FULL PAPER

Heat Treatment in an Alloy $Al_{64}Cu_{27}Fe_{15}$

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Abstract:

Aluminum-based alloys containing quasicrystalline phases have good wear resistance due to their low wear coefficient and high hardness. The formation of quasicrystalline phases depends on the composition of the alloy and the imposition of high cooling rates on the molten metal. In the raw state of fusion, presenting β-$Al_2Fe_5(Cu)$ monoclinic phases, they are present together with the quasicrystalline phase-ω. 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 $Al_{64}Cu_{27}Fe_{15}$ obtained by smelting, in a controlled atmosphere. To understand the microstructural evolution, characterizations were made using SEM and XRD. The thermal treatment carried out for 24 hours, to obtain a microstructure with icosahedral phase coexisting with small increases in existing crystalline phases.

Keywords: quasicrystalline phases; microstructural evolution; phases type β-$Al_2Fe_5(Cu)$

1. Introduction

Quasicrystals are known as the third state of the solid mater, after the classical crystal and amorphous materials [1]. A large number of quasicrystalline alloys have been discovered, the most investigated being alloys of Al systems with transition d-metals. These alloys have a combination of physical, thermal and mechanical properties, such as low electrical and thermal conductivity, good resistance to corrosion and oxidation, low friction coefficient, high hardness at room temperature. Obtaining a quasicrystalline icosahedral phase is the result of an expert reaction between a β phase and its remaining liquid. Detailed equilibrium phase of the Al-Cu-Fe ternary system are identified in the stable region of the icosahedral phase (i-phase) and the neighboring phases, which provides a useful guideline for phase selections and appropriate thermal processes for the phase synthesis. The metastable icosahedral phase-ω transforms directly to the β-phase (with a change in the composition), which is the stable phase of the composition of the alloy Al-Cu-Fe. Many structures can be either three-dimensional icosahedral (IQC) or two-dimensional decagonal

(DQC) in most of the Al-based quasicrystalline alloys. The icosahedral quasicrystalline phase present in the Al-Cu-Fe alloy is formed by peritectic solidification of high temperature crystalline phases reacting with a liquid phase. This process is necessarily slow, and mostly some crystalline phases are retained out of equilibrium at room temperature together with the quasicrystal. In the ternary system $Al_{64}Cu_{27}Fe_{15}$ in addition to the ψ-Al_6Cu_2Fe icosahedral phase, some crystalline phases are found, which can be mentioned: type B_2 structures (still called β), which can be further subdivided into β_1-$AlFe_3$ - (CCC), β - $Al_5[(Cu,Fe)_5$, $AlFe(Cu)$-(cubic), type(CsCl)]; λ-$Al_{13}Fe_4$-(monoclinic); λ-Al_7Fe_2-(orthorhombic); ω-Al_7Cu_2Fe (tetragonal); μ-Al_5Fe_2; τ-$AlCu(Fe)$-(cubic tetragonal), allows the formation of thermodynamic stability with icosahedral quasicrystalline phase, being thermodynamically stable under normal conditions of temperature and pressure [2].

Even in small proportions, approximate crystalline phases, when found retained in the quasicrystalline material, can significantly impair the properties of quasicrystals. The composition range of a purely quasicrystalline material is found

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in a very small fraction in the ternary phase diagram $Al_{64}Cu_{27}Fe_{15}$ [3].

Obtaining a purely quasicrystalline material depends on the preparation conditions. The production of quasicrystals, via conventional solidification, provides a quasicrystalline material along with a fraction of "approximate" crystalline phases. Through thermal treatments, a significant reduction of the crystalline phases is achieved to the detriment of the increase of the quasicrystalline phase. Iron, copper and aluminum powders are used, which are added to reduce the temperature of adiabatic combustion and, thus, avoid the vaporization of the other components with subsequent thermal treatment, obtaining a single-phase quasicrystalline material. Therefore, an additional heat treatment is necessary to promote the formation of icosahedral quasicrystalline phase. Due to crystalline and quasicrystalline phases exhibit significant composition and atomic volume differences; the formation of porosity has been reported, but as unwanted effect. Therefore, different ways have been suggested to reduce the porosity to a minimum while pure quasicrystal is obtained.

