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The Determination of the Solidification Paths and the Liquidus Surface in the Quasicrystalline Region of the Al-Cu-Ru System

by

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INTRODUCTION

Preliminary measurements on the properties of quasicrystals have indicated that they may be useful as light-weight structural materials and hard, wear-resistant, non-stick surface coatings.^[1,2,3] In order to determine the applicability of quasicrystals to these areas, and to devise more applications, a more thorough understanding of the mechanical properties and deformation mechanisms is needed. This will only come when it is possible to produce larger and less flawed quasicrystals.^[2] Several studies are under way to develop a means of producing both fine-grained polycrystalline and single-crystal quasicrystals.^[1,4] But a lack of accurate phase diagrams for these materials, and a questionable understanding of the reactions that occur upon cooling from the liquid, are severely hindering these efforts.

The Al-Cu-Ru system has been shown to contain a phase region that exhibits icosahedral symmetry.^[5,6] This face-centered icosahedral (FCI) phase is stable at high temperatures, but the transformation kinetics of this phase are such that it can be maintained during slow cooling to room temperature in the absence of a second phase.^[5,6,7] The objective of this research is to study the solidification reactions and determine the liquidus surface in the quasicrystalline region of the Al-Cu-Ru system to determine if conventional slow-growth methods will be successful for growing single-quasicrystals.

Initial experimental work will cover a large portion of the known region of quasicrystalline stability. Studies will focus on reaction temperatures and solidification paths in order to qualitatively form the reaction schemes and liquidus surface. Subsequent work will focus more in depth on certain regions of the system to more accurately determine the reaction schemes and liquidus surface. In this research, the liquidus and reaction temperatures will be determined with differential thermal analysis (DTA), and the phases present and order of reaction will be identified by using powder X-ray diffraction, energy dispersive spectroscopy (EDS), standard optical microscopy and directional solidification (DS).

BACKGROUND

The discovery of icosahedral order in rapidly solidified Al_6Mn by D. Shechtman et al. in 1984 opened up a new field of study in materials science called quasicrystals.^[8,9] Before the discovery of quasicrystals it was generally believed that solid matter existed in only two states, crystalline and amorphous. Quasicrystals, however, are a general class of alloys that exhibit long range positional order but non-crystallographic orientational order.^[4,8,10] Sharp diffraction patterns have verified the existence of positional order and have revealed the lack of periodic translational order.^[5,8,9] Quasicrystals exhibit 5-fold symmetry, which is a forbidden symmetry for normal crystalline materials since pentagons cannot fill a plane without leaving voids and, hence, cannot be used as unit cells for crystalline materials. The energetics which cause the icosahedral phase to form and the nature of the atomic structuring which gives rise to the 5-fold symmetry are not well understood, but several models have been suggested to explain the formation of 5-fold symmetry.^[5]

One model used to describe the growth of quasicrystals is known as the icosahedral Glass model. It is the leading model for non-equilibrium quasicrystal growth.^[11] In this model atomic clusters join in a manner that preserves icosahedral orientation but does not necessarily preserve long range orientational order (Figure 1a).^[10,12] This model produces tears, or surfaces within the glass along which positional order breaks down. Growth algorithms have been developed that minimize these tears and result in diffraction peak widths that correspond well to experimental data.^[4,10] Another model describes the growth of quasicrystals using equilibrium rules to produce structures with infinite positional correlation lengths in thermodynamic equilibrium. Examples are the Penrose tiling and Random tiling models.^[4,10,12] The Penrose tiling model utilizes 36° and 72° rhombi (Figure 1b) and matching rules to fill space (Figure 1c). The Random tiling model utilizes tiles but does not require any long-range matching rules, only local growth rules. Figures 2a - 2f show the quasiperiodic structures resulting from the glass model (Figure 2a), and the Penrose (Figure 2c) and Random (Figure 2e) tiling models. The glass model yields blurry diffraction spots, as can be seen in Figure 2b. The random tiling model produces a quasiperiodic structure that resembles the Penrose model structure and yields similar diffraction patterns, but the peaks from the Random tiling model are surrounded by faint halos as can be seen in Figure 2f.^[4,10]

The discovery of metastable icosahedral phases maintainable to room temperature using conventional cooling rates opened up the study of quasicrystals to conventionally solidified samples. Before this discovery, all quasicrystals had been prepared by using rapid

solidification techniques.^[6,9] The metastability of the Al-Cu-Ru icosahedral phase was discovered by A. P. Tsai.^[6] Studies of the quasicrystals in this system showed that these quasicrystals generally lack the phason strain which is present in quasicrystals in other systems.^[13-15] In other words, the quasicrystals in the Al-Cu-Ru system are almost defect free. With these discoveries it became feasible to attempt to grow single-quasicrystals of Al-Cu-Ru by conventional slow growth methods. These single-quasicrystals could be used in inelastic-neutron-scattering measurements.^[16] These measurements are well defined for normal crystalline materials, and the study of this phenomenon in quasicrystals could lead to a better understanding of the atomic stacking sequences of quasicrystals which lead to the 5-fold symmetry. Single-quasicrystals could also be used in X-ray Debye-Waller factor measurements.^[7] The information provided by these measurements could establish whether the Penrose or Random tiling model best describes the structure of quasicrystals in Al-Cu-Ru. However, these experimental techniques require as large a single crystal as possible, and attempts at growing single-quasicrystals of $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$ using the Bridgman technique at Ames Laboratory have not been successful.^[17,18]

Figure 1: Pentagons and rhombi. (a) Arrangement of pentagons as per the Glass model. (b) 36° and 72° rhombi from the Penrose tiling model. (c) Structure formed from Penrose model with indicated matching rules. [a & b from reference 4, c from reference 5]

