

Quasicrystalline phase formation of the $Al_{67}Cu_{26}Fe_{15}$ alloy

Formação de fase quasicristalina da liga $Al_{67}Cu_{26}Fe_{15}$

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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 $Al_{67}Cu_{26}Fe_{15}$. The ternary alloy with nominal composition of $Al_{67}Cu_{26}Fe_{15}$ was processed by High Power Mechanical Milling 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). On the surface of the quasicrystalline alloy, we can observe in the SEM the presence of $\gamma-Al_2O_3$ alumina, which contributes to the textural properties of the catalytic support, revealing its catalytic activity, aiming at a higher performance in methanol oxidation reactions. The diffraction patterns of $Al_{67}Cu_{26}Fe_{15}$ showed the presence of $\omega-Al_7Cu_2Fe$, $\beta-Al(Fe,Cu)$ and $\lambda-Al_{13}Fe_4$ phases that coexist with the thermodynamic quasicrystalline phase- ϕ . 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. High power mechanical milling. Quasicrystal $Al_{67}Cu_{26}Fe_{15}$.

Resumo

O presente trabalho teve como objetivo caracterizar a microestrutura da fase icosaedral (ϕ -fase quasicristalina) do sistema com composição estequiométrica do quasicristal $Al_{67}Cu_{26}Fe_{15}$. A liga ternária com composição nominal de $Al_{67}Cu_{26}Fe_{15}$ foi processada por Moagem Mecânica de Alta Energia, 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). Na superfície da liga quasicristalina, podemos observar no SEM a presença da alumina $\gamma-Al_2O_3$, que contribui para as propriedades texturais de suporte catalítico devida a sua atividade catalítica, visando maior desempenho em reações de oxidação do metanol. De acordo com os resultados de XRD, os padrões de difração da liga $Al_{67}Cu_{26}Fe_{15}$ mostraram a presença das fases $\omega-Al_7Cu_2Fe$, $\beta-Al(Fe,Cu)$ e $\lambda-Al_{13}Fe_4$ 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-chave: Fase icosaedral. Moagem mecânica de alta energia. Quasicristal $Al_{67}Cu_{26}Fe_{15}$.

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Introduction

Quasicrystals are a new class of materials characterized by quasi-periodic order. Since then, quasicrystals have been observed in a wide range of intermetallic alloys. The stable icosahedral *Al-Cu-Fe* phase of a face-centered icosahedral (FCI) that can coexist with rational approximant crystalline structures. Alternatively, rapid cooling from molten state can be used. Mechanical alloying (MA) is a versatile technique capable of producing metastable and non-equilibrium phases, and may offer a cheap viable method of preparing quasicrystalline alloy powders suitable for subsequent manipulation. Surprisingly, quasicrystalline order has also been discovered recently in several soft-matter systems, ranging from spherical dendrite micelles, block copolymers to binary mixtures of nanoparticles. In addition, soft-matter quasicrystals can also be fabricated in colloidal systems using external fields such as holography or laser beams. Quasicrystalline behavior arises due to the presence of two competing length scales, either induced by the different sizes of the two particle species in the case of binary mixtures, or due to an effective pair interaction that favors two length scales. This leads to a broad classification of soft-matter quasicrystals in to two categories:

1. binary mixtures, for example, of nanoparticles interacting with simple isotropic pair potentials, and
2. single-component systems, like micelles, with effective pair interactions that favor two length scales.

Evidence of spontaneous formation of quasicrystalline order in soft-matter systems belonging to both categories have been observed in computer simulation studies. In order to prove the thermodynamic stability of quasicrystals, one has to show that the quasicrystal corresponds to the lowest free-energy state of the system.

Quasicrystals can be either energetically or entropically stabilised. An energetically stabilised quasicrystal results when the quasicrystal is the minimum-energy configuration at zero temperature. On the other hand, when the configurational entropy outweighs the energetic contribution, the quasicrystal may be entropically stabilised at finite temperatures. 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

(SHECHTMAN et al., 1984). These materials can be manufactured by mechanical alloying (MA), fast or conventional solidification (melt-spinning), physical deposition of vapors and plasma processing.

