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# Formation of the Icosahedral Al–Cu–Fe Phase by Solid State Reaction

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Al–Cu–Fe alloys with a nominal composition of $Al_{63}Cu_{24}Fe_{13}$, $Al_{62}Cu_{25.5}Fe_{12.5}$ and $Al_{65}Cu_{20}Fe_{15}$ have been fabricated by solid-state reaction at 550, 650, and 750 °C. The synthesized alloys mainly consist of icosahedral $Al_{65}Cu_{20}Fe_{15}$, body-centered cubic $\beta$-AlFe(Cu) and monoclinic $\lambda$-$Al_{13}Fe_4$ phases. After synthesis under optimal conditions the fraction of the icosahedral phase was 100, 80, and 85 weight per cent in $Al_{63}Cu_{24}Fe_{13}$, $Al_{62}Cu_{25.5}Fe_{12.5}$, and $Al_{65}Cu_{20}Fe_{15}$, respectively.

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## 1. Introduction

In the context of potential applications, quasicrystals [1] attract much attention because of a unique combination of properties such as high hardness, low surface energy, low coefficient of friction, high corrosion and wear resistance, low electrical and thermal conductivity [2, 3]. The uses of quasicrystals as bulk materials, however, are limited due to their high fragility. The most promising is the use in the form of coatings and powder [4–6]. Quasicrystal powders show potential as composite materials fillers, especially for metal matrix [7–10] and polymer composite [11–13].

A metal matrix composite usually consists of a light matrix reinforced by particles or short fibers of a hard material. Metal matrix composites are very promising from the point of view of their use in the aircraft industry and other fields that require lightweight durable materials. Aluminum is often used as the matrix, which is reinforced by ceramic silicon carbide or aluminum oxide. Since quasicrystals exhibit remarkable mechanical properties at low and intermediate temperatures such as high hardness and yield stress, they make an alternative to ceramic silicon carbide and aluminum oxide. Because of the low cost of the constituent elemental metals the icosahedral phase in the Al–Cu–Fe ternary system deserves particular attention among other quasicrystalline phases for the purpose of industrial uses [2, 14, 15].

Quasicrystal powders can be obtained using a variety of methods [16–18], among which mechanical alloying recently attracted much attention. First used to produce the Al–Cu–Mn quasicrystalline phase [19], mechanical alloying successfully used to obtain other quasicrystalline phases, including Al–Cu–Fe. In the case of Al–Cu–Fe this method is a combination of ball milling and subsequent annealing [9, 20–22]. The mechanical alloying method allows for production of quasicrystal powders of varying dispersity containing up to 100% of the quasicrystalline phase. However, when using this method it is difficult to control the composition of the synthesized powders and obtain materials with reproducible properties [23]. Furthermore, the use of this method on an industrial scale appears difficult because of the high cost and complexity of the process — less expensive and more efficient synthesis techniques are therefore needed. An important consideration here is that the content of quasicrystalline phase in the powders used as fillers in metal-matrix composites should be high enough, but not necessarily very close to 100%.

A possible candidate technique is the conventional solid-state synthesis, a very simple and low cost method of fabricating quasicrystalline Al–Cu–Fe in large quantities. When comparing the solid-state synthesis and mechanical alloying, the question to address is this — is it possible to eliminate the step of the preliminary mechanical alloying processing and obtain the Al–Cu–Fe material with high content of the icosahedral phase using heat treatment only? According to the published Al–Cu–Fe equilibrium phase diagrams the icosahedral phase forms within the composition range approximately 62–65 at.% of Al [24, 25]. Below the peritectic reaction temperature of about 820 °C, the stability area of the icosahedral phase extends over the whole vertical section. Thus, from the thermodynamic point of view it is possible to obtain icosahedral Al–Cu–Fe phase by the conventional solid-state synthesis without prior mechanical alloying processing. The purpose of this study was to investigate the formation of the Al–Cu–Fe icosahedral phase in the solid-state synthesis, depending on the initial composition and annealing conditions.

