Materials Research. 2012; 15(5): 749-752
DOI: 10.1590/S1516-14392012005000046

The Formation of Quasicrystal Phase in Al-Cu-Fe System By Mechanical Alloying

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Received: November 30, 2011; Revised: February 15, 2012

In order to obtain quasicrystalline (QC) phase by mechanical alloying (MA) in the Al-Cu-Fe system, mixtures of elementary Al, Cu and Fe in the proportion of 65-20-15 (at. %) were produced by high energy ball milling (HEBM). A very high energy type mill (spex) and short milling times (up to 5 hours) were employed. The resulting powders were characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). QC phase was not directly formed by milling under the conditions employed in this work. However, phase transformations identified by DSC analysis reveals that annealing after HEBM possibly results in the formation of the ψ QC phase.

Keywords: *Al-Cu-Fe system, mechanical alloying, quasicrystals*

1. Introduction

Since the discovery of quasicrystals (QCs) about 30 years ago, many efforts have been made in understanding the structure, properties and the synthesis of these materials. Hundred of systems have been identified as QC formers on both, stable and metastable conditions. Most of these systems 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 $Al_{63}Cu_{25}Fe_{12}$ (at. %), in equilibrium with other crystalline phases like β-AlFe(Cu), λ-$Al_{13}Fe_4$, λ1-Al_3Fe, θ-Al_2Cu, ω-Al_7Cu_2Fe and ϕ-$Al_{10}Cu_{10}Fe$[1]. Among these crystalline phases, ω shows a great similarity with the icosaedral ψ phase. The coordination of the Fe atoms is very similar in both structures[2].

From the solidification route, the ψ phase seems to be formed in equilibrium conditions, by a peritectic reaction from a primary crystalline phase[1,3,4]. Non-equilibrium processes like rapid solidification or MA can extend the compositional range of ψ, as well as to form metastable disordered approximant phases. HEBM process seems to be suitable for the production of nano-particles due to the continuous process of mixture and fragmentation. However, it seems that quasicrystals are destabilized in presence of high concentration of structural defects[5] that are common in the HEBM powders.

The composition of the ψ phase, when formed, depends on the alloy composition, as well as on the composition of the co-existing phases[4]. These aspects make complex the mechanism of QC formation by MA, which is very dependent on the process variables, as well as on the contamination level. Fe excess from the milling media can result in significant changes in the composition of the mixture. The particles initial size, the use of PCA (process control agents), the milling atmosphere, time and energy, which are related to the temperature reached during the process and to the contamination level, strongly affect the alloying mechanisms during the milling. Furthermore, the success in obtaining the QC ψ phase by HEBM in the Al-Cu-Fe system is frequently related to a subsequent annealing at temperatures from 400 to 800 °C after milling. However, the mechanisms involved in this process are not clearly described. 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.

In the Al-Cu-Fe system, at compositions richer in iron like $Al_{60}Cu_{20}Fe_{15}$, the ψ phase can be formed as a minor component by rapid solidification, and its proportion increases significantly after annealing[3]. HEBM of the same composition can lead to the formation of the ψ phase after annealing at temperatures ranging from 440 to 550 °C[6] or at temperatures as high as 750 °C[7], or even with no additional annealing, as a minor phase[8,9]. In compositions with lower

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Fe content (10-12 at. %), the ψ phase can be obtained by MA without subsequent annealing[2,9,10], but in this case Fe contamination, mainly from longer milling times, can change the overall composition of the mixture.

Immerse in this context, the present work aims to investigate the formation of the ψ phase in the Al-Cu-Fe system by mechanical alloying, under very high energy conditions (spex type mill) and short milling times (up to 5 hours). In addition, the thermal stability of the phases present in the milled powders is also evaluated.

2. Experimental Procedures

Al, Cu (powder) and Fe (1-2 mm pellets), in the proportion of $Al_{65}Cu_{20}Fe_{15}$, atomic %, were HEBM in a Spex ball mill, for 1, 2, 3 and 5 hours, under argon atmosphere. Ball to powder ratio was 10:1 and 1% (weight) of stearic acid was employed as a process control agent.

