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FULL PAPER

Characterization in the Icosahedral Phase of $Al_{63}Cu_{25}Fe_{12}$ System

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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 $Al_{63}Cu_{25}Fe_{12}$. 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 was determined by dispersive energy spectroscopy (DES). The diffraction patterns of $Al_{63}Cu_{25}Fe_{12}$ showed the presence of quasicrystalline phase-ϕ, ω-Al_7Cu_2Fe, β-Al(Fe, Cu) and λ-$Al_{13}Fe_4$ phases that coexist with the thermodynamic quasicrystalline phase-ϕ. In icosahedral phase oxidation of aluminum forms a dense layer on the passivating outer most surface of the quasicrystal which causes depletion in both copper and iron. It was observed not only the presence of alumina, γ-Al_2O_3, but also the formation of hematite and copper oxide in the dense layer. 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; mechanical alloying; characterization; quasicrystal $Al_{63}Cu_{25}Fe_{12}$

1. Introduction

The quasicrystalline phases are a new class of intermetallic compounds that 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 $Al_{86}Mn_{14}$ alloy [1]. These materials can be manufactured by mechanical alloying (MA), fast or conventional solidification (melt-spinning), physical deposition of vapors and plasma processing.

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 have been exploited for application 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 are potentially toxic, but in the same time they are economically viable. Al-Cu-Fe alloys are an exception 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. It was reported that the quasicrystalline phase formed in the conventionally solidified $Al_{65}Cu_{20}Fe_{15}$ alloy is

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thermodynamically stable and does not undergo transformation phase to the melting point (primary crystalline phase peritonetic reaction) at 1135 K [4]. Therefore, the discovery of the thermodynamically stable quasicrystalline phase in the $Al_{63}Cu_{25}Fe_{12}$ 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. Another technique that is widely used to enhance densification is mechanical alloying (MA). MA is a powder metallurgy process that was developed in the mid-1960s by the International Nickel Company (INCO) as a solid route for introducing and retaining fine refractory oxide particles in high temperature alloys mainly for gas turbine applications [5]. It is a solid-state powder processing method through repeated welding, fracturing, and rewelding of powder particles in a high energy ball mill [6].

The present work aims to investigate the formation of the quasicrystalline phase in the $Al_{63}Cu_{25}Fe_{12}$ system by mechanical alloying method using a planetary mill (processing time – thirty hours). The quasicrystalline phases, morphological and structural characteristics of the conventionally solidified $Al_{63}Cu_{25}Fe_{12}$ alloy were investigated using techniques X-ray diffraction (XRD), scanning electron microscopy (SEM) and dispersive energy spectroscopy (DES). In addition, it was studied the conditions of grinding and thermal treatment to obtain the icosahedral phase and quasicrystalline phase-ϕ in the quasicristal $Al_{63}Cu_{25}Fe_{12}$.

2. Results and Discussion

3.1 X-Ray diffraction

The X-ray diffraction of the sample with $Al_{63}Cu_{25}Fe_{12}$ stoichiometry is shown in Figure 1 in the crude state of fusion. The following phases are observed in the diffractogram: cubic phase of type β-Al (Fe, Cu), ω-Al_7Cu_2Fe and quasicrystalline phase-ϕ, which is a solid solution with cubic structure isomorphic of cesium chloride structure (CsCl) and the isomorphic phase λ-$Al_{13}Fe_4$ is completely monoclinic [7]. For the $Al_{63}Cu_{25}Fe_{12}$ alloy composition the presence of β-Al (Fe, Cu) and λ-$Al_{13}Fe_4$ 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 [8]. It is possible to predict the main intermetallic phases that are present: FeAl, Fe_3Al, $FeAl_2$, Fe_2Al_5, $FeAl_3$ and Fe_2Al_9 and $FeAl_6$ metastable phases.