Figure 2: Growth models. The Glass model produces the structure shown in (a). Its calculated diffraction pattern (b) is blurry, implying too much disorder. The Penrose tiling model produces the structure shown in (c). Its calculated diffraction pattern (d) has bright, sharp peaks. The Random tiling model produces the structure shown in (e). Its calculated diffraction pattern (f) is surrounded by faint halos. [reference 10]

PREVIOUS STUDIES

Work performed by Shield et al. and others has shown that the FCI phase is not an equilibrium phase in Al-Cu-Ru at room temperature; rather, it is a high temperature phase that is stable above 700°C.^[6,7] Figures 3a - 3c show powder X-ray diffraction scans taken of as-spun $\text{Al}_{70}\text{Cu}_{20}\text{Ru}_{10}$ material annealed at 500°C and 800°C. The appearance of the FCI phase signature peak upon annealing at 800°C (indicated by arrow in Figure 3b) verifies its stability at high temperatures. The disappearance upon reannealing at 500°C (Figure 3c) proves that the FCI phase is metastable and reverts to the low-temperature tetragonal phase (note that the material in Figure 3b is not single phase FCI). Differential thermal analysis (DTA) measurements have verified this transformation (Figures 4a - 4d), and have shown the reaction temperature to be around 700°C.^[19]

However, it has been shown that the icosahedral phase can be maintained at room temperature and during slow-cooling from elevated temperatures in the absence of a second phase.^[7] Figures 5a - 5c show powder X-ray diffraction scans of as-spun material annealed at various temperatures. The sample was annealed at 800°C for a long enough time to produce single-phase FCI before it was annealed at 500°C. These plots verify the stability of the FCI phase in the absence of a second phase. Also, slow cooling from annealing at 800°C has been shown to produce only the icosahedral phase in the absence of a second phase.^[7] Figure 6 shows powder X-ray diffraction scans of slow-cooled pure $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$ which is the composition suggested by Shield to be a congruently melting quasicrystalline phase. This information suggests that the stability of the icosahedral phase is such that conventional solidification techniques should be successful in producing a single-quasicrystal if a composition can be found which does not produce any second phases upon cooling.

The existence of an approximant phase to the FCI phase in Al-Cu-Ru has also been studied by Shield et al.^[20] Approximant phases are normal crystalline phases which contain structurally similar units to those found in icosahedral phases. In the Al-Cu-Ru system, an approximant has been discovered which has been identified as simple cubic with a lattice parameter of $a = 12.38\text{\AA}$. It belongs to the point group $m\bar{3}$ and space group $\text{Pm}\bar{3}$.^[20] Figure 7 shows powder X-ray diffraction scans of the FCI phase and the cubic approximant phase. When this information is combined with the knowledge provided by inelastic-neutron-scattering measurements and X-ray Debye-Waller factor measurements, a much better understanding could be obtained of the atomic ordering which occurs to produce the 5-fold symmetry in quasicrystals.

Figure 3: Powder X-ray diffraction scans of $\text{Al}_{70}\text{Cu}_{20}\text{Ru}_{10}$. Sample was annealed at the following temperatures: (a) 500°C for 24 hours, which contains the tetragonal and Al_2Cu phases; (b) 800°C for 24 hours, which contains the FCI phase (signature peak marked with an arrow); and (c) at 500°C again, which no longer contains the FCI phase. [reference 7]

Figure 4: Differential thermal analysis scans showing FCI transformation temperature. (a) $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$, (b) $\text{Al}_{70}\text{Cu}_{15}\text{Ru}_{15}$, (c) $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ and (d) $\text{Al}_{70}\text{Cu}_{20}\text{Ru}_{10}$. The top scans are of material annealed at low temperatures to obtain the tetragonal phase, and the bottom scans are of material in the FCI phase, obtained by annealing at 800°C . The endothermic peaks (marked with an arrow) correspond to the transformation to the FCI phase. [reference 19]

Figure 5: Powder X-ray diffraction scans of as-spun material. Sample was annealed for 24 hours at the following temperatures: (a) 500°C, showing the pure tetragonal phase; (b) 500°C then 800°C, showing the FCI phase; and (c) 500°C, then 800°C and then again at 500°C, showing the irreversibility of the tetragonal to FCI transformation in the absence of a second phase. [reference 7]

Figure 6: Powder X-ray diffraction scan of $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$. Sample was cooled at 16°C/hr from 800°C to 450°C. This illustrates the kinetic limitations of the FCI to tetragonal transformation upon cooling. [reference 5]

Figure 7: Powder X-ray diffraction scans of $\text{Al}_{60}\text{Cu}_{25}\text{Ru}_{15}$. Sample was annealed at 800°C for (a) 24 hours and (b) 96 hours. In (a) the phases present are the FCI, Al_2Cu and AlRu . In (b) the material has transformed to a cubic approximant phase. The related diffracting maxima for the two phases are marked. [reference 5]

Attempts to grow single-quasicrystals of $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$ at Ames Laboratory have been performed using the Bridgman technique.^[17,18] The sample is first arc-melted into a homogeneous button and drop-cast into a copper mold designed to fit the alumina crucibles used. It is then superheated above the melting point using a platinum resistance furnace and slowly withdrawn out of the furnace to produce directional solidification. Initial results were less than successful as the crystals came out multiphase and very brittle. However, upon subsequent annealing, homogenization and quenching these multiphase ingots transformed to 100% FCI.^[17,18] Incorrect starting compositions, second phases precipitating during cooling, and a lack of understanding of the solidification reactions are possible explanations for the inability to successfully grow single-quasicrystals in the Al-Cu-Ru system. An equilibrium phase diagram could provide the necessary information to solve these problems, but a complete one is not available at this time.^[21]

OBJECTIVE

The objective of this research is to examine the quasicrystalline region of the Al-Cu-Ru system to determine a method of growing single-quasicrystals. The interest in this study is based on the need to understand the phase diagram and reaction schemes so that the correct starting composition can be determined to successfully produce single-quasicrystals using conventional slow-growth methods. Large single-quasicrystals are needed for use in inelastic-neutron-scattering studies and X-ray Debye-Waller factor measurements. The information provided by these studies may lead to the determination of the atomic arrangements that occur to produce 5-fold symmetry and the how these arrangements affect the properties of the alloy.