The produced powders were characterized by X-ray diffraction (XRD), using a Rigaku Geiger-Flex equipment, at 40 kV × 30 mA, Cu Kα radiation (λ = 1,54056 Å) and 2θ from 5 to 90° at 2°/min and a step of 0,032 degree/s, in order to verify the level of mixture during the milling, as well as to identify the phases eventually formed during HEBM. Differential scanning calorimetry (DSC) Netzsch DSC 200 F3 Maia, under constant argon flux and heating rate of 40 K/min, was also performed in order to evaluate the thermal stability of the mixture and to verify the occurrence of phase transformations induced by heating. Scanning electron microscopy (SEM) FEI Magellan 400 L was employed to verify the powder morphological and size evolution along the process.

3. Results and Discussion

Figure 1 shows the XRD analysis of the as milled powders. Peaks of elementary Al, Cu and Fe are predominant in the powders milled for 1 hour, but small peaks identified as the θ phase are already present. As the milling time increases, Al and mainly Cu peaks decrease significantly. The θ peaks seems to reach its maximum intensity in the powder milled for 2 hours, decreasing thereafter. Fe peaks remain visible even in powders milled for 5 hours. It seems that the lower solubility and diffusivity of Fe than Cu in Al is responsible for this effect. Besides, the starting size of the Fe pellets was greater than the Al and Cu powders. Some weak unidentified peaks occur for all milling times. Similar results were obtained in several works using planetary mills and longer milling times[2,8,9-12], although the presence of β or even ψ phases, besides the θ phase, are also reported in these works. The presence of X-ray diffraction lines from the elementary powders after 2 and 3 hours of milling made difficult the identification of other phases having diffraction lines at 2θ ranging from 43 to 45° and that were supposed to form.

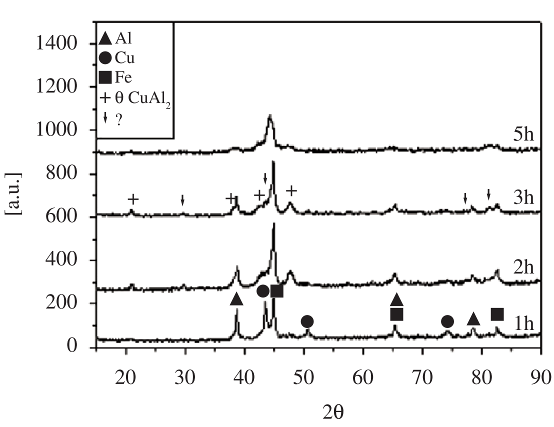


Figure 1. XRD spectra obtained for the powders milled for different times: 1, 2, 3 and 5 hours.

An unidentified peak appears at the edge of the mean Fe peak, becoming more evident in the powder milled for 5 hours. This peak at 2θ = 44°, in association to other unidentified peak at the position around 2θ = 81° could be associated to λ, β1-$AlFe_3$ or even to a metastable γ-Al_4Cu_9 phase[13]. However the small amount of peaks that could be related to these phases does not allow a precise identification.

DSC spectra of the milled powders are seen in Figure 2a. A detailed view reveals that an exothermic peak around 150 °C is observed in the powder milled for 1 hour (Figure 2b). This peak decreases after 2 hours of milling (Figure 2c), disappearing for greater milling times. This peak could be associated to the θ phase formation, as it reduces for higher milling times, where θ forms directly from the milling process as observed in XRD (Figure 1). DSC peaks at this temperature were also related to powder stress relief[14], but it seems to be not the case in the present work, as their intensity reduces and disappear with longer milling times. Salimon et al. observed the formation of θ and β phases after annealing the Al-Cu-Fe mechanically alloyed powders at this temperature range[15]. However, higher temperatures are also reported for θ formation: 330 °C (along with the ω phase)[6], 400[2,10] and 580 °C[7].

