JOURNAL OF MATERIALS SCIENCE **38** (2003) 885–889

Solidification behavior of decagonal quasicrystal in the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melt

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The microstructural evolution of $Al_{72}Ni_{12}Co_{16}$ alloy at various undercoolings was investigated in this paper. A single-phase decagonal quasicrystal (D-phase) was obtained in the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melts. Different microstructure morphologies of the D-phase were formed with increasing undercoolings. Based on Toner's model of the step growth of quasicrystals, the growth mechanisms of the D-phase under various undercoolings were discussed. The D-phases formed at various undercoolings in the undercooled melts show different microstructures owing to the change of preferential growth direction from the quasiperiodic to periodic direction. © *2003 Kluwer Academic Publishers*

1. Introduction

Since the discovery of an icosahedral phase [1] in the rapidly solidified Al-Mn alloy, the quasicrystals have attracted much attention owing to their special quasiperiodic structure. 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. The discoveries of these stable quasicrystals have brought a great progress in the studies of quasicrystal structure as they are free of defects and strain resulted from rapid solidification. Unlike icosahedral quasicrystals, the decagonal quasicrystals possess both quasiperiodic and periodic directions in one crystal [5–7]. For this structure feature, 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 the D-phase was found, the Al-Ni-Co system is considered to be the easiest one in which single-grain decagonal quasicrystal can be formed by a 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 D-phase. Besides, Sato [9] and Jeong *et al.* [10] respectively confirmed that $Al_{72}Ni_{12}Co_{16}$ melt becomes single D-phase just below the melting point temperature under the slow cooling condition, indicating a congruent solidification. But for the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melts, few investigations on phase composition and microstructural evolution were reported. In this work, we applied the electromagnetic melting and cyclic superheating method to study the solidification behavior of $Al_{72}Ni_{12}Co_{16}$ alloy melts. This technique enables an alloy melt to reach high undercooling levels during slow-cooling rate because the heterogeneous nucleation of melt is avoided to a great extent. Besides, it provides us with an effective method to investigate phase composition, phase morphology and growth mechanism involving quasicrystal and crystalline phases under various undercoolings.

2. Experimental procedure

High purity aluminum, nickel and cobalt (purity better than 99.98%) were used to form an alloy with a stoichiometry of $Al_{72}Ni_{12}Co_{16}$. Prior to melting, the surfaces of the metals were cleaned mechanically by grinding off the surface oxide layers and chemically by etching in HCl solution diluted with water. The melting process was carried out in a vacuum arc furnace under an Ar atmosphere. 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 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, each sample was cyclically superheated by 300 K for 5 min. The thermal behavior of samples was monitored by an infrared pyrometer with a relative accuracy of 3 K, and response time of 5 ms [11]. Before the experiments the pyrometer was calibrated with a standard $PtRh_{30}$-$PtRh_6$ thermal couple.

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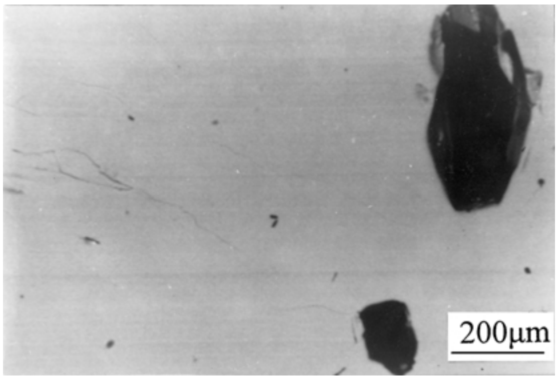

Figure 1 BEI photograph of the arc-melted $Al_{72}Ni_{12}Co_{16}$ alloy.

