Heat Treatment in an Alloy $Al_{63}Cu_{24}Fe_{12}$

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Abstract. Structural characteristics and thermal behaviour of the conventionally solidified Al–Cu–Fe alloys with nominal compositions of $Al_{63}Cu_{24}Fe_{12}$ were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Results show that a single quasicrystalline phase forms in a conventionally solidified $Al_{63}Cu_{24}Fe_{12}$ alloy, being thermodynamically stable without phase transition. In the raw state of fusion, presenting icosahedral phase-ω and cubic β-$Al_2Fe_5(Cu)$ in solid solution, identified β phase and icosahedral phase-ω, in which coexist with the quasicrystalline phase for $Al_{63}Cu_{24}Fe_{12}$ alloy. A careful chemical composition control and an efficient heat treatment are necessary to obtain quasicrystalline phases. The objective of this work was to study the heat treatment in the homogenization of the quasicrystalline alloy $Al_{63}Cu_{24}Fe_{12}$ obtained by smelting, in a controlled atmosphere. SEM micrographs for $Al_{63}Cu_{24}Fe_{12}$ alloy after annealing at 700ºC for 4 h revealed the formation of pentagonal dodecahedrons in the quasicrystalline phase, with an edge size of about 30 µm

Keywords: Quasicrystalline Phases, $Al_{63}Cu_{24}Fe_{12}$, Phases ω/β-$Al_2Fe_5(Cu)$.

1. Introduction

Quasicrystals show the characteristics of both crystalline (i.e. generation of sharp peaks and spots in X-ray diffraction and electron diffraction patterns, respectively) and non-crystalline materials (i.e. absence of translational symmetry) [1]. Quasicrystalline materials have unique set of mechanical, electrical, thermal, optical, corrosion and biocompatible properties, use as a mass catalyst in methanol catalytic reactions and quantum and thermal fluctuations in the light cone in quasicrystalline systems, which makes them suitable for many practical applications [2]. Among various quasicrystals, Al-Cu-Fe is an attractive alloy system as the constituent elements of this system are non-toxic, easily available and of favorable cost. Al-Cu-Fe quasicrystals have the potential to be used for heat flow detection,

in solar absorbance devices, as coating material, in catalytic applications and as reinforcing phase in metal matrix composites. Among the available Al-based quasicrystalline alloys, the ternary Al-Cu-Fe quasicrystalline alloys are most popular due to non-toxicity, wide availability and cost-effectiveness of the constituent's elements.

Metastable QCs are formed in a wide range of binary alloy systems of Al with the d-transition metals. Stable QCs can be obtained when the third element is added to one of these binary systems. The third element could be one of the transition metals for example, coppe [3]. Examples of these stable ternary quasicrystalline systems are icosahedral Al-Cu-Fe and decagonal Al-Cu-Co.

Adding of the fourth element, not necessary a transition metal, to these ternary systems may result in a quasicrystalline structure. The quasicrystalline alloys contained more than four elements were also obtained. Either three-dimensional icosahedral (IQC) or two-dimensional decagonal (DQC) structures are formed in most of the Al-based quasicrystalline alloys [4]. Physical properties of IQC and DQC, in particular, electronic transport strongly differ. In spite of that, there exists a close relationship between the icosahedral and decagonal structures [5]. Thus, for example, direct transformation from IQC to DQC by heat treatment was observed.

Knowledge of phase diagram is critical for guiding the growth of single quasicrystals, and thus significant efforts have been made to establish the Al-Cu-Fe phase diagram, primarily focusing on the phase region in the vicinity of the I phase. Consequently, the phase equilibria associated with the ω phase in the Al-rich corner have been well determined and critically assessed [6]. However, the experimental phase equilibrium data is still very limited in the Cu-Fe-rich portion. So far, only one isothermal section at 600°C has been experimentally established over the whole composition range [7].