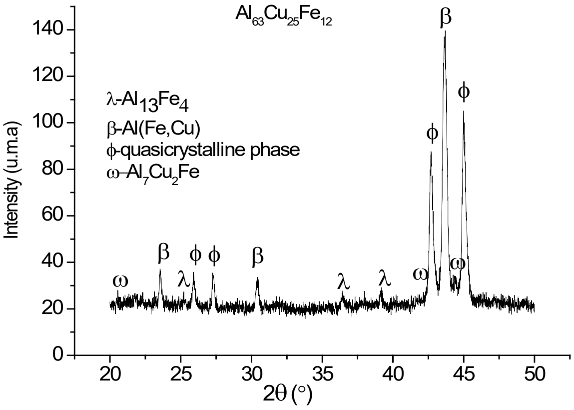

Figure 1. The XRD of $Al_{63}Cu_{25}Fe_{12}$ alloy in the crude state of fusion.

Therefore, it can be seen 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 is characterized by a solid/liquid interface in each phase. In addition, the β-phase transforms below 750°C into the λ,ω and β-phases, which are solid solutions induced by the solubility of Cu and Fe. In the $Al_{63}Cu_{25}Fe_{12}$ alloy, the formation of the icosahedral phase is the result of a peritoneal reaction between phase β-Al (Fe, Cu) with the remaining liquid.

For 30 hours of milling and treating at 700°C, a small presence of ω-Al_7Cu_2Fe intermetallic phase is observed in the x-ray diffractogram (see Figure 1) and with the increase of the milling time, the appearance of the icosahedral quasicrystalline phase-ϕ, together with the formation of the solid solution β-Al (Fe, Cu) and diluted in intermetallic phase ω-Al_7Cu_2Fe, these phases become very stable with a time.

Crude molten sample, composition $Al_{63}Cu_{25}Fe_{12}$, 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. It can be seen that, in addition to the peaks associated to the β-Al (Fe, Cu) cubic phase, previously mentioned, a greater definition of the peaks is showing the to the icosahedral phase and quasicrystalline phase-ϕ [9].

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

The $Al_{63}Cu_{25}Fe_{12}$ quasicrystalline alloy in its crude state of fusion was observed by 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. At 30 hours of milling, new peaks have appeared along with those of Al, Al_2Cu (intermetallic phase) and the λ-$Al_{13}Fe_4$ phase, being the quasicrystalline phase –φ phase and the most predominant β-Al (Fe, Cu) phase with formation of the icosahedral phase and their ordering are observed after heating. In addition, the heat treatment of the milled sample for 30 hours leads to the stabilization of the phase β-Al (Fe, Cu). In addition, the heat treatment of the milled sample for 30 hours leads to the stabilization of the β-Al (Fe, Cu) phases and the φ-quasicrystalline phase. At 30 hours there is an increase in the peaks of the icosahedral phase and a decrease of the phase ω-Al_7Cu_2Fe that is diluted with the quasicrystalline phase-ϕ. After a time of 30 hours, it was noticed that there is an evolutionary increase of the icosahedral phase and the phase β-Al (Fe, Cu) appears.

The maximum limit for the heat treatment temperature is 858 ºC, which is the melting point of the icosahedral structure. After mixing the $Al_{63}Cu_{25}Fe_{12}$ powder, typical composition for the icosahedral, quasicrystalline phase, milled, most of the structure produced, consists of β-Al(Fe,Cu) and ω-Al_7Cu_2Fe intermetallics, the quasicrystalline phase-ϕ is a secondary phase. This result of the microstructural morphology was 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 β-Al (Fe, Cu) pentagonal prism in column structure and small cauliflower nodules showing the λ-$Al_{13}Fe_4$ monoclinic phase coexisting with the quasicrystalline phase-ϕ, in solution solid [10]. The average grain size that this sample reaches after 30 hours of milling is ~ 19nm. Therefore, it is emphasized that a slight change in the compositions would cause a significant difference in the microstructural evolution during metallurgical processing.

