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Characterization in the Icosahedral Phase of the System $Al_{64}Cu_{25}Fe_{12}$

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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 $Al_{64}Cu_{25}Fe_{12}$. The ternary alloy with nominal composition of $Al_{64}Cu_{25}Fe_{12}$ 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 $Al_{64}Cu_{25}Fe_{12}$ showed the presence of $\beta - Al(Fe, Cu)$ and $\lambda - Al_{13}Fe_4$ 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: lcosahedral Phase,Characterization, Quasicrystal $Al_{64}Cu_{25}Fe_{12}$.

Caracterización en la Fase Icosaédrica del Sistema $Al_{64}Cu_{25}Fe_{12}$

Resumen
El presente trabajo tuvo como objetivo caracterizar la microestructura de la fase icosaédrica (fase cuasicristalina-ϕ) del sistema con composición estequiométrica del cuasicristal $Al_{64}Cu_{25}Fe_{12}$. La aleación ternaria con composición nominal de $Al_{64}Cu_{25}Fe_{12}$ se procesó mediante aleación mecánica (MA) como un método de procesamiento de estado sólido viable para producir varias fases cuasicristalinas metaestables y estables. La caracterización estructural de las muestras obtenidas se realizó mediante difracción de rayos X (XRD) y Microscopía electrónica de barrido (SEM), mientras que la composición elemental de los elementos químicos Al, Fe y Cu se determinó mediante la técnica de espectroscopía de rayos X por dispersión. energía (EDS). Según los resultados de XRD, los patrones de difracción de $Al_{64}Cu_{25}Fe_{12}$ mostraron la presencia de fases $\beta - Al(Fe, Cu)$ y $\lambda - Al_{13}Fe_4$ coexistiendo con la fase ϕ termodinámica cuasicristalina. Finalmente, el análisis elemental indica que durante la síntesis de la aleación hay poca variación de la composición ideal. Los resultados indican que se pueden obtener aleaciones con alto porcentaje de fase icosaédrica mediante colada al aire.

Palabras clave: Fase lcosaédrica, Caracterización,Cuasicristal $Al_{64}Cu_{25}Fe_{12}$.

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. Schechtman first discovered the icosahedral phase in 1984 in a rapidly solidified $Al_{86}Mn_{14}$ alloy [1]. Hundred of systems have been identified as QC formers on both, stable and metastable conditions. Most of these systems

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are based in aluminum alloyed to transition metals. Although much scientific knowledge has already been raised about the QCs, a technological use of these materials has yet to be achieved. A very promising application seems to be the use as a reinforcing phase in aluminum alloys, due to a set of intrinsic properties.The icosaedral quasicrystalline ψ phase is stable in a narrow composition range of the $Al-Cu-Fe$ system. This composition is around $Al_{62}Cu_{25}Fe_{12}$-$SIat.\%$)), in equilibrium with other crystalline phases like $\beta-AlFe(Cu)$, $\lambda-Al_{13}Fe_4$, λ_1-Al_3Fe, $\theta-Al_2Cu$, $\omega-Al_7Cu_2Fe$ and $\varphi-Al_{10}Cu_{10}Fe_1$. Among these crystalline phases, ω shows a great similarity with the icosahedral ψ phase. The coordination of the Fe atoms is very similar in both structures. From the solidification route, the ψ phase seems to be formed in equilibrium conditions, by a peritectic reaction from a primary crystalline phase. Non-equilibrium processes like rapid solidification or MA can extend the compositional range of ψ, as well as to form metastable disordered approximant phases.

In the $Al-Cu-Fe$ system, at compositions richer in iron like $Al_{60}Cu_{20}Fe_{15}$,the phase-ψ can be formed as a minor component by rapid solidification, and its proportion increases significantly after annealing. However, the mechanisms involved in this process are not clearly described. However, the mechanism of local atomic ordering in the transition from a crystalline to a quasicrystalline state is not well understood.The coordination numbers (CN) and atomic distances for QCs and other crystal structures for $Al-Cu-Fe$ have been observed at room temperature.

Some authors relate that during the annealing of the milled powder, the ψ phase can be formed from disordered metastable phases that are ordered by the effect of the heating. Other authors state that annealing at high temperatures can lead to liquid formation and the ψ phase could be formed from equilibrium phases through a peritectic reaction.

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 [2]. 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 [3].

