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Growth morphologies of decagonal quasicrystal in highly undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melt①

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[Abstract] The electromagnetic melting and cyclic superheating method was applied to undercool the $Al_{72}Ni_{12}Co_{16}$ alloy melt, and a maximum undercooling, 180 K was obtained. Growth morphologies were characterized by using optical microscopy, scanning electron microscope(SEM) and transmission microscopy(TEM). The microstructural morphologies indicate that a continuous growth mode of D-phase along the periodic orientation of ten-fold axis is preferred at large undercoolings. According to the Toner's step growth mode of quasicrystal, the preferred continuous growth along the periodic orientation of ten-fold axis is caused by the loss of potential barrier for nucleating steps along this direction.

[Key words] $Al_{72}Ni_{12}Co_{16}$; high undercooling; decagonal quasicrystal; growth morphology
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1 INTRODUCTION

Since the discovery of an icosahedral phase[1] in the rapidly solidified Al-Mn alloy, quasicrystals have attracted more and more attentions owing to their special quasiperiodic structure. The stable icosahedral and decagonal quasicrystals were discovered in Al-Cu-TM (TM= Fe, Ru or Os)[2, 3] and Al-Co-TM(TM= Cu or Ni)[4] alloy systems, respectively. The discoveries of these stable quasicrystals have brought a great progress in the studies of quasicrystal structure without high density of defects and strain resulted from rapid solidification. Unlike icosahedral quasicrystals, the decagonal quasicrystals possess both quasiperiodic and periodic directions in one grain[5~7]. According to this particular structure, one can simultaneously compare the physical properties in the two directions. Thus it is obviously advantageous to perform experiments on the decagonal quasicrystals. Among all alloy systems in which D-phase was found, the Al-Ni-Co system is considered to be the easiest one to form single-grain D-phase by the slow-cooling method. Yokoyama et al[8] constructed a partial isothermal phase diagram including D-phase in the Al-Ni-Co system and determined the composition of the liquid which is in equilibrium with the stoichiometric decagonal phase. Furthermore, Sato[9] and Jeong et al[10] respectively confirmed that $Al_{72}Ni_{12}Co_{16}$ melt became single D-phase just below the melting point temperature under the slow cooling condition, indicating a congruent solidification.

Up to now only a few investigations on high undercooling of the quasicrystal-forming alloy melt were reported. In this work, we apply the electromagnetic melting and cyclic superheating method to study the growth morphologies of D-phase in the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melt. This technique enables melt to reach high undercooling levels during slow cooling because the heterogeneous nucleation in melt is avoided in a great extent. Besides, it provides us with an effective method to investigate phase morphology and growth mechanism under various undercoolings.

2 EXPERIMENTAL

High purity aluminum, nickel and cobalt (purity better than 99.98%) were taken to form an alloy with a stoichiometry of $Al_{72}Ni_{12}Co_{16}$. The melting process was carried out in a vacuum arc furnace under high-purity Ar atmosphere(purity higher than 99.999%). Button ingots approximately 3 cm in diameter were remelted three times to get a completely homogeneous composition.

The undercooling experiments of samples were carried out in an electromagnetic levitation melting apparatus manufactured by Edmuld Buhler Co, Germany. The working chamber was initially evacuated to about 10^{-4} Pa, and then back-filled with high-purity Ar gas. For the purpose of deactivating heterogeneous nucleation sites, each sample was cyclically superheated to a super-

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heating of 300 K for 5 min. The thermal behavior of samples was monitored by an infrared pyrometer with relative accuracy of 3 K, and response time of 5 ms, respectively[11]. Before experiments the pyrometer was calibrated with a standard $PtRh_{30}$-$PtRh_6$ thermal couple.

The crystallographic features were mainly examined by Rigaku X-ray powder diffraction with a Cu K_α source. Composition was examined by the backing-scattering electron images (BEI) of a JXA-840 scanning electron microscope (SEM). The slice was electrolytically thinned using an electrolyte of 5% $HClO_4$ in ethanol at − 30 ℃ and investigated using JEM-200cx transmission electron microscopy (TEM). In addition, differential thermal analyzer (DTA) was adopted to determine the liquidus and transition temperature of the alloy (heating rate: 10 K/min).

3 RESULTS AND DISCUSSION

3.1 Alloy composition

Fig. 1 shows BEI photograph of the arc-melted $Al_{72}Ni_{12}Co_{16}$ alloy. Except for the black holes, the image contrast is almost the same for all the surface regions, suggesting a homogeneous composition was obtained.

