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Thermal stability of decagonal quasicrystal prepared from undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melt

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Abstract

The thermal stability of the single-phase decagonal quasicrystal produced directly from the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melt was investigated by different heat treatments. The optical microscopy, TEM, X-ray powder diffractometer (XRD) and differential thermal analyzer (DTA) techniques were adopted to observe the microstructure and to characterize the phase composition, respectively. Based on the analyses of the X-ray diffraction patterns and the DTA curves, two modifications of the decagonal quasicrystal existed in the annealed samples, which have a close structural relationship to the decagonal quasicrystal.

Keywords: Decagonal quasicrystal; Undercooling; Thermal properties; Heat treatment; X-ray technique

1. Introduction

Since the discovery of an icosahedral phase in the rapidly solidified Al–Mn alloy [1], quasicrystals (QCs) have attracted much attention owing to their special quasiperiodic structure. Whereafter, the icosahedral and decagonal QCs were found in Al–Cu–TM (TM = Fe, Ru or Os) [2,3] and Al–Co–TM (TM = Cu or Ni) [4] alloy systems. These discoveries of QCs have brought a great progress in the studies of quasicrystal properties. However, the recent researches indicated that due to the large entropy of QCs, many of the discovered QCs prepared by conventional methods are only stable at higher temperatures while precipitation of a second phase or decomposition into a mixture of crystalline phases occurs in these QCs at lower temperatures [5–7]. Thus it is necessary to perform experiments on the thermal stability of the prepared QCs.

In the present work, we applied the electromagnetic melting and cyclic superheating method to prepare the single-phase decagonal quasicrystal in the highly undercooled $Al_{72}Ni_{12}Co_{16}$ alloy melt. Because the number of nucleation sites decreases considerably, this technique enables an alloy melt to reach high undercooling levels. Besides, the thermal stability of single-phase decagonal quasicrystal obtained from the undercooled melt was studied by different heat treatments.

2. Experimental procedure

High purity aluminum, nickel and cobalt (purity better than 99.98%) were used to form an alloy with a stoichiometry of $Al_{72}Ni_{12}Co_{16}$. The melting process was carried out in a vacuum arc furnace under an Ar atmosphere. The master ingots approximately 3 cm in diameter were remelted three times to get a completely homogeneous composition. Subsequently, 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 at 300 K for 5 min. The thermal behavior of samples was monitored by an infrared pyrometer with a relative accuracy of 3 K, and a response time of 5 ms [8]. At temperatures of 1100 K and 1200 K, the prepared decagonal quasicrystals from the undercooled melt were annealed for 7 h in an evacuated silica tubes, respectively.

The samples were examined in a JEM-200cx transmission electron microscopy (TEM) and a Rigaku X-ray powder

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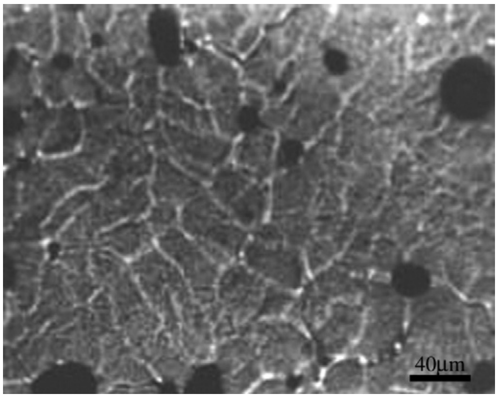

Fig. 1. Microstructure of the $Al_{72}Ni_{12}Co_{16}$ alloy obtained with an undercooling of 78 K.

diffractometer (XRD) with a Cu K_{α} source. TEM investigations were carried out on the powered materials which were spread on Cu grids cover by carbon films. The same powders were used for X-ray diffractions. Besides, differential thermal analyzer (DTA) was carried out to determine the phase transformation with a heating rate of 10 K/min under an Ar atmosphere. Kroll's etching reagent was used for observing the microstructure.

3. Experimental results

According to the previous experiments [9–11], various microstructures with increase of undercooling were obtained in the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy. At low undercoolings, the microstructure was usually composed of decagonal quasicrystal and other crystalline phases. The single-phase decagonal quasicrystal was only achieved under high undercoolings. Fig. 1 presents the microstructure of the $Al_{72}Ni_{12}Co_{16}$ alloy with an undercooling of 78 K. It is very obvious that except for black holes, the equiaxed grains are distributed in the solidified microstructure. From the X-ray diffraction spectrums in Fig. 3a, it indicated that this microstructure with the equiaxed grains is the single-phase decagonal quasicrystal.