## 2. Experimental

The pellets for the solid-state synthesis with the nominal compositions $Al_{62}Cu_{25.5}Fe_{12.5}$, $Al_{63}Cu_{24}Fe_{13}$ and $Al_{65}Cu_{20}Fe_{15}$ were prepared from Al, Cu, and Fe (99.9% purity) powders of 1–10 $\mu$m nominal particle size. The

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starting materials were mixed in ethanol and pressed into pellets. The pellets were placed in alumina crucibles, encapsulated into quartz ampoules under a pressure of helium 0.05 MPa and then annealed at 550, 650, and 750 °C for periods from 2 to 20 h with subsequent rapid cooling.

The compositional and phase characterization of the specimens were based on X-ray diffraction patterns and scanning electron microscopy. Phase identification was carried out by X-ray diffraction using BRUKER AXS D8 Advance difractometer with Cu $K_\alpha$ radiation. The microstructure of the specimens before and after annealing was studied with a high resolution scanning electron microscope model Supra 50VP Carl Zeiss equipped with an energy dispersive spectrometer INCA Energy Oxford.

## 3. Results and discussion

Figure 1a shows the X-ray diffraction patterns for $Al_{63}Cu_{24}Fe_{13}$ samples after annealing at 650 °C for 2, 10 and 20 h. The diffraction patterns after 2 h of annealing show the presence of icosahedral $Al_{65}Cu_{20}Fe_{15}$ phase along with body-centered cubic $\beta$-AlFe(Cu) and monoclinic $\lambda$-$Al_{13}Fe_4$ phases. With increasing annealing time up to 10 h, the intensities of the peaks corresponding to the $\beta$ and $\lambda$ phases decrease and the intensity of the peaks corresponding to icosahedral phase increase. After annealing for 20 h only the peaks related to the icosahedral phase were observed.

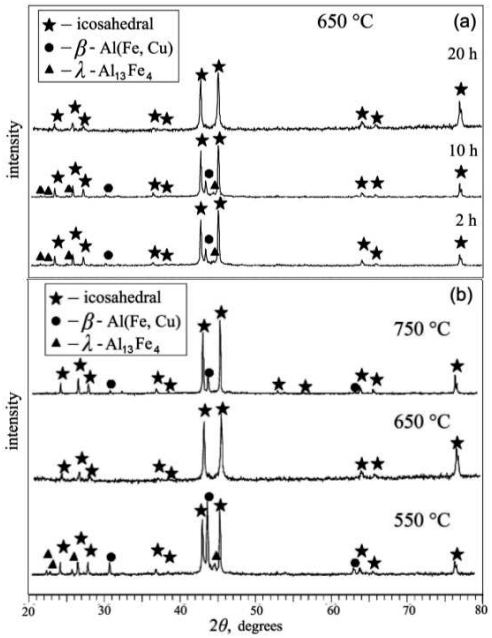


Fig. 1. X-ray diffraction patterns for $Al_{63}Cu_{24}Fe_{13}$ after annealing at 650 °C for 2, 10, and 20 h (a) and after annealing at temperatures of 550, 650, and 750 °C for 20 h (b).

Figure 1b shows the X-ray diffraction patterns for $Al_{63}Cu_{24}Fe_{13}$ sample after annealing at temperatures of 550, 650, and 750 °C for 20 h. After annealing at 550 °C the icosahedral, cubic, and monoclinic phases were present in the sample. With increasing annealing temperature the intensities of the peaks of the $\beta$ and $\lambda$ phases decrease and the intensity of the peaks of the icosahedral phase increases. After annealing at 650 °C the diffraction pattern shows only peaks corresponding to $i$-phase and traces of $\beta$-phase. With further increase of the annealing temperature up to 750 °C the intensity of peaks corresponding to the $\beta$ phase increases.