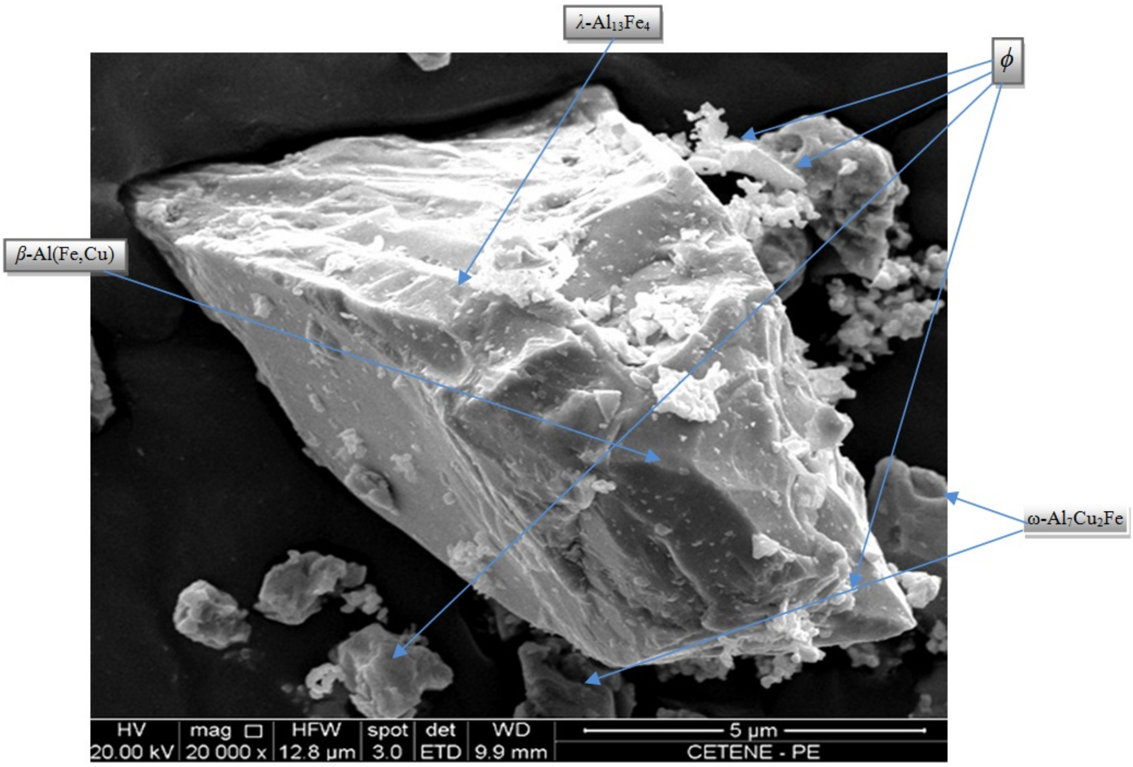

Figure 2. SEM of the quasicrystalline alloy $Al_{63}Cu_{25}Fe_{12}$ obtained after 30 hours of milling.

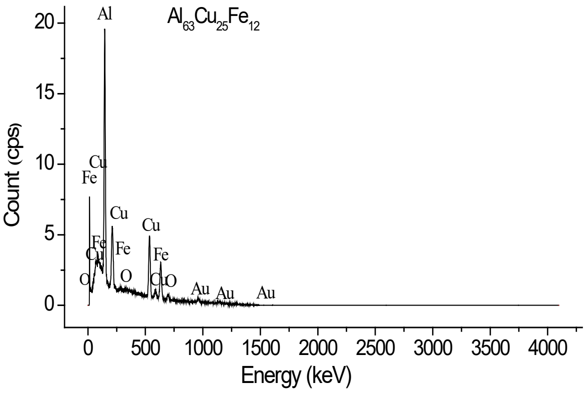

Figure 3. DES spectrum of the sample on $Al_{63}Cu_{25}Fe_{12}$.