Mechanical alloying (MA) is a solid-state and powder processing technique involving repeated cold welding, fracturing, and re-welding of blended powder particles in a high-energy ball mill to produce a homogeneous material. Some neighbouring $Al_{13}TM_4$ phases (*TM*: transition metals, e.g. *Fe, Co, Ni*) and related ternaries consist of the same type of large icosahedral clusters and the same periodicity of stacking of planes with similar structure motifs, but are periodical three directions, sometimes with very large unit cells. Therefore, they are called approximants to the decagonal quasicrystals.

Originally developed to produce oxide-dispersion strengthened (ODS) nickel- and iron-base superalloys for applications in the aerospace industry, MA has now been shown to be capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or pre-alloyed powders.

The non-equilibrium phases synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys. Non-equilibrium processing of materials has attracted the attention of a number of scientists and engineers due to the possibility of producing better and improved materials than is possible by conventional methods. Quasicrystal and approximant phases exist at certain alloy compositions usually defined by valence electron concentrations and represent a kind of Hume-Rothery phases. The crystal energy is lowered by contact of the Fermi level to the Brillouin zone planes formed by strong diffraction peaks. Historically, Hume-Rothery phases were considered first in the *Cu-Zn* alloys and related binary systems of *Cu*-group elements with the neighboring elements of higher valences.

Rapid solidification processing (RSP) and mechanical alloying (MA) are two such processing methods with somewhat similar capabilities. MA is a dry powder processing technique and has been used to synthesize both equilibrium and metastable phases of commercially useful and scientifically interesting materials. These intermetallics were the intermediate products formed during to gradual mechanical and thermal homogenization and excitation. The quantitative phase composition of mechanically alloyed powders was determined using interactively controlled database phase analysis, fitting procedures and modelling of X-ray patterns for different structures. The process of MA consists of loading the powder mix and the

grinding medium (generally hardened steel or tungsten carbide balls) in a stainless steel container sealed under a protective argon atmosphere (to avoid/minimize oxidation and nitridation during milling) and milling for the desired length of time. About 1–2 wt.% of a process control agent (PCA) (usually stearic acid) is normally added to prevent excessive cold welding amongst the powder particles, especially when powders of ductile metals are milled.

The types of mills generally used are SPEX mills (wherein about 10g of the powder can be processed at a time), attritors (where a large quantity of about a few pounds of powder can be processed at a time), or Fritsch Pulverisette mills (where powder in more than one container can be processed simultaneously) (SURYANARAYANA et al., 2001). The times required for processing are short in the SPEX mills whereas they are longer in the attritors or Fritsch mills. Thermodynamic stability of the icosahedral quasicrystalline phase in $Al-Cu-Fe$ alloys has attracted lots of interest because it can hopefully give us a challenging opportunity for the potential industrial usage of the quasicrystalline materials.

Many investigations have been focused on the solidification behaviour and phase selection criterion of the $Al-Cu-Fe$ alloys, and a peritectic reaction has been suggested as a formation mechanism of the icosahedral phase in an appropriate cooling rate range. Meanwhile, the complex multiphase solidification structures of these alloys together with extreme brittleness retard the development activities for practical applications.

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 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 (YIN et al., 2008). 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, $Al-Cu-TM$ ($TM=Fe, Co, Ni, Zr, Nb, Mo, W, Hf, Os, Re$ etc.) 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 thermodynamically stable and does not undergo transformation phase to the melting point (primary crystalline phase peritectic reaction) at 1135 K (OCHIN et al., 1999).

Therefore, the discovery of the thermodynamically stable quasicrystalline phase in the $Al_{67}Cu_{26}Fe_{15}$ 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 $Al_{67}Cu_{26}Fe_{15}$ system by mechanical alloying method using a planetary mill (processing time – thirty hours). The quasicrystalline phases, morphological and structural characteristics of the conventionally solidified $Al_{67}Cu_{26}Fe_{15}$ 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 quasicrystal $Al_{67}Cu_{26}Fe_{15}$.

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 $Al_{67}Cu_{26}Fe_{15}$ were duly weighed, using a SHIMADZU model scale Ay 220, with precision of the order of 10^{-4} g. The $Al_{67}Cu_{26}Fe_{15}$ quasicrystalline alloy powder was obtained after the occurrence of the reaction in a Pulverizette 5 Fritsch planetary mill, for 30 hours 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.

The milling speed was set to 300 rpm, to obtain fine powder of $Al_{67}Cu_{26}Fe_{15}$ 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.