Similar results were obtained when the $Al_{62}Cu_{25.5}Fe_{12.5}$ and $Al_{65}Cu_{20}Fe_{15}$ pellets were annealed at 550, 650, and 750 °C within 2–20 h. X-ray diffraction patterns for $Al_{62}Cu_{25.5}Fe_{12.5}$ and $Al_{65}Cu_{20}Fe_{15}$ annealed at 650 °C for 2 and 20 h are shown in Fig. 2. After annealing for 2–10 h the powder diffraction patterns contain peaks corresponding to monoclinic, cubic, and icosahedral phases. No other phases were observed. With increasing annealing time up to 20 h the intensities of the peaks corresponding to the $\beta$ and $\lambda$ phases decrease and the intensity of the peaks of the icosahedral phase increase. The maximum content of the icosahedral phase was observed after annealing at 650 °C for 20 h. However, unlike in the samples $Al_{63}Cu_{24}Fe_{13}$ even after annealing of under optimal conditions there are significant amount of $\beta + \lambda$ and $\lambda$ phases in the $Al_{62}Cu_{25.5}Fe_{12.5}$ and $Al_{65}Cu_{20}Fe_{15}$ samples, respectively. Further increase of the annealing temperature and time did not increase the icosahedral phase content.

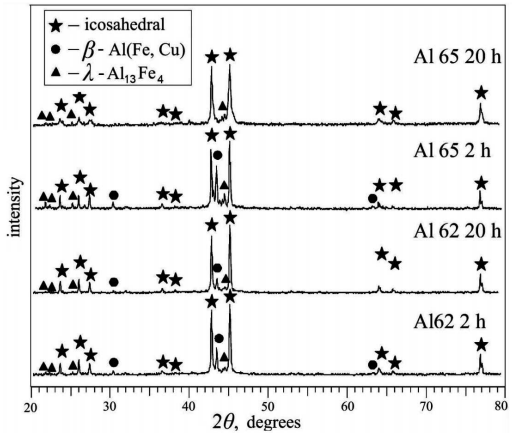


Fig. 2. X-ray diffraction patterns for $Al_{62}Cu_{25.5}Fe_{12.5}$ (Al62) and $Al_{65}Cu_{20}Fe_{15}$ (Al65) annealed at 650 °C for 2 and 20 h.

The results of the quantitative phase analyses for $Al_{62}Cu_{25.5}Fe_{12.5}$, $Al_{63}Cu_{24}Fe_{13}$, and $Al_{65}Cu_{20}Fe_{15}$ samples annealed for 20 h are given in Table. The data indicates that the maximum content of the icosahedral phase in excess of 95 wt% was obtained after annealing of the $Al_{63}Cu_{24}Fe_{13}$ pellets at 650 °C. Scanning electron microscopy images (Fig. 3) show the microstructure of the $Al_{63}Cu_{24}Fe_{13}$ samples before, and after annealing at

650 °C for 10 h. The microstructure of the sample before annealing consists of isometric particles of the constituent elements Al, Cu, and Fe with diameters of the order of 10 $\mu$m. After annealing the maximum size of particles increases significantly reaching 30–40 $\mu$m in diameter. Smaller particles of about 10 $\mu$m in diameter are also present. The X-ray energy dispersive spectroscopy data indicated that while the composition of the large and medium-sized particles is close to the composition of the icosahedral phase $Al_{65}Cu_{20}Fe_{15}$, the compositions of smaller particles correspond to that of $\beta$-AlFe(Cu) and $\lambda$-$Al_{13}Fe_4$ phases. All the studied $Al_{62}Cu_{25.5}Fe_{12.5}$ and $Al_{65}Cu_{20}Fe_{15}$ samples displayed similar microstructure, i.e., formed by large particles of the icosahedral phase and smaller particles of the $\beta$ and $\lambda$ phases.

