

Formation of nanostructured ω -Al₇Cu₂Fe crystalline phase by the ball milling technique

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Abstract Crystalline ω -Al₇Cu₂Fe bulk samples were prepared by arc furnace and then by means of milling, the average grain size of these samples is reduced to the nanometer scale. The structural and magnetic properties of the nanostructured ω -Al₇Cu₂Fe phase have been studied by X-ray diffraction employing Rietveld method, Mössbauer spectroscopy and vibrating sample magnetometry. The results indicate that the average grain size of the synthesized sample (ω -phase) rapidly decreases from 79 to 12 nm after 5 h of milling. Furthermore, the hyperfine parameters of the nanostructured samples are higher than the values for the bulk ω -phase. Magnetic measurements show a weak ferromagnetic behavior with $M_s = 0.46 \text{ emu.g}^{-1}$ for the bulk ω -phase. After the milling process this value increases to $M_s = 1.50 \text{ emu.g}^{-1}$ due to the formation and growth of a magnetic interstitial region after reducing the average grain size of the sample.

Keywords ω -Al₇Cu₂Fe phase · Nanostructured materials · X-ray diffraction · Mössbauer spectroscopy

1 Introduction

The discovery of quasicrystals in 1984 opened a new field of research for the study of aperiodic solids: systems with long range order but without periodicity [1]. The

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unusual physical properties (e.g., high electrical resistance, low coefficient of friction, low surface energy [2], high hardness [3], good wear resistance [4]) of these systems is normally related to this new kind of order. Moreover, it is pointed out that also the chemical order is of crucial importance to define the properties of quasicrystals. Moreover, it is remarkable that in the Al-Cu-Fe phase diagram [5], quasicrystals occupy a narrow region normally surrounded by crystalline and amorphous phases. This is the case for the well studied icosahedral $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ quasicrystal (*i*-phase) [6–8] where a small variation of the composition means a new crystalline structure like the ω - $\text{Al}_7\text{Cu}_2\text{Fe}$ phase (tetragonal unit cell, space group $P4/mnc$ and lattice parameters $a = 6.33 \text{ \AA}$ and $c = 14.81 \text{ \AA}$) [9]. The structure and some physical properties of the ω -phase have been studied [10]. However, the magnetic behavior of this system still been an open question. Furthermore, it is interesting to note that even though the ω -phase have a chemical composition close to the *i*-phase its properties are significantly different [11, 12]. Additionally, the nanostructuring of the samples gives us the possibility to improve their physical properties as function of their average grain size [13–15].

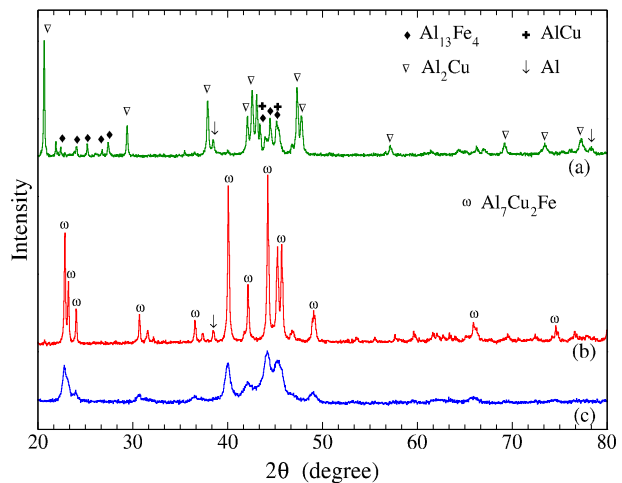
In this sense, the main aim of the present work is to investigate the structural and microstructural order of the nanostructured ω - $\text{Al}_7\text{Cu}_2\text{Fe}$ phase as well as its magnetic properties. As mentioned above, the study of the crystalline ω -phase is important to understand more the effect of aperiodicity on the physical properties of the *i*-phase. The paper is organized as follow. The experimental details are described in the next section. Section 3 is devoted to the results and discussion. In Section 4 we summarize the main results of the present work.

