Growth Condition and X-ray Analysis of Single $Al_{64}Cu_{23}Fe_{13}$ Icosahedral Quasicrystal by the Czochralski Method

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Growth conditions for the preparation of a single $Al_{64}Cu_{23}Fe_{13}$ icosahedral (I-) quasicrystal with excellent quasicrystallinity were examined using the Czochralski method. The appreciation of the quasicrystallinity of the grown single quasicrystal was performed by X-ray structural analysis. The full widths at half-maximum (FWHM) of the Bragg reflections along 2-, 3- and 5-fold symmetry directions have no $Q_{\parallel}$ and $Q_{\perp}$ dependence. Where the $Q_{\parallel}$ and $Q_{\perp}$ mean the phason momentum and real scattering vector. Furthermore, peak shifts from ideal Bragg positions were not observed. These means that the grown $Al_{64}Cu_{23}Fe_{13}$ quasicrystal by the Czochralski method has perfect I-phase structure.

1. Introduction

Although an Al–Cu–Fe stable I-quasicrystal was found 14 years ago,[1] preparation of the single Al–Cu–Fe I-quasicrystal from the melt had not been reported till September 1999.[2] The formation mechanism of Al–Cu–Fe I-quasicrystal is characterized by the wide compositional redistribution through the peritectic reaction between Cu-enriched liquid and Fe-enriched $(Al + Cu)_{13}Fe_4$ solid phases.[3] That is why researchers have tried to prepare the single I-quasicrystal with various annealing methods.[4,5] However, single Al–Cu–Fe I-quasicrystals grown by the annealing methods usually contain defects *i.e.*, phason strain and porosity.[6] The preparation of single quasicrystals directly from melt is a necessary factor to prepare a single quasicrystal with excellent structural quality. In actually, it is difficult to confirm the liquid region, which is equilibrate with I-phase region. The liquid region is determined by the functions of temperature and composition. Prevarskiy has already reported[7] the existence of I- and liquid two-phase region in Cu-enriched compositional area. Some recent reports[8,9] have described about the existence of I- and liquid two-phase region, which implies the possibility of an i-crystallization as a primary crystal from the melt. Previous our report[10] has suggested that the liquid composition with equilibrium to the I-phase is located in the narrow composition region around $Al_{60}Cu_{37}Fe_3$, and the equilibrate temperature is 1073 K.

Also, we have found the scavenging effect of adding a small amount of Si element to restrain the crystallization of $(Al + Cu)_{13}Fe_4$. Consequently, the single Al–Cu–Fe I-quasicrystal could be directly grown from the melt at 1073 K by choosing the molten alloy with a composition of $Al_{57.7}Cu_{37.7}Fe_{3.5}Si_{1.1}$. The grown single Al–Cu–Fe I-quasicrystal has been reported to show distinct facet planes and sharp back scattering X-ray Laue spots.[11] However, the detail evaluation of the quasicrystallinity of the single Al–Cu–Fe I-quasicrystal has not been achieved.

The aim of this paper is to prepare the single quasicrystal with high quality using the Czochralski method, and to evaluate the quasicrystallinity of the single $Al_{64}Cu_{23}Fe_{13}$ I-sample using X-ray diffraction analysis.

2. Experimental Procedure

The single $Al_{64}Cu_{23}Fe_{13}$ I-quasicrystal was prepared by the Czochralski method with following growth conditions;
  (1) molten alloy composition of $Al_{57.7}Cu_{37.7}Fe_{3.5}Si_{1.1}$,
  (2) growth temperature of 1073 K,
  (3) seed composition of $Al_{64}Cu_{23}Fe_{13}$, and
  (4) growth rate of about 0.05 μm/s.