The crystallographic features were mainly examined by a Rigaku X-ray powder diffractometer (XRD) with a Cu K_α source. The solidified samples were comminuted into powders prior to XRD. For metallographic examinations we used a JXA-840 scanning electron microscope (SEM). Composition was examined by backing-scattering electron imaging (BEI) in the SEM. The slice was electrolytically thinned using an electrolyte of 5% $HClO_4$ in ethanol at $-30°C$ and investigated using a JEM-200cx transmission electron microscopy (TEM). In addition, differential thermal analyzer (DTA) was used to determine phase composition and the liquidus temperature of the alloy (heating rate: 10 K/min). Kroll's etching reagent was used for observing the microstructure.

3. Experimental results and discussion

3.1. Experimental results

Fig. 1 shows a 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 surface regions, suggesting a homogeneous composition was obtained.

Fig. 2 presents four types of microstructural morphologies of the $Al_{72}Ni_{12}Co_{16}$ alloy at undercoolings, ΔT, of less than 150 K. Fig. 2a shows the microstructure of a sample undercooled by 70 K. It is composed of gray stripe branches, which represent the D-phase according to the X-ray diffraction spectrums in Fig. 4. The black parts are holes located at the boundaries. At higher undercoolings, equiaxied structures were formed in the solidified samples. Fig. 2b is the microstructure of a sample undercooled by 90 K. It is mainly composed of coarse equiaxied structures. Fig. 2c presents the structure of samples undercooled by 120 K, which consists of finer equiaxied grains. Furthermore, the coarse microstructure occurs repeatedly at the undercooling of 150 K, which can be seen in Fig. 2d.

In Fig. 3, growth morphologies of the same solidified samples undercooled by 70 K and 90 K are shown. Fig. 3a gives the deeply-etched image of the directional D-phase. The facet morphology can be seen along the growth direction (indicated by the arrow). Therefore, the D-phase grew in a lateral pattern and formed the stripe morphology, which can be seen in Fig. 2a. Fig. 3b reveals the growth morphology of the D-phase found in a shrinkage cavity of the same sample undercooled by

