A FASE ICOSAEDRAL DO SISTEMA Al$_{63}$Cu$_{25}$Fe$_{12}$

THE ICOSAHEDRAL PHASE OF Al$_{63}$Cu$_{25}$Fe$_{12}$ SYSTEM

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Resumo: presente trabalho teve como objetivo caracterizar a microestrutura da fase icosaedral (ϕ-fase quasicristalina) do sistema com composição estequiométrica do quasicristal Al$_{63}$Cu$_{25}$Fe$_{12}$. A liga ternária com composição nominal de Al$_{63}$Cu$_{25}$Fe$_{12}$ foi processada por Moagem de Alta Energia (MAE), como um método viável de processamento no estado sólido para a produção de várias fases quasicristalinas metaestáveis e estáveis. A caracterização estrutural das amostras obtidas foi realizada por difração de raios-X (DRX) e Microscopia Eletrônica de Varredura (MEV), enquanto a composição elementar dos elementos químicos Al, Fe e Cu foram determinados pela técnica de Espectroscopia de raios X por energia dispersiva (EDS). De acordo com os resultados de XRD, os padrões de difração da liga Al$_{63}$Cu$_{25}$Fe$_{12}$ mostraram a presença das fases β-Al(Fe,Cu) e λ-Al$_{13}$Fe$_4$ coexistem com a ϕ-fase quasicristalina em regime termodinâmico. Finalmente, a análise elementar indica que durante a síntese da liga existe pequena variação da composição ideal. Os resultados indicam que ligas com alto percentual de fase icosaedral podem ser obtidas por fundição ao ar.

Palavras-chaves: Fase Icosaedral. Caracterização. Quasicristal Al$_{63}$Cu$_{25}$Fe$_{12}$.

Abstract: The present work aimed to characterize the microstructure of the icosahedral phase (quasicrystalline phase-ϕ) of the system with stoichiometric composition of the quasicrystal Al$_{63}$Cu$_{25}$Fe$_{12}$. The ternary alloy with nominal composition of Al$_{63}$Cu$_{25}$Fe$_{12}$ was processed by mechanical alloying (MA) as a viable solid state processing method for producing various metastable and stable quasicrystalline phases. The structural characterization of the obtained samples was performed by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM), while the elemental composition of the chemical elements Al, Fe and Cu were determined by the technique of X-ray spectroscopy by dispersive energy (EDS). According to the results of XRD, the diffraction patterns of Al$_{63}$Cu$_{25}$Fe$_{12}$ showed the presence of β-Al(Fe,Cu) and λ-Al$_{13}$Fe$_4$ phases coexist with the thermodynamic ϕ-phase quasicrystalline. Finally, elemental analysis indicates that during alloy synthesis there is little variation of the ideal composition. The results indicate that alloys with high percentage of icosahedral phase can be obtained by casting in the air.

Keywords: Icosahedral Phase. Characterization. Quasicrystal Al$_{63}$Cu$_{25}$Fe$_{12}$

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1 INTRODUCTION

The quasicrystalline phases are a new class of intermetallic compounds which exhibit conventionally forbidden rotational symmetries in their diffraction patterns, which are incompatible with translational periodicity. The icosahedral phase was first discovered in 1984 by Schechtman in a rapidly solidified Al\textsubscript{86}Mn\textsubscript{14} alloy (SHECHTMAN et al., 1984).

These materials can be manufactured by Mechanical Alloying (MA), fast or conventional solidification (Melt-spinning), Physical Deposition of Vapors (PVD) and Plasma Processing (PP). The quasicrystals have many attractive properties, such as high hardness, low electrical and thermal conductivities, low surface energy, accompanied by low coefficient of friction, high resistance to oxidation and corrosion, and unusual optical properties that were not observed for crystalline alloys (DANIELS et al., 2005). Such properties of quasicrystalline materials were exploited for applications of heterogeneous catalysts in processes and catalytic supports in catalytic oxidation reactions of methanol. So far, several quasicrystals have been obtained in various binary, ternary and multicomponent systems. Generally, quasicrystalline phases form in systems based on Al, Mg, Zr, Fe, Co, Nb, Ti, Zn and Cu. As the variety of base metals forming quasicrystalline phases is broad, the spectrum of alloying elements is even broader (YIN et al., 2008). However, the alloying elements of these elements are potentially toxic, or economically viable. Al-Cu-Fe alloys are an exception. They are interesting due to the low degree of toxicity, easy availability and reasonable acquisition costs. Therefore, in the last two decades, Al-Cu-TM (TM = Fe, Co, Ni, Zr, Nb) quasicrystalline alloy systems have been intensively researched.