The composition of the grown single Al–Cu–Fe I-quasicrystal was determined by Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The microstructure of the single Al–Cu–Fe I-quasicrystal was examined by high-resolution transmission electron microscopy (HRTEM). In HRTEM observation, a 400 kV electron microscope (JEM-4000EX) with a resolution of 0.17 nm was used. To determine the quality of the single Al–Cu–Fe I-quasicrystal, X-ray diffraction structural analysis was performed using Mo Kα radiation monochromated by flat highly oriented pyrolytic graphite (HOPG) with a conventional four-circle X-ray diffractometer (Rigaku AFC-5) operated at 40 kV and 20 mA. Detailed line-profiles of Bragg reflections along three different directions of 2-, 3- and 5-fold symmetrical axes were measured in the Q-scan mode, which means that a step scan with equal intervals were carried out in reciprocal space. High-resolution determination of both positions and peak-widths in the scans, which corresponds to θ-2θ scan, was achieved using a sharp slit with a horizontal width of 0.067? and a vertical width of 0.5° was used. The momentum resolution along the three directions is 3.3×10^{-2} nm^{-1}.

3. Results and Discussion

Figure 1 shows photo images of the growing single Al–Cu–Fe I-quasicrystal by the Czochralski method. The seed qua-
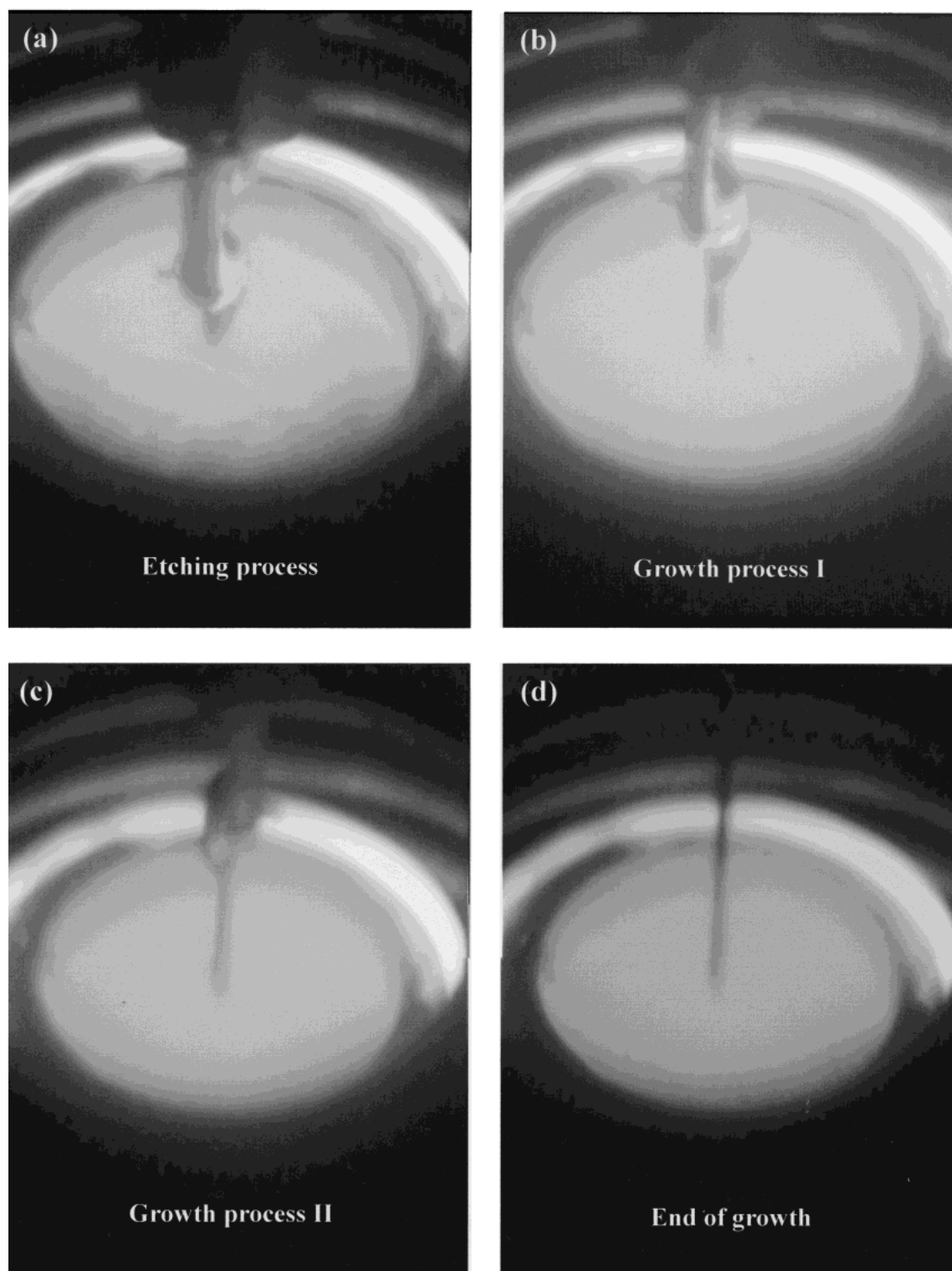
Single Al$_{64}$Cu$_{23}$Fe$_{13}$ Icosahedral Quasicrystal Growth