A small exothermic peak is observed at 350 °C in the powder milled for 2 hours. This peak is also present in the powders milled for longer times and can be associated with the formation of the ω phase[6,14]. As the phase ω is identified as a precursor of the simultaneous formation of the ψ and β phases[6,13], the high energy exothermic peaks observed in all milling times in the range of 432 to 458 °C, could be associated to a massive formation of both phases. Finally, the endothermic peaks at 540 and 585 °C, observed in the powders milled for 1 hour, can be associated with θ and Al fusion, respectively. The peaks are very small in the powder milled for 2 hours and disappear in powders milled for 3 and 5 hours. The pseudo binary λ - θ phase diagram[7] reveals that the θ melts at 585 °C. Although the melting temperature of Al is normally around 660 °C, it can be reduced by the presence of small amounts of Cu as an impurity[14].

Figure 3 shows SEM micrographs from the as milled powders. As verified in the XRD analysis, the mixture is not complete after 1 hour of milling. Back-scattering electrons contrast reveals a fine unmixed lamellar structure, along with Cu and mainly Fe isolated particles (Figure 1). Although unmixed, the intimate lamellar contact of elements in some particles of the powder can promote solid state reactions under heating, as observed in DSC analysis. Increasing

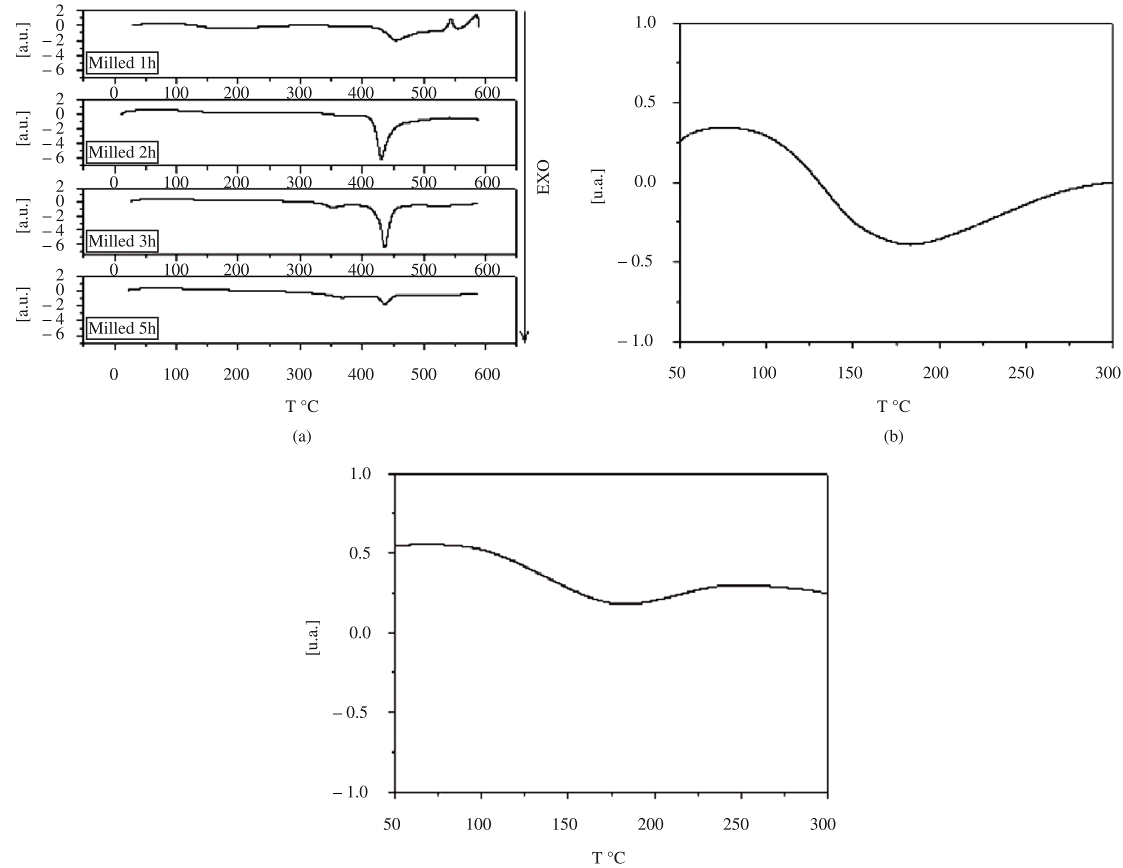
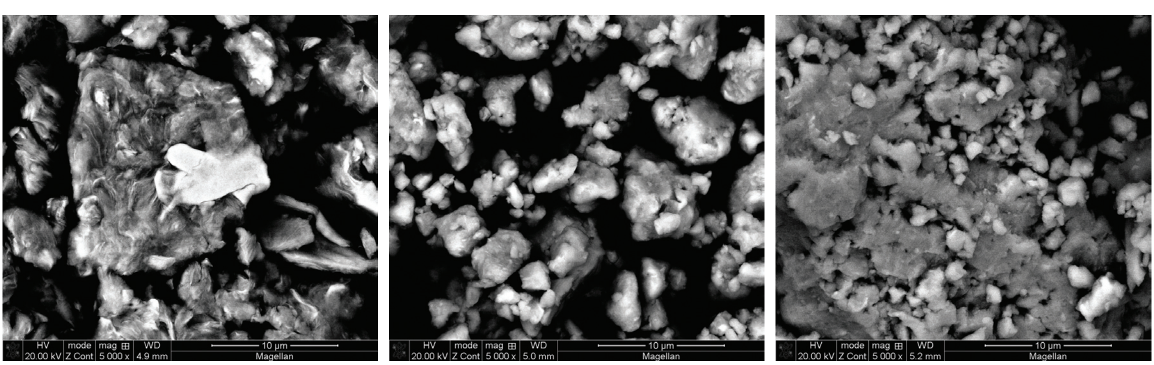


