Growth of a Single Al_{64}Cu_{23}Fe_{13} Icosahedral Quasicrystal Using the Czochralski Method and Annealing Removal of Strains

Yoshihiko Yokoyama,¹ Ryunosuke Note,² Kenzo Fukaura,¹ Hisakichi Sunada,¹ Kenji Hiraga² and Akihisa Inoue²

¹Faculty of Engineering, Himeji Institute of Technology, Shosha, Himeji 671-2201, Japan
²Institute for Materials Research, Tohoku University, Katahira, Aobaku, Sendai 980-8577, Japan

Phase relations between the liquid and the solid icosahedral (I-) phases were examined at different temperatures to determine the growth condition of a single Al–Cu–Fe I-quasicrystal using the Czochralski method. The composition of the single I-quasicrystal was chosen to be Al_{64}Cu_{23}Fe_{13} due to the superior thermal stability. We found that the liquid composition, which equilibrates to the Al_{64}Cu_{23}Fe_{13} I-phase at 1073 K, was Al_{17.7}Cu_{27.7}Fe_{32.5}Si_{11}. Based on the phase relation, production of a single Al_{64}Cu_{23}Fe_{13} I-quasicrystal was attempted by using the Czochralski method. As a result, we succeeded in the growth of a single Al_{64}Cu_{23}Fe_{13} I-quasicrystal, and we also measured the Vickers hardness of annealed single I-quasicrystal samples with different anneal times to estimate the structural improvement by annealing.

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1. Introduction

Preparation of a single quasicrystal with high structural quality is an important procedure to reveal the intrinsic properties of quasicrystals. The processes of single quasicrystal growth include the Czochralski method and the floating zone method (traveling solvent type). Control of incongruent solidification is easier with the Czochralski method than with the floating zone method, because controlling the floating zone (e.g. shape, composition, and temperature) for a long time, over one month, is difficult. In the Al–Cu–TM alloy system,¹ the liquid phase in equilibrium with the I- or decagonal (D-) quasicrystal is only located in a Cu-enriched area. This is very different from Al–Pd–Mn² and Al–Ni–Co³ systems, where the liquid composition in equilibrium with the I- or D-phase is located in an Al-enriched region. Al–Cu–Fe ternary phase diagrams, which included an I-phase as an unknown phase, had already been provided⁴–⁶ before the discovery of the Al–Cu–Fe I-phase in 1987.⁷ These phase diagrams pointed out the difficulty of single quasicrystal growth from a melt because there is no two-phase (I + L) region (L: liquid), and only the λ₂-phase was observed as a primary crystal in the wide composition range of Fe + Cu < 40 at%. The primary λ₂-phase was reported⁸ to be a family of the λ₁-phase with an Al₁Fe₂ orthorhombic structure with over 5 at% Cu. I-phase formation was reported by Dong et al.⁹ with the peritectic reaction of L + λ₂ → I. This quasicrystal formation mechanism was also different from Al–Pd–Mn and Al–Ni–Co systems because the primary solid phase of the I-phase formation peritectic reaction was a β₃-phase with a cubic CsCl type structure. The β₃-phase was only seen in much higher temperatures in the Al–Cu–Fe system, and was recognized in the λ₂-phase formation reaction to the peritectic reaction between the liquid and the β₃-phases. Since Al₁₁Fe₁₃-type intermetallic compounds exhibit superior thermal stability in an Al–Cu–Fe alloy, the primary crystal of the I-formation peritectic reaction might not be a cubic β₃-phase but an orthorhombic λ₂-phase. The same I-phase formation mechanism was observed in Al–Cu–Ru, Al–Cu–Os, and Al–Pd–Re systems. This indicates the difficulty of I-quasicrystal growth from a melt in these alloy systems.⁸

The aim of this paper is to reveal the phase relation between the I-phase and the liquid phase in a two-phase (I + L) region, which can contact a single liquid phase region. Several partial isothermal sections, including an I-phase, were examined in this work. Based on these phase diagrams, we attempted to grow a single Al–Cu–Fe I-quasicrystal from a melt using the Czochralski method.