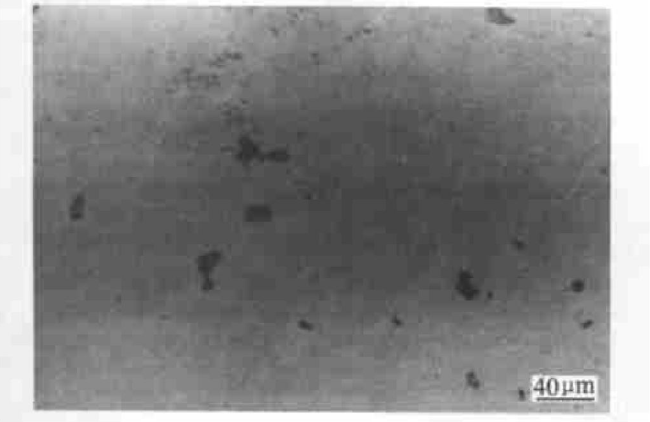

Fig. 1 BEI photograph of arc-melted $Al_{72}Ni_{12}Co_{16}$ alloy

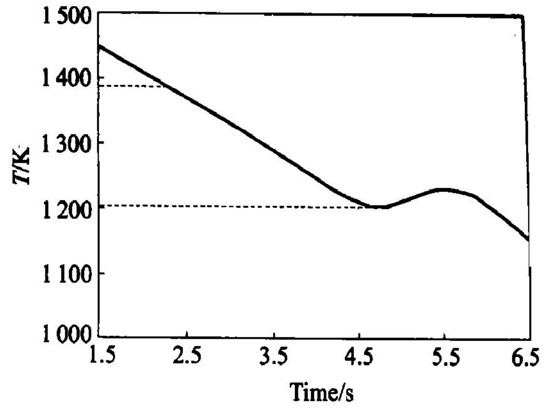

Fig. 2 Temperature-time profile of experiment obtained from $Al_{72}Ni_{12}Co_{16}$ sample

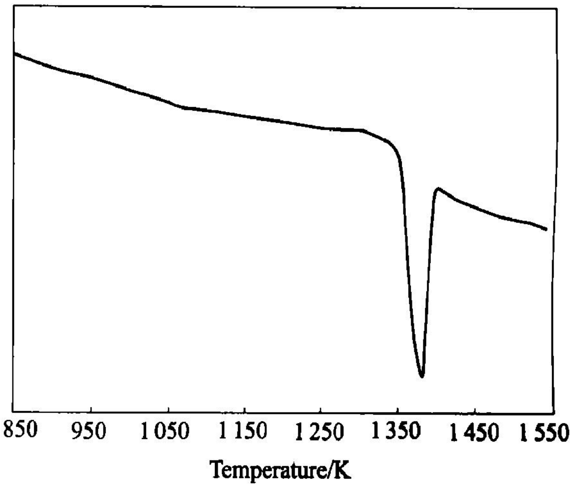

Fig. 3 DTA-heating curves obtained from $Al_{72}Ni_{12}Co_{16}$ sample solidified after maximum undercooling of 180 K

3.2 Growth morphologies of undercooled decagonal quasicrystal

Fig. 2 shows a curve of temperature vs time of $Al_{72}Ni_{12}Co_{16}$ alloy in solidification process. The differential temperature analysis (DTA) curve of this alloy is given in Fig. 3, and the liquidus temperature T_l can be determined from the DTA curve. It can be seen in Fig. 2 that there occurs undercooling in the melt below the liquids temperature of the quasicrystal phase (T_l = 1 385 K), and there initiates nuclei at T_n = 1 205 K. Therefore, the undercooling of the sample is $\Delta T = T_l - T_n = 180$ K. A reproducible undercooling of maximum $\Delta T = 180$ K is observed. In addition, X-ray diffraction spectrum of the undercooled sample is shown in Fig. 4. According to the indices of D-phase calibrated by Yamamoto et al[12], all peaks in the pattern can be indexed as a single D-phase without other phases. Thus, we have produced a sample consisting of single-phase decagonal quasicrystal by the solidification of the ternary alloy $Al_{72}Ni_{12}Co_{16}$ from the undercooled melt.