TEM analyses were conducted to confirm the formation of decagonal quasicrystal in the undercooled $Al_{72}Ni_{12}Co_{16}$ alloy. Fig. 2a shows an important ten-fold axis pattern, exhibiting the rotational symmetries of decagonal quasicrystal. Besides, Fig. 2b is the diffraction pattern of the same sample along the P arrow in Fig. 2a, which confirmed that the decagonal quasicrystal is a two-dimensional quasiperiod and one-dimensional period. These patterns indicated that the microstructure obtained in the $Al_{72}Ni_{12}Co_{16}$ melt undercooled at 78 K consists of a single-phase decagonal quasicrystal.

In order to identify the phase compositions of the undercooled and the annealed samples, XRD, and DTA methods were adopted. X-ray diffraction spectrums of the samples are shown in Fig. 3. All the diffraction peaks of decagonal quasicrystal were calibrated by using the indices of Sato et al. [12]. Fig. 3a, b and c is the powder diffraction patterns of the undercooled and the annealed samples at 1100 K and 1200 K, respectively. In Fig. 3a, the diffraction pattern shows particularly sharp diffraction peaks and all peaks can be indexed as the decagonal quasicrystal without other phases, which indicated that a high quality of single-phase decagonal quasicrystal is produced from the $Al_{72}Ni_{12}Co_{16}$ alloy melt with an undercooling of 78 K. Although the diffraction patterns in Fig. 3b and c are similar to that in Fig. 3a, there are some differences between them. By the local magnifications (in Fig. 4) of Fig. 3, the strong reflection peak of the (13422) plane in the decagonal quasicrystal obtained from the undercooled melt are split in the samples with heat treatments and the peak intensities decrease with the increase of the annealed temperature. It indicated that the structural modifications of the decagonal quasicrystal exist in the annealed samples.

The differential temperature analysis (DTA) curves of the undercooled and the annealed samples are given in Fig. 5. It can be seen that although the heating histories of the annealed samples are quite similar, they are different to that of the undercooled sample. From an approximate temperature of 1100 K, the slopes of the annealed samples are steeper than that of the undercooled sample. A comparison of the heating curves for the annealed samples at 1100 K and 1200 K shows the different liquidus temperatures, which indicated that there are various modifications of the decagonal quasicrystal in the annealed samples.

It can be seen that the equiaxed grains of the single-phase decagonal quasicrystal solidified directly from the $Al_{72}Ni_{12}Co_{16}$ alloy melt with the undercooling of 78 K. The comparisons of the XRD patterns and the DTA curves of the undercooled and the annealed samples show that there were different structure modifications of the decagonal quasicrystal in the annealed samples.

4. Discussion

Usually, the microstructure of a material is determined by its solidification processing. According to the previous experiment

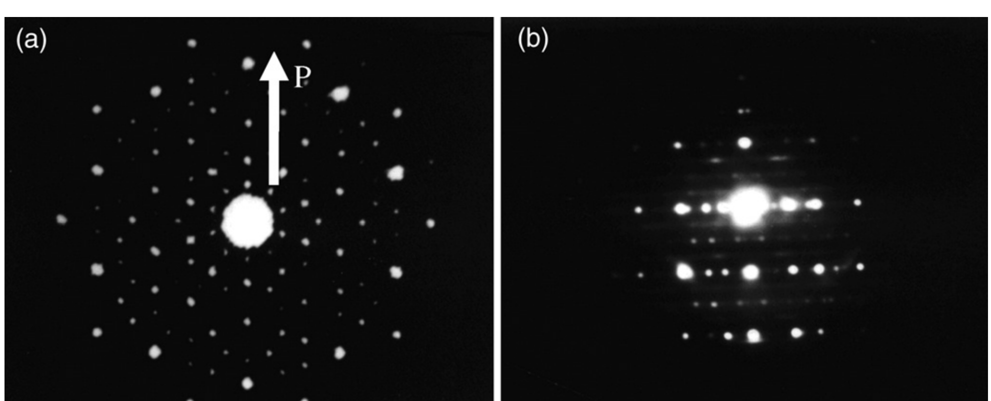

Fig. 2. Electron diffraction patterns exhibiting the rotational symmetries of decagonal quasicrystal in the $Al_{72}Ni_{12}Co_{16}$ alloy melt undercooled at 78 K. (a) Ten-fold axis and (b) two-fold axis.