Crystalline Phases Relating to Stable Al–Cu–Fe Quasicrystal

By V. S. Raghunathan*, D. Sundararaman* and R. Divakar*

Analytical electron microscopic studies have been carried out in the rapidly solidified Al$_{50}$Cu$_{30}$Fe$_{15}$ alloy to relate the phase constitution and microstructure of the stable quasicrystal. The quasicrystalline phase was found to coexist with two distinct crystalline phases, one based on orthorhombic AlCu and the other based on monoclinic AlFe binary intermetallic compounds. The quasicrystalline phases in proximity to each of these were of different compositions as compared to that of the bulk of the quasicrystalline phases. A spread in the short range order, stabilized by the presence of defects could result in the observed variation in the chemical composition of the quasicrystalline phase; this in turn could result in the nucleation of crystalline phases outside the composition range of the quasicrystalline phase.

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**Keywords:** stable quasicrystal, coexisting crystalline phases, short range order, defects in quasicrystals, analytical electron microscopy

I. Introduction

Since the discovery of a quasicrystalline phase with icosahedral symmetry in the binary Al–Mn system$^{(4)}$, it has been found that a large number of metallic systems could be obtained in the quasicrystalline state through non-equilibrium processes such as quenching from the melt$^{(5)}$. Metastability as a consequence of the non-equilibrium nature of production of the phase was thought to be a necessary property of these phases, until the discovery of the T2 phase in the Al–Li–Cu system, which could be produced by slow cooling or by precipitation reactions. T2 phase is a stable icosahedral phase and large grains measuring up to a mm have been produced$^{(6)}$. A number of systems, notably the ternary alloys of the type Al–Cu–M (M=Fe, Co, Ru and Os)$^{(7)}$, have been found to form a stable quasicrystalline phase close to the compositions Al$_{50}$Cu$_{30}$M$_{15}$. In particular, Al–Cu–Fe has been investigated by using methods that include X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM), Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA) with the main purpose of determining the nature of the quasicrystalline phase and its thermal stability$^{(8)}$.

Apart from the reports detailing the nature of the quasicrystalline phase in the Al–Cu–Fe system, very little attention has been paid to the studies on the exact composition of the quasicrystalline phase, coexistence of any other crystalline phases, their composition and crystallography. The present paper reports in detail the analytical electron microscopy results of rapidly solidified Al$_{50}$Cu$_{30}$Fe$_{15}$ in which the quasicrystalline phase is predominant. The interest in the system stemmed from the fact that mostly single phase, stable quasicrystals are produced by rapid solidification as well as by isothermal heating processes$^{(9)}$. In this system much of the work so far is directed towards obtaining structural information, in order to verify whether the icosahedral twinning model$^{(10)}$, icosahedral glass model$^{(11)}$ or the icosahedral quasicrystalline model based on projection method or Penrose tilings$^{(12)}$ could satisfactorily explain the structure of quasicrystals. Efforts are also aimed at identifying atomic sites and defect sites by nuclear techniques such as Mössbauer spectroscopy$^{(13)}$ or Positron annihilation$^{(14)}$. These questions are certainly related to the chemistry of the quasicrystalline phase and the coexisting crystalline phases. It has been known that crystalline phases coexist$^{(15)}$ with the quasicrystals in the Al–Mn system as indeed in several other quasicrystalline systems. Generally, such a phase separation is assumed to occur during the solidification process when the alloy composition deviates from the ideal stoichiometry of the quasicrystalline phase. The focus in this study is to characterize these phases and relate them in terms of crystal structure, defect state and composition. The paper mainly deals with the observation of two crystalline phases along with the quasicrystalline phase, with respect to their composition, crystal structure and morphology.