Fig. 1 Photo images of the growing single Al$_{64}$Cu$_{23}$Fe$_{13}$ I-quasicrystal by the Czochralski method, etching process (a), stable growth process (b), (c) and end of the growth (d).

sicrystal was prepared by the Bridgman Method,[11] and cut off into a quadrangular pyramid shape. The seed quasicrystal was set the growth direction in parallel with a 3-fold symmetry axis. Because the 3-fold direction is the preferential growth direction of an I-quasicrystal. To keep on the clean molten al-loy surface, the multi-layered crucible is composed by the in-ner P-BN crucible, outer BN crucible and Mo susceper. How-ever, the Czochralski method in this study is not a special one but a ordinary method as shown in Fig. 1. In the growth of sin-gle Al–Cu–Fe I-quasicrystals by the Czochralski method, an
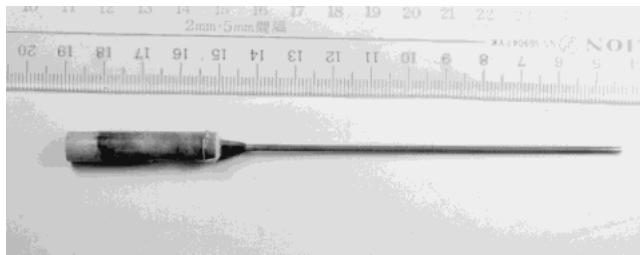
Fig. 2 Outer appearance of the grown single $Al_{64}Cu_{23}Fe_{13}$ I-quasicrystal.

Fig. 3 FWHM changes as a function of and $Q_\perp$ (a) and Bragg reflections shift from ideal position as a function of $Q_\perp$ (b) along 2-, 3- and 5-fold symmetrical axes.

etching process should be a most important process to grow up the single quasicrysals with superior quasicrystallinity. Because the liquid composition and growth temperature are limited in too narrow ranges to accomplish the necking process by the growing temperature change. Since the tip of a seed quasicrystal is composed of a single I-grain, the necking process can be substituted by a careful etching process. In actually, there is no difference in the diameter of the growing single I-quasicrystal as shown in Fig. 1. Figure 2 shows the outer appearance of the grown single I-quasicrystal by the Czochralski method. The length of the single I-quasicrystal is about 100 mm, and the diameter is about 2 mm. In order to keep on the superior structural quality of the single I-quasicrystal, the diameter of the growing single I-quasicrystal should be restricted less than 2 mm, whose value can be determined by the previous experimental data.