Figs. 5(a) and (b) are microstructure and growth morphology of D-phase in the same undercooled sample, respectively. In Fig. 5(a), microstructure of the undercooled sample is mainly composed of the equiaxied structures, which could be a continuous growth mode. Additionally, it can be clearly seen that the growth of the primary stem is quicker than that of arms in Fig. 5(b). The electron diffraction patterns along the orientations of primary stem, and arms, are displayed in Fig. 6 respectively. The patterns indicate that the orientation of primary stem parallels the ten-fold of D-phase, and the orientation of arms parallels the two-fold of D-phase. These results confirm that a continuous growth of D-phase along the periodic orientation of ten-fold axis is preferred under

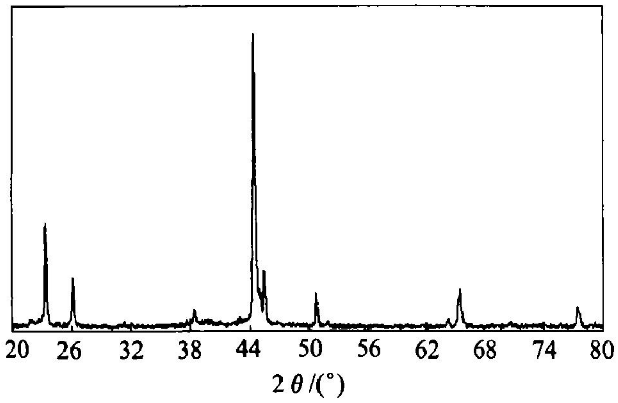

Fig. 4 X-ray powder diffraction patterns of $Al_{72}Ni_{12}Co_{16}$ alloy undercooled by ΔT 180 K

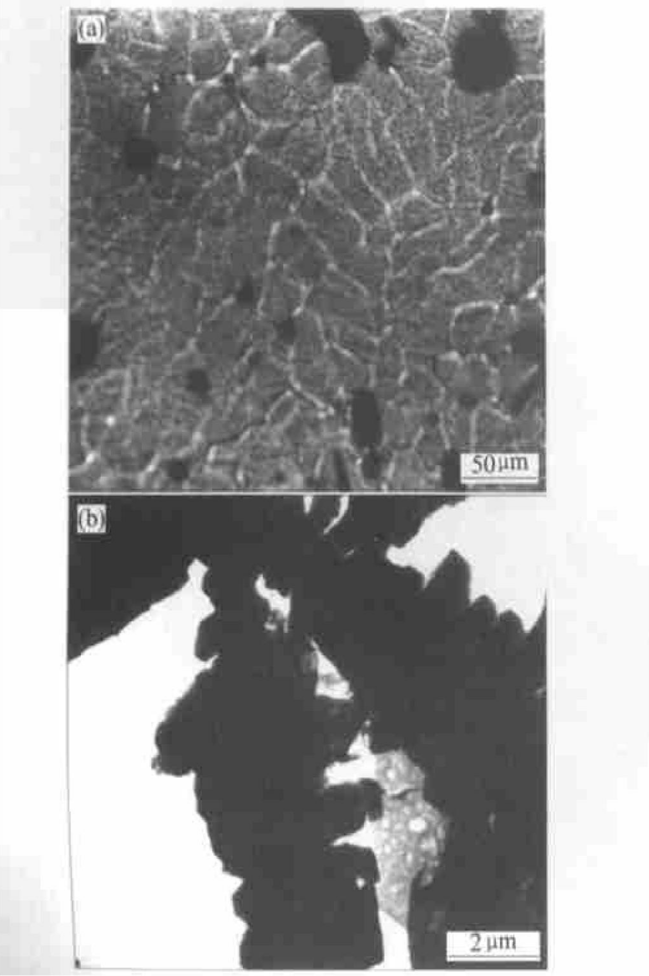

Fig. 5 Optical microstructure and TEM morphology of D-phase formed in $Al_{72}Ni_{12}Co_{16}$ alloy melt with maximum undercooling of 180 K
(a) —Equiaxied microstructure;
(b) —Dendrite growth morphology

large undercoolings. In addition, Fig. 7 shows growth morphology of D-phase formed in a shrink cavity of the same undercooled sample. It further confirms that the continuous growth along ten-fold axis is preferred under the large undercoolings.