2. Experimental Procedure

The samples used in the present study were ternary Al–Cu–Fe alloys in a compositional range from 5 to 45 at% Cu and from 0 to 25 at% Fe. These alloy ingots were prepared by arc melting in an argon atmosphere. The alloys were annealed at several temperatures for 173 to 720 ks to obtain an equilibrium state. Water quenching was performed after the anneal treatment to freeze the structure, which could reveal the compositional relation between the solid and liquid phases. The compositions of several phases in the quenched samples were determined by an electron probe microanalyzer (EPMA). Quenched structures were observed by a scanning electron microscope (SEM). Single quasicrystallinity and orientation determination were examined by backscattering X-ray Laue diffractometry. The compositions on the top and bottom sides of the grown single I-quasicrystal were examined by inductively coupled plasma-emission mass spectroscopy (ICP-MS).

3. Results and Discussion

Pseudo-binary phase diagrams of a Cu-enriched compositional area provide useful information for research into a molten alloy that can crystallize an I-quasicrystal as a primary crystal, because the melting point of the Al–Cu–Fe de-
creases significantly in the Cu-enriched compositional area. Figure 1\(^5\) shows an Al\(_{17-x}\)Cu\(_x\)Fe\(_3\) (\(X = 0\) to \(40\) at\%) pseudo binary phase diagram that was extracted from a study reported by Phillips in 1953. The distinctions among the Al\(_3\)Fe, \(\lambda_2\)- and \(\lambda_1\)-phases, and \(\beta\)- and \(\beta_2\)-phases were not described in his report; we presumed that Al\(_3\)Fe and \(\beta\) represent the \(\lambda_2\)-phase and \(\beta_2\)-phase in Ref. 4). In this paper, the names of the phases in the Al–Cu–Fe system follow those in Ref. 4). There is no description of an I-phase in his reports, whereas some other reports\(^9,10\) suggest the existence of the I-phase shown in Fig. 1. For example, Prevarskiy\(^9\) reported the existence of a two-phase (I + L) region in the same compositional range as in Fig. 1. Furthermore, our previous report\(^1\) suggested that the liquid composition with equilibrium to the I-phase was located in the narrow region around Al\(_{63}\)Cu\(_{37}\)Fe\(_3\) at 1073 K. The Al\(_{67-x}\)Cu\(_x\)Fe\(_3\) pseudo binary phase diagram shown in Fig. 1 should be modified to contain the I-phase. The structure of the I-quasicrystal was limited in Cu-enriched composition (\(>23\) at\%) in the Czochralski method because the liquid composition in equilibrium with the I-phase was located in a more Cu-enriched region. The structural change of an Al–Cu–Fe I-quasicrystal due to annealing was examined by Y. Calvayrac et al.\(^12\) using Al\(_{60}\)Cu\(_{30}\)Fe\(_{15}\) and Al\(_{63}\)Cu\(_{37}\)Fe\(_{12}\) alloys, and a nearly single I-phase was obtained in the Al\(_{63}\)Cu\(_{37}\)Fe\(_{12}\) alloy by full annealing treatment at just below the resolve temperature. Figure 2 shows SEM images of the annealed samples with nominal composition of Al\(_{64}\)Cu\(_{32}\)Fe\(_{12}\) at 1073 K for 180 ks (a), 360 ks (b), and 720 ks (c). The Al\(_{64}\)Cu\(_{32}\)Fe\(_{12}\) composition was determined by preliminary experiments to estimate the thermal stability in Al–Cu–Fe I-alloys (not shown); this Al\(_{64}\)Cu\(_{32}\)Fe\(_{12}\) composition was also close to the Al\(_{63}\)Cu\(_{37}\)Fe\(_{12}\) composition, which was described as a stable I-phase composition in Ref. 12). Most of the sample was composed of I-phase, and the second phase was seen in interfaces among the I-phases. In Fig. 2, the structure becomes a more homogeneous one with annealing time. This indicates that the Al\(_{64}\)Cu\(_{32}\)Fe\(_{12}\) I-phase demonstrated superior thermal stability. Structural changes of these three samples were examined by X-ray diffractometry, as shown in Fig. 3. The X-ray diffraction spectra of the I-phase in this figure became strong with annealing time, and most of the X-ray spectra were identified as those of I-phase for 720 ks annealing at 1073. The second phase was identified as the \(\chi\)-phase with a hexagonal structure, and it can be seen as an Al\(_{62}\)Cu\(_{34}\)Fe\(_{14}\) (Al\(_3\)Cu\(_{10}\)Fe) ternary intermetallic compound. Figure 4 shows the Al–Cu–Fe constitutional phase diagram. The second phase of the \(\chi\)-phase can be seen in this phase diagram. Since the \(\chi\)-phase has no phase relation with the I-phase, the \(\chi\)-phase was probably formed by the remaining liquid quenching. As seen in Figs. 3 and 4, the second phase has a tendency to disappear with annealing. Consequently, we selected Al\(_{63}\)Cu\(_{37}\)Fe\(_{13}\) as an ideal I-quasicrystal composition in an Al–Cu–Fe system because of its superior thermal stability.