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, Cr, Nb) quasicrystalline alloy systems have been intensively researched. Was reported that the quasicrystalline phase formed in the conventionally solidified $Al_{65}Cu_{20}Fe_{15}$ alloy is thermodynamically stable and does not undergo phase transformation to the melting point (primary crystalline phase peritetic reaction) at 1135K [4]. Therefore, the discovery of the thermodynamically stable quasicrystalline phase in the $Al_{65}Cu_{20}Fe_{15}$ 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 $Al_{64}Cu_{25}Fe_{12}$ system by mechanical alloying (planetary mill) for 5 hours. The identification of quasicrystalline phases, morphological and structural characteristics of the conventionally solidified $Al_{64}Cu_{25}Fe_{12}$ 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.

Experimental Procedures

In the experiment, aluminum powders (purity-$99,99\%$)), copper (purity-$99,99\%$) and iron (purity-$99,99\%$) with nominal stoichiometric composition (expressed as %) of $Al_{64}Cu_{25}Fe_{12}$ were duly weighed, using a SHIMADZU model scale Ay 220, with precision of the order of 10^{-4} g. A Frittsch 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 $CuK_\alpha(\lambda = 1,5406\text{Å})$, $0.01^\circ s^{-1}$ sweep step, in a 2θ (2-theta) 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 20 kV, 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.

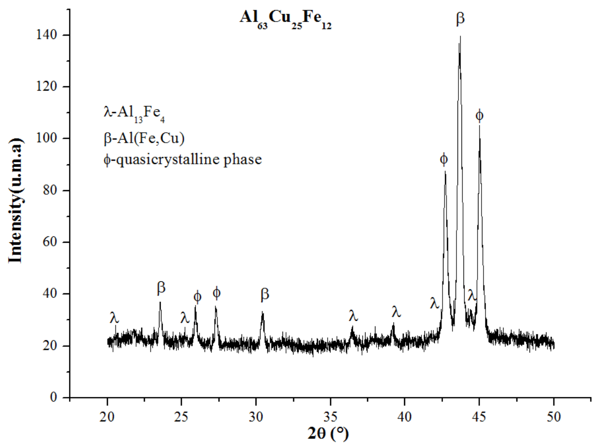

Figure 1: X-ray diffractogram of $Al_{64}Cu_{25}Fe_{12}$ alloy in the crude state of fusion.

Results and Discussion

The X-ray diffraction spectrum of the sample with $Al_{64}Cu_{25}Fe_{12}$ stoichiometry is shown in Figure 1, in the crude state of fusion. The following phases are observed in the diffractogram: cubic phase of type $\beta - Al(Fe, Cu)$ and quasicrystalline phase-ϕ, which is a solid solution with cubic structure isomorphic of cesium chloride structure ($CsCl$) and the isomorphic phase $\lambda - Al_{13}Fe_4$ is completely monoclinic [5]. In the $Al - Cu - Fe$ system, a large number of phases intermetallic crystals may be present depending on the composition of the alloy manufactured. Among these phases, the ones that occur most frequently are the phases referred to in the literature as, $\lambda - Al_{13}Fe_4$, $\lambda_2 - Al_3Fe$, $\beta - AlFe(Cu)$ (solid cubic solution with the structure of type CsCl), $\omega - Al_7Cu_2Fe$ among others. For the alloy with the composition of the present work, it was reported that the quasicrystalline phase is formed by the reaction between the phases $\lambda - Al_3Fe$, $\beta - AlFe(Cu)$ and the liquid.

For the alloy of $Al_{64}Cu_{25}Fe_{12}$ compositions the presence of $\beta - Al(Fe, Cu)$ and $\lambda - Al_{13}Fe_4$ phases coexist with the quasicrystalline phase-ϕ, which depends on kinetic and thermodynamic processes. This result also suggests that the $\beta - Al(Fe, Cu)$ is formed directly from the liquid phase. It is possible to predict which the main intermetallic phases present are: $FeAl$, Fe_3Al, $FeAl_2$, Fe_2Al_5, $FeAl_3$ and Fe_2Al_9 and $FeAl_6$ 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 [6]. 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 $Al_{64}Cu_{25}Fe_{12}$, the formation of the icosahedral phase is the result of a peritoneal reaction between phase $\beta - Al(Fe, Cu)$ with the remaining liquid.