2 Experimental details

Alloys in the composition $\text{Al}_7\text{Cu}_2\text{Fe}$ (ω -phase) were prepared from a mixture of high-purity chemical elemental powders of Al (99.999+%), Cu (99.99+%) and Fe (99.9+%) in an arc furnace in argon atmosphere. Then, the samples were heat treated at 600°C in evacuated quartz tubes for up to 48 h. In order to obtain a nanostructured ω -phase these samples were milled for five hours in a high energy ball milling SPEX 8000 employing a 7:1 charge ratio. The milling was made under argon atmosphere. Ethanol was added during the milling process as a surfactant in order to reduce the adherence of the powder to the vial walls and grinding balls.

The phase purity of the samples was confirmed by powder x-ray diffraction (XRD) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and, additionally, in order to determine the percentage of the phases present in the samples as well as the accurate microstructural parameters (such as cell parameters, grain size and lattice strain) of the ω -phase nanostructured, the XRD patterns were analyzed by Rietveld method using the Topas software V10.0 (Bruker AXS) [16]. The local structure around the Fe sites was analyzed by transmission Mössbauer spectroscopy (TMS) employing a $25 \text{ mCi } ^{57}\text{Co/Rh}$ radioactive source. Mössbauer spectra, recorded at room temperature, were fitted using the NORMOS fitting program [17]. The isomer shift values are given relative to the α -Fe value, obtained at room temperature. The study of the magnetic properties of the samples was done using vibrating sample magnetometer (VSM) of Quantum Design, at room temperature, with a magnetic field in the range of $\pm 20 \text{ kOe}$.

Fig. 1 (Color online) X-ray diffraction patterns of the ω -Al₇Cu₂Fe sample **a** as prepared by arc furnace, **b** after heat treatment, and **c** after 5 h milling.



3 Results and discussion

Figure 1 shows the powder XRD patterns of the Al₇Cu₂Fe sample (a) as prepared by a arc furnace, (b) after heat treatment, and subsequently (c) after 5 h milling. The X-ray diffraction peaks for the as-prepared sample show the presence of θ -Al₂Cu, λ -Al₁₃Fe₄, AlCu and fcc-Al phases with a weight percentage of 44.89 %, 42.51 %, 7.74 % and 4.86 %, respectively. The presence of these phases, mainly Al₂Cu and Al₁₃Fe₄, are usually associated to the formation process of the quasicrystalline phase [18]. In Fig. 1b, can be seen that after heat treatment the peaks corresponding to the θ , λ and AlCu phases disappear completely to form the ω -Al₇Cu₂Fe phase. This is result of the interdiffusion of the atoms (Al, Cu, Fe) of these phases which leads to the formation of a new type of structure, such as the intermetallic ω -phase [19]. In situ XRD measurements of Al-Cu-Fe thin films reported by Haidara et. al. are in agreement with this results [20]. The cell parameters corresponding to the ω -phase, obtained by Rietveld method, are $a = 0.633(2)$ Å and $c = 1.480(8)$ Å which is in good agreement with the literature [9]. Furthermore, the average grain size is $\sim 79.2(17)$ nm while the lattice strain is approximately zero, 0.00(5). Additionally, in Fig. 1b can be identified traces of fcc-Al (3.80 %) which indicates that part of Al atoms still unreacted due to the larger concentration of the Al component [10]. In fact, measurements of energy dispersive X-ray spectroscopy (EDS) show the composition of Al₇₁Cu₁₉Fe₁₀, which is close to the ideal one.