Was reported that the quasicrystalline phase formed in the conventionally solidified Al\textsubscript{65}Cu\textsubscript{20}Fe\textsubscript{15} alloy is thermodynamically stable and does not undergo phase transformation to the melting point (primary crystalline phase peritonic reaction) at 1135K (DUN et al., 2014). Therefore, the discovery of the thermodynamically stable quasicrystalline phase in the Al\textsubscript{65}Cu\textsubscript{20}Fe\textsubscript{15} alloy opened a new path for its experimental investigations. The preparation, properties, structure and application of these quasicrystalline alloys have been the main topics of interest in the field of the science of materials related to powder metallurgy.

The present work aims to investigate the formation of the quasicrystalline phase in the Al\textsubscript{63}Cu\textsubscript{25}Fe\textsubscript{12} system by mechanical alloying (planetary mill) for 5 hours. The identification of quasicrystalline phases, morphological and structural characteristics of the conventionally solidified Al\textsubscript{63}Cu\textsubscript{25}Fe\textsubscript{12} alloy were investigated in the present study using techniques X-ray diffraction (XRD), scanning electron microscopy (SEM) and dispersive energy spectroscopy (EDS). In addition, the thermal stability of the phases present in the ground powders is also evaluated.

2 MATERIALS AND METHODS

In the experiment, aluminum powders (purity-99.99%), copper (purity-99.99%) and iron (purity-99.99%) with nominal stoichiometric composition (expressed as%) of Al\textsubscript{63}Cu\textsubscript{25}Fe\textsubscript{12} were duly weighed, using a SHIMADZU model scale Ay 220, with precision of the order of 10\textsuperscript{-4}g. A Fritsch Pulverisette 5 planetary ball mill was used with cylindrical
pitchers 77 mm in diameter by 80 mm in height and balls (20, 12 and 7 mm in diameter), both being balls and tungsten jars. The identification of the phases and microstructural analysis and energy spectrum of the chemical elements alloys quasicrystalline made using the techniques X-ray diffraction (XRD), scanning electron microscopy (SEM) and dispersive energy spectroscopy (EDS).

The DRX analysis was performed using a SIEMENS diffractometer, Model D-5000, with CuKα (λ = 1,5406 Å), 0.01 °/s sweep step, in a 2θ ranging from 20° to 120°. The MEV/EDS analysis was performed by a LEO scanning electron microscope model 1430 with OXFORD microprocessor for EDS model 7353 coupled with a voltage between 5 and 20kV, after the sample was coated with a layer of gold deposited under vacuum in order to increase the contrast.

The load of the powder mixture was maintained at 20 g for all tests, as well as the 10:1 powder-to-powder ratio. The assay speed adopted was 200 rpm and grinding time was for 30 hours. Finally, 3 g of polyethylene additive was used as grinding medium and argon atmosphere. Polyethylene was used as a process controlling agent and added before grinding in order to reduce the adhesion of ductile aluminum particles to the bead spheres and walls.

3 RESULTS AND DISCUSSION

3.1 X-Ray Diffraction

The X-ray diffraction spectrum of the sample with Al₆₃Cu₂₅Fe₁₂ stoichiometry is shown in Figure 1, in the crude state of fusion. The following phases are observed in the diffractogram: cubic phase of type β-Al(Fe,Cu) and quasicrystalline phase-ϕ, which is a solid solution with cubic structure isomorphic of cesium chloride structure (CsCl) and the isomorphic phase λ-Al₁₃Fe₄ is completely monoclinic (DUN et al., 2014). For the alloy of Al₆₃Cu₂₅Fe₁₂ compositions the presence of β-Al(Fe,Cu) and λ-Al₁₃Fe₄ phases coexist with the quasicrystalline phase-ϕ, which depends on kinetic and thermodynamic processes. This result also suggests that the β-Al(Fe,Cu) is formed directly from the liquid phase (YOSHIOKA et al., 1995). It is possible to predict which the main intermetallic phases present are: FeAl, Fe₃Al, Fe₁₂Al₅, Fe₁₃Al₃ and Fe₂Al₉ and Fe₆Al₆ metastable phases. Therefore, we see that in a Fe-Al diffusion pair, there is a smaller drop in the circularity and a tendency to stabilize indicating a different kinetic behavior, thus causing the nodule to grow increasing the number of new complex phases with Cu and Fe, this can facilitate the appearance of facets, nodules and influences a cubic geometry characterized by a solid / liquid interface in each phase.