II. Experimental

An ingot of Al$_{50}$Cu$_{30}$Fe$_{15}$ was prepared by induction melting with a graphite crucible as susceptor and cast in a brass mould. Rapidly quenched ribbons were prepared from the alloy using a melt spinning apparatus. This consists of a copper wheel rotated at speeds such that tangential velocities in the range 20–30 m/s were achieved. The alloy was melted in a quartz tube with an orifice of about 0.6 mm dia, the atmosphere above the melt being argon gas. The molten metal is ejected on the spinning copper
wheel by increasing the gas pressure, and ribbons of about 3 mm width and 30 μm thick and a few centimetres long are produced. Optical microscopy and scanning electron microscopy was done to study the morphology on both, the wheel side and the air side of the spun ribbons. X-ray diffraction was carried out using the CuKα radiation.

The surface of the as-produced ribbons was undulated and hence ground on fine emery paper before electrochemical thinning was attempted. Electrochemical thinning, in an electrolyte of 20 vol% HNO₃ in methanol, at a DC potential of 6 V and bath temperature of around 243 K, produced foils thin enough for electron microscopic observation. The samples were observed in a Philips EM400T transmission electron microscope operating at 120 kV. Microchemical analysis of the quasicrystalline and coexisting crystalline phases (very small, but observable volume fraction) using a LINK Analytical 10/85 S EDX system attached to the microscope. The compositions were determined using the ratio thin section (RTS-2) software in conjunction with the virtual standards package (VSP) by the standarless analysis procedure. Theoretical k-factors were calculated and a nominal thickness of 100 nm was used in all the calculations. The accuracy of the analysis depends mainly on the counting statistics, the absorption corrections used and the accuracy of the calculated k-factors. Multiple determinations of composition for the same phase give a measure of the variation due to counting statistics in terms of the root mean square deviations (RMSD). Deviations from actual composition due to uncertainties in the k-factors calculated by the RTS software from experimentally determined k-factors is small for higher atomic numbers (approximately above 22)⁹. The absolute compositions are therefore only correct to within 3 at% of the actual compositions.

III. Results

1. Optical microscopy and X-ray diffraction

Figure 1(a) shows the typical appearance of the surface of the ribbon in contact with air. It is clearly seen that dendritic morphology with river like pattern has formed, in contrast to the wheel side where the growth morphology is as shown in Fig. 1(b). It is evident that on the wheel side of the ribbon, the structure assumes pentagonal dodecahedron shaped grains which reflect the 5-fold symmetry of the structure. The size of such grains was estimated to be around 25 μm. Similar structures have been reported in scanning electron microscopic study of Al–Mn–Si melt spun ribbons, where the sizes of such structures were an order of magnitude smaller than in our case. Tsai et al.⁹ also report formation of well developed grains of pentagonal dodecahedron morphology in annealed conventionally cast Al–Cu–Fe alloy. The sizes of these grains are in the range 20 μm. This class of quasicrystals, assume macroscopic shapes that reflect the microscopic symmetry of atomic arrangements and so underlines the existence of preferential growth direction, an aspect that needs a careful future study.

X-ray diffraction data as obtained from the sample have been analysed and summarised in Table 1. All the peaks were indexed using six index scheme proposed by Bancel et al.¹⁹ for icosahedral phases and it is found that except for two peaks at Q values of 18.47 and 30.47