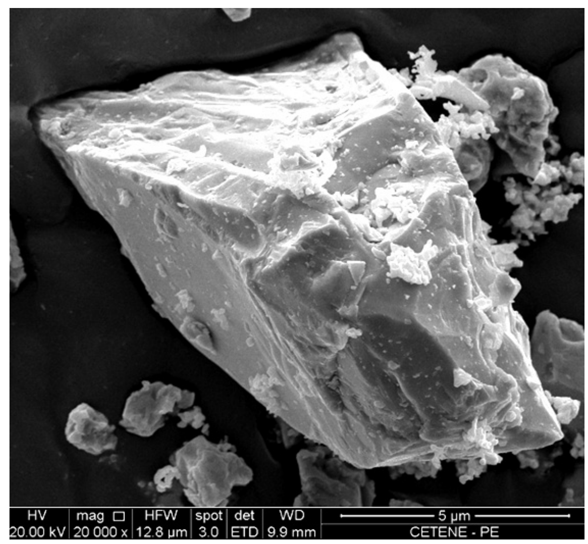

Figure 2: SEM of the quasicrystalline alloy $Al_{64}Cu_{25}Fe_{12}$.

The crude melt sample, composition $Al_{64}Cu_{25}Fe_{12}$, showed peaks associated with the $\lambda - Al_{13}Fe_4$ 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 $\beta - Al(Fe, Cu)$ cubic phase, previously mentioned, a greater definition of the peaks referring to the icosahedral phase and the quasicrystalline phase-ϕ [7]. The $Al - Cu - Fe$ system have a deleterious effect on the formation of the icosahedral quasicrystalline phase. Instead, a primitive cubic phase with the $B2$ structure is formed at the expense of the icosahedral phase. In the monoclinic $\lambda - Al_{13}Fe_4$ phase was also observed to form due to the higher Fe concentration for this composition, the $\beta - Al(Fe, Cu)$ cubic phase and the icosahedral quasicrystal was observed in the XRD pattern [8]. The unmasked $Al_{64}Cu_{25}Fe_{12}$ 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 $Al_{64}Cu_{25}Fe_{12}$, shown Figures 2 and 3 below. 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.

Figure 3 shows the elemental analysis spectrum of the Energy-dispersive X-ray spectroscopy (EDS). There is a greater predominance of aluminum than the other elements (copper and iron) that make up the quasicrystalline alloy.

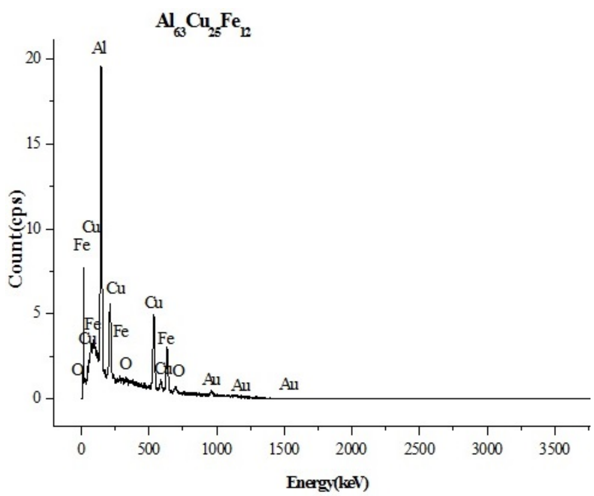

Figure 3: EDS spectrum of the sample on alloy $Al_{64}Cu_{25}Fe_{12}$.

The existence of $\varphi - Al_2O_3$ favors the formation of spinel on $CuAl_2O_4$ oxidation in the presence of Cu or CuO. However, the possibility of formation of other spinel oxides such as $CuFe_xAl_{2-x}O_4$, are essential to surface catalysis and the $CuAl_2O_4$ and Fe_3O_4 composites are complexes that form a thin film, which passive quasicrystalline alloy structure [9, 10].

Conclusions

- The icosahedral phase is directly transformed into the $\lambda - Al_{13}Fe_4$ monoclinic structure. In the case of the nominal stoichiometric composition $Al_{64}Cu_{25}Fe_{12}$ the icosahedral phase is completely transformed in the cubic phase $\beta - Al(Fe, Cu)$ in solid solution at 700 °C, being evidenced in the XRD analysis.