The initial samples will encompass a large portion of the Al-Cu-Ru system including the region where the quasicrystalline phase has been shown to exist. Differential thermal analysis (DTA) will be used to find the liquidus and solidification temperatures. The liquidus temperature is critical in the growth of single-crystals, and this can be determined with DTA.^[22,23] The phases present in an as-cast structure will be determined using optical microscopy, powder X-ray diffraction and energy dispersive spectroscopy (EDS). The solidification sequences and the dynamics of growth will be studied using directional solidification (DS). With powder X-ray diffraction a fine powder is used and very sharp diffraction peaks are generated which can be indexed to the phases present in the sample.^[24,25] With EDS, the composition of phases is determined by bombarding the sample with an electron beam and measuring the different energy levels of the electrons emitted from the sample.^[26] The main intent in using EDS is to determine the distribution of the ruthenium, so a standardless-semi-quantitative analysis software will provide sufficient information. The shape of the growth front, the composition of the solid and liquid phases at the growth front, the composition and transformation characteristics of the lower temperature phases, and the composition profile from the liquid to the solid can be determined with DS.^[27,28]

Figures 8a - 8c show the binary phase diagrams for the combinations of the three elements involved in this study. The intersection of the isopleths intended for initial study are marked on the Al-Cu (Figure 8a) and Al-Ru (Figure 8b) phase diagrams. These isopleths were chosen based on the ternary phase equilibria studied by Shield et al.^[5,7,19] Shield constructed approximate isotherms at 500°C (Figure 9a) and 800°C (Figure 9b) which provided the compositional region of phase stability of the face-centered-icosahedral (FCI) phase. The compositions studied in this work are plotted in ternary space in Figure 10. The FCI region is also shown on Figure 10 for reference.

Figure 8: Binary phase diagrams. (a) Al-Cu and (b) Al-Ru. The intersections of the 65 and 70 atomic percent aluminum isopleths are marked on both diagrams. [reference 29]

Figure 8 (cont.): (c) Cu-Ru. [reference 29]

Figure 9: Approximate isotherms. (a) 500°C and (b) 800°C. Filled circles mark the compositions studied for the determination of this figure. α = Al, θ = Al_2Cu , δ = Al_2Ru , ω = $\text{Al}_7\text{Cu}_2\text{Ru}$, L = liquid, ϵ = Al_6Ru , γ = Al_3Ru , β = AlRu , α' = α -AlCuRu (approximant), a and b were not indexable. [reference 19]

Figure 10: Ternary space plane showing compositions studied and FCI region.

PROCEDURE

For the initial samples, buttons weighing approximately 30 grams were made of $\text{Al}_{65}\text{Cu}_x\text{Ru}_y$ where x ranges from 35 to 10 atomic percent and y ranges from 0 to 25 atomic percent, and $\text{Al}_{70}\text{Cu}_x\text{Ru}_y$ where x ranges from 30 to 10 atomic percent and y ranges from 0 to 20 atomic percent, in increments of 5, by combining appropriate quantities of aluminum, copper and ruthenium (all >99.9% pure) in an arc-melter. The buttons were melted and turned 8 times to ensure complete mixing. Specimens were cut from these buttons and mounted in diallyl phthalate with a layer of copper filled diallyl phthalate on the face of each mount. The layer of copper powder was necessary for the mount to have good conductivity when used in a scanning electron microscope (SEM). Powder specimens for differential thermal analysis (DTA) runs and powder X-ray diffraction scans were prepared by crushing a part of each of the remaining arc-melted buttons using a mortar and pestle.

Liquidus temperatures were measured for the initial 65 and 70 atomic percent aluminum series samples using a Perkin-Elmer model DTA-1700 Differential Thermal Analysis furnace (Figure 11) with a System 7/4 Thermal Analysis Controller. The DTA-1700 furnace uses alumina cups to hold the sample and reference powders. For each run, approximately 55 mg of powder was used from each sample, and pure alumina powder was used as the reference material. The sample and reference cups were loaded into the furnace and the system was purged with flowing argon for 20 minutes in order to obtain an inert atmosphere. Both heating and cooling runs were performed using a rate of $10^\circ\text{C}/\text{min}$, and all samples were run under flowing argon (106 cc/min).

Powder X-ray diffraction scans of both series were run using a Philips PW 1830 X-ray Generator and a Philips PW 1820 θ - 2θ Powder Goniometer. The samples were prepared by coating a glass slide with vacuum grease and sprinkling the sample powder onto the slide covering an area of 4 cm^2 . The slide was then loaded into the θ - 2θ goniometer. All scans were run from 20° to 80° 2θ in increments of 0.05° 2θ with a duration of 3 seconds per increment. Copper K_α radiation was used for all scans. Standard optical microscopy was then conducted on all mounted samples, and optical micrographs were taken of representative areas. Finally, the mounted samples from both series were examined in a Cambridge S200 Scanning Electron Microscope (SEM) using a Tracor-Northern model 5500 Energy Dispersive Spectrometer (EDS) with a polymer thin window. Standardless semi-quantitative (SSQ) analysis software was used to qualitatively identify the phases present and the distribution of the ruthenium.