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 $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$), $0.01^{\circ}/\text{s}$ sweep step, in a 2θ (2-theta) ranging from 20° to 120° . Thus, we increased the proportion of the quasicrystalline phase, and thus performed a heat treatment to favor the peritectic transformation of these phases. In this case, we use a radiant oven, 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 $750\text{-}780^{\circ}\text{C}$. The formation of the stable structure and quasicrystals appear to result from the ordering of metastable intermetallic with crystalline phases. We heat the oven and the sample simultaneously at a heating rate of $30^{\circ}\text{C}/\text{min}$. Before and during the treatment, we perform intermediate washes with argon 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

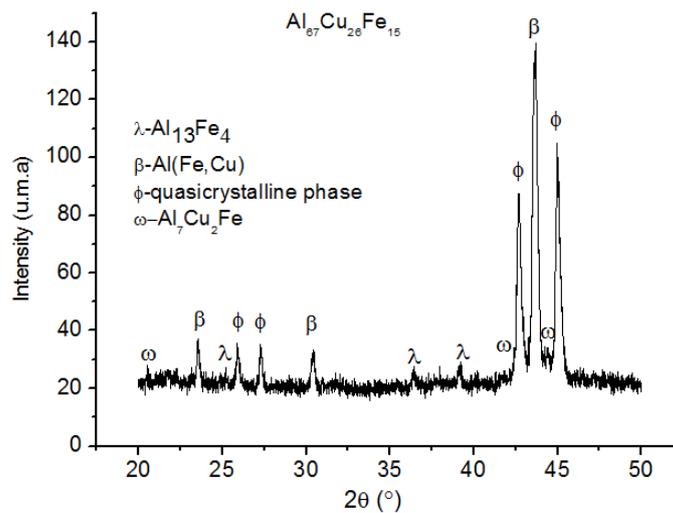
before grinding in order to reduce the adhesion of ductile aluminum particles to the bead spheres and walls.

Results and Discussion

The X-ray diffraction spectrum of the sample with $\text{Al}_{67}\text{Cu}_{26}\text{Fe}_{15}$ stoichiometry is shown in Figure 1 in the crude state of fusion. The following phases are observed in the diffractogram: cubic phase of type $\beta\text{-Al}(\text{Fe},\text{Cu})$, $\omega\text{-Al}_7\text{Cu}_2\text{Fe}$ and quasicrystalline phase- ϕ , which is a solid solution with cubic structure isomorphic of cesium chloride structure (CsCl) and the isomorphic phase $\lambda\text{-Al}_{13}\text{Fe}_4$ is completely monoclinic (TSAI, 2013). For the $\text{Al}_{67}\text{Cu}_{26}\text{Fe}_{15}$ alloy composition the presence of $\beta\text{-Al}(\text{Fe},\text{Cu})$ and $\lambda\text{-Al}_{13}\text{Fe}_4$ phases coexist with the quasicrystalline phase- ϕ , which depends on kinetic and thermodynamic processes. This result also suggests that the $\beta\text{-Al}(\text{Fe},\text{Cu})$ is formed directly from the liquid phase (YOSHIOKA et al.,1995). 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. 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 $\text{Al}_{67}\text{Cu}_{26}\text{Fe}_{15}$ alloy, the formation of the icosahedral phase is the result of a peritectic reaction between phase $\beta\text{-Al}(\text{Fe},\text{Cu})$ with the remaining liquid. From 725°C for 30 hours, in the $\text{Al}_{63}\text{Cu} - 25\text{Fe}_{12}$ alloy the quasicrystalline phase was obtained along with the $\beta\text{-Al}(\text{Fe},\text{Cu})$ and $\lambda\text{-Al}_{13}\text{Fe}_4$ phases for this milling time.

During the 30 hours of milling at a temperature of 700°C , the quasicrystalline- ϕ phase was obtained that coexists with the phases $\beta\text{-Al}(\text{Fe},\text{Cu})$ and $\lambda\text{-Al}_{13}\text{Fe}_4$. Frequently, the chemical formula of β phase in Al-Cu-Fe system is written in the form of $\beta\text{-Al}(\text{Fe},\text{Cu})$, to represent the fact that part of Fe is replaced by Cu .

The forces of repulsion between Cu and Fe have a pronounced effect on the elements distributions over the phases during the transformations caused by heating and also by a longer milling processing. Upon further heating, the chemical composition of the coexisting phases gradually approaches the average composition of the alloy.