Systematic studies of Al–Cu–Fe phase diagrams were carried out, and they revealed the liquid composition in equilibrium with the Al\(_{64}\)Cu\(_{32}\)Fe\(_{12}\) I-phase; some of them are shown in Fig. 5. Partial isothermal sections in the Cu-enriched area were investigated by three alloys with the nominal compositions of Al\(_{63}\)Cu\(_{37}\)Fe\(_{13}\), Al\(_{61}\)Cu\(_{38}\)Fe\(_{13}\), and Al\(_{60}\)Cu\(_{39}\)Fe\(_{13}\) to avoid the complicated phase relation between the I- and other solid phases. The boundary between the two-phase (I + L)
region and the single L region was observed in a much narrower composition area than that of previous reports.\textsuperscript{5,9} These isothermal sections indicated that the composition of the I-phase in equilibrium with the liquid phase becomes a Cu-enriched one with decreasing temperature. Second phase precipitation may occur at low temperatures. The growth temperature of the I-phase must be higher in the Czochralski method to avoid second phase formation, and we also kept the growing I-quasicrystal composition as Al\textsubscript{64}Cu\textsubscript{23}Fe\textsubscript{13}. Control of the liquid composition and the growth temperature are important factors in the Czochralski method to keep a stable I-quasicrystal growing. However, compositional control of the molten alloy was difficult in the Al–Cu–Fe ternary alloy system because of the much narrower compositional range of the boundary between the (I + L) and L regions. To solve this problem, the stability of the primary I-crystallization was improved\textsuperscript{11} by adding a small amount of Si, and the primary $\lambda_2$-crystals were completely eliminated by the cyclic melting process. The structural and compositional changes of the two-phase (I + L) region of the Al\textsubscript{69}Cu\textsubscript{27}Fe\textsubscript{4}Si\textsubscript{1} quenched samples after annealing at 1073, 1023, and 923 K are shown in Fig. 6. Adding a small amount of Si did not change the phase relation between the liquid and the I-phases. However, the primary $\lambda_2$-crystals are removed entirely from the molten alloy by the preliminary cyclic melting process. This figure clearly reveals that Al\textsubscript{57.7}Cu\textsubscript{37.7}Fe\textsubscript{3}Si\textsubscript{1} is the optimum composition of a molten alloy that can crystallize an Al\textsubscript{64}Cu\textsubscript{23}Fe\textsubscript{13} I-quasicrystal as a primary crystal. The temperature and compositional ranges of liquid that can crystallize Al\textsubscript{64}Cu\textsubscript{23}Fe\textsubscript{13} I-quasicrystal as a primary crystal are too narrow to control the necking process by growing temperature changes. We attempted to use this phase relation for the growth of a single Al\textsubscript{64}Cu\textsubscript{23}Fe\textsubscript{13} I-quasicrystal with the Czochralski method. We
finally succeeded in growing an I-quasicrystal from the melt under the conditions below.

1. The molten alloy composition was Al_{57.7}Cu_{37.7}Fe_{3.5}Si_{1.1}
2. The growth temperature was 1073 K
3. The seed quasicrystal composition was Al_{64}Cu_{23}Fe_{13}