Figure 11: Schematic of the differential thermal analysis furnace. [Reference 30]

For the directional solidification (DS) experiments, preparation of the sample involved arc-melting the proper amounts of aluminum, copper and ruthenium (all >99.9% pure) into buttons of $\text{Al}_{65}\text{Cu}_{25}\text{Ru}_{10}$. These buttons were then used in a vacuum-static-casting process. For this process, an array of 8 quartz tubes of 4 mm ID was designed by cementing one end of the tubes into a fixture using refractory cement. This fixture was connected to a vacuum pump through a quick release valve. After superheating the buttons, the tubes were lowered into the melt and the quick-release valve was opened, causing the liquid to be sucked up into the tubes. The array was then raised above the melt to allow the rods to solidify.

The first attempt at making the rods was unsuccessful. The buttons were covered with a slag which is typical of this material. The slag prevented complete mixing of the buttons during the super-heat of the vacuum-static-casting run. Also, this sample expands a great deal very rapidly upon cooling due to the presence of the FCI phase, so the quartz tubes were shattered when the metal was sucked up into them. This contaminated the remaining liquid so the material was not salvageable. New buttons and a new quartz tube setup were made for a second vacuum-static-casting attempt. In order to save material, only 6 quartz tubes were used in the array for the second attempt. To prevent the slag from causing problems during the second attempt, the new buttons were drop-cast into an 0.6" copper chill-cast mold which caused the slag to solidify on top of the drop-cast, leaving clean metal for use in the second

vacuum-static-casting. But, the problem of expansion upon cooling again caused the quartz tubes to shatter as the metal cooled, and the rods broke into several pieces. However, enough rods were obtained for three DS runs. The pieces were cleaned by beadblasting them, which decreased the diameter of the pieces considerably but cleaned them sufficiently.

The directional solidification furnace is shown in Figure 12. The 5 mm ID recrystallized Al_2O_3 tubes used to hold the sample are closed at one end so the sample rod sits on the bottom of the tube. The tube is held in place with an o-ring seal connected to a vacuum/inert-gas system. An alumina stirring rod is inserted through a second o-ring seal at the top of the tube. A Pt/Rh furnace was used to melt the sample. The carriage, furnace and cold finger are moved upward on three ball-bushing guide-rods at a constant rate controlled by a computer connected to a stepper motor. For the runs the samples were heated under vacuum to 500°C . The system was then flushed twice with argon and backfilled to +2 psi with argon. The furnace then continued to heat the sample to the desired temperature. Once the furnace reached the desired temperature, the alumina stirring rod was run up and down through the liquid to cause the bubbles of trapped gas to rise out of the column of liquid. At this time the furnace assembly was raised at a rate of $61\text{ }\mu\text{m/sec}$ for 1 inch. The system was then allowed to stabilize for 60 minutes before the directional solidification run was started. After the run, the samples were quenched in water by releasing the o-ring seal holding the top of the Al_2O_3 tube allowing the tube to drop into a cold water bath.

The first DS run was performed at a temperature of 925°C and a speed of $5\text{ }\mu\text{m/sec}$. This temperature was chosen based on the DTA data available for the $\text{Al}_{65}\text{Cu}_{25}\text{Ru}_{10}$ sample, but upon inspection of the sample after the run it was discovered that the pieces were only partially molten. Three of the pieces were mounted for optical metallography and the rest were used in a second DS run at 1200°C and $5\text{ }\mu\text{m/sec}$. At this temperature the sample was completely molten. Due to the expansion of the quasicrystalline phase upon cooling, the sample became stuck inside the alumina tube. This material is very brittle so the sample broke into pieces when the alumina tube was broken away from the rod. Several of the pieces were mounted, polished and etched for optical metallography and EDS work. Upon study of the sample, it was discovered that there was no directionality to the phases, so a third DS run was performed at a temperature of 1500°C and a speed of $5\text{ }\mu\text{m/sec}$. The pieces from this run were also mounted, polished and etched for optical metallography and EDS work. Upon study of this sample, it was discovered that there was no directionality to the phases in this sample, either. This third DS run exhausted the supply of rods and after careful consideration of the difficulties surrounding DS of this alloy, it was decided to wait on further runs.

Figure 12: Schematic of the directional solidification furnace. [Reference 28]

Once the initial set of samples had been analyzed, a rough ternary liquidus was sketched. From the information in this sketch, several series of samples were made to more accurately determine the boundaries of the phase regions. The series $\text{Al}_{65}\text{Cu}_{34-31}\text{Ru}_{1-4}$, $\text{Al}_{65}\text{Cu}_{24-21}\text{Ru}_{11-14}$, $\text{Al}_{70}\text{Cu}_{29-26}\text{Ru}_{1-4}$, $\text{Al}_{70}\text{Cu}_{24-21}\text{Ru}_{6-9}$, $\text{Al}_{66-69}\text{Cu}_{24-21}\text{Ru}_{10}$, $\text{Al}_{66-69}\text{Cu}_{19-16}\text{Ru}_{15}$, and $\text{Al}_{72.5}\text{Cu}_{26.5-23.5}\text{Ru}_{1-4}$ were chosen for further study. Appropriate quantities of aluminum, copper and ruthenium (all >99.9% pure) were weighed to make 5 gram buttons. The samples from each series were placed into separate alumina crucibles and loaded into an NRC Crystal Growth unit equipped with a Eurotherm temperature controller. The lower ruthenium content samples were heated to 1200°C, held for 8 hours to obtain equilibrium and furnace cooled. The higher ruthenium content samples were heated to 1200°C, held for 12 hours to obtain equilibrium and furnace cooled. The samples were removed from the crucibles, cut in half and polished. The phases present were optically identified and the composition of the samples in which the primary phase changed was used to more accurately draw the ternary liquidus surface. Finally, one sample from each series was crushed into powder and run in the Perkin-Elmer DTA to determine the liquidus and reaction temperatures.