In addition, the β phase transforms below 750°C to form the phases λ and β, which are solid solutions induced by the solubility of Cu and Fe. In the Al₆₃Cu₂₅Fe₁₂ alloy, the formation of the icosahedral phase is the result of a peritoneal reaction between phase β-Al(Fe,Cu) with the remaining liquid. The crude melt sample, composition Al₆₃Cu₂₅Fe₁₂, showed peaks associated with the λ-Al₁₃Fe₄ monoclinic phase, possibly due to a higher percentage of iron and aluminum in the alloy.

It can be seen that, in addition to the peaks associated to the β-Al(Cu,Fe) cubic phase,
previously mentioned, a greater definition of the peaks referring to the icosahedral phase and the quasicrystalline phase-$\phi$(ROSAS & PEREZ, 2001).

![Spectrum of XRD of Al$_{63}$Cu$_{25}$Fe$_{12}$ alloy in the crude state of fusion.](image1)

**Figure 1.** Spectrum of XRD of Al$_{63}$Cu$_{25}$Fe$_{12}$ alloy in the crude state of fusion.

3.2 Scanning Electron Microscopy / Dispersive Energy Spectroscopy - SEM/EDS

The unmasked Al$_{63}$Cu$_{25}$Fe$_{12}$ quasicrystalline alloy in its crude state of fusion, observed in the scanning electron microscope (SEM) with the x-ray emission peaks of the chemical elements (Al, Cu and Fe) constituents in the sample of Al$_{63}$Cu$_{25}$Fe$_{12}$, shown Figures 2 and 3 below.

![SEM of the quasicrystalline alloy Al$_{63}$Cu$_{25}$Fe$_{12}$.](image2)

**Figure 2.** SEM of the quasicrystalline alloy Al$_{63}$Cu$_{25}$Fe$_{12}$. 
This result of the microstructural morphology observed in SEM showed a typical structure of a quasicrystalline grain in the shape of a pentagonal prism, structure in the form of a ladder and surrounded by small cauliflower nodules, according to Figure 2. It can be observed in the image of (Fe, Cu) "pentagonal prism in column structure" and small cauliflower nodules showing the $\lambda$-Al$_{13}$Fe$_4$ monoclinic phase coexisting with the quasicrystalline phase-ϕ, in solution solid (BAKER et al., 2017).

![Figure 3. EDS spectrum of the sample on Al$_{63}$Cu$_{25}$Fe$_{12}$.](image)

Figure 3 shows the elemental analysis spectrum of the ESD. There is a greater predominance of aluminum than the other elements (copper and iron) that make up the quasicrystalline alloy. The existence of $\gamma$-Al$_2$O$_3$ favors the formation of spinel on CuAl$_2$O$_4$ oxidation in the presence of Cu or CuO. However, the possibility of formation of other spinel oxides such as CuFe$_x$Al$_{2-x}$O$_4$, are essential to surface catalysis and the CuAl$_2$O$_4$ and Fe$_3$O$_4$ composites are complexes that form a thin film, which passive quasicrystalline alloy structure (ESTRELLA et al., 2009).

4 CONCLUSIONS

The main conclusions of this article are as follows:
- The icosahedral phase is directly transformed into the $\lambda$-Al$_{13}$Fe$_4$ monoclinic structure. In the case of the nominal stoichiometric composition Al$_{63}$Cu$_{25}$Fe$_{12}$, the icosahedral phase is completely transformed in the cubic phase $\beta$-Al(Cu,Fe) in solid solution at 700ºC, being evidenced in the XRD analysis;
From 700°C for 5 h in the Al$_{63}$Cu$_{25}$Fe$_{12}$ quasicrystalline alloy, it is possible to obtain and see the phases and the quasicrystalline phase presence of the β-Al(Fe,Cu) and λ-Al$_{13}$Fe$_{4}$ phases coexist with the quasicrystalline phase-ϕ up to a time 30-hour grinding time;

The Al$_{63}$Cu$_{25}$Fe$_{12}$ quasicrystalline alloy with high percentage of icosahedral phase can be produced by melting in the air, avoiding leakage of composition and certain impurities;

The SEM images of the quasicrystalline alloy Al$_{63}$Cu$_{25}$Fe$_{12}$ showed three phases: β-Al(Fe,Cu), λ-Al$_{13}$Fe$_{4}$ presenting similarity of both the present phases and the "pentagonal prism in column structure" morphology, surrounded by small cauliflower nodules. The existence of γ-Al$_2$O$_3$ favors the formation of spinel on Fe$_3$O$_4$/CuAl$_2$O$_4$ oxidation in the presence of Cu or CuO, having excellent properties for its use in heterogeneous catalysis.

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REFERENCES