The current study intends to systematically investigate the Al-Cu-Fe phase diagram using a set of three identical $Cu/Fe/Al_5Fe_2$ diffusion triples and forty-seven equilibrated alloys [8]. The structural characteristics, morphological features and thermal behaviour of the conventionally solidified $Al_{63}Cu_{24}Fe_{12}$ alloy were investigated in the present study, using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Material and Methods

The aluminum, iron and copper powders, according to their granulometry and stoichiometric composition, having a purity of 99.9%, from Alcoa in Brazil-Alcoa Alumínio

and Aldrich Chemical, were weighed in an analytical balance PR Series 4 Ohaus houses (0.0001g) maximum capacity 220g and 0.1mg resolution in proportions adequate to the composition $Al_{63}Cu_{24}Fe_{12}$, mechanically homogenized and compacted in the form of disc with diameters of 10 mm and 2 mm thick, in a uniaxial hydraulic press. Initially, a pre-pressing was carried out under a maximum load of 5 tonnes for 3 minutes.

The precursor alloy was obtained by direct fusion of the compacted constituents. The fusion was carried out in an arc furnace under controlled atmosphere of analytical Argon 5.0, with 99.99% purity. The electric induction arc furnace is powered by a BALMER static rectified generator which power is 22 KVA. For phase identification, a Shimadzu XRD 6000 diffractometer was used, using CuK_α radiation with a wavelength of $\lambda = 1.5406$ Å.

X-ray diffraction (DRX)/Malvern Panalytical software coupled with OriginPro 8 was used for graphing and phase analysis. To increase the proportion of the quasicrystalline phase in the alloy, thermal treatments were carried out, whose objective was to favor the transformation of the crystalline phases in the icosahedral phase. The heat treatments were carried out under a helium atmosphere in a tubular oven with electrical resistance NABERTHERM model RHT 17, equipped with a quartz cylindrical chamber with $\varphi = 75$ mm by 700 mm in length, where the samples were stored. The samples were placed in the quartz chamber accommodated in a stainless steel boat covered by an alumina blanket, after which at least three vacuum operations were performed following filling with helium, and, finally, a negative pressure of 0.5 bar, followed by heating at a rate of 30^oCmin^{-1}. The thermal treatments were carried out at the following times: 6, 12 and 24 h.

The measurements were taken for a wide range of diffraction angles (2θ) ranging from 20º to 50º with an angular pitch of 0.05º and with counting time per point equal to 4 s. To analyze the morphology of quasicrystalline powders using a LEO Scanning Electron Microscope, Model 1430, coupled to an OXFORD probe, with an acceleration voltage of 0.5 to 30kV with a 10V step, after the sample has been coated with a layer of gold deposited in a vacuum to improve contrast.

3. Results and discussion

The diffractogram curves shown in Figure 1 represent the evolution of the phases of the raw melting alloy and the heat-treated alloys in the 6, 12 and 24h times.
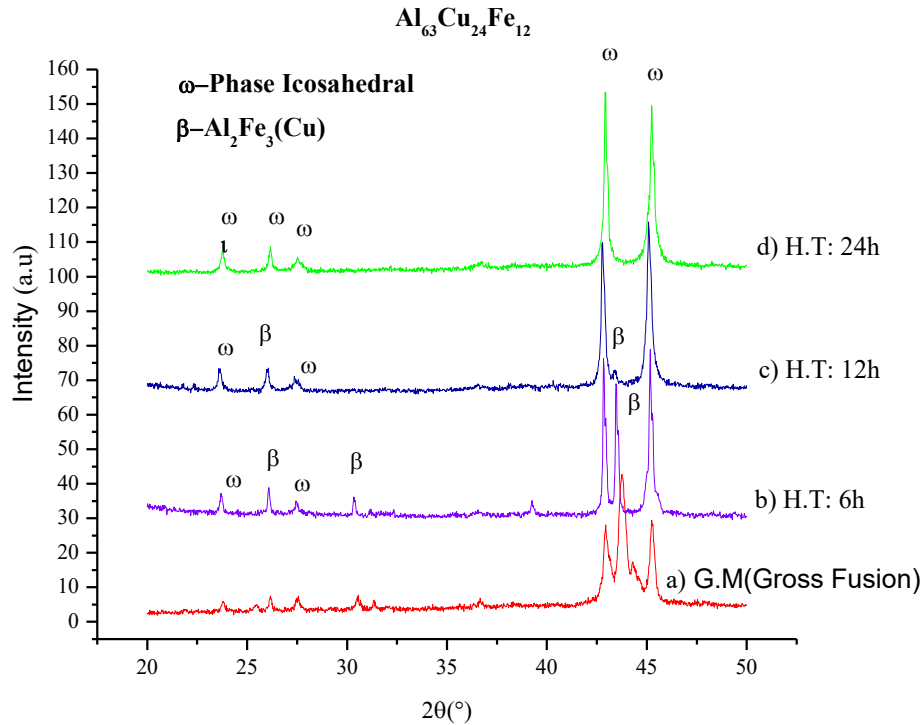
Figure 1: X-ray diffractograms (XRD) of samples of $Al_{63}Cu_{24}Fe_{12}$: a) G.M (Gross Fusion), b) H.T: 6h, c) H.T: 12h and d) H.T: 24h.