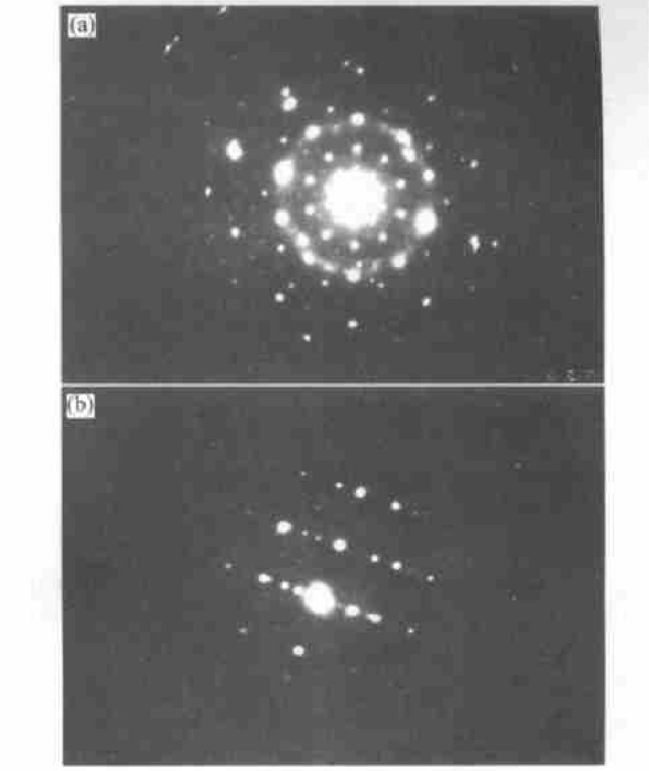

Fig. 6 Electron diffraction patterns exhibiting rotational symmetries of D-phase in $Al_{72}Ni_{12}Co_{16}$ alloy melts with maximum undercooling of 180 K
(a) —Ten fold; (b) —Two fold

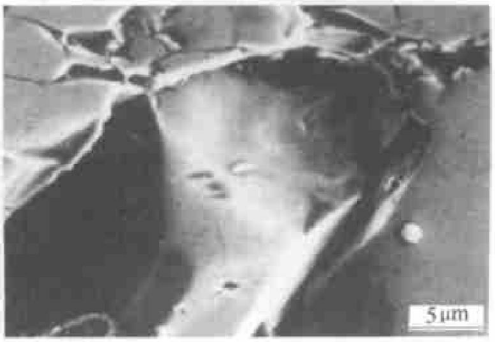

Fig. 7 SEM growth morphology of D-phase in shrink cavity of $Al_{72}Ni_{12}Co_{16}$ alloy melts with maximum undercooling of 180 K

3.3 Discussion

For a decagonal quasicrystal, there are periodic direction (along the ten-fold axis) and quasiperiodic direction (along the two-fold axis). The quasiperiodicity of D-phase yields dramatic difference in the growth behavior of this phase in comparison to crystals. For a regular crystal, the faceted growth takes place below the roughening transition temperature. Since the quasicrystal can be considered as a periodic crystal with infinite periodicity, the roughening transition temperature should be infinity. Toner[13] proposed a simple step growth model of the faceted quasicrystalline interface in comparison to the regular crystal. In his model the quasicrystals grew by nucleating a step height(h_s) , which was related to the chemical potential difference across the interface($\Delta\mu$) as

$$h_s \propto (\Delta\mu)^{-1/3} \qquad (1)$$

Thus, as the chemical potential increases, the height of steps needed for the quasicrystal growth decreases. On the other hand, the step height for a crystal growth is related to the lattice parameter and is independent of the chemical potential difference. Furthermore, for a crystal, the critical potential barrier for nucleation of steps vanishes at the roughening transition temperature, while for quasicrystals, it always remains finite.

The above analyses indicate that the step growth along the quasiperiodic direction is the nature of D-phase. At small undercoolings, the potential barrier for nucleating steps along the periodic direction is so large that the step growth along this direction is impossible. Therefore, the D-phase takes the only step growth mode along the quasiperiodic direction. When the undercooling of the melt is large enough, the potential barrier for nucleating steps along the periodic direction vanishes and continuous growth along the periodic direction is preferred by D-phase. Thus, in the periodic direction, D-phase must be like a regular crystal to possess a continuous growth mode and form the equiaxied structures which consist of dendrite elements, as can be clearly seen in Fig. 5.

4 CONCLUSIONS

1) A maximum undercooling, 180K, is achieved, and single-phase decagonal quasicrystal is prepared by means of electromagnetic melting and cyclic superheating in the $Al_{72}Ni_{12}Co_{16}$ alloy.

2) A continuous growth mode of D-phase along the periodic orientation of ten-fold axis is preferred at the large undercoolings.

3) The microstructure of D-phase formed in the large undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melt consists of the equiaxied grains, and the latters are composed of dendrite elements.

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