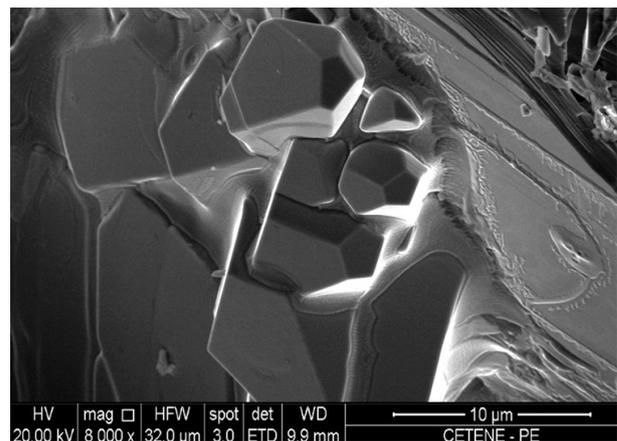
Figure 1 – The XRD Spectrum of $Al_{65}Cu_{25}Fe_{15}$ alloy.

Source: The authors.

The crude melt sample, composition $Al_{67}Cu_{26}Fe_{15}$, 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 $\beta-Al(Cu,Fe)$ cubic phase that were previously mentioned, a greater definition of the peaks referring to the icosahedral phase and the quasicrystalline phase- ϕ (ROSAS & PEREZ, 2001).

The $Al_{65}Cu_{25}Fe_{15}$ 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 $Al_{67}Cu_{26}Fe_{15}$, 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 $\lambda-Al_{13}Fe_4$ phase, being the quasicrystalline phase- ϕ phase and the most predominant $\beta-Al(Fe,Cu)$ 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 $\beta-Al(Fe,Cu)$.

In addition, the heat treatment of the milled sample for 30 hours leads to the stabilization of the $\beta-Al(Fe,Cu)$ phases and the quasicrystalline phase- ϕ . It is well known that the product phases in the case of peritectic as well as peritectoid reactions heterogeneously nucleate at the interface of the parent reactant phases. Subsequently, the product phase grows along the interface to form an intervening layer between the reactants. The transformation in both cases proceeds by solute diffusion through the product phase. Therefore, the diffusion of solute through product phase has been found to be the determining factor for the growth of the pro-

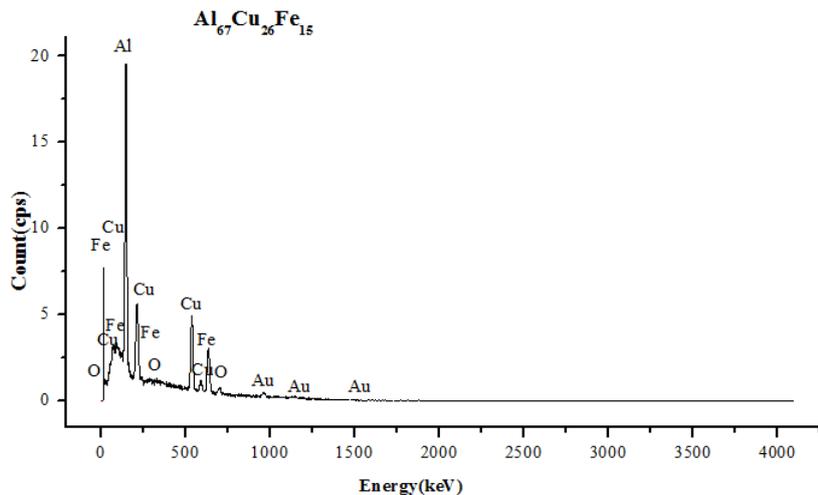
Figure 2 – SEM of the quasicrystal $Al_{67}Cu_{26}Fe_{15}$ in 30 hours of milling.

Source: The authors.

duct phase. This diffusion during a peritectoid reaction is extremely slow.

During the 30 hours there is an increase in the peaks of the icosahedral phase and a decrease of the phase $\omega-Al_7Cu_2Fe$ that is diluted with the quasicrystalline phase- ϕ . After a time of 30 hours, we notice that there is an evolutionary increase of the icosahedral phase and the phase $\beta-Al(Fe,Cu)$ appears. The maximum limit for the heat treatment temperature is $858^\circ C$, which is the melting point of the icosahedral structure.