A subsequent heat treatment is observed, in the X-ray diffractogram Figure 1, the increase in icosahedral phase-ω, peaks and β-Al_2Fe_3(Cu) phase peaks. After heat treatment at 700ºC in 4h, a) G.F (Gross Fusion), b) H.T : 6h, c) H.T: 12h and d) H.T: 24h, presents compositional stability of the quasicrystal with icosahedral phases phase-ω, peaks and β-Al_2Fe_3(Cu) with well refined and identified peaks that are expected in the Al-Cu-Fe system.

The peaks found in the diffractograms are phases, icosahedral phase-ω and the β-Al_2Fe_3(Cu) phase. The crystalline β-Al_2Fe_3(Cu) phase is also present in the as cast alloy. It is observed that, depending on the composition, the presence of two or three of the following phases: icosahedral phase-ω with quasicrystalline structure, β-Al_2Fe_3(Cu) phase, which is a solid solution with isomorphic cubic structure of the structure of cesium chloride (CsCl) and the λ phase isomorphic of the structure of the compound $Al_{13}Fe_4$, which is monoclinic that will be assigned to the icosahedral phase, when compared to the JCPD sheet [9].

The β-Al_2Fe_3(Cu) phase is cubic primitive, presenting diffraction patterns characteristic of the amorphous/nanocrystalline phase. The presence of an amorphous phase after heat treatment at this temperature is very difficult, as this would indicate that the system

has a high stability of the amorphous phase consequently a high tendency to form amorphous phase, which is not reality.

The composition that show characteristic XRD patterns of amorphous / nano phase are around the stability region of the quasicrystalline phase, following the same trend of the compositions that showed this behavior after treatment at 700ºC. Some of the compositions close to the QC region, slightly enriched in Fe, began to show the two most intense peaks, characteristic of the icosahedral phase, together with the β-$Al_2Fe_3(Cu)$ phase. The i-QC phase is formed between the ω and β-$Al_2Fe_3(Cu)$ phases, and forms a two-phase equilibrium field with both.

The β and ω phases coexist with the quasicrystalline phase when the process of obtaining does not provide the kinetic conditions for the alloy to become almost quasicrystalline. In the $Al_{63}Cu_{24}Fe_{12}$ alloy, the formation of the icosahedral phase is the result of an expert reaction between the primary β phase and the remaining liquid. Therefore, only after a heat treatment at 700ºC for 4h is a pure quasicrystalline material obtained. Thus, no single-phase icosahedral structure is obtained in $Al_{63}Cu_{24}Fe_{12}$ without promoting a rigorous heat treatment.