The outer appearance of the grown Al-Cu-Fe I-quasicrystal is shown in Fig. 7. A seed quasicrystal was prepared by the Bridgman Method\textsuperscript{[11]} and cut into a quadrangular pyramid shape. The seed quasicrystal was set at a three-fold direction to the growth direction. The necking process was substituted for careful etching since the tip of the seed quasicrystal was composed of a single I-grain. The single quasicrystallinity of the I-quasicrystal growing toward a three-fold direction could be confirmed by the growth morphology, which appeared to be a hexagonal prism shape, as shown in Fig. 8(a). The growth morphology of the I-quasicrystal along a three-fold direction was considered to simply be an expanded dodecahedron shape oriented toward a three-fold direction. The grown I-quasicrystal in Fig. 8(a) was characterized by distinct three-facet planes due to the hexagonal prism shape. Backscattering X-ray Laue diffraction patterns were taken from six different points on the bottom side to determine the single quasicrystallinity, and all of them were equal. One of them is shown in Fig. 8(b) as an example. The symmetry of the backscattering X-ray Laue diffraction pattern was equivalent to that of the single I-quasicrystal shown in Fig. 8(a). The orientation of the grown I-quasicrystal was also equivalent to that of the seed quasicrystal. Consequently, we concluded that the single grown I-quasicrystal was a sin-
gle I-quasicrystal. The slow growth rate was the most important factor for avoiding compositional deviation in the growth of the single I-quasicrystal because much more extensive compositional redistribution is required to grow the I-solid phase. The top and bottom side compositions of the single I-quasicrystal were examined by the ICP-MS method and were Al_{65.5}Cu_{22.2}Fe_{13.3} and Al_{63.4}Cu_{23.7}Fe_{12.7}. The analyzed positions are shown in Fig. 7 and marked “Top” and “Bottom.” The compositional deviation was less than 0.6 at%, and the growth rate of the single I-quasicrystal was about 0.05 μm/s. This growth rate was the smallest value in a series of quasicrystal growths in Al-based ternary alloy systems, though the growth rate should be smaller yet to prepare a single I-quasicrystal with superior quality.

The annealing treatment of a single quasicrystal is an important procedure for removing strains and unsuitable atom replacements that are introduced by the unidirectional growth in the Czochralski method. In this study, we attempted to estimate the quality of the I-quasicrystal by Vickers hardness, the value of which is affected by strains and unsuitable atom replacements. A higher Vickers hardness is caused by a more superior structural quality of the quasicrystal. The sample used for the hardness measurement is shown in Fig. 9(a). The rhombohedron shape was formed by three paired five-, three-, and two-fold symmetrical planes, which were confirmed by the backscattering X-ray Laue diffraction patterns shown in Figs. 9(b), (c), and (d). The rhombohedron sample was cut from the bottom part of the single I-quasicrystal under the conditions below.

1. The three-fold symmetrical plane was perpendicular to the growth direction.
2. The two-fold symmetrical plane was perpendicular to the three-fold symmetrical plane.
3. The five-fold symmetrical plane was perpendicular to the two-fold symmetrical plane, and the angle between the five- and three-fold symmetrical planes was about 79 degrees.

Figure 10 shows the Vickers hardness changes of several symmetrical planes as a function of the annealing time. The load value in the micro Vickers hardness measurement was determined by the indented surface morphology with no cracks. The maximum load to measure micro Vickers hardness with
no cracks was 0.254 N; the apparent hardness was usually larger at over 0.254 N due to the formation of cracks. The three-fold symmetrical plane showed the highest Vickers hardness of several symmetrical planes in the grown state; this phenomenon was equal to that of a single Al30Pd30Mn10 I-quasicrystal,14) where the three-fold symmetrical plane is perpendicular to the growth direction. Hardness anisotropy was eliminated by annealing treatment, and the hardness values of several symmetrical planes were similar, about 810 HV for over 10 ks of annealing time. Each Vickers hardness value increased with annealing time and saturated at over 360 ks. The lengths of the error bars of several symmetrical planes shortened with annealing time. Figure 10 shows that the hardness of the Al64Cu23Fe13 I-phase was about 810 HV with no orientational dependence. The figure also indicates the optimum annealing conditions to remove the strains and unsuitable atom replacements; the annealing temperature and time were 1073 K and over 360 ks.

4. Summary

Some partial isothermal sections were prepared to determine the tie lines between the I- and liquid phases at several temperatures. These tie lines between the I- and liquid phases indicated that the liquid composition was in equilibrium with the Al42Cu23Fe13 I-phase at high temperatures. Growth of a single Al64Cu23Fe13 I-quasicrystal was attempted based on this data by using the Czochralski method. The results obtained can be summarized as follows.

(1) Adding a small amount of Si element effectively prevents $\lambda_2$-crystallization. The optimum molten alloy composition was Al37.5Cu7.5Fe3.5Si1.1, which is in equilibrium with the Al64Cu23Fe13 I-phase at 1073 K. The molten alloy was treated by preliminary cyclic melting to avoid $\lambda_2$-crystallization.

(2) A single Al64Cu23Fe13 I-quasicrystal was grown from the melt using the Czochralski method.

(3) Annealing treatment is a useful procedure for removing strains and unsuitable atom replacement, which could be estimated by the Vickers hardness. Annealing conditions with the temperature at 1073 K and the time over 360 ks are suggested to remove strains and unsuitable atom replacement.

REFERENCES