Figure 2. DSC results obtained for the powders milled for different times: a) overall results; b) detail of exothermic peak of the powder milled for 1 hour, around 150 °C; and c) detail of exothermic peak of the powder milled for 2 hours, around 150 °C.



(a) (b) (c)

Figure 3. SEM micrographs of the as milled powders, for different milling times: a) 1 hour; b) 3 hours; and c) 5 hours. Back scattering electrons contrast.

the milling time, the lamellar structure becomes hardly visible, suggesting that alloying starts to occur. In fact, XRD results reveal the θ phase forms, along with some unidentified phases, mainly in the powders milled for 2, 3 and 5 hours. Further, the size of the unmixed Cu and Fe particles becomes significantly smaller (clear particles in Figure 3b). After milling for 5 hours, the amount of unmixed particles becomes significantly reduced and the powders tend to agglomerate.

4. Conclusions

Based on the experimental conditions employed in this work and its corresponding results, the following conclusions can be drawn:

The complete mixture of the elementary powders was not complete up to 5 hours milling. However, a fine lamellar structure was obtained, mainly between Al and Cu, even after only 1 hour milling. This enabled the formation of θ phase during the milling and several other solid state reactions observed in DSC analysis;

QC phase was not directly formed in the $Al_{65}Cu_{20}Fe_{15}$ alloy by HEBM, using a very high energy mill, even after milling for 5 hours. Instead, θ and other unidentified phases seem to form after 2 hours of milling. The λ, β1 or the metastable γ phases could be related to these peaks;

DSC analysis of the milled powders shows that some exothermic phase transformations take place during heating, the most significant around 440 °C. The literature supports the hypothesis that this reaction can be associated to the formation of the β and ψ-QC phases, from a previous ω phase formed at lower temperatures. Further XRD analysis on annealed powders is necessary to support this hypothesis.

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