<table>
<thead>
<tr>
<th>Q (nm⁻¹)</th>
<th>q (nm⁻¹)</th>
<th>l₁</th>
<th>d (nm)</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.81</td>
<td>0.21</td>
<td>19</td>
<td>0.3739</td>
<td>110001</td>
</tr>
<tr>
<td>18.47</td>
<td>0.17</td>
<td>14</td>
<td>0.3401</td>
<td>—</td>
</tr>
<tr>
<td>19.37</td>
<td>0.14</td>
<td>11</td>
<td>0.3243</td>
<td>11010</td>
</tr>
<tr>
<td>25.66</td>
<td>0.20</td>
<td>8</td>
<td>0.2449</td>
<td>21001</td>
</tr>
<tr>
<td>29.80</td>
<td>0.13</td>
<td>100</td>
<td>0.2108</td>
<td>100000</td>
</tr>
<tr>
<td>30.47</td>
<td>0.13</td>
<td>8</td>
<td>0.2062</td>
<td>—</td>
</tr>
<tr>
<td>31.39</td>
<td>0.16</td>
<td>80</td>
<td>0.2002</td>
<td>11000</td>
</tr>
<tr>
<td>43.25</td>
<td>0.30</td>
<td>10</td>
<td>0.1453</td>
<td>11100</td>
</tr>
<tr>
<td>44.33</td>
<td>0.19</td>
<td>8</td>
<td>0.1417</td>
<td>11100</td>
</tr>
<tr>
<td>50.68</td>
<td>0.22</td>
<td>24</td>
<td>0.1240</td>
<td>10100</td>
</tr>
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</table>
nm$^{-1}$, the remaining correspond to the quasicrystalline phase. The two peaks are believed to arise from crystalline phases coexisting with the quasicrystalline phase. It is to be mentioned here that asymmetry in peak profiles was seen to be associated with the peaks corresponding to the quasicrystalline phase.

2. Electron microscopy and electron diffraction

(1) Quasicrystalline phase

A systematic examination of the quasicrystalline nature of the alloy samples was carried out by electron microscopy. Figure 2 shows the SAD patterns from the icosahedral quasicrystalline phase showing (a) five, (b) three, and (c) two fold symmetries.

Fig. 3 Typical bright field electron micrographs showing (a) grain boundaries and (b) defect structures in quasicrystalline Al$_{62}$Cu$_{27}$Fe$_{15}$.

Fig. 4 CBED pattern along a five fold axis.

| Table 2 Composition of the quasicrystalline phase in the absence of crystalline phases. |
|---------------------------------|---|---|---|
| at% Al | Cu | Fe |
| RMSD | 1.2 | 4.9 | 3.6 |
diffraction analysis, that includes micro-diffraction of the grains and by convergent beam electron diffraction patterns (CBED). Energy dispersive X-ray analysis of various regions of the sample was done to see any variation in the chemical composition of the quasicrystalline phases. Figures 2(a)-(c) show typical SAD patterns obtained with the electron beam carefully oriented parallel to the five-fold, three-fold, and two-fold symmetry axes of the icosahedral phase. Figures 3(a), (b) show the typical appearance of the icosahedral regions. It can be clearly seen that the microstructure of the quasicrystalline phase exhibits sharp inter-crystalline boundaries that are characteristic of crystalline phases. Defects have been found to respond to tilting experiments and the contrast changes associated with tilting will be illustrated elsewhere.

A CBED pattern oriented along five fold symmetry axis is shown in Fig. 4. The pattern has perfect five fold symmetry. The widths of the successive sidebands on the Kikuchi bands scale by 1.6 which is close to the golden mean. The diameters of the HOLZ rings, three of which are seen, scale by 1.27 which is the square root of the golden mean. This indicates a scaling factor equal to the golden mean along the five fold axis, since the reciprocal

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**Fig. 5** Crystalline phase C-1 of the orthorhombic AlCu type (a) bright field image, (b) micro-diffraction pattern (c) Key to microdiffraction pattern. The unit outlined corresponds to the position of weak spots in the pattern. EDX spectra of (d) C-1 phase, and (e) QC-1 phase. The Ni peak in (e) is from the grid.
lattice spacing in the direction perpendicular to the reciprocal lattice section of the CBED pattern is proportional to the square of the HOLZ ring diameters. Hence the CBED pattern demonstrates quasiperiodicity of the structure in three dimensions.

EDX analysis was done on a number of quasicrystalline grains and the results are summarized in Table 2. Analyses were also carried out on various locations within an icosahedral phase with a view to detect any local inhomogeneity. It is to be mentioned here that no significant variations were found in the concentrations of Al, Cu and Fe.

