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Abstract
The phase equilibria of the Al-Cu-Fe quasicrystalline phase (y phase) is complex and conventional crystal growth techniques like the Bridgman and Czochralski methods are not applicable in preparation of large crystals. Large single grains of the y phase been have prepared by either slow cooling or isothermal anneals. In the later technique, arc melted ingots were subjected to either single or multiple heat treatments between 825 and 840°C to encourage grain growth. Following heat treatment, grains of the icosahedral phase are found either as isolated pentagonal-faceted crystals within the ingot or within clusters of intergrown grains. The growth of the large grains is independent of the sample processing history of the sample, is facilitated by the presence of liquid at the growth temperatures and is constrained by the physical dimension of the ingot. The microstructure of both grain types is similar containing a minor quantity (on the order of 5–10 %) of a second phase and a high degree of porosity in the as-grown state. The second phase is usually present as a thin layer between adjacent grains or associated with a pore within a single grain. The grain porosity is distributed throughout the ingot. These defects can be removed through post-growth hot isostatic pressing and anneal treatments.

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PROCESSING OF AL-CU-FE SINGLE GRAINS

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ABSTRACT

The phase equilibria of the Al-Cu-Fe quasicrystalline phase is complex and conventional crystal growth techniques like the Bridgman and Czochralski methods are not applicable in preparation of large crystals. Large single grains of the $\psi$ phase have prepared by either slow cooling or isothermal anneals. In the later technique, arc melted ingots were subjected to either single or multiple heat treatments between 825 and 840 °C to allow for grain growth. Following heat treatment, grains of the icosahedral phase are found either as isolated pentagonal-faceted crystals within the ingot or within clusters of intergrown grains. The growth of the large grains is independent on the processing history of the sample, facilitated by the presence of liquid at the growth temperatures and is constrained by the physical dimension of the ingot. The microstructure of both grain types are similar containing a minor quantity (on the order of 5-10 %) of a second phase and a high degree of porosity in the as-grown state. The second phase is usually present as a thin layer between adjacent grains or associated with a pore within a single grain. The porosity is spread throughout the ingot. These defects can be removed through post-growth hot isostatic pressing and anneal treatments

INTRODUCTION

Quasicrystalline alloy systems contain complex phase equilibria that require careful considerations when attempting to prepare these materials in single crystal form. Since the discovery of thermodynamically stable quasicrystals, large improvements have been made in the size; quality and availability of single grain samples of some quasicrystalline alloys while other systems remain more challenging. The development of methods for preparation of single grains of the icosahedral $\psi$ phase in the Al-Cu-Fe alloy system has lagged behind other alloy systems primarily due to inability of accessing the $\psi$ phase via the liquid. Referring to the suggested liquidus surface [1], the icosahedral phase $\psi$ in the Al-Cu-Fe system forms during solidification via the peritectic reaction, $P_1$, at 860 °C: $L + \beta$ (FeCuAl) + $\lambda$(Al$_{13}$Fe$_4$) $\rightarrow \psi$ [1,2]. Furthermore the primary solidification field for the $\psi$ phase is quite narrow both in composition and temperature and is centered far from the composition of solid $\psi$ phase.

Previous work on the preparation of single grains of $\psi$ - Al$_{63}$Cu$_{25}$Fe$_{12}$ [3-5] used an annealing method in which multiphase samples were heated to just below the peritectic reaction at 860 °C for 4 days. Stoichiometric starting material was cast from the liquid state and then melt spun or rapidly solidified into ribbons or flakes. The size of crystals extracted was reported to be typically less than a millimeter in size. Krakow et.al. [6] also reported the growth of large grains of the icosahedral phase using a single annealing treatment below the peritectic temperature. Ingots of nominal composition Al$_{63}$Cu$_{25}$Fe$_{12}$ were induction melted and cooled. The ingots were then annealed at 840 °C for several days and faceted grains were extracted from
the ingot. Ishimasa and Mori [7] were able to produce single grains of the $\psi$ - $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$, 3mm in diameter, using a slow cooling process through the peritectic reaction followed by a 50 hour anneal at 822 °C. Ishimasa noted that grain growth in their specimen was not uniform across the sample and that grain growth seemed to be associated with the formation of liquid during the annealing treatment above the peritectic temperature. Furthermore, grain growth was not observed if the lower temperature anneal was omitted suggesting that both the formation of liquid and annealing below the peritectic temperature was necessary for the growth of large grains.