RESULTS

The DTA plots for the initial 65 and 70 atomic percent aluminum series samples are shown in Figures 13a - 13k. The scans are cooling curves for all samples, evidenced by the large exothermic peaks signifying the transition to a more stable phase. The DTA plots for the 65 atomic percent aluminum series samples and the lower ruthenium content samples in the 70 atomic percent aluminum series have end effects that were disregarded after finding the same effect upon rerunning several samples to higher temperatures. As can be seen, some of the higher ruthenium content samples in the 70 atomic percent aluminum series appear to have a liquidus temperature at or above 1400°C.

The powder X-ray diffraction scans for the initial 65 and 70 atomic percent aluminum series samples are shown in Figures 14a - 14k. The peaks were identified using information from the JCPDS^[31] files and Shield's scans of the pure Al_2Cu (θ), FCI and tetragonal (ω) phases. All scans were completely indexed except the higher ruthenium content 70 atomic percent aluminum series samples where peak shift, peak overlap, sharing of similar peaks and high background noise made differentiation of phases impossible.

Figures 15a - 15f show the optical micrographs of the 65 atomic percent aluminum series samples. The $\text{Al}_{65}\text{Cu}_{35}$ sample consists of AlCu (η) dendrites in a matrix of θ . The $\text{Al}_{65}\text{Cu}_{30}\text{Ru}_{05}$ sample and the $\text{Al}_{65}\text{Cu}_{25}\text{Ru}_{10}$ sample consist of FCI primary dendrites, a secondary phase of η , and a matrix of θ . The $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ sample and the $\text{Al}_{65}\text{Cu}_{15}\text{Ru}_{20}$ sample consist of Al_2Ru (δ) primary dendrites, a secondary phase of FCI, and a matrix of α - AlCuRu (α'). The $\text{Al}_{65}\text{Cu}_{10}\text{Ru}_{25}$ sample consists of δ primary dendrites in a matrix of FCI.

Figures 15g - 15k are the optical micrographs of the 70 atomic percent aluminum series samples. The $\text{Al}_{70}\text{Cu}_{30}$ sample consists of θ dendrites and the $\theta + \text{Al}$ eutectic. The $\text{Al}_{70}\text{Cu}_{25}\text{Ru}_{05}$ sample consists of FCI primary dendrites, a secondary phase of θ , and the $\theta + \text{Al}$ eutectic. The $\text{Al}_{70}\text{Cu}_{20}\text{Ru}_{10}$ sample and the $\text{Al}_{70}\text{Cu}_{15}\text{Ru}_{15}$ sample consist of $\text{Al}_{13}\text{Ru}_4$ primary dendrites, a secondary phase of FCI, a tertiary phase of θ , and the $\theta + \text{Al}$ eutectic in the interdendritic regions. The $\text{Al}_{70}\text{Cu}_{10}\text{Ru}_{20}$ sample consists of $\text{Al}_{13}\text{Ru}_4$ primary dendrites, a secondary phase of δ , and a tertiary phase of FCI. The structure in the interdendritic region on this sample was too fine to accurately identify the phases present.

Table 1 lists the results from the energy dispersive spectroscopy analysis using the scanning electron microscope on the initial 65 and 70 atomic percent aluminum samples. The phases were identified based on the relative amounts of each element present, the results of the powder X-ray diffraction scans, and information from work performed by Shield et al.

Figure 13: Differential thermal analysis plots of the initial samples.

Figure 13 (cont.):

Figure 13 (cont.):

Figure 14: Powder X-ray diffraction scans of the initial samples.

Figure 14 (cont.):

Figure 14 (cont.):

Figure 15: Optical micrographs of the initial samples. (a) $\text{Al}_{65}\text{Cu}_{35}$ (100X), (b) $\text{Al}_{65}\text{Cu}_{30}\text{Ru}_{05}$ (250X), (c) $\text{Al}_{65}\text{Cu}_{25}\text{Ru}_{10}$ (250X) and (d) $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ (250X). All samples were etched in Keller's etch.

(e)

(f)

(g)

(h)

Figure 15 (cont.): (e) $\text{Al}_{65}\text{Cu}_{15}\text{Ru}_{20}$ (500X DIC), (f) $\text{Al}_{65}\text{Cu}_{10}\text{Ru}_{25}$ (250X DIC), (g) $\text{Al}_{70}\text{Cu}_{30}$ (250X) and (h) $\text{Al}_{70}\text{Cu}_{25}\text{Ru}_{05}$ (1000X DIC). All samples were etched in Keller's etch.

Figure 15 (cont.): (i) $\text{Al}_{70}\text{Cu}_{20}\text{Ru}_{10}$ (1000X DIC), (j) $\text{Al}_{70}\text{Cu}_{15}\text{Ru}_{15}$ (1000X DIC) and (k) $\text{Al}_{70}\text{Cu}_{10}\text{Ru}_{20}$ (1000X DIC). All samples were etched in Keller's etch.

Table 1: Compositional analysis of the initial samples. Numbers are atomic percent. Data for eutectic phases was taken by scanning entire eutectic region.