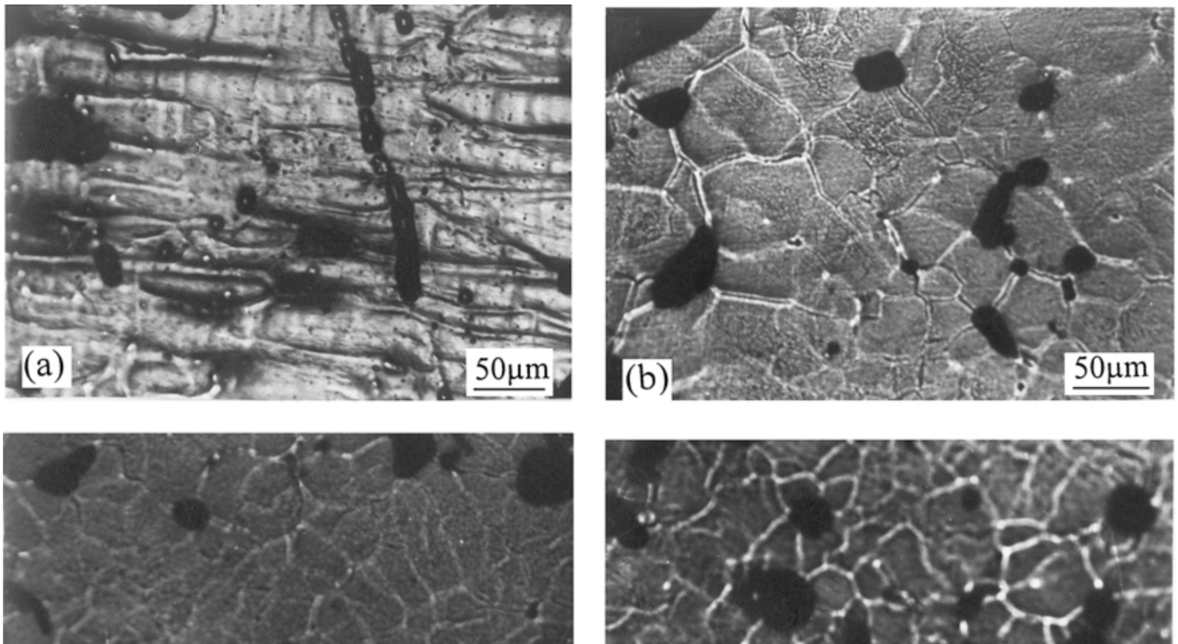

Figure 2 Microstructures of $Al_{72}Ni_{12}Co_{16}$ alloy melts undercooled by (a) $\Delta T = 70$ K, (b) $\Delta T = 90$ K, (c) $\Delta T = 120$ K and (d) $\Delta T = 150$ K.

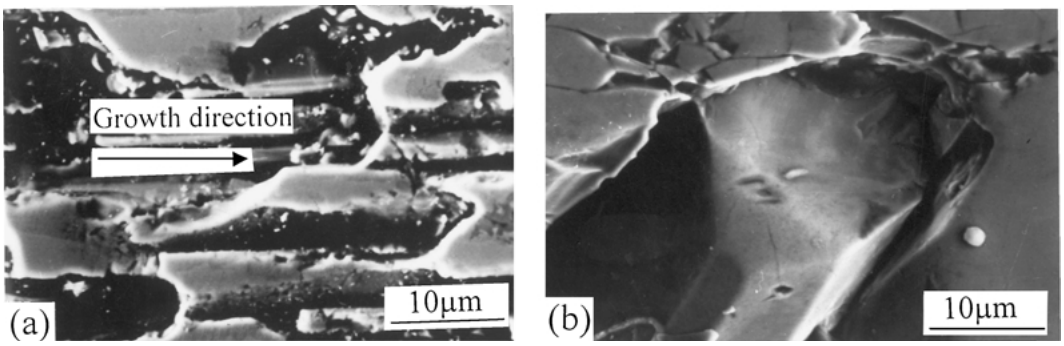

Figure 3 Scanning electron micrographs of a D-phase in $Al_{72}Ni_{12}Co_{16}$ alloy melts undercooled by (a) $\Delta T = 70$ K and (b) $\Delta T = 90$ K.

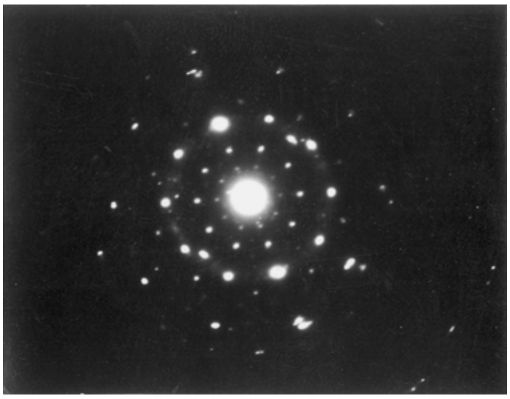

Figure 4 Ten-fold diffraction pattern exhibiting the rotational symmetries of D-phase in $Al_{72}Ni_{12}Co_{16}$ melts undercooled by 70 K.

90 K. The facet reveals a microcolumnar structure with the facets stepping out along the two-fold direction. It indicates that the growth of the D-phase is fastest along the periodic ten-fold axis and slowest along the two-fold direction.

TEM analyses were conducted to confirm D-phase formation in the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy. Fig. 4 shows an important ten-fold axis pattern, exhibiting the rotational symmetries of decagonal quasicrystals. The pattern indicates that the samples undercooled by 70 K consisted of single-phase decagonal quasicrystal.

X-ray diffraction spectrums of the undercooled $Al_{72}Ni_{12}Co_{16}$ alloys are shown in Fig. 5. All the diffraction peaks of D-phase can be calibrated by using the indices of Yamamoto and Ishihara [12]. Fig. 5a–d are the powder diffraction patterns of the samples undercooled by 70 K, 90 K, 120 K and 150 K, respectively. All peaks in these patterns can be indexed as a single D-phase pattern without other phases according to their plane spacing (*d*-value) and relative intensity, which also indicates that single-phase decagonal quasicrystals are obtained in the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melts.