After ball-milling a nanostructured ω -phase is formed (see Fig. 1c), which is indicated by the a reduction of the peak intensity and the broadening of the diffraction peaks. Therefore, from Rietveld refinement of the X ray diffraction pattern of the nanostructured sample, it is observed that the average grain-size reduces to 12.79(3) nm while the lattice strain increases reaching the value of 0.19(2). In the same way, a slightly increase of the cell parameters, $a = 0.634(2)$ Å and $c = 1.485(6)$ Å, it is observed as a result of the milling process. Moreover, in Fig. 1c can be observed that there is no evidence of the formation of another phases. It is worth mentioning that due to the lattice strain which is a result of the milling process, the

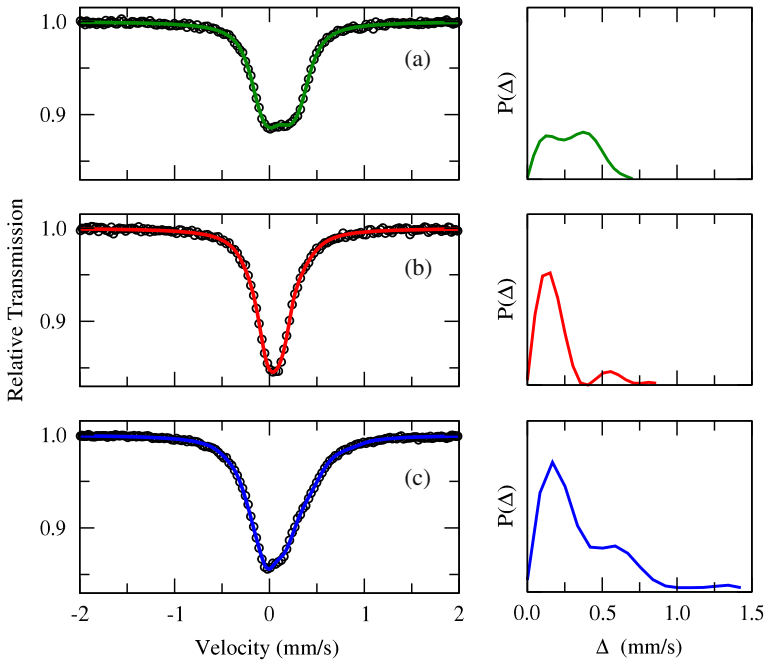


Fig. 2 (Color online) Room temperature Mössbauer spectra of the ω -Al₇Cu₂Fe sample **a** as prepared by arc furnace, **b** after heat treatment, and **c** after 5 h milling. The right panels correspond to the distributions $P(\Delta)$ for each case of the left.

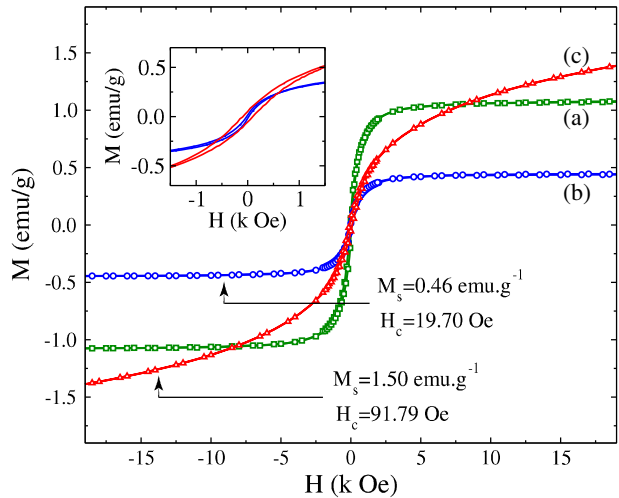
Scherrer equation is not the best way to calculate the average grain size of the studied samples.