After mixing the $Al_{65}Cu_{25}Fe_{15}$ powder, typical composition for the icosahedral, quasicrystalline phase, milled, most of the structure produced, consists of $\beta-Al(Fe,Cu)$ intermetallics, the quasicrystalline phase is a secondary phase.

Figure 3 – DES spectrum of the sample on $Al_{67}Cu_{26}Fe_{15}$.

Source: The authors.

This result of the microstructural morphology observed in SEM showed a typical structure of a quasicrystalline grain in the form of dodecahedron polyhedral with by nodules small cauliflower, according to Figure 2.

The high cooling rates promote the formation of metastable phases. 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). The average grain size that this sample reaches after 30 hours of milling is ≈ 19 nm.

The quasicrystalline phase- ϕ has equilibrium phase fields with three phases of $\beta-Al(Fe, Cu)$, $\lambda-Al_{13}Fe_4$, and liquid phases at $800^\circ C$, with four phases of β , λ , $\omega-Al_7Cu_2Fe$, and liquid at $720^\circ C$, and with three phases of $\beta-Al(Fe, Cu)$, ω , and liquid at $680^\circ C$. The large droplets, which experience less undercooling, contain higher heat content prior to deposition and undergo nucleation and growth of the primary $\lambda-Al_{13}Fe_4$ phase in the liquid.

After deposition, the remaining undercooled liquid phase leads to the formation of the quasicrystalline phase- ϕ . As the precipitates of the $\lambda-Al_{13}Fe_4$ phase are observed to be located in the centre of grains, this indicates that the quasicrystalline phase forms during deposition of undercooled droplets.

It is observed that even very small over-sprayed particles, which would have experience a very high cooling rate, reveal the presence of $\beta-Al(Fe, Cu)$ phase. This must be seen in view of the fact that the composition of the quasicrystalline phase- ϕ depends on the cooling condi-

tions and the coexisting phases that are in equilibrium with the $\beta-Al(Fe, Cu)$ phase. 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. After annealing at $750^\circ C$ for 30 hours, the precipitates of the $\lambda-Al_{13}Fe_4$ phase dissolve in the quasicrystalline phase- ϕ . Compared to $\beta-Al(Fe, Cu)$ phase, $\lambda-Al_{13}Fe_4$ is featured by its relatively high Cu concentration, thus is considered to be non-equilibrium, transforming to other phases upon annealing.

The equilibrium of these phases depends on the thermodynamic temperature. The change of the phase composition between the composite materials and the initial blend indicates that during the hot pressing process the reaction between the quasicrystalline particles and the matrix takes place. The formation of the $\omega-Al_7Cu_2Fe$ phase leads to an increase in the volume fraction of reinforcement with respect to the nominal value due to the higher molar volume of the $\omega-Al_7Cu_2Fe$ phase. It has been reported that the transformation of the ϕ -phase into crystalline phases depends on the consolidation conditions, especially temperature of the process.

The formation of the $\omega-Al_7Cu_2Fe$ phase was found in the composites consolidated at different temperatures and pressures. In our experiments the ϕ -phase transformed to $\omega-Al_7Cu_2Fe$ at lower temperature (about $400^\circ C$), contrary to the results presented above.

Reduction of this temperature could be correlated with the presence of the $\beta-Al(Cu, Fe)$, phase, which coexists with the i -phase in the initial melt spun ribbon. In the rapidly solidified ribbons observed phases are in the

metastable state and they can transform into stable equivalents during annealing at certain temperatures.

The temperature used for the compaction (about $400^{\circ}C$) is much lower than the temperature (above $600^{\circ}C$) of the transformation of two-phase $\beta+\phi$ structure to the single ϕ -phase. Therefore, it can be suggested that diffusion of the aluminium and copper between β and ϕ -phases facilitates change of the ϕ -phase composition towards that typical for stable i -phase variant and subsequent formation of small grains of the ω -phase (containing 71.3 at.% of Al , 19 at.% of Cu and 9.6 at.% of Fe) in the areas enriched in Al close to the β/ϕ -phase interface. Similar phenomena of the $\omega-Al_7Cu_2Fe$ phase nucleation on quasicrystalline/matrix interfaces. In the peritectic transformation, the reaction proceeds by advancement of the peritectic/primary interface. The compositional measurements clearly reveal that the transformation leading to formation of ω particles involves diffusion of aluminium and copper across the quasicrystalline phase- ϕ/ω interface. One can carry out calculations based on diffusional growth to show whether it is possible to form the ω phase in the solid state.