SAMPLE	REGION	Al	Cu	Ru	PHASES
Al ₆₅ Cu ₃₅	primary	75.3	24.7		AlCu (η)
	matrix	70.5	29.5		Al ₂ Cu (θ)
Al ₆₅ Cu ₃₅ Ru ₀₅	primary	62.0	23.7	14.4	FCI
	secondary	47.7	52.2	0.2	η
	matrix	74.5	25.5		θ
Al ₆₅ Cu ₂₅ Ru ₁₀	primary	74.0	12.4	13.7	FCI
	secondary	46.7	48.8	4.6	η
	matrix	76.4	22.4	1.2	θ
Al ₆₅ Cu ₂₀ Ru ₁₅	primary	62.9		37.1	Al ₂ Ru (δ)
	secondary	54.0	24.2	21.8	FCI
	matrix	38.0	34.3	27.7	α -AlCuRu (α')
Al ₆₅ Cu ₁₅ Ru ₂₀	primary	64.0		36.0	δ
	secondary	51.9	18.0	30.1	FCI
	matrix	32.5	28.2	39.3	α'
Al ₆₅ Cu ₁₀ Ru ₂₅	primary	67.5		32.5	δ
	matrix	58.5	21.0	20.6	FCI
Al ₇₀ Cu ₃₀	primary	76.2	23.8		θ
	eutectic	80.8	19.2		θ + Al
Al ₇₀ Cu ₂₅ Ru ₀₅	primary	73.1	7.0	19.9	FCI
	secondary	77.1	22.9		θ
	eutectic	83.8	16.2		θ + Al
Al ₇₀ Cu ₂₀ Ru ₁₀	primary	76.1		23.9	Al ₁₃ Ru ₄
	secondary	66.6	19.7	13.7	FCI
	tertiary	62.6	37.1	0.3	θ
	eutectic	81.4	17.3	1.2	θ + Al
Al ₇₀ Cu ₁₅ Ru ₁₅	primary	74.5		25.5	Al ₁₃ Ru ₄
	secondary	65.5	19.9	15.6	FCI
	tertiary	69.5	27.9	2.6	θ
	eutectic	82.1	16.9	1.0	θ + Al
Al ₇₀ Cu ₁₀ Ru ₂₀	primary	78.0		22.2	Al ₁₃ Ru ₄
	secondary	66.6		33.4	δ
	tertiary	60.8	22.4	16.8	FCI

Figures 16a - 16b show the optical micrographs of the first DS run solidified at 925°C and 5 $\mu\text{m}/\text{sec}$. The sample contains primary FCI surrounded by AlCu (η). Figures 17a - 17d are the optical micrographs of the second DS run sample solidified at 1200°C and 5 $\mu\text{m}/\text{sec}$. Optical examination and the results of the EDS analysis suggest that this sample consists of the FCI primary phase with η as the secondary phase and Al₂Cu (θ) as the matrix. Figures 18a - 18d show the optical micrographs of the third DS run sample solidified at 1500°C and 5 $\mu\text{m}/\text{sec}$. Optical examination and the results of the EDS analysis suggest the same reaction scheme as in the second DS run sample.

Table 2 lists the results of the optical examination of the secondary samples. The main objective in making these samples was to more accurately determine where the primary phases change, so the samples between which the primary phases change are listed. From this information the primary phase boundaries were drawn on the ternary liquidus surface. One sample was chosen from each series for differential thermal analysis runs in the Perkin-Elmer DTA-1700 and the liquidus temperatures were added to the isopleths. Figures 19a - 19g show the DTA plots from these samples.

Figure 16: Optical micrographs of first directionally solidified sample. (a) Longitudinal and (b) transverse cuts. Magnification is 100X. Sample was etched in Keller's etch.

Figure 17: Optical micrographs of second directionally solidified sample. (a) Initial unmelted structure, (b) DS liquid at beginning of run, (c) DS liquid farther up sample and (d) DS liquid near solid/liquid interface. Magnification is 100X. Sample was etched in Keller's etch.

Figure 18: Optical micrographs of the third directionally solidified sample. (a) Structure at end of 61 $\mu\text{m}/\text{sec}$ run (50X), (b) DS liquid at beginning of run, (c) DS liquid farther up sample and (d) DS liquid near solid/liquid interface. Magnification is 100X on b-d. Sample was etched in Keller's etch.

Table 2: Optical analysis of the secondary samples.

SERIES	SAMPLE	PRIMARY PHASE
$\text{Al}_{65}\text{Cu}_{34-31}\text{Ru}_{01-04}$	$\text{Al}_{65}\text{Cu}_{34}\text{Ru}_{01}$	AlCu (η)
	$\text{Al}_{65}\text{Cu}_{33}\text{Ru}_{02}$	FCI
$\text{Al}_{65}\text{Cu}_{24-21}\text{Ru}_{11-14}$	$\text{Al}_{65}\text{Cu}_{22}\text{Ru}_{13}$	FCI
	$\text{Al}_{65}\text{Cu}_{21}\text{Ru}_{14}$	Al_2Ru (δ)
$\text{Al}_{70}\text{Cu}_{29-26}\text{Ru}_{01-04}$	$\text{Al}_{70}\text{Cu}_{29}\text{Ru}_{01}$	Al_2Cu (θ)
	$\text{Al}_{70}\text{Cu}_{28}\text{Ru}_{02}$	FCI
$\text{Al}_{70}\text{Cu}_{24-21}\text{Ru}_{06-09}$	$\text{Al}_{70}\text{Cu}_{25}\text{Ru}_{05}$	FCI
	$\text{Al}_{70}\text{Cu}_{24}\text{Ru}_{06}$	$\text{Al}_{13}\text{Ru}_4$
$\text{Al}_{66-69}\text{Cu}_{24-21}\text{Ru}_{10}$	$\text{Al}_{67}\text{Cu}_{23}\text{Ru}_{10}$	FCI
	$\text{Al}_{68}\text{Cu}_{22}\text{Ru}_{10}$	$\text{Al}_{13}\text{Ru}_4$
$\text{Al}_{66-69}\text{Cu}_{19-16}\text{Ru}_{15}$	$\text{Al}_{68}\text{Cu}_{17}\text{Ru}_{15}$	δ
	$\text{Al}_{69}\text{Cu}_{16}\text{Ru}_{15}$	$\text{Al}_{13}\text{Ru}_4$
$\text{Al}_{72.5}\text{Cu}_{26.5-23.5}\text{Ru}_{01-04}$	$\text{Al}_{72.5}\text{Cu}_{26.5}\text{Ru}_{01}$	θ
	$\text{Al}_{72.5}\text{Cu}_{25.5}\text{Ru}_{02}$	FCI
	$\text{Al}_{72.5}\text{Cu}_{24.5}\text{Ru}_{03}$	$\text{Al}_{13}\text{Ru}_4$

Figure 19: Differential thermal analysis plots of the secondary samples.