Figure 2 shows the Mössbauer spectra of the samples and the corresponding distribution of the quadrupole splitting, $P(\Delta)$. For the present fit, the full width at half maximum has been fixed at the value of $\Gamma = 0.248$ mm/s for all sites, similar as the case for the i -phase [8]. As can be seen, the Mössbauer spectrum in Fig. 2a corresponds to such expected for the crystalline Al₁₃Fe₄ phase with values of $\langle\delta\rangle = 0.222(1)$ mm/s, $\langle\Delta\rangle = 0.296(1)$ mm/s, and $\chi^2 = 0.98$, as reported in the literature [18]. Moreover, considering the crystallographic data, this system is characterized by two local arrangements for the Fe-sites: the first one with only Al neighbors and the second one with Al and Fe neighbors [18]. The local order around Fe in Al₁₃Fe₄ could be explained by two distribution curves between 0.13 and 0.37 mm/s, respectively.

On the other hand, Mössbauer spectra in Fig. 2b and c correspond to the bulk ω -phase and its nanostructured phase after five hours milling. The hyperfine parameters are $\langle\delta\rangle = 0.170(1)$ mm/s, $\langle\Delta\rangle = 0.198(1)$ mm/s, $\chi^2 = 1.02$ and $\langle\delta\rangle = 0.208(1)$ mm/s, $\langle\Delta\rangle = 0.370(1)$ mm/s, $\chi^2 = 1.66$, respectively. These values are very close to those reported in the literature [11, 21].

Furthermore, the shape of the quadrupole distribution of bulk ω -phase can be observed in the right panel of Fig. 2b. This distribution has a maximum value around $\Delta = 0.13$ mm/s which confirms that this phase has only one crystallographic site for the Fe sites [9]. However, due to the employed technique for the preparation of the samples, we considered a small distribution close to $\Delta = 0.55$ mm/s as a product

Fig. 3 (Color online) Variation of magnetization with applied field, $M(H)$, for the ω -Al₇Cu₂Fe sample **a** as prepared by arc furnace, **b** after heat treatment, and **c** after 5 h milling. The inset shows the zoom view of the hysteresis loop near the origin.



of small disorder in the grain boundary. Thus, after five hours milling these two distributions are noticeably broadened which indicates the formation of new Fe-sites in the interstitial region due to the reduction of the grain size during the milling process.

Figure 3 shows the magnetization as a function of the magnetic field for the studied samples. The obtained saturation magnetization (M_s) and the coercive field (H_c), at room temperature, are $M_s = 1.10 \text{ emu.g}^{-1}$ and $H_c = 39.17 \text{ Oe}$ for the as-cast sample; $M_s = 0.46 \text{ emu.g}^{-1}$, and $H_c = 19.70 \text{ Oe}$ for the heat-treated sample (bulk ω -phase); and $M_s = 1.50 \text{ emu.g}^{-1}$ and $H_c = 91.79 \text{ Oe}$ for the five hours milled sample (nanostructured phase). It is interesting to note that the magnetization values (M_s and H_c) of the nanostructured sample are higher than those obtained for the bulk ω -phase. These differences between the nanostructured and bulk samples are attributed to the formation and growth of a magnetic interstitial region after reducing the grain size of the sample. It is worth mentioning that this small magnetic contribution cannot be detected by Mössbauer spectroscopy (see Fig. 2). Similar results have been observed in the i -Al₆₄Cu₂₃Fe₁₃ quasicrystal [22].

4 Summary

In summary, we have shown that a nanostructured ω -Al₇Cu₂Fe phase can be obtained after milling its solid counterpart. In fact, after 5 h milling the ω -Al₇Cu₂Fe reduces its average grain size up to $\sim 12 \text{ nm}$. There are also evidences of a weak ferromagnetic behavior due to the formation and growth of a magnetic interstitial region after reducing the grain size of the sample. The next step is to find the dependence of the milling time with the grain-size in order to study the physical properties of these nanostructured ω -phase as a function of the grain-size. A systematic comparative study of the ω -Al₇Cu₂Fe and the corresponding i -Al₆₄Cu₂₃Fe₁₃ quasicrystal is fundamental to determine if the unusual properties of these new

materials are mainly due to the aperiodic or chemical order, or both. This study is under way.

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