The interfaces do not bear any evidence of a peritectic reaction. The absence of anti-phase domains clearly indicates that the ω phase has not been formed in the solid state. The growth rate calculations using peritectoid transformation kinetics underestimates the observed experimental values. Therefore, it can be concluded that the ω crystallites precipitate on quasicrystals by heterogeneous nucleation and grow into the aluminium-rich melt until the supersaturation is exhausted.

Reduction of this temperature could be correlated with the presence of the $\beta-Al(Cu, Fe)$ phase, which coexists with the ϕ -phase in the initial melt spun ribbon. In the rapidly solidified ribbons observed phases are in the metastable state and they can transform into stable equivalents during annealing at certain temperature. Figure 3 shows the elemental analysis spectrum of the DES. There is a greater predominance of aluminum than the other elements (copper and iron) that make up the quasicrystalline alloy. The existence of $\gamma-Al_2O_3$ favors the formation of spinel on $CuAl_2O_4$ oxidation in the presence of Cu or CuO .

Among the different transition aluminas known, γ -alumina ($\gamma-Al_2O_3$) is perhaps the most important with direct application as a catalyst and catalyst support in the automotive and petroleum industries. The usefulness of this oxide can be traced to a favorable combination of its textural properties, such as surface area, pore volume, and poresize distribution and its acid/base characteristics,

which are mainly related to surface chemical composition, local microstructure, and phase composition.

Nevertheless, the chemical and hydrothermal stability of $\gamma-Al_2O_3$ are still a critical point for catalytic applications. For example, the use of $\gamma-Al_2O_3$ as a support for Co based catalysts in the Fischer–Tropsch (FT) process for the production of clean fuels is not lacking in practical problems. $\gamma-Al_2O_3$ is reported to appear at temperatures between 350 and $1000^{\circ}C$ when it is formed from crystalline or amorphous precursors, and is stable at temperatures as high as $1200^{\circ}C$ when the latter is used as the starting material.

The structure of $\gamma-Al_2O_3$ is traditionally considered as a cubic defect spinel type, the defective nature derives from the presence of only trivalent Al cations in the spinel like structure, i.e., the magnesium atoms in the ideal spinel $CuAl_2O_4/FeAl_2O_4/MgAl_2O_4$ are replaced by aluminum atoms.

The oxygen lattice is built up by a cubic close-packed stacking of oxygen layers, with Al atoms occupying the octahedral and tetrahedral sites. To satisfy the $\gamma-Al_2O_3$ stoichiometry some of the lattice positions remain empty (vacancies), although their precise location is still controversial.

When $\gamma-Al_2O_3$ is derived from amorphous aluminas it has always been reported to possess a cubic lattice. Both a cubic lattice and tetragonal distortion] are found for boehmite [$AlO(OH)$] or gibbsite [$Al(OH)_3$] derived $\gamma-Al_2O_3$. Other studies, however, have proposed the existence of only a tetragonal structure.

Recently, tetragonal $\gamma-Al_2O_3$ obtained from highly crystalline boehmite was reported to be present between 450 – $750^{\circ}C$. A reduction of the tetragonal distortion can be produced by increasing the temperature, but at no stage is cubic $\gamma-Al_2O_3$ obtained. A new phase has been identified with more obvious cation ordering above $750^{\circ}C$, designated as $\gamma'-Al_2O_3$, which approaches the structure of $\delta-Al_2O_3$ above $900^{\circ}C$.

The main difference is considered to be in the arrangement of the Al atoms: the vacancies are distributed between octahedral and tetrahedral sites in $\gamma-Al_2O_3$, while they are only in octahedral sites in $\delta-Al_2O_3$; the oxygen lattice is the same for both phases.

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. Fe is not as much oxidised probably because it is embedded in

$CuAl_2O_4$ grains, but the 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. Alumina (Al_2O_3) presents Lewis-type acid sites which are formed during the dehydration process by combination of two surface hydroxyl groups. Silica-alumina ($SiO_2 : Al_2O_3$) has acid-sites of the Lewis and Brönsted types.