(2) Crystalline phases

Two distinct crystalline phases have been identified to be associated with the quasicrystalline phase. The two crystalline phases differ in morphology, composition and crystal structure. The interface boundaries are quite sharp and it is interesting to note that the compositions of the quasicrystalline regions coexisting with the crystalline phases are very different from each other and also different from the nominal composition of the icosahedral phase free of any crystalline phase reported in the last section. Essentially the melt spun ribbons of Al_{60}Cu_{35}Fe_{15} alloy contain three distinguishable regions:

(a) the region with only quasicrystalline phase,
(b) the region with crystalline phase-1 (C-1) and quasicrystalline phase (QC-1), and
(c) the region with crystalline phase-2 (C-2) and quasicrystalline phase (QC-2).

Figure 5(a) shows the typical appearance of the C-1 region. The C-1 phase can be described as a monolithic plate with internal fine structures. The composition of this C-1 crystalline phase is estimated by EDX to be Al=52.7 at%, Cu=40.9 at%, Fe=6.4 at%. Only a single micro-diffraction pattern could be obtained from this region which is shown in Fig. 5(b). The analysis of the pattern was tried by comparing the d-spacing of the crystal structure of the various phases reported in the binary Al-Cu system. Though not conclusive, the structure of the C-1 phase is found to be closely related to the primitive orthorhombic AlCu phase with lattice parameters \(a=0.4015 \text{ nm}, b=1.202 \text{ nm}, c=0.8652 \text{ nm}\), based on which a key to the micro-diffraction pattern is drawn in Fig. 5(c). EDX spectra for the C-1 and QC-1 phases are presented in Fig. 5(d) and (e).

The other crystalline C-2 phase associated with a quasicrystalline region QC-2, is significantly different both in morphology and composition. Figures 6(a) and (b) show the typical morphology of the C-2 phase containing very closely spaced parallel planar faults. In this orientation the diffraction pattern obtained is shown in Fig. 6(c). The diffraction pattern contains ordered spots in alternate rows of the reciprocal lattice section. Two other reciprocal lattice sections taken from the C-2 phase are shown in Figs. 6(d), (e). The composition of the C-2 phase was found to be Al=70.3 at%, Fe=21.9 at%, Cu=7.8 at%, close to the Al_{60}Fe stoichiometry. Hence as a natural choice, the three SAD patterns (Figs. 6(c)-(e)) were analysed in terms of the monoclinc structure of Al_{60}Fe with the reported lattice parameters \(a=1.5489 \text{ nm}, b=0.80831 \text{ nm}, c=1.2476 \text{ nm}, \beta=107.72^\circ\) and it was found that a reasonable match exists, as shown in the keys to the SAD patterns in Fig. 6(f)–(h). The pattern shown in Fig. 6(d) corresponds to a slightly distorted zone of [021] of the monoclinic structure. The planar faults are found to be along [001]. Figures 6(i) and (j) show the EDX spectra from the coexisting phases C-2 and QC-2 respectively.

In Table 3 we summarise the compositions of C-1, QC-1, C-2 and QC-2 phases. The differences in the compositions of QC-1 and QC-2 phases and the nominal composition of the icosahedral phase regions are brought out clearly. In this context, another important observation made in the alloy is the occurrence of C-2 with coexisting QC-2 regions are much larger in frequency than C-1 with QC-1 regions. The frequency of occurrence is of the order 10:1.