Figure 19 (cont.):

DISCUSSION

Isopleths showing liquidus temperatures were constructed from the temperature data from the DTA runs (Figures 20a - 20b). The information from the isopleths implies that there may be a peak in the liquidus near the 15 atomic percent ruthenium samples in both series. The change of primary phases from the Al-Cu side of the ternary composition plane to the Al-Ru side also implies that there is a peak in the liquidus. This peak may correspond to the congruently melting FCI phase which has been proposed to exist. Shield stated that the $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$ composition is a congruently melting phase. Also, recent work on predicting congruently melting icosahedral compositions found that $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ is the most likely composition.^[32] The existence of this phase, at least in as much as it is a congruent melter, is still under investigation. Single crystal growth attempts of $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$ have not been successful at Ames Laboratory. However, Shield has shown that the thermodynamic stability of the FCI phase is such that it will decompose to the low temperature tetragonal phase in the presence of a second phase during cooling, so a starting composition slightly off $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$ may cause a second phase to form upon cooling. It is also possible that the liquidus in the higher ruthenium content samples is above 1400°C, which would imply that the liquidus slopes gradually upward from the Al-Cu to the Al-Ru diagram.

A reaction scheme has been pieced together by using all of the information available from the DTA and powder X-ray diffraction runs, the EDS work and the micrographs. With the 65 atomic percent aluminum series samples (Table 3), the FCI phase begins to form as the primary dendrites in the 2 atomic percent ruthenium sample, and continues as the primary phase through the 13 atomic percent ruthenium sample. The secondary phase in these samples is the AlCu (η) phase, and the matrix is Al_2Cu (θ). With more ruthenium the primary phase changes to the Al_2Ru (δ) phase and FCI becomes the secondary phase. The matrix then becomes the α -AlCuRu (α') phase. This scheme continues through the 20 atomic percent ruthenium sample. In the 25 atomic percent ruthenium sample, the reaction scheme is the same except for the absence of the α' phase. The 15 atomic percent ruthenium sample was very hard to analyze in the SEM as it had very fine structures and contained a lot of porosity. It was not possible to conclusively distinguish the phases using the micrographs, and the EDS analysis was also inconclusive. However, based on the powder X-ray diffraction scan and the reaction schemes of the surrounding samples the reaction scheme for the 15 atomic percent ruthenium sample was derived.

Figure 20: Isopleths. (a) 65 atomic percent aluminum series samples and (b) 70 atomic percent aluminum series samples. The temperatures for $\text{Al}_{65}\text{Ru}_{35}$ and $\text{Al}_{70}\text{Ru}_{30}$ were taken from the phase diagram.

In the 70 atomic percent aluminum series samples the FCI phase again forms as primary dendrites in the 2 atomic percent ruthenium sample. The matrix is θ and the binary eutectic $\theta + \text{Al}$ is present in the interdendritic regions. In the 6 atomic percent ruthenium sample the primary dendrites are $\text{Al}_{13}\text{Ru}_4$ and the FCI phase forms as the secondary phase. The tertiary phase is θ and the interdendritic region is composed of the $\theta + \text{Al}$ binary eutectic. This scheme continues through the 15 atomic percent ruthenium sample. Finally, much like the 15 atomic percent ruthenium 65 series sample, the 20 atomic percent ruthenium sample is almost too complicated to analyze. It appears as though the primary phase is still $\text{Al}_{13}\text{Ru}_4$, but the secondary phase is now Al_2Ru (δ), and the tertiary phase becomes FCI. This is supported by the X-ray data and by the EDS analysis. There is a lot of porosity and a very fine microstructure in the interdendritic region, so accurate analysis of the composition of this region was not possible using the EDS. Table 4 shows the general reaction scheme for the 70 atomic percent aluminum series samples.

Finally, by correlating all of the available data from the initial and secondary samples, including the powder X-ray diffraction scans, the differential thermal analysis runs and the optical micrographs, a ternary liquidus surface was constructed showing the phase fields and the general order of reaction (Figure 21). The placement of the troughs separating the fields is correct to within ± 1 atomic percent ruthenium. The arrows giving the order of reaction are also correct based on the preliminary and subsequent work. The reactions are not given because the appearance and disappearance of phases is not completely understood. Further DS work would allow the exact determination of the reactions, but this work seems too complicated to perform on this system. Reaction temperatures are also not listed because some of the DTA data does not seem to correlate with the expected phases.

When the location of the FCI phase in this ternary liquidus surface is matched with the FCI phase fields from the work of Shield, it appears as though there is no composition which will produce single phase FCI during cooling. Any composition chosen would cool through at least a two-phase field and the FCI phase would decompose in the presence of another phase. In other words, single-crystal growth attempts on quasicrystalline Al-Cu-Ru will not be successful due to the fact that a starting composition can not be found which will not produce second phases upon cooling. The information available also seems to discredit the claim that the $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$ composition is a congruently melting quasicrystalline phase. This composition has been studied under several conditions including slow-cooling from the melt, drop-casting from the melt, directional growth using the Bridgman technique and differential thermal analysis. None of the methods have produced single phase FCI.