Consequently, the relative amounts of QC, $\beta$and ω phases (determined by XRD analysis) appears to significantly affect surface properties (wettability) and hardness; a lower amount of secondary phases (e.g. , β and ω) yields better surface and hardness properties [10]. The intensity of the peaks corresponding to ω-phase is greater than the peaks specifically related to β-phase. The composition of $Al_{65}Cu_{27}Fe_{18}$ has phases in equilibrium with other crystalline phases such as icosahedral phase-ω and the β-$Al2Fe_3(Cu)$ phase coexist with a small amount in solid solution [11]. For the $Al_{63}Cu_{24}Fe_{12}$ alloy, the presence of the quasicrystalline phase coexists with a small fraction of the β-phase. It can also be observed that there is a small displacement of the β phase peaks to the left; this is due to the increase in the network parameter of this phase, caused by the excess of copper, in the β cubic structure, as the sample is heat-treated. As can be seen in the diffractograms of the heat-treated samples, the diffraction peaks attributed to the β phase decrease as the heat treatment time increases. With 24 hours of heat treatment, the quasicrystalline material is homogeneous and practically monophasic. Figures 2 and 3 represent the results obtained from quasicrystals samples by Scanning Electron Microscopy. In Figure 2, SEM micrographs of the Al-Cu-Fe alloy the morphology can be observed that the heat-treated Al-

Cu-Fe alloy already has crystallites with a dodecahedral shape (the same symmetry as the icosahedron) and with small amounts of Al_2O_3 oxide on its surface [12].
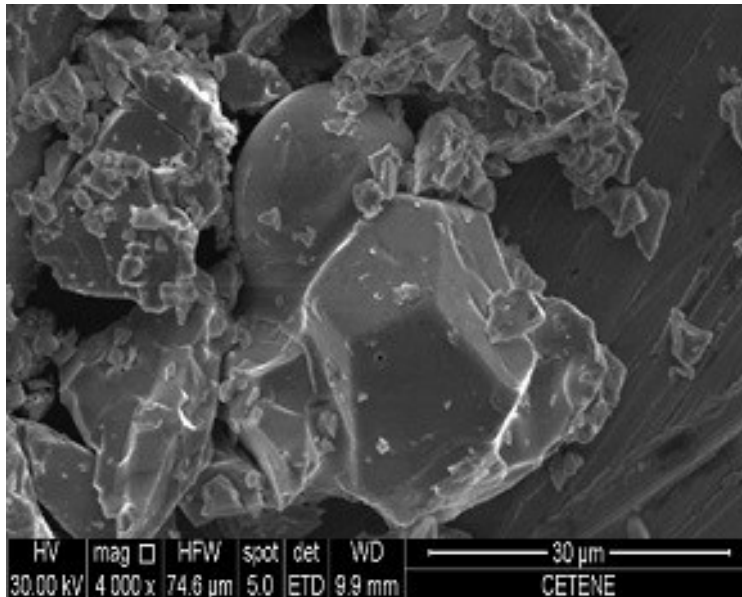

Figure 2. SEM micrographs of the Al-Cu-Fe alloy: Characteristic dodecahedral crystals of the quasicrystalline phase of alloy $Al_{63}Cu_{24}Fe_{12}$.

The size of these crystallites is 30μm and corresponds to the quasicrystalline phase $Al_{63}Cu_{24}Fe_{12}$. However, the SEM micrograph of $Al_{63}Cu_{24}Fe_{12}$ alloy after annealing for 4h at 700ºC shows an array of the pentagonal dodecahedral crystals in the shape of a cauliflower, as seen in Figure 3.
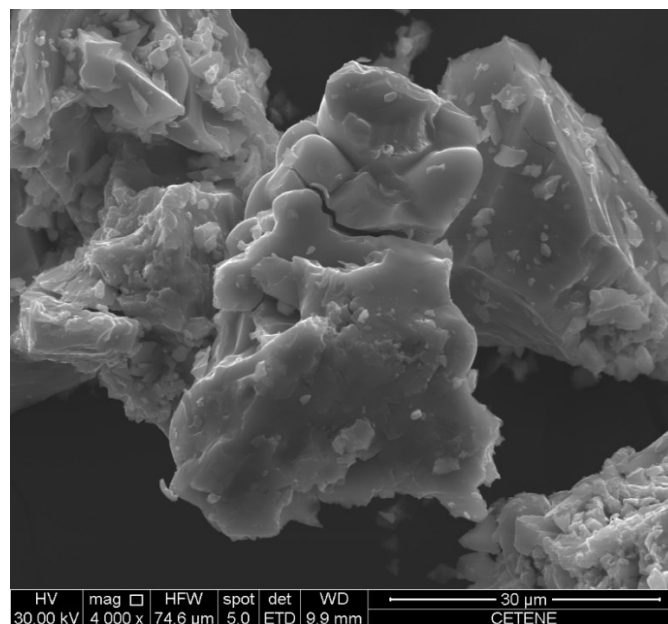

