Journal of Alloys and Compounds 509 (2011) 10036–10039

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

XRD and HREM studies from the decomposition of icosahedral AlCuFe single-phase by high-energy ball milling

C. Patiño-Carachure, O. Téllez-Vázquez, G. Rosas*

Instituto de Investigaciones Metalúrgicas, UMSNH, Edificio U, Ciudad Universitaria, Morelia, Michoacan 58000, Mexico

ARTICLE INFO

Article history:
Received 18 March 2011
Received in revised form 4 August 2011
Accepted 6 August 2011
Available online 12 August 2011

Keywords:
Quasicrystals
Mechanical alloying
Transmission electron microscopy (TEM)
X-ray diffraction

ABSTRACT

In this investigation the $Al_{64}Cu_{24}Fe_{12}$ alloy was melted in an induction furnace and solidified under normal casting conditions. In order to obtain the icosahedral phase (i-phase) in a single-phase region, the as-cast sample was subject to a heat treatment at 700 °C under argon atmosphere. Subsequently, the i-phase was milled for different times in order to evaluate phase stability under heavy deformation. X-ray diffraction (XRD) and high-resolution electron microscopy (HREM) analysis were conducted to the structural characterization of ball-milled powders. XRD results indicated a reduction in quasicrystal size during mechanical ball milling to about 30 h. HREM analysis revealed the presence of aperiodic nano-domains, for example, with apparent fivefold symmetry axis. Therefore, the i-phase remains stable over the first 30 h of ball-milling time. However, among 30–50 h of mechanical milling the i-phase transforms progressively into β-cubic phase.

1. Introduction

It is well known that icosahedral quasicrystalline phase (QC) Al–Cu–Fe has an intermetallic nature, because intermetallic phases are their precursors. In addition, this phase has a narrow solubility of its elements in the phase diagram, which is commonly obtained in some intermetallic materials. Thus, both types of phases share structural properties; however, the quasicrystalline phases are characterized by a complex atomic ordering. The QC alloys possess unusually and interesting physical properties such as high hardness, good corrosion resistance, low friction coefficients and high wear resistance [1–3]. However, due to atomic ordering they are brittle in nature, which limits their practical applications. It is well known that the crystal size reduction at nanoscale regime improve the mechanical properties. Mechanical milling/alloying (MM/MA) is a specific technique to obtain crystals with nanometric size dimensions [4]. However, it is well known that this technique can induce disordering in ordered materials. Atomic disordering can subsequently induced phase transformations in intermetallic compounds [5–8]. On the other hand, MA process has also been used to produce Al–Cu–Fe icosahedral quasicrystals starting from elemental powders [9–12]. Most of these studies were dedicated to investigate the icosahedral phase formation close to the perfect composition. However, there are few investigations dedicated to explore the structural aspects and stability of pure i-phase out to the perfect composition when it is subjected to heavy deformation induced by high-energy ball-milling [13,14]. Thus, in this paper, we present a systematic investigation by high-resolution electron microscopy combined with XRD studies after the mechanically milled of single i-phase pre-alloyed specimen.

2. Materials and methods

Al–Cu–Fe alloy ingots were prepared by conventional casting using an induction furnace (Power-Trak 35-95) starting from high purity materials (99.9%). The ingots were prepared in air with a nominal composition of $Al_{64}Cu_{24}Fe_{12}$ at.%. The as-cast alloy was annealed at 700 °C by 96 h to obtain pure i-phase. After that, the sample was subjected to high-energy ball milling using a SPEX 8000 mixer mill for 1, 3, 5, 10, 20, 30, 40 and 50 h periods of time. Hardness steel vial and balls were used as milling media with ball-to-powder weight ratio equal to 8:1. The size of the grinding medium was 12.7 mm in diameter. All materials were characterized by X-ray diffraction (Siemens D5000), using Cu Kα radiation. For the morphology and structural analysis scanning (JEOL-6400) and transmission electron microscopy (FEG Philips Tecnai F20) were used.

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction pattern of as-cast specimen with atomic composition of $Al_{64}Cu_{24}Fe_{12}$. This XRD pattern illustrate a typical mixture of phases; the ternary solid solution with bcc structure $Al_5(Cu,Fe)_5$ and the icosahedral-stable quasicrystalline (QC) phase (i-Al_6Cu_2Fe). According to the phase diagram obtained by previous works [15–18], in order to obtain icosahedral single phase it is necessary to carry out an annealing treatment at 700 °C. The XRD pattern from Fig. 1(b) corresponds to the heat treatment alloy, only peaks related with the QC phase can clearly observed.