We recently described a processing method for the preparation of large single grains of $\psi$ phase using multiple isothermal anneals to enhance the growth of the single grains of icosahedral Al-Cu-Fe [8,9]. Stoichiometric $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$ were chill cast and then annealed at temperatures between 825 and 840 °C for periods of time from 14 to 28 days and yielded isolated faceted grains as large as 5 mm x 5mm x 10 mm. It was also apparent, especially in the second composition, that liquid was present at the annealing temperatures even though the peritectic temperature was not exceeded. We speculated that the grain growth was a direct result of the multiple heat treatments analogous to abnormal grain growth or secondary recrystallization. In this paper we review the physical and structural changes during processing, discuss the results additional isothermal annealing experiments and microstructural characterization of the as-grown crystals and present evidence that confirms that liquid formation is a necessary condition for the observed exaggerated grain growth. As a consequence of this condition, the as-grown crystals contain a high density of defects (second phases and porosity) related to the presence of liquid.

**Figure 1** Suggested liquidus projection for the icosahedral region of the Al-Cu-Fe alloy system from Gayle et.al. [1]
**EXPERIMENTAL PROCEDURE**

Appropriate quantities of aluminum, copper and iron (99.99% purity, metals basis) are cleaned and arc melted into buttons weighing approximately 50 grams. The buttons are melted up to four times under an argon atmosphere to ensure compositional homogeneity. The buttons are then drop cast into a copper chill mold into ingots roughly 50-75 mm long. Ingots of compositions $\text{Al}_63\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_65\text{Cu}_{23}\text{Fe}_{12}$ in diameters of 12 mm and 25 mm were prepared. Ingots were sealed in quartz ampoules under a partial pressure of argon and heat treated isothermally at various temperatures between 750 °C and 835 °C for varying lengths of time between 7 and 28 days. Specifically, three heat treatments were employed; 1) two-step anneals at 825 °C and 835°C for 7 days each, 2) single isothermal anneal at 835 °C for 28 days and 3) homogenization anneal at 750 °C for 7 days followed by an isothermal anneal at 835 °C for 28 days. Differential thermal analysis (DTA) and microstructural characterization was conducted on samples both before and following heat treatments.

**RESULTS**

**As-Cast Ingots**

The as-cast microstructure of the ingots is shown in Figure 2. The structure consists of large dendrites of $\lambda$ ($\text{Al}_{13}\text{Fe}_4$) with icosahedral phase $\psi$ and $\beta$ phase in the interdendritic regions. This phase distribution is consistent along the length of the ingot although there is a slight increase in microstructural scale from the bottom to the top of the ingot, reflecting the variation in cooling rates during chill casting. Also note the relative low density of porosity present in the structure. Heating traces taken in the DTA, Figure 3, indicates the as-cast structure undergoes two major melting events below 900 °C. At approximately 695 °C, the fairly sharp endothermic peak most likely corresponds to the eutectic reaction $U_2, L + \psi \rightarrow \beta + \omega (\text{Al}_7\text{Cu}_2\text{Fe}_1)$, as shown in Figure 1. The second endothermic peak occurs over a wider temperature range and can be separated into two melting events. The initial deviation of heating trace from the baseline begins at onset temperature of approximately 835 °C and suggests a partial melting of the solid. Partial melting continues up to 877 °C where again a large release of heat suggests an isothermal reaction. Referring again to Figure 1, the isothermal reaction corresponds to the peritectic reaction $P_1, L + \beta + \lambda \rightarrow \psi$, whereas the partial melting prior to the peritectic reaction is the direct melting of the $\psi$ phase. The microstructural and DTA data is consistent with solidification sequence proposed by Gayle et.al. [1].