Figure 3. SEM micrographs for conventionally solidified $Al_{63}Cu_{24}Fe_{12}$ alloys annealed for 4 h at 700°C.

Small nodules in cauliflower formats are seen, this is due to the coexistence of the two phases, icosahedral phase-ω and the β-Al$_2$Fe$_5$(Cu) phase, both being diluted in the peritoneal reactions [13].

Thus, the present investigation demonstrates that during the heat treatment of Al$_{63}$Cu$_{24}$Fe$_{12}$ alloy, the icosahedral phase-ω melted and peritectic reaction occurred between liquid and β-Al$_2$Fe$_5$(Cu). It is therefore reasonable to assert that the ω phase in Al$_{63}$Cu$_{24}$Fe$_{12}$ alloy formed as the result of a peritectic reaction. However, the ordering and stability of the icosahedral phase-ω can then be achieved by heat treatment at 700-780°C [14].

The formation of the stable structure and ordering of quasicrystals seem the result of the ordination of metastable intermetallics, the coexistence of different intermetallic phases including phases ω and β, of which β-phase in orientation has the highest volume fraction. The ω and β phases coexist with the quasicrystalline phase when the process of obtaining does not provide the kinetic conditions for the alloy to become completely quasicrystalline.

The formation of a phase with icosahedral structure in an alloy of composition Al$_{63}$Cu$_{24}$Fe$_{12}$, together with the phases: icosahedral phase-ω and the β-Al$_2$Fe$_3$(Cu), in addition to small quantities of the λ-Al$_{13}$Fe$_4$ phases completed in solid solution. In the Al$_{63}$Cu$_{24}$Fe$_{12}$ alloy, the formation of the icosahedral phase is the result of an expert reaction between the primary phase β and the remaining liquid. Therefore, only after a heat treatment at 700°C for 4h a pure quasicrystalline material is obtained [15].

4. Conclusion

SEM micrographs of this alloy in as-solidified state and after heat treatment at 700ºC for 4h, showed an array of the pentagonal dodecahedral crystals in the shape of a cauliflower. The sample of stoichiometric composition of the type Al$_{65}$Cu$_{27}$Fe$_{18}$, has equilibrium phases with the icosahedral phase-ω and the β-Al$_2$Fe$_5$(Cu) phase coexisting in solid solution. The peaks found in the diffractograms are phases icosahedral phase-ω and the β-Al$_2$Fe$_5$(Cu) presents stable thermodynamic stability between the phases ω and β. As-solidified Al$_{63}$Cu$_{24}$Fe$_{12}$ alloy exhibited icosahedral phase-ω together with β-Al$_2$Fe$_5$(Cu). The formation of the stable structure and ordering of quasicrystals seem the result of the ordination of metastable intermetallics, the coexistence of different intermetallic phases including phases ω and β. Additionally, the grains of the β-Al$_2$Fe$_5$(Cu) icosahedral phase located at the Al$_{63}$Cu$_{24}$Fe$_{12}$ particle/matrix interface were observed.

5. Acknowledgment

6. Bibliography

[1]. KLYUEVA, M.; SHULYATEV, D.; ANDREEV, N.; SVIRIDOVA, T.; SUSLOV, A. New stable icosahedral quasicrystal in the system Al-Cu-Co-Fe. *Journal of Alloys and Compounds 801*. p. 478–482, 2019.

[2]. DUBOIS, J.M. Properties-and applications of quasicrystals and complex metallic Al alloys. *Chemical Society Reviews 41(20)*. p. 6760–6777, 2012.