- From 700 °C for 5 h in the $Al_{64}Cu_{25}Fe_{12}$ quasicrystalline alloy, it is possible to obtain and observe the phases and the quasicrystalline phase presence of the $\beta - Al(Fe, Cu)$ and $\lambda - Al_{13}Fe_4$ phases coexist with the quasicrystalline phase-ϕ up to a time 30 hour grinding time.

- The $Al_{64}Cu_{25}Fe_{12}$ 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 $Al_{64}Cu_{25}Fe_{12}$ showed three phases: $\beta - Al(Fe, Cu)$ and $\lambda - Al_{13}Fe_4$ presenting similarity of both the present phases and the pentagonal prism in column structure morphology, surrounded by small cauliflower nodules. The existence of $\gamma - Al_2O_3$ favors the formation of spinel on $Fe_3O_4/CuAl_2O_4$ oxidation in the presence of Cu or CuO, having excellent properties for its use in heterogeneous catalysis.

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References

[1] D. Schechtman, I. Blech, D. Gratias, J.W. Cahn. Metallic Phase with Long-Range Orientational Order and No Translational Symmetry. Physical Review Letters **53**, 1951-1953. https://doi.org/10.1103/. (1984).

[2] M.J. Daniels, D. King, L. Fehrenbacher, J.S. Zabinski, J.C. Bilello. Physical Vapor Deposition Route for Production of $Al - Cu - Fe - Cr$ and $Al - Cu - Fe$ Quasicrystalline and Approximant Coatings. Surface and Coatings Technology. **191**, 96-101. https://doi.org/10.1016/j.surfcoat.2004.07.117. (2005).

[3] S. Yin, C. Li, Q. Blanb, M. Lua. Effect of composition on the formability of quasicrystalline phase in mechanically alloyed $Al - Cu - Fe$ powders. Materials Science and Engineering. **496**, 362-365. https:

//doi.org/10.1016/j.mex.2021.101305. (2008).

[4] D. Dun, H. Liu, L. Hou, L. Xue, L. Dou, W. Yang, Y. Zhao, B. Shen. Ductile $Co - Nb - B$ bulk metallic glass with ultrahigh strength. Journal of Non-Crystalline Solidspowders. Materials Science and Engineering. **386**, 121-123. https://doi.org/10.1016/j.jnoncrysol.2013.12.004. (2014).

[5] A.P. Tsai. Discovery of Stable Icosahedral Quasicrystals: Progress in Understanding Structure and Properties. Journal of Non-Crystalline Solids powders. **42**, 5352-5365. https://iopscience.iop.org/article/10.1143/JJAP.34.1606. (2013).

[6] A. Yoshioka, K. Edagawa, K. Kimura, S. Takeuchi. Production of High-Quality Thin-Film Samples of Al-Cu-Fe Icosahedral Quasicrystal. Japanese Journal of Applied Physics. **34(2)**, 1606-1609. https://doi.org/10.1039/c3cs35388e. (1995).

[7] G. Rosas, R. Perez.On the transformations of the $\psi - AlCuFe$ icosahedral phase Quasicrystal. Material Letters. **47**, 225-230. https://doi.org/10.1016/S0167-577X(00)00239-1. (2001).

[8] W. Wolfa, F.G. Coury, M.J. Kaufman, C. Bolfarini, C.S. Kiminami, W.J. Botta. The formation of quasicrystals in $Al-Cu-Fe-(M = Cr, Ni)$ melt-spun ribbons. Journal of Alloys and Compounds. **731**, 1288-1294. https://doi.org/10.1016/j.jallcom.2017.09.139. (2018).

[9] A. Baker, M. Caputo, H. Hampikian, L. Simpson, C. Li.Icosahedral Quasicrystal Layer Observed on λ Phase in $Al - Cu - Fe$ Alloy Materials Sciences and Applications. **8**. 509-520. https://doi.org/10.4236/msa.2017.87035. (2017).

[10] M. Strella, L. Barrio, G. Zhou, X. Ang, Q. Wang, W. Wen; J.C Hanson, A.I. Frenkel, A.J. Rodriguez. In Situ Characterization of $CuFe_2O_4$ and Cu/Fe_3O_4 Water-Gas Shift Catalysts. The Journal of Physical Chemistry **C**. **113**, 14411-14417. http://dx.doi.org/10.1021/jp903818q. (2009).