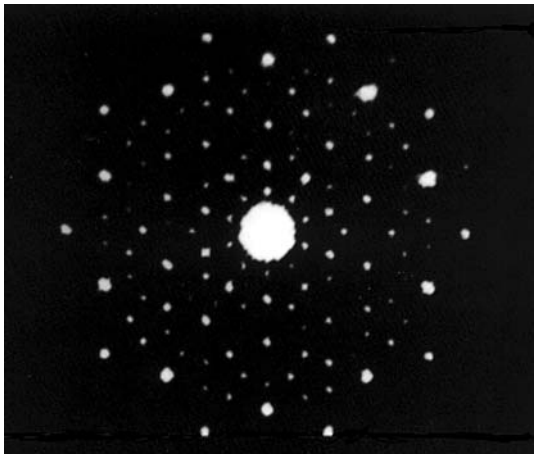

Figure 6 Electron diffraction pattern exhibiting the rotational symmetries of decagonal quasicrystal formed in the $Al_{72}Ni_{12}Co_{16}$ alloy melts undercooled by 65 K.

interesting to note that the higher the undercooling, the stronger the anisotropy of the growth kinetics of the decagonal quasicrystal is, which leads to fast growth in the periodic direction along the needle axis. In the quasiperiodic direction, however, there is not sufficient time to complete the cross section or even the needles themselves. Indeed, most of the needles are hollow (see in Fig. 4). Fig. 5 shows the X-ray diffraction spectrum of the sample undercooled by 65 K. The diffraction peaks of decagonal quasicrystal can be calibrated by using the indices of Yamamoto *et al.* [15]. All the peaks of the diffraction patterns in Fig. 5 belong to the decagonal quasicrystal without other phases. TEM analyses were also conducted to confirm decagonal quasicrystal in the samples formed in the undercooled melts. Fig. 6 shows an important ten-fold axis pattern, exhibiting the rotational symmetries of decagonal quasicrystals.

In addition, it was found that the decaprisms of quasicrystals become thin in diameter with the increasing undercooling of melts (see in Fig. 2). From the point of Toner [16], the growth along the quasiperiodic directions is the nature of decagonal quasicrystals. At smaller undercoolings, the growth of decagonal quasicrystal is along the quasiperiodic directions without other direction. With the increase of undercooling, the potential barrier for nucleating steps along the periodic direction of the ten-fold axis vanishes and the growth along ten-fold axis begins. The continuous growth rate along the ten-fold axis is greater than that along the quasiperiodic directions [17]. So the growth of decagonal quasicrystal along the ten-fold axis is preferred. Therefore, the diameter of decagonal quasicrystal becomes thinner as the undercooling increases. In addition, the directional growth in the undercooled melt occurs only under a certain condition. It is essential that the thermal undercooling is greater than the solutal undercooling [18]. So the solidification processing is dominantly controlled by the thermal diffusion. Therefore, the higher the undercooling, the stronger the thermal diffusion, which makes the diameter of the decagonal quasicrystal decrease.

4. Conclusions

The directional growth of the decagonal quasicrystal was achieved in the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melts. The diameter of the decagonal quasicrystal becomes thin as the undercooling increases. The maximum diameter of the single-grain decagonal quasicrystal is approximately 0.5 mm with an undercooling of 65 K. These results could bring out a novel idea to prepare bulk single-grain quasicrystals by the directional solidification of the highly undercooled melt.

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