The differential temperature analysis (DTA) curve of the same sample formed in $Al_{72}Ni_{12}Co_{16}$ alloy melt undercooled by 70 K is given in Fig. 6. It indicates that the sample consists of single-phase decagonal quasicrystal as checked by XRD, and that the liquidus temperature T_m is 1363 K.

It can be seen that with increasing undercooling, the microstructure of the solidified samples and growth mode of the D-phase varied. The results of these experiments indicate that the D-phase is directly formed in the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melts. With increase of undercooling, the morphology of the D-phase varied from the stripe morphology, indicating a lateral growth pattern, to the equiaxied structures, which could result from a continuous growth.

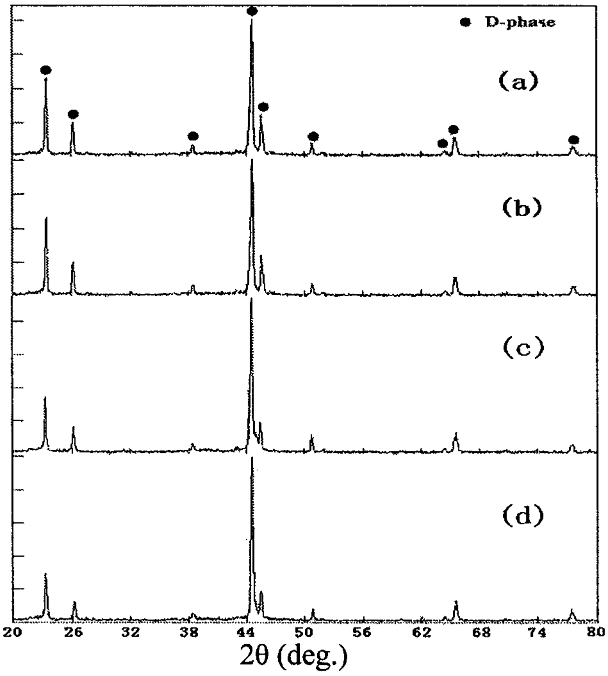

Figure 5 X-ray powder diffraction patterns of $Al_{72}Ni_{12}Co_{16}$ alloy undercooled by (a) $\Delta T = 70$ K, (b) $\Delta T = 90$ K, (c) $\Delta T = 120$ K and (d) $\Delta T = 150$ K.

3.2. Discussion

The above-mentioned experiments indicated that single-phase decagonal quasicrystals are prepared in the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melts, which is corresponding to the experimental results of Sato [9] and Jeong *et al.* [10].

Furthermore, the D-phase shows various morphologies depending on the prior undercooling of melt. This phenomenon was caused by the change of growth mechanism of the D-phase [19]. Generally, the D-phase possesses quasiperiodic (along the two-fold axis) and periodic (along the ten-fold axis) directions in one crystal. The quasiperiodicity yields dramatic difference in the growth behavior of quasicrystals in comparison to