According to the theoretical explanations, the effects of the phason strain on the X-ray diffraction patterns can be divided into two classes. One is the random phason strain. In this case, the peak profile causes broadening of the FWHM with $Q_\perp$ dependence.[12] The second case is the linear phason strain. In this case, the peak show shifts from the ideal positions proportional to $Q_\perp$. So that, to evaluate the quality of the grown single Al–Cu–Fe I-quasicrystal by the Czochralski method, the FWHM and peak shifts of the reflection peaks along 2-, 3- and 5-fold symmetrical axes were measured by X-ray diffractometry using a sphere-shaped single I-sample of 0.3 mm in diameter which was cut off from master single I-quasicrystal. The FWHM along 2-, 3- and 5-fold symmetrical axes are plotted against $Q_\perp$ in Fig. 3(a). The FWHM has no $Q_\perp$ dependence. The peak shifts from the ideal Bragg reflections are plotted as a function of $Q_\perp$ in Fig. 3(b). As can be seen in the figure, for all directions, the shifts has no $Q_\perp$ dependence. Furthermore, the lowest value of the FWHM of the present single Al–Cu–Fe sample have same magnitude to that of the single Al-Pd-Mn sample,[13] which is known to be a high quality I-quasicrystal. These facts mean that the grown $Al_{64}Cu_{23}Fe_{13}$ I-quasicrystal by the Czochralski method in this study is almost phason free I-structure. The grown single Al–Cu–Fe quasicrystal was also examined using a HRTEM technique. Figure 4 shows a HRTEM image of as grown single Al–Cu–Fe sample, taken with the incident electron beam along a 5-fold axis. A Fourier diffractogram of the HRTEM image is also shown on the right side in Fig. 4. In the HRTEM image, one can see that all of lines of bright dots have no kink and no dead-end. These facts mean the phason free structure in the grown single Al–Cu–Fe sample in atom scale. Consequently, the grown single Al–Cu–Fe sample exhibits superior quasicrystallinity in the both of macro- and microscopic studies.
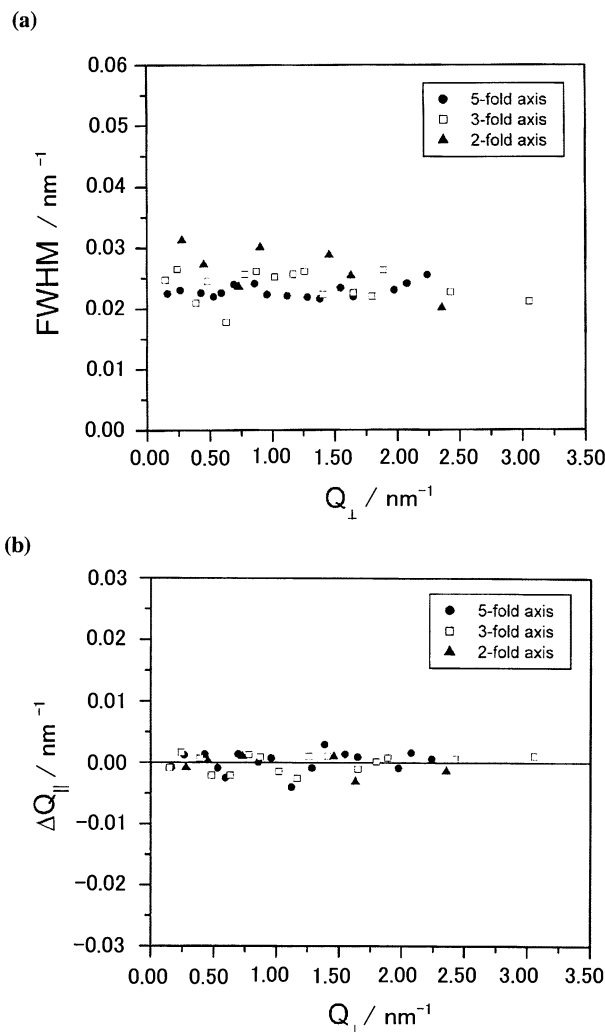
4. Conclusions

The single $Al_{64}Cu_{23}Fe_{13}$ I-quasicrystal was prepared by the Czochralski method, which is peculiar to the etching process to keep on the same diameter during the growing-up process. The grown single $Al_{64}Cu_{23}Fe_{13}$ sample in this study shows superior quasicrystallinity, which can be estimated by no $Q_\parallel$ and $Q_\perp$ dependency of FWHM values of diffraction peaks along 2-, 3- and 5-fold symmetry directions. We conclude the single $Al_{64}Cu_{23}Fe_{13}$ I-quasicrystal is almost phason free quasicrystalline structure.