In an advanced stage of oxidation, the formation of oxide nodules was observed by SEM. However, the possibility of formation of other spinel oxides such as $CuFe_xAl_{2-x}O_4$, are essential to surface catalysis and $CuAl_2O_4$ and Fe_3O_4 composites are complexes that form a thin film on the surface of quasicrystalline alloy [11]. Fe is not as much oxidised probably because it is embedded in $CuAl_2O_4$ grains, but Cu is only partly oxidised. The growth of an Al-oxide layer is controlled by diffusion of Al and O ions towards the metal-oxide interface involving predominantly the formation of Al–O bonds. For the oxidation of Al, the oxide films formed at low temperatures (T<200ºC) are amorphous and can be described by a close packing of oxygen anions with the Al cations distributed over the octahedral and tetrahedral interstices and exhibit a deficiency of Al cations [12]. In addition, an Al-deficient oxide film of self-limiting thickness grows which prevents Al to diffuse to the interface to further react with oxygen. A stoichiometric γ-Al_2O_3 may form if the exact amount of Al is available for a given oxygen dose. At the high-temperature limit of 858°C, the diffusivity does not prevent the supply of Al and O, thus, the surface film establishes a stoichiometric condition, which favors crystallization, correspondingly, and the oxidation of the clean pentagonal surface of $Al_{63}Cu_{25}Fe_{12}$ quasicrystal leads to the growth of an amorphous oxide layer, very fine film type. In order to obtain a proper quasicrystal–oxide interface, Al segregation from the bulk to the surface is required that first restores the quasicrystalline order and (only) then binds to oxygen to form the oxide layer. The high heat of formation for Al_2O_3, however, favors most likely the oxide formation on the crystalline $Al_{63}Cu_{25}Fe_{12}$ surface before the quasicrystalline stoichiometry and order is restored. The oxide bed which forms is very dense and has a damping and inhibitory property in the presence of Cu or CuO and Fe_3O_4 / $CuAl_2O_4$ due to the adhesion/sorption properties of amorphization on its surface. The oxide coating formed inorganic compound Al_2O_3 (alumina) that is a passivation layer which thickness is lower than two nanometers at room temperature, whatever the exposure to oxygen in which passivates quasicrystalline alloy structure. The dense layer passivates and inhibits the oxidation of copper property, since it influences the adhesion properties/adsorption. Therefore, these nodules consist of α-Al_2O_3 and γ-Al_2O_3, although the morphology of the nodule is very unusual for this oxide phase in the icosahedral phase.

3. Material 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 $Al_{63}Cu_{25}Fe_{12}$ were duly weighed , using a SHIMADZU model scale Ay 220, with precision of the order of 10^{-4} g. The $Al_{63}Cu_{25}Fe_{12}$ quasicrystalline alloy powder was obtained after the occurrence of the reaction in a Pulverizette 5 Fritsch planetary mill, for 30 hours. The milling speed was set to 300 rpm, to obtain fine powder of $Al_{63}Cu_{25}Fe_{12}$ alloy. The amount of material to be milled was kept constant for the experiment, being 25 g of powder per test, and the BPR dilution ratio changed between 10: 1 (5 and 10 kg of beads, respectively) under argon atmosphere. High purity argon is the most commonly used inert gas to prevent oxidation and/or contamination of powders. Generally, some considerable temperature increases can be achieved during grinding, reaching temperatures above 680°C in the confined contact region between 8 mm diameter stainless steel grinding bodies. There are very few reports of studies on the effects of intentionally altered grinding temperature. Usually, this is done by adding liquid N_2 in the grinding container to lower the temperature or by heating the grinding container to increase the temperature. The milling time depends on the material and its structure.

The ternary alloy with nominal composition of $Al_{63}Cu_{25}Fe_{12}$ was processed thirty hours by mechanical alloying (MA) method using a Frittsch

Pulverisette 5 planetary ball mill with cylindrical pitchers 77 mm in diameter by 80 mm in height and balls (8,12 and 20 mm in diameter), both being balls and tungsten jars.