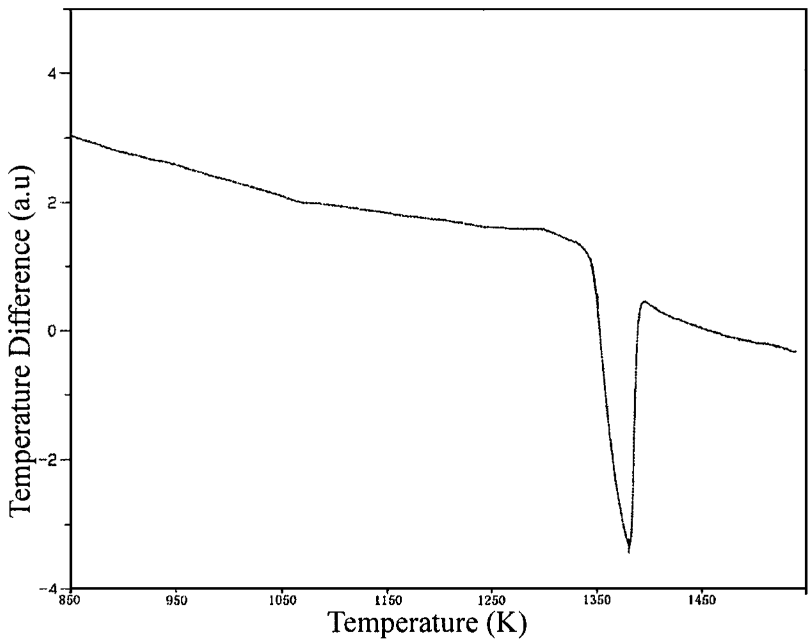

Figure 6 DTA-heating curve obtained from an $Al_{72}Ni_{12}Co_{16}$ sample solidified after undercooling of $\Delta T = 70$ K.

crystals. For a regular crystal step (or lateral) growth of a crystal takes place above the roughening transition temperature. Since the quasicrystal can be considered as a periodic crystal with infinite periodic, the roughening transition temperature should be infinity. Toner proposed a model of step growth of the faceted quasicrystalline interface in comparison to the regular crystal [20]. It was found that quasicrystals grow by nucleating a step height (h_S) which is proportional to $(\Delta\mu)^{-1/3}$, where $\Delta\mu$ is the chemical potential difference across the interface. Thus as the chemical potential difference increases, the height of steps needed to grow a quasicrystal decreases. On the other hand, the step height for crystal growth is related to the lattice parameter and is independent of the difference in chemical potential. Further 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 step growth is the nature of D-phase and the advancing of solid-liquid interface is along the quasiperiodic direction of two-fold axis. When the undercooling is lager than the roughening transition temperature, the chemical barrier for nucleation steps along the periodic direction of ten-fold axis vanishes and a continuous growth mode of D-phase along that is preferred. The growth of D-phase along the quasiperiodic direction could be regarded as the movement of larger steps which can be clearly seen in Fig. 3a, and it takes a lateral growth pattern and finally forms stripe morphology. However, samples solidified after larger undercooling prefer a continuous growth mode along the periodic direction of ten-fold axis, which can be seen in Fig. 3b.

In addition, the finer equiaxied-grain structure of samples undercooled by 120 K (in Fig. 2c) was caused by the break-up of the original dendrites [21]. Near the undercooling of 120 K, the solidified dendrites have the maximum tendency to be remelted, and the equiaxied finer grains occurring under the action of remelting. In contrast, at the undercoolings of less or larger than 120 K, because the remelting is not severe enough to make the original structure disintegrate into fine grains, the coarse microstructures of D-phase which were initially formed were kept (in Fig. 2b and d).

4. Conclusion

In this study, the microstructure evolution of decagonal quasicrystals in $Al_{72}Ni_{12}Co_{16}$ alloy was investigated by the electromagnetic melting and cyclic superheating method. A maximum undercooling, 150 K, is achieved and single-phase decagonal quasicrystals are prepared in the $Al_{72}Ni_{12}Co_{16}$ alloy. With the increase of undercooling, the decagonal quasicrystals show various microstructures due to the change of growth mechanism. At small undercoolings, a lateral growth pattern of the D-phase along the quasiperiodic direction is adopted, and at larger undercoolings a continuous growth mode along the periodic direction of ten-fold axis is preferred.

Acknowledgments

This work was carried out under the financial supports of the National Natural Science Foundation of China (Grant No. 59971036), the State Key Fundamental Research of China (Grant No. G2000067202) and the Doctorate Foundation of Northwestern Polytechnical University.

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Received 23 June
and accepted 16 October 2002