Therefore, as the time of the heat treatments increases, the amount of the quasicrystalline icosahedral phase-ω and liquid phases also increases. However, the ordering and stability of the icosaedral phase can then be achieved by heat treatment at 750-780ºC. The formation of the stable structure and ordering of quasicrystals seems to be the result of the ordering of metastable intermetallic. Because, there are transformations at the thermodynamic level between the formation of the solid solution β-$Al(Cu,Fe)$ and compound Al_7Cu_2Fe. This is due, the β and λ 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 $Al_{62}Cu_{25,5}Fe_{12,5}$ composition, together with the β-$Al(Cu,Fe)$ and τ-$AlCu(Fe)$ phases, in addition to small amounts of the λ-$Al_{13}Fe_4$ phase are attributed the icosaedral phase, after heat treatment. The objective of this work is the study of obtaining a material with phases of the type icosahedral-ω and β-$Al_2Fe_5(Cu)$ as a function of the heat treatment times.

2. Material and Methods

The aluminum, iron and copper powders, according to their granulometry and stoichiometric composition, having a purity of 99.99%, from Alcoa in Brazil-Alcoa Alumínio and Aldrich Chemical, were weighed in the proportions adequate to the composition $Al_{64}Cu_{27}Fe_{15}$, mechanically homogenized and compacted in the form of a disk 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 a controlled argon atmosphere. The electric induction arc furnace is powered by a BALMER static rectified generator whose 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. 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. For heat treatments, an oven with tubular resistance Nabertherm was used, at a temperature of 750 °C. The heating of the oven, together with the samples, was carried out with a heating rate of 30 °C min^{-1}. The thermal treatments were carried out at the following times: 6 am, 12 pm and 24 h.

The measurements were taken for a wide range of diffraction angles (2θ) ranging from 20° to 100° with an angular pitch of 0.05° and with counting time per point equal to 4s. 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, show the evolution of the phases of the raw melting alloy and of the heat treated alloys in the 6, 12 and 24h times. The X-ray diffraction peaks of low-iron-content and high-iron-content samples corresponding to the decagonal and icosahedral

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structures were identified and are marked in Figure 1. The X-ray diffraction patterns obtained from two different studied compositions where the icosahedral phase coexist with these crystalline phases (β is liquid). It is interesting to point out that the cubic phase β-Al_2Fe_5(Cu) always coexists with the icosahedral phase in all the explored compositions where the quasicrystalline icosahedral phase-ω was obtained. The diagram also indicates that the nucleation of the quasicrystalline icosahedral phase-ω is obtained in the ranges of ~70–56 at.% of aluminum, 40–5 at.% of copper and 20–5 at.% of iron. In the composition ranges, where only the icosahedral phase-ω and the β-Al_2Fe_5(Cu) cubic phase are present, the amount of the icosahedral phase depends on the Al:(Cu+Fe) ratio.

The peaks found in the diffractograms are ω-icosahedral phase phases and the β-Al_2Fe_5 (Cu) phase in a solid solution of Al_{50-x} (Cu, Fe)$_{50 + x}$ composition, since the structure of the β phase belongs to a group spatial Pm_3m (CsCl type structure) and its network parameter is approximately 2.9Å [4]. The methods used for preparation, the region of existence, the structure and the properties of icosahedral quasicrystalline phase (QC) formed in the Al-Cu-Fe system are thermodynamically stable. The β-phase is an Al(Cu,Fe) cubic crystalline phase and the i-phase is an Al_6Cu_2Fe icosahedral quasicrystalline phase.

The intensity of the peaks corresponding to i-phase is higher than the peaks specifically related to β-phase. The composition of $Al_{64}Cu_{27}Fe_{15}$ has phases in equilibrium with other crystalline phases such as ω-icosaedral phase and the β-Al_2Fe_5 (Cu) phase coexist with a small amount in solid solution [5]. 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.