Table 3: Reaction scheme for 65 atomic percent aluminum series samples. Numbers in top row are atomic percent ruthenium.

0, 1	2, 5, 10, 13	14, 15, 20	25
Liquid	Liquid	Liquid	Liquid
↓	↓	↓	↓
$L \rightarrow \text{AlCu}$	$L \rightarrow \text{FCI}$	$L \rightarrow \text{Al}_2\text{Ru}$	$L \rightarrow \text{Al}_2\text{Ru}$
↓	↓	↓	↓
$L + \text{AlCu}$ $\rightarrow \text{Al}_2\text{Cu}$	$L + \text{FCI}$ $\rightarrow \text{AlCu}$	$L + \text{Al}_2\text{Ru}$ $\rightarrow \text{FCI}$	$L + \text{Al}_2\text{Ru}$ $\rightarrow \text{FCI}$
	↓	↓	↓
	$L + \text{AlCu}$ $\rightarrow \text{Al}_2\text{Cu}$	$L + \text{FCI}$ $\rightarrow \text{AlCuRu}$	

Table 4: Reaction scheme for 70 atomic percent aluminum series samples. Numbers in top row are atomic percent ruthenium.

0, 1	2, 5	6, 10, 15	20
Liquid	Liquid	Liquid	Liquid
↓	↓	↓	↓
$L \rightarrow \text{Al}_2\text{Cu}$	$L \rightarrow \text{FCI}$	$L \rightarrow \text{Al}_{13}\text{Ru}_4$	$L \rightarrow \text{Al}_{13}\text{Ru}_4$
↓	↓	↓	↓
$L + \text{Al}_2\text{Cu}$ $\rightarrow \text{Al} + \text{Al}_2\text{Cu}$	$L + \text{FCI}$ $\rightarrow \text{Al}_2\text{Cu}$	$L + \text{Al}_{13}\text{Ru}_4$ $\rightarrow \text{FCI}$	$L + \text{Al}_{13}\text{Ru}_4$ $\rightarrow \text{Al}_2\text{Ru}$
	↓	↓	↓
	$L + \text{Al}_2\text{Cu}$ $\rightarrow \text{Al} + \text{Al}_2\text{Cu}$	$L + \text{FCI}$ $\rightarrow \text{Al}_2\text{Cu}$	$L + \text{Al}_2\text{Ru}$ $\rightarrow \text{FCI}$
		↓	↓
		$L + \text{Al}_2\text{Cu}$ $\rightarrow \text{Al} + \text{Al}_2\text{Cu}$

Figure 21: Ternary liquidus surface.

CONCLUSIONS

Reaction schemes, isopleths, and a ternary liquidus diagram were constructed using information from differential thermal analysis, powder X-ray diffraction, standard optical microscopy and energy dispersive spectroscopy on samples from the Al-Cu-Ru ternary system. The initial samples tracked isopleths of 65 and 70 atomic percent aluminum through the region of icosahedral phase stability within this system. Subsequent samples tracked between the initial samples so that more accurate information could be obtained for the determination of the liquidus surface. The information from these studies is inconclusive as to the existence of the congruently melting icosahedral phase. The apparent peak in the liquidus temperatures shown in the isopleths, and the change in the primary phases shown in the reaction schemes, both suggest a peak in the liquidus near the predicted compositions of $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$ or $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$. Whether this implied peak is actually a congruently melting phase is not clear. The construction of both the ternary liquidus surface from this work, and the isotherms from the work of Shield et al., show that the FCI phase field does include these compositions. Further study of samples surrounding these compositions would be necessary to verify the existence of a congruently melting phase. It is obvious from the phase fields defined in the liquidus surface that a composition does not exist which produces the FCI phase as the primary phase without producing any secondary phases upon cooling. In other words, there appears to be no composition for which slow-growth methods will produce a single-quasicrystal.

Directional solidification studies were performed on the $\text{Al}_{65}\text{Cu}_{25}\text{Ru}_{10}$ composition in order to study the growth front characteristics of the icosahedral phase and to examine the change from primary to secondary and subsequent phases. The expansion of the icosahedral phase upon cooling, and the existence of the exterior layer, made study of this sample difficult and interpretation of the results unreliable. Further study of this composition is not practical. However, other compositions which contain the FCI phase as the primary phase may warrant further study, such as the $\text{Al}_{65}\text{Cu}_{30}\text{Ru}_{05}$. Since this sample is closer to the Al-Cu binary side of the ternary diagram, it should contain less FCI and hence should expand less upon cooling. Also, directional solidification of the $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$ sample may prove to be of interest. No direct work of this nature has yet been done on this composition, and the results may warrant further study of this system.

CONTINUED RESEARCH

The $\text{Al}_{65}\text{Cu}_{23}\text{Ru}_{12}$ sample could be cast directly into an alumina tube for use in the DS apparatus by melting the sample in an alumina crucible under vacuum, lowering the alumina tube into the melt and backfilling the chamber with argon. This samples could then be used in the directional solidification apparatus. Then, standard optical microscopy and SEM work could be performed on a sample of this composition. This work would conclusively determine whether or not this composition is a congruent melter.

Several more series could be made to more accurately map out the liquidus surface surrounding the quasicrystalline region and closer to the aluminum corner to determine the exact location of the phase fields in these areas. Also, differential thermal analysis could be performed on all of the samples available to more accurately construct the ternary liquidus surface. Finally, study of the transformation characteristics of these samples could be performed in order to gain a better understanding of the reaction sequences.

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