3.1 Characterization Methods

The identification of the phases and also microstructural analysis and alloys quasicrystalline were done using the techniques X-ray diffraction (XRD), scanning electron microscopy (SEM) and dispersive energy spectroscopy (DES). The *XRD analysis* was performed using a SIEMENS diffractometer, Model D-5000, with CuK_α (λ= 1,5406 Å), 0.01 °/s sweep step, in a 2θ (2-theta) ranging from 20º to 120º.

A heat treatment was performed to favor the peritoneal transformation of these phases increasing the proportion of the quasicrystalline phase. In this case, a radiant oven was used, brand ANALOGICA and model AN8000, initially each sample was treated for 24 hours at a temperature of 750°C. However, the ordering and stability of the icosahedral phase can then be obtained by heat treatment at 750-780°C. The formation of the stable structure and quasicrystals appears to result from the ordering of metastable intermetallic with crystalline phases. The oven and the sample were simultaneously heated at a heating rate of 30°C/min. Before and during the treatment, intermediate washes with argon were performed in order to reduce the effects of oxidation and treat the samples in an inert atmosphere.

The *SEM/ DES analysis* was performed by a LEO scanning electron microscope model 1430 with OXFORD microprocessor for DES 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 25 g for all tests, as well as the 10:1 powder-to-powder ratio. The adopted assay speed was 300 rpm and grinding time was 30 hours. Finally, 2 g of polyethylene additive were 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.

4. Conclusions

The icosahedral phase is directly transformed into the λ-$Al_{13}Fe_4$ 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 β-Al (Fe, Cu) in solid solution at 700ºC, being evidenced in the XRD analysis. In 700°C during 30 hours in $Al_{65}Cu_{25}Fe_{15}$ quasicrystalline alloy, it is possible to obtain 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 30-hour grinding time. During the nanostruction process, the formation of new phases is poorly evidenced, only dependent on the grinding time and the heat treatment to be given in the $Al_{63}Cu_{25}Fe_{12}$ sample. This confirms the stability of this phase under the grinding process. The average grain size that this sample reaches after 30 hours of milling is ~19nm. The morphological analysis of $Al_{63}Cu_{25}Fe_{12}$ alloy performed by SEM, presents a crystallite with a structure of the column structure in the shape of a pentagonal prism with small platelets of aluminum oxide (γ-Al_2O_3) surrounded in the upper part and with small nodules of cauliflower. In grinding the obtained product is a solid metastable solution that acquires more energy as the increase in the milling time and which transformation in the icosahedral phase occurs by a faster diffusion process, justifying a less thermal treatment time. From 600°C in the $Al_{63}Cu_{25}Fe_{12}$ alloy the quasicrystalline phase was obtained along with the β-Al (Fe, Cu) and λ-$Al_{13}Fe_4$ phases up to a grinding time of 30 hours. When the quasicrystalline alloy is subjected to high temperatures, the formation of a sequence of metastable aluminas before the formation of the γ-Al_2O_3 alumina is observed. Oxidation has been found to be accompanied by a phase transformation of the phase-ϕ in to the β-Al (Fe, Cu) and ω-Al_7Cu_2Fe. Such a reaction can be understood by assuming Fe and Cu segregation which in turn might be responsible for the nodular growth of the oxide. Orientational oxide growth of γ-Al_2O_3 is detected at the surface of oxidized $Al_{63}Cu_{25}Fe_{12}$. The transformation phase could be detected due to diffusion of oxygen into the quasicrystals. This diffusion can be detected by other characterization techniques. The oxide bed, which is forming, is very dense and has a damping and inhibitory property in the presence of Cu or CuO and Fe_3O_4/$CuAl_2O_4$ due to the adhesion/sorption properties of amorphization on its surface. In an advanced stage of oxidation, the formation of oxide nodules was observed by SEM. Therefore, these nodules consist of α, γ -Al_2O_3, although the morphology of the nodule is very unusual for this oxide phase in the icosahedral phase.

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