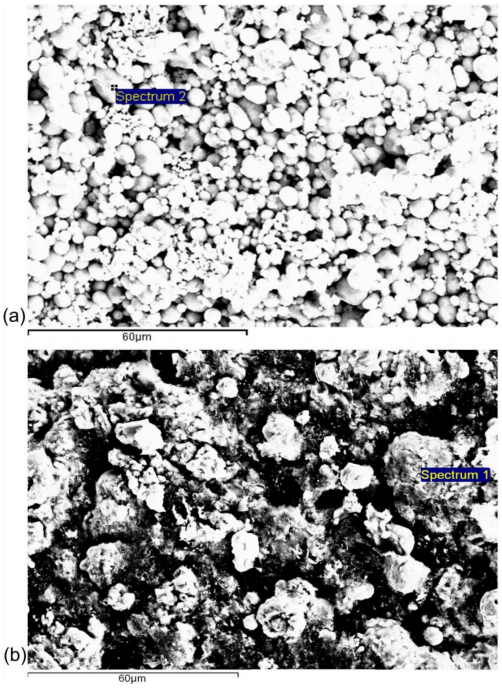


Fig. 3. Microstructure of $Al_{63}Cu_{24}Fe_{13}$ before and after annealing at 650 °C for 10 h.

Our X-ray diffraction and energy dispersive spectroscopy data suggests that the icosahedral phase evolution during annealing of the investigated samples proceeds via the dissolution of the $\beta$ and $\lambda$ phases formed at the initial stage of annealing. The maximum content of the icosahedral phase in the samples depends on the composition, temperature, and annealing time. Single-phase samples were obtained only after annealing the $Al_{63}Cu_{24}Fe_{13}$ pellets. Second phases were always present in the samples obtained from the $Al_{62}Cu_{25.5}Fe_{12.5}$ and $Al_{65}Cu_{20}Fe_{15}$ pellets. The content of the icosahedral phase in all our samples increased with increasing annealing temperature from 550 to 650 °C and reached its maximum value of 95–100, 80 and 85 per cent for $Al_{63}Cu_{24}Fe_{13}$, $Al_{62}Cu_{25.5}Fe_{12.5}$, and $Al_{65}Cu_{20}Fe_{15}$, respectively. Further increase of the annealing temperature leads to a decrease of the icosahedral phase content in the samples and to an increase of the content of the $\lambda$ and $\beta$ phases.

TABLE

Quantitative phase analyses for $Al_{63}Cu_{24}Fe_{13}$, $Al_{62}Cu_{25.5}Fe_{12.5}$ and $Al_{65}Cu_{20}Fe_{15}$ samples annealed for 20 h.

| Sample | Annealing temperature | Phase composition [wt%] | | |
|---|---|---|---|---|
| | | $i$ | $\beta$ | $\lambda$ |
| $Al_{63}Cu_{24}Fe_{13}$ | 550 °C | 50 | 35 | 15 |
| | 650 °C | >95 | *a* | *a* |
| | 750 °C | 80 | 20 | *a* |
| $Al_{62}Cu_{25.5}Fe_{12.5}$ | 550 °C | 55 | 30 | 15 |
| | 650 °C | 80 | 15 | 5 |
| | 750 °C | 80 | 15 | 5 |
| $Al_{65}Cu_{20}Fe_{15}$ | 550 °C | 55 | 15 | 30 |
| | 650 °C | 85 | *a* | 15 |
| | 750 °C | 80 | *a* | 20 |

[a] Below detection limit.

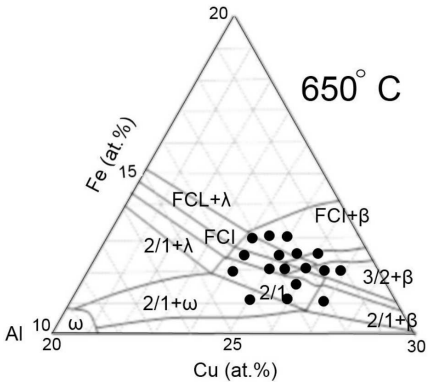


Fig. 4. Isothermic section of the ternary Al–Cu–Fe phase diagram near the icosahedral phase forming region at 650 °C according to Ref. [26].