In Figure 3, the morphology of the heat-treated sample is observed for 24 hours. Small nodules in cauliflower formats are seen, this is due to the

coexistence of the two phases, icosahedral phase-ω and the β-Al_2Fe_5(Cu) phase, both being diluted in the peritoneal reactions [6].
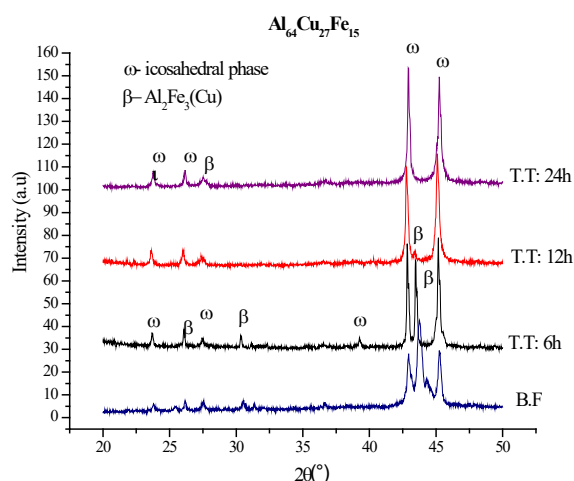

Figure 1. X-ray diffractograms (XRD) of samples of $Al_{64}Cu_{27}Fe_{15}$: Gross fusion heat treated at 6, 12 and 24 h.

Figures 2 and 3 represent the results obtained from quasicrystals samples by Scanning Electron Microscopy. In Figure 2, a morphology of colonies of particles with irregular flattened spherical shapes are observed, obtained in the raw state of fusion.
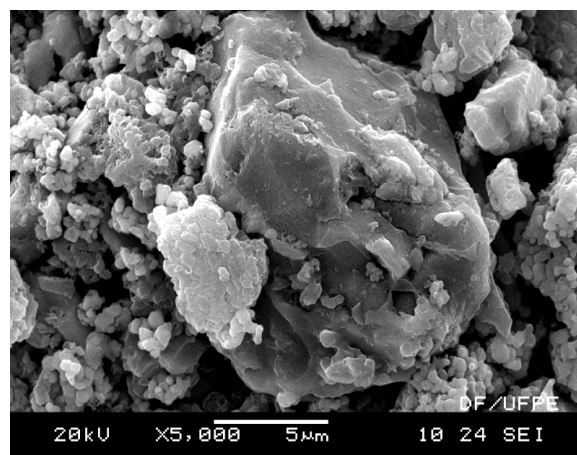

Figure 2. Scanning Electron Microscopy image of particles with flattened spherical shapes of the raw melting $Al_{64}Cu_{27}Fe_{15}$ alloy.

It can be observed in the image of β-Al_2Fe_5(Cu) pentagonal prism in column structure and small cauliflower nodules showing the λ-$Al_{13}Fe_4$ monoclinic phase coexisting with the quasicrystalline icosahedral phase-ω in solution solid. In the $Al_{65}Cu_{20}Fe_{15}$ alloy the icosahedral

phase is in equilibrium with the copper-poor λ-$Al_{13}Fe_4(Cu)$ phase, while in the $Al_{62.5}Cu_{25}Fe_{12.5}$ alloy it is in equilibrium with the Cu-rich β–Al(Cu,Fe) phase. The structure have been identified as λ-phase (or ω-phase) with chemical formula of $Al_{13}Fe_4$ or Al_7Cu_2Fe. Thus, the quasicrystalline phase in an $Al_{l65}Cu_{20}Fe_{15}$ alloy contains less copper compared to that $Al_{62.5}Cu_{25}Fe_{12.5}$ alloy. The crude fusion sample composed of $Al_{64}Cu_{27}Fe_{15}$, showed peaks associated with the λ-$Al_{13}Fe_4$ monoclinic phase, possibly due to a higher percentage of iron and aluminum in the alloy.