**Heat Treated Ingots**

A. **Macroscopic Examination**

The appearance of the chill cast ingots after heat treatment is similar irrespective of the number of heat treatments, annealing temperatures, or time at temperatures. Upon removal from
Figure 2 Microstructure of an Al$_{63}$Cu$_{25}$Fe$_{12}$ as-cast ingot. The structure consists of $\lambda$ dendrites surrounded by a mixture of icosahedral phase (light gray) and cubic phase (white).

Figure 3 Heating trace of the chill cast Al$_{63}$Cu$_{25}$Fe$_{12}$ alloy. Two major melting events at 695 °C and 877 °C are observed.
Figure 4 Comparison of the macro appearance of Al$_63$Cu$_{25}$Fe$_{12}$ ingots before and after heat treatment. Distortion, cracking and grain growth within the ingot is apparent.

In the furnace the ingots were distorted and evidence of partial melting could be observed as shown in Figure 4 for the Al$_63$Cu$_{25}$Fe$_{12}$ alloy composition. The upper ingot is an example of an as-cast ingot. The ingot has a uniform diameter and a smooth surface appearance. The two lower ingots were subjected to the two-step anneal treatment. The ingots have swelled, become distorted and crack and the surface has taken on a fine crystalline but porous appearance. This change in ingot appearance was also observed on the ingots following the homogenization anneal at 750 °C but prior to subsequent high temperature anneal. Evidence of partial melting can be seen on the left side of the middle ingot where liquid has exuded out from the ingot forming a small, globular appendage. Ingots of the slightly enriched aluminum composition, Al$_{65}$Cu$_{23}$Fe$_{12}$, exhibited the same behavior on heat treatment but the amount of liquid formed was greater, pooling in the bottom of the crucible.

Also evident in the center of the annealed ingots of Figure 4 is formation of large, single grains of the icosahedral phase that can be easily removed from the surrounding ingot. For the

Figure 5 Isolated single grains of icosahedral phase found in the interior of two-step annealed, 12-mm diameter ingots of Al$_{63}$Cu$_{25}$Fe$_{12}$. 
two-step annealing treatment of 14 days, the single grains are not found uniformly along the length of the ingot. This is clearly evident when the ingots are broken open and isolated grains exhibiting five-fold faceting, are found within the ingot as shown in Figure 5. The isolated grains appear to nucleate along the centerline of the ingot and grow outward until the surface of the ingot is reached. When annealing is conducted for longer times, the grains grow sufficiently large to impinge on each other, forming large agglomerations of inter-grown grains as shown in Figure 6. Isolated grains can still be found in these ingots. Low temperature, homogenization annealing at 750 °C had no effect on the physical changes described above nor did the low temperature treatment inhibit the growth of large grains during the subsequent high temperature anneals. The size of the grains formed in the long annealing treatments appears to be limited by
Figure 8 Microstructure of a single grain showing high levels of porosity with second phase adjacent to the pores.

the overall dimension of the ingot. When ingot diameter is doubled, the average size of the resultant grains increases by a comparable factor as shown in Figure 7.

B. Microstructural Characterization

Overall, the different annealing sequences had no apparent effect on the microstructure of the as-grown grains. In all cases, the isolated single grains were found to contain a small amount of second phase and a high degree of porosity as shown in Figure 8. The second phase was identified to be the cubic $\beta$ (CsCl) phase and was primarily located adjacent to a pore. The pores show a bimodal distribution with the smaller pores averaging approximately 25 microns in diameter whereas the larger pores were on the order of 80 microns. Total porosity levels were measured to be approximately 10% by volume.

The microstructure of the intergrown grains is similar to the isolated grains as shown in Figure 9. A thin layer of $\beta$ phase separates each grain from one another. In addition large porosity is found along the intergranular boundary suggesting that a liquid layer at the annealing temperature isolated the grains. Upon cooling from the growth temperatures the liquid solidifies to the $\beta$ phase and shrinkage porosity in the intergranular region.