IV. Discussion

In order to examine the consequences of our analytical results, we construct a ternary Gibbs triangle, Fig. 7, which shows the various phases found in our study. The quasicrystalline phase stoichiometry was on an average quite close to the alloy composition chosen. While the compositional variance could be ascribed to the analytical method used, it is also to be expected that rapid solidification could cause this effect. That is, even if there is a tendency to form a line compound, a composition fluctuation should be expected. What is of importance, however, is the change in quasicrystalline stoichiometry in close proximity to the two crystalline phases C-1 and C-2. The quasicrystalline phases in contact with C-1 and C-2 are distinctly different from the average composition as shown in Tables 2 and 3. An earlier study indicates the presence of only one crystalline phase based on Al–Fe ordered solid solution indexed to a simple cube of unit cell parameter 0.29 nm (23). To reconcile the observation of two coexisting phases in the system, we consider the following points:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Al</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1 (AlCu type)</td>
<td>52.7</td>
<td>40.9</td>
<td>6.4</td>
</tr>
<tr>
<td>RMSD</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>QC-1 (with C-1)</td>
<td>64.8</td>
<td>19.0</td>
<td>16.2</td>
</tr>
<tr>
<td>RMSD</td>
<td>0.9</td>
<td>2.1</td>
<td>1.4</td>
</tr>
<tr>
<td>C-2 (Al_{60}Fe type)</td>
<td>70.3</td>
<td>7.8</td>
<td>21.9</td>
</tr>
<tr>
<td>RMSD</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>QC-2 (with C-2)</td>
<td>64.0</td>
<td>23.9</td>
<td>12.1</td>
</tr>
<tr>
<td>RMSD</td>
<td>0.8</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>
phase giving rise to simultaneous formation of C-1, C-2 and QC as per stoichiometry observed. Though small fluctuations in the liquid could lead to formation of nuclei of C-1 and C-2 and growth during rapid solidification, the observed repartitioning of solutes between the quasicrystalline phase and the crystalline phase associated with it is difficult to explain. Hence the observed features can be ascribed to the solidification process.

In this context we have examined the available data of local chemistry and short range order variations reported in the system. Fe\(^{57}\) Mössbauer spectra of Al\(_{55}\)Cu\(_{20}\)Fe\(_{15}\) indicate that there are two Fe sites\(^{(22)}\), and these could be justified on the assumption that the two units prolate and oblate rhombohedra required for 3D Penrose tiling have unique decoration with one transition metal site in each. Necessarily this approach assumes existence of two distinct but perfect short range order in the structure of the quasicrystals. However, a recent experiment and re-evaluation of the Mössbauer data\(^{(10)}\) seems to suggest that there exists a distribution of Fe sites in the Al–Cu–Fe quasicrystals, which is at variance with the two site approach and suggests a distribution of short range order, as in the case of amorphous materials. Also recently, positron annihilation spectroscopy experiments indicate that there exists definitely a high concentration of defects of the vacancy type as well as their associated forms in the quasicrystals. In Al–Mn–Si\(^{(23)}\) these have been identified as di-vacancy type defects. In Al–Cu–Fe these are found to be monovacancy type defects. Thus these studies show that the icosahedral phase has a distribution of short range order accompanied by defects. We suggest that these two effects would lead to significant fluctuations in composition in the quasicrystalline state while retaining the icosahedral structures. The solidifying
quasicrystal by virtue of the spread in short range order and the occurrence of defects, could result in variation in chemical composition in the quasicrystal, leading eventually to the crystallisation of C-1 and C-2 corresponding to the extremum in Fe and Cu compositions. Our evidence supports the fact that such fluctuations in composition do exist and that these are probably sustained by the defects. Indeed, for amorphous materials, local chemistry and topology variations, providing new sites for chemical activity have been hypothesised\(^{26}\). It is of interest to determine the scale of the compositional fluctuations that could be sustained in the quasicrystalline lattice.

V. Conclusions

The study illustrates that under identical conditions of cooling and solidification, two distinct crystalline phases coexist with the quasicrystals of Al-Cu-Fe system. C-1 phase is similar to AlCu phase (orthorhombic) and C-2 phase to AlFe phase (monoclinic). The chemical composition of the quasicrystalline phase in contact with these phases is significantly different from that in the bulk of the quasicrystals. The volume of C-2 phase is larger by an order of magnitude than the C-1 phase. The observations are consistent with the idea that there exists a significant distribution of chemical short range order in the as-formed quasicrystalline phase.

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