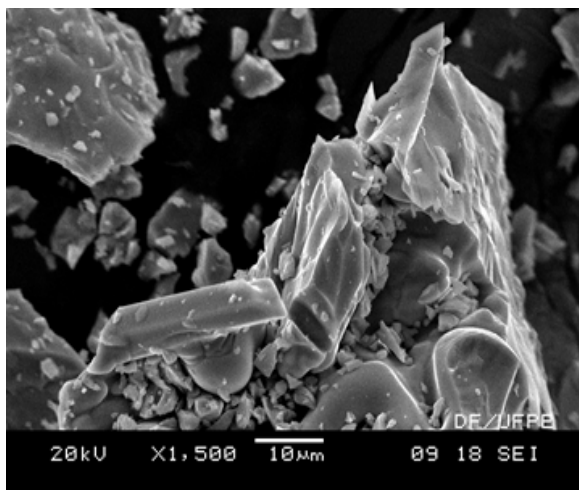**Figure 3.** Scanning Electron Microscopy image of the heat-treated sample for 24h of the $Al_{64}Cu_{27}Fe_{15}$ alloy with cauliflower nodules.

In the phase diagram, the icosahedral quasicrystalline phase is obtained by the peritoneal reaction of the β-Al(Cu,Fe) phase, the λ-Al_3Fe phase and the remaining liquid phase. This reaction starts at a temperature of approximately 860°C. This temperature indicates the beginning of an expert reaction responsible for the formation of the icosahedral phase that occurs between the λ_2-Al_3Fe, β-AlFe(Cu) phases and the remaining liquid. The β and λ phases fuse at temperatures above 1100°C. The λ-phase has a nominal composition of λ_2-Al_3Fe and extends within the ternary phase diagram replacing Cu with Fe.

The β-phase is a cubic Al(Cu,Fe) solution with type (B_2) structure. It converges to the binary phase AlFe, but admits an extensive substitution of Cu to Fe, according to the indications in the phase diagram. Between 700 to 872°C, the icosahedral phase is subjected to an expert test. In this temperature scale, the remaining liquid and the β or λ phase coexist, depending on the composition of the alloy. Because of the high fusion temperatures β and λ, it is not possible to form the i-phase directly by the fusion: one or both phases β or λ always appear first.

Due to the high melting temperature of β and λ, care in controlling the composition is essential to study the transformations of the i-phase. This observation indicates that the composition of the icosahedral phase in Al-Cu-Fe alloys not only depends on the cooling condition and the equilibrium temperature, but also on the coexisting phases that are in equilibrium with the icosahedral structure.

It is observed that even very small over-sprayed particles, which would have experience a very high cooling rate, reveal the presence of β-Al(Fe,Cu) phase. This must be seen in view of the fact that the composition of the quasicrystalline icosahedral phase-ω depends on the cooling conditions and the coexisting phases that are in equilibrium with the β-Al(Fe,Cu) phase [7]. The high heat content of the liquid could also be inferred from the shrinkage porosity observed in the regions having large grain size. This kind of porosity is absent in the small-grained regions.

4. Conclusions

It appears that the longer the heat treatment time, for samples treated up to 24h, the greater the homogeneity of the ω-icosahedral phase and the β-$Al_2Fe_5(Cu)$ phases. The sample of stoichiometric composition of the type $Al_{64}Cu_{27}Fe_{15}$, has equilibrium phases with the icosahedral phase-ω and the β-$Al_2Fe_5(Cu)$ phase coexisting in solid solution. The peaks found in the diffractograms are phases, icosahedral phase-ω and the β-$Al_2Fe_5(Cu)$, in a solid solution of $Al_{50-x}(Cu, Fe)_{50+x}$ composition. The presence of different morphologies was observed. In the fusion blends, there are particle morphology with flat spherical shapes of the $Al_{64}Cu_{27}Fe_{15}$ alloy. In the 24h heat treated sample of the $Al_{64}Cu_{27}Fe_{15}$ alloy, small nodules of colonies of particles in the shape of cauliflower are presented. Additionally, the grains of the β-$Al_2Fe_5(Cu)$ and icosahedral phase-ω located at the $Al_{64}Cu_{27}Fe_{15}$ particle/matrix interface were observed.

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Acknowledgments

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