DISCUSSION

The physical and structural changes observed in the annealing of Al-Cu-Fe chill cast ingots occur in two stages, low temperature chemical homogenization and exaggerated grain growth at high temperatures. These two stages can be correlated to the two distinct melting events as the ingots are heated.

A. Low Temperature Chemical Homogenization

The main physical changes occurring in the low temperature anneals are the chemical homogenization of the as cast structure and the swelling and distortion of the ingots. During this
first stage of annealing, there is a strong driving force for chemical homogenization as the as-cast structure is multi-phased, containing a mixture of high and low melting phases, and therefore chemically inhomogeneous. According to Gayle et.al. [1], alloys of composition Al\textsubscript{63}Cu\textsubscript{25}Fe\textsubscript{12} lie within the single phase icosahedral region between 700 °C and 800 °C. Upon heating above 695 °C, the formation of liquid aids in the homogenization of the structure by providing a medium for fast mass transport, however, the liquid is transient and ultimately the structure will become single phase. This homogenization process is analogous to the transient liquid phase sintering of powder metals [10].

It is well known in transient liquid phase sintering, large chemical differences between the solid and liquid phases coupled with differential rates of mass transport between species and phases can lead to swelling and distortion of the powder compact. This swelling or formation of porosity within the compact results from both the change in volume of liquid as it is consumed (solidifies) and the formation of Kirkendall porosity as the chemical species interdiffuse through the solid phases. The degree to which swelling occurs is proportional to the compositional differences between the phases and inversely proportional to the amount of liquid formed [10]. Unfortunately the phase equilibria of the Al-Cu-Fe system does not allow for wide variation of these parameters.

B. Exaggerated Grain Growth

The primary result of the different processing methods is that the ability to prepare large single grains of the icosahedral phase through heat treatment at 835 °C is unaffected by any prior heat treatment at lower temperatures and is insensitive the initial microstructure of the ingot. Therefore the conditions that favor the growth of large grains must exist at 835 °C. The DTA
results indicated the alloy begins to melt at approximately 835 °C and both the macrostructure and microstructure of the as-grown grains provide indirect evidence of the presence of liquid at the growth temperature. First the five-fold faceting of the grains must result from contact with a liquid phase, which allows the crystal the flexibility to grow surfaces of low energy that is not available in the solid state. Furthermore when the growth of the grains began to impinge upon another they remained separated by a layer of second phase, which is formed as the alloy is cooled, and the liquid solidifies. The separation of grains with a liquid layer also explains why significant porosity is found in the intergranular region. With the mixture of solid ψ and liquid, the grains of icosahedral are free to coarsen and grow.

The formation of liquid at the growth temperature is presumed to result from passing from the single-phase ψ field into a two-phase (ψ + Liquid) phase field. While an isothermal section of the phase diagram is not available for 835 °C, Gayle et.al. [1] determined the phase relations and solubility ranges for the ψ icosahedral phase at both 700 and 800 °C. The composition of the alloys used in this study lie entirely within the single-phase ψ region at these two temperatures. This is corroborated by the single-phase microstructure observed following homogenization at 750 °C. Gayle et.al. [1] also found that the stability range of the ψ phase shifts to higher Fe and lower Cu concentrations from 700 °C to 800 °C. Above 800 °C, the compositional stability is likely to continue to shift to higher Fe and lower Cu content. This is a common feature of peritectic systems and is shown in the schematic drawing in Figure 10.

**SUMMARY**

Large single grains of Al-Cu-Fe icosahedral ψ can be prepared by long-term thermal annealing treatments. Several physical and structural changes occur during heat treatment including swelling, distortion and cracking of the ingots. These physical changes can be
correlated to the formation of liquid at approximately 700 °C and the chemical homogenization of the as-cast structure. The ability to prepare large single grains of the icosahedral phase through heat treatment at 835 °C is unaffected by any prior heat treatment at lower temperatures and is insensitive the initial microstructure of the ingot, but relies on the presence of the liquid at the annealing temperatures. The growth of the grains is a result of the coarsening of existing grains within the liquid-solid mixture.

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