[3]. LI, L.;BI, Q.; YANG, J.; FU, L.;WANG, L.; WANG, S.; LIU, W. Large-scale synthesis of Al–Cu–Fe submicron quasicrystals. *Scripta Materialia* 59, p. 587–590, 2008.

[4]. MISRA,S.K.; KAHRIZI, M. ; SINGH,K.; VENKATRAMANI,N.; BAHADUR,D. EPR, X-ray, and magnetization studies of metastable alloys Ti_2Fe, $Al_{40}Cu_{10}Mn_{25}Ge_{25}$ and $Al_{65}Cu_{20}Fe_{15}$ as prepared by mechanical alloying. *Journal Magnetic Materials 150*, p.430–436., 1995.

[4]. MISRA,S.K.; KAHRIZI, M. ; SINGH,K.; VENKATRAMANI,N.; BAHADUR,D. EPR, X-ray, and magnetization studies of metastable alloys Ti_2Fe, $Al_{40}Cu_{10}Mn_{25}Ge_{25}$ and $Al_{65}Cu_{20}Fe_{15}$ as prepared by mechanical alloying. *Journal Magnetic Materials 150*, p.430–436, 1995.

[5]. HUTTUNEN-SAARIVIRTA, E. Microstructure, fabrication and properties of quasicrystalline Al-Cu-Fe alloys: a review. *Journal of Alloys and Compounds 363 (1–2)*.p.154–178, 2004

[6]. CHEN, H.-L.; YONG, D.; HONGHUI, X.; WEI, X. Experimental investigation and thermodynamic modeling of the ternary Al-Cu-Fe system. *Journal of Materials Research 24 (10)*.p. 3154–3164, 2009.

[7]. SHIELD, J.E.; CAMPBELL, J.A.; SORDELET, D.J. Mechanical properties of Al-Cu-Fe-based quasicrystalline coatings. *Journal of Materials Science Letters 16 (24)*.p.2019–2021, 1997.

[8]. MUKHOPADHYAY, N.K.; UHLENWINKEL, V.; SRIVASTAVA, V.C. Synthesis and characterization of bulk Al-Cu-Fe based quasicrystals and composites by spray forming. *Journal of Materials Engineering and Performance 24(6)*.p. 2172–2178, 2015.

[9]. ROY, M. Formation and magnetic properties of mechanically alloyed $Al_{65}Cu_{20}Fe_{15}$ quasicrystal. *Journal of Magnetism and Magnetic Materials 302*, p.52–55, 2006.

[10]. SALES, M.; MERSTALLINGER, A.; USTINOV, A. I.; POLISHCHUK, S. S.; MELNICHENKO, T. V. Effect of the addition of crystalline β-phase in Al–Cu-Fe quasicrystalline coatings on their tribological properties. *Surface & Coatings Technology 201*, p.6206–6211, 2007.

[11]. ROSAS, G., PEREZ, R On the transformations of the ψ-AlCuFe icosahedral phase. *Materials Letters 47*.p. 225–230, 2001.

[12]. BISWAS ,K. GALUN , R. ;MORDIKE , N. L; CHATTOPADHYAY , K. Laser cladding of quasicrystal forming Al-Cu-Fe on aluminum. *Journal of Non-Crystalline Solids 334*. 517–523, 2004.

[13]. WIDJAJA, E. J.; MARKS, L. D. Microstructural evolution in Al–Cu–Fe quasicrystalline thin films. *Thin Solid Films 441*, p.63–71, 2003.

[14]. LEPESHEV , A.A.; ROZHKOVA ,E.A.; KARPOV , I.V.; USHAKOV ,A.V. ; FEDOROV , L.Y. PHYSICAL, mechanical, and tribological properties of quasicrystalline Al-Cu-Fe coatings prepared by plasma spraying. *Physics of the Solid State 55 (12)*.p. 2531–2536, 2013.

[15]. DUBOIS, J.M.; KANG, S.S.; ARCHAMBAULT, P. COLLERET, B. Thermal diffusivity of quasicrystalline and related crystalline alloys. *Journal of Materials Research 8 (1)*.p. 38–43, 1993.