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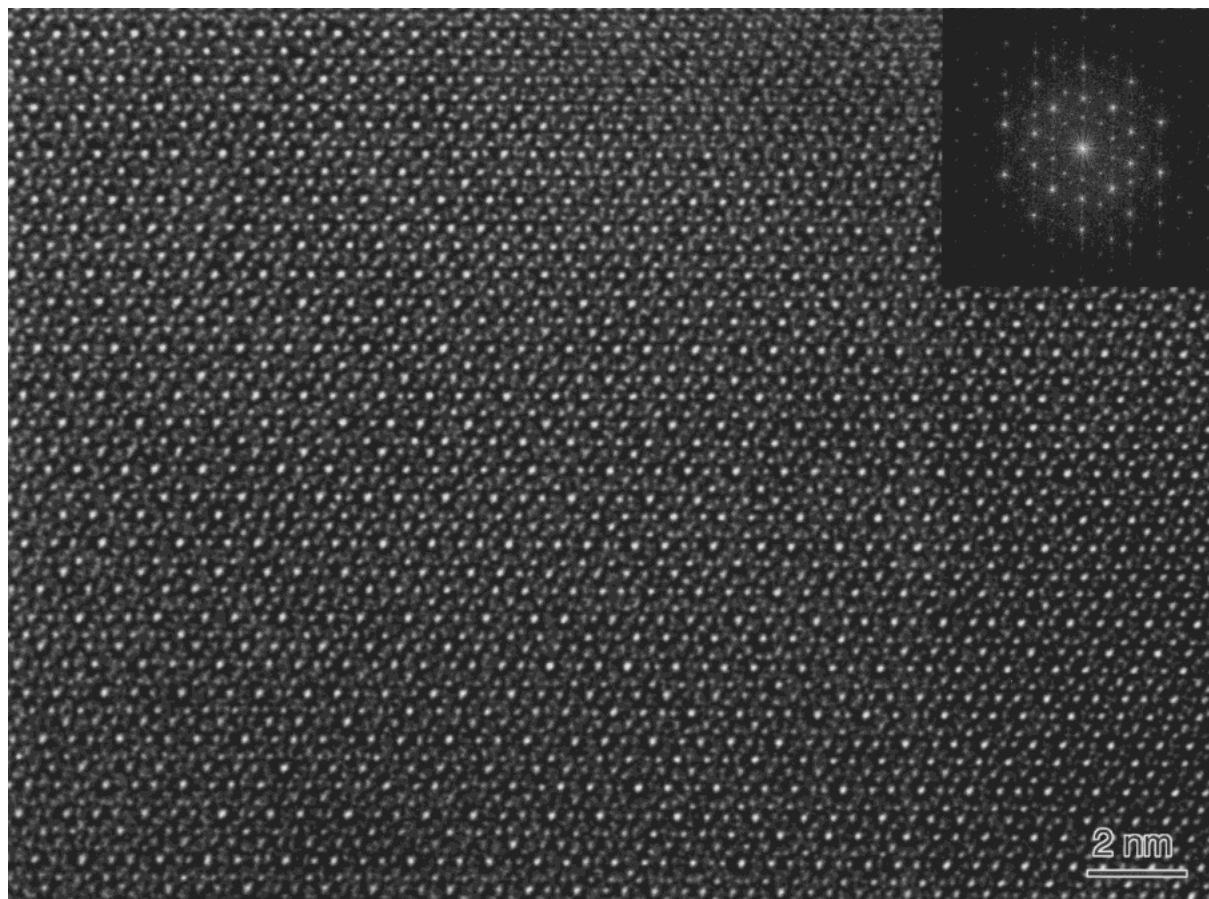Fig. 4   HRTEM image of as grown single Al$_{64}$Cu$_{23}$Fe$_{13}$ I-quasicrystal with incident electron beam along a 5-fold axis. Digital diffractogram of the HRTEM image on right side in this figure.

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