According to the isothermic section of the Al–Cu–Fe equilibrium phase diagram at 650 °C (Fig. 4) reported in Ref. [26], the composition corresponding to 65 at.% Al, 20 at.% Cu and 15 at.% Fe falls into the two-phase $i + \lambda$ region (see Fig. 4). The $\lambda$ phase is therefore expected to be present in the samples synthesized from the $Al_{65}Cu_{20}Fe_{15}$ pellets. The composition corresponding to 62 at.% Al, 25.5 at.% Cu, and 12.5 at.% Fe is on the boundary of the single $i$ phase region and the two-phase $i + \beta$ region [26]. That explains the presence of small amounts of the $\beta$ phase in the samples synthesized from the $Al_{62}Cu_{25.5}Fe_{12.5}$ pellets. The presence of the $\lambda$ phase in these samples may be indicative of an incomplete synthesis. The composition corresponding to 63 at.% Al, 24 at.% Cu and 13 at.% Fe is within the icosahedral phase region, and the single-phase samples were obtained from the $Al_{63}Cu_{24}Fe_{13}$ initial composition by annealing at 650 °C and rapid cooling. According to the pseudo-

-binary phase diagram reported in Ref. [24], the homogeneity area of the icosahedral phase becomes narrower at higher temperature and the probability of the second phase formation due to local composition variations in the samples is expected to increase. That may explain the presence of second phases in the $Al_{63}Cu_{24}Fe_{13}$ samples annealed at 750 °C.

We now compare our results with the data on the icosahedral phase formation during mechanical alloying with following annealing. The phase composition of the ball milled and un-milled powders of $Al_{65}Cu_{20}Fe_{15}$ annealed at 600–800 °C for 4 h was reported in Ref. [21]. After annealing at 600 °C the un-milled sample did not contain the icosahedral phase, while some of the ball milled samples contained small amounts of the icosahedral phase. With increasing annealing temperature up to 700 °C significant amounts of the icosahedral phase were formed — 82 and 72 wt% in ball milled and un-milled samples, respectively. With further increase of the annealing temperature up to 800 °C, however, the weight fractions of the icosahedral phase decreased in both samples. We can therefore conclude that our findings are in qualitative agreement with the results reported in Ref. [21]. We also note that weight fractions of the icosahedral phase did not differ significantly in the milled and un-milled powders but did strongly depend on the annealing temperature. A comparative analysis of the phase composition of the samples obtained by solid-phase synthesis and by mechanical alloying with subsequent annealing suggests that for powders with composition close to the stability area of the icosahedral phase annealing at temperatures of 650–700 °C is the determining stage in the formation of the icosahedral phase.

## 4. Summary

Formation of the Al–Cu–Fe icosahedral phase in the solid-state synthesis, depending on the initial composition and annealing conditions was studied. Pellets with nominal compositions of $Al_{63}Cu_{24}Fe_{13}$, $Al_{62}Cu_{25.5}Fe_{12.5}$, and $Al_{65}Cu_{20}Fe_{15}$ have been annealed at 550, 650, and 750 °C between 2 and 20 h and subsequently rapid cooled. It was found that the evolution of the icosahedral phase during annealing is due to dissolution of the $\beta$ and $\lambda$ phases formed at initial stages of annealing. The concentration of the icosahedral phase in all the samples studied increased with increase of annealing temperature from 550 to 650 °C and reached its maximum value after annealing for 20 h at 650 °C. The maximum concentration of icosahedral phase obtained by conventional solid-state synthesis is close to 100 per cent in $Al_{63}Cu_{24}Fe_{13}$, that allow to use this method for producing of large amounts of quasicrystalline powder for industrial applications.

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