The Brönsted type is able to give away a proton, in such a way that the mechanism of the dehydration reaction may be of the ionic type. For the oxidation of Al , the oxide films formed at low temperatures ($T < 200^\circ C$) 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. A stoichiometric Al_2O_3 may form if the exact amount of Al is available for a given oxygen dose.

At the high-temperature limit of $858^\circ C$, 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 $Al_{65}Cu_{25}Fe_{15}$ quasicrystal leads sheets at room temperature exhibited field-effect mobilities of $6-9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which are almost one order of magnitude higher than those reported for the growth of an amorphous oxide layer. 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 $Al_{67}Cu_{26}Fe_{15}$ surface before the quasicrystalline stoichiometry and order is restored. The oxide thin layer that forms is very dense and has a damping and inhibitory property in the presence of Cu , forming a rich variety of compounds with oxidation states of +1 and +2. The removal of oxygen results in excess electrons that are redistributed on the cation empty levels, thus changing their oxidation state from M^{n+} to $M^{(n-1)+}$. Transition-metal oxides such as CuO , TiO_2 , Fe_3O_4 , WO_3 , NiO , Fe_2O_3 , $CuAl_2O_4$, Al_2O_3 , CeO_2 , etc., just to mention a, belong to this category which remain on the surface of the quasicrystalline alloy due to the adhesion/sorption properties of amorphization on its surface.

Oxides can be used as inert supports of finely dispersed active metal nanoparticles or directly as catalysts. In this latter case, the oxide surface must be able to exchange chemical species with the liquid- or gas-phase surroundings or to adsorb chemical species

and promote dissociation and regeneration of chemical bonds.

The great flexibility of oxide surfaces stems from the presence on the surface of both Lewis and Brönsted acid and basic sites, sometimes acting in a cooperative way (ESTRELLA et al., 2009). Therefore, these nodules consist of $\alpha-Al_2O_3$ and $\gamma-Al_2O_3$, although the morphology of the nodule is very unusual for this oxide phase in the icosahedral phase.

Conclusions

The icosahedral phase is directly transformed into the $\lambda-Al_{13}Fe_4$ monoclinic structure. In the case of the nominal stoichiometric composition $Al_{67}Cu_{26}Fe_{15}$, the icosahedral phase is completely transformed in the cubic phase $\beta-Al(Cu, Fe)$ in solid solution at $700^\circ C$, being evidenced in the XRD analysis. In $700^\circ C$ during 5 hours in $Al_{65}Cu_{25}Fe_{15}$ quasicrystalline alloy, it is possible to obtain 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 30-hour grinding time. During the nanostructure process, the formation of new phases is poorly evidenced, only dependent on the grinding time and the heat treatment to be given in the $Al_{65}Cu_{25}Fe_{15}$ 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 $\approx 19\text{nm}$. The morphological analysis of $Al_{65}Cu_{25}Fe_{15}$ 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 (Al_2O_3) surrounded in the upper part and with small nodules of cauliflower. The ω phase precipitates on the icosahedral phase by heterogeneous nucleation and grows into the aluminium-rich melt until the supersaturation is exhausted. The phase evolution during laser processing can be explained using concepts available in the literature.

In grinding the obtained product is a solid metastable solution that acquires more energy as the increase in the milling time and whose transformation in the icosahedral phase occurs by a faster diffusion process, justifying a less thermal treatment time. From $600^\circ C$ in the $Al_{67}Cu_{26}Fe_{15}$ alloy the quasicrystalline phase was obtained along with the $\beta-Al(Fe, Cu)$ and $\lambda-Al_{13}Fe_4$ 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 $\gamma-Al_2O_3$ alumina is observed.

The ϕ -phase partially transformed to ω -Al₇Cu₂Fe phase in all hot compacted composites, which involved an increase in the volume fraction. The ω -phase nucleated in the form of small grains as a product of Al₆₇Cu₂₆Fe₁₅ particle transformation. Additionally, the grains of the β -Al(Cu, Fe) icosahedral phase located at the Al₆₇Cu₂₆Fe₁₅ particle/matrix interface were observed. The oxide bed which forms is very dense and has a damping and inhibitory property in the presence of Cu or CuO and Fe₃O₄/CuAl₂O₄ 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 -Al₂O₃, although the morphology of the nodule is very unusual for this oxide phase in the icosahedral phase.

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