* Corresponding author.
E-mail addresses: grtrejo@umich.mx, grtrejo07@yahoo.com.mx (G. Rosas).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.08.026

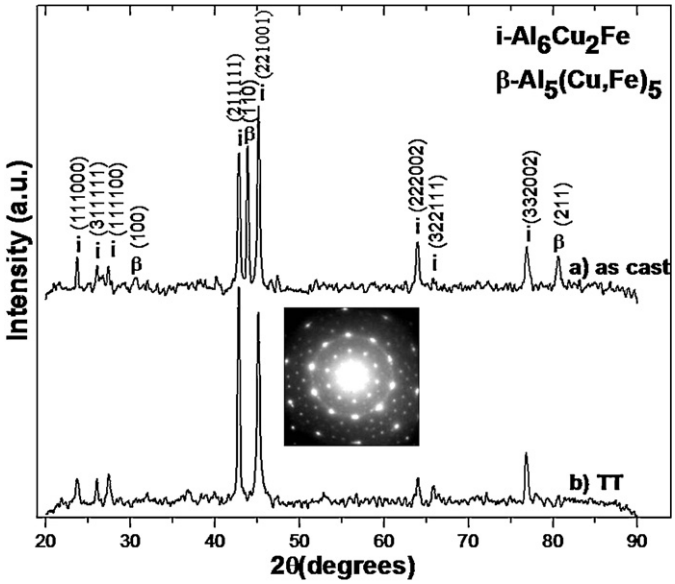

Fig. 1. XRD patterns of specimens (a) as-cast, where i and β phases coexist, (b) icosahedral phase as a single phase after a heat treatment at 700 °C by 96 h followed by slow cooling.

Electron diffraction pattern shown in the inset, which shows diffuse points consistent with scattering from the imperfect quasicrystals.

Few structural features from this phase before and after annealing can be commented, for example, before thermal treatment (Fig. 1(a)) the i-phase XRD peaks clearly show a Gaussian profile, however, peaks in Fig. 1(b) indicates broadening near to the background line like to Lorentzian profile. It is well-known from XRD crystal theories that a Lorentz peak profile corresponds to peak broadening due to crystal size diminished. However, after annealing process of the QC phase peaks like a Lorentzian profile are obtained. Thus, this structural behavior is contrary to that expected in the crystalline materials, where sharp peaks are obtained by stress relaxation of the material after the heat treatment.

Another feature observed from both XRD patterns, are related to the intensities of the main diffraction peaks (2 1 1 1 1 1), (2 2 1 0 0 1) proposed by Cahn et al. [19]. After annealing treatment, we can see that the (2 1 1 1 1 1) principal reflection decrease in intensity, now being the (2 2 1 0 0 1) reflection the most intense in the XRD pattern. This structural behavior has been observed in early investigations [9,10,20]. According to the XRD crystalline statements, this result suggests preferential QC orientation and the oriented reflections could be quasi-crystallographically related.

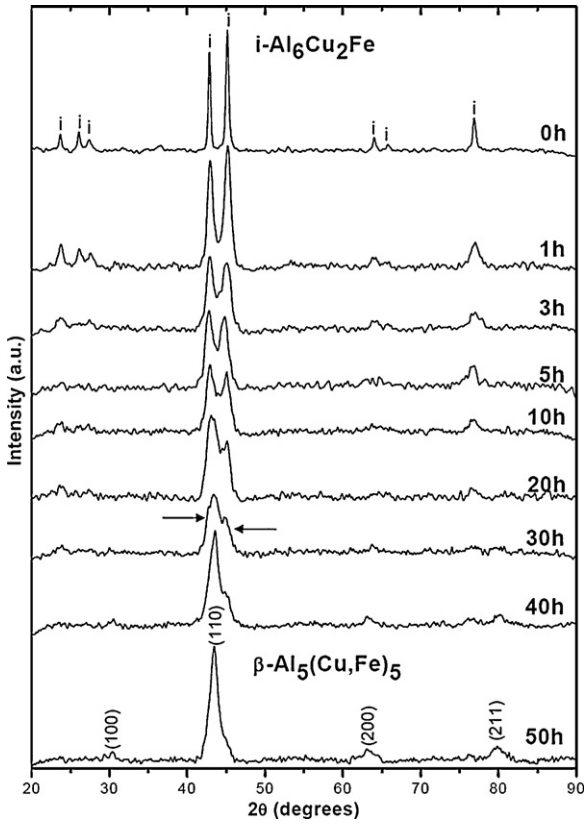

Fig. 3. XRD patterns from ball-milled samples for different times illustrating the i-to-β phase transformation.

To complement the structural characterization of the starting material HREM analysis of the ingot were performed. Thus, Fig. 2 shows different HREM images and its corresponding FFT pattern. For example, in (a) fivefold, (b) twofold, and (c) pseudo twofold zone axes are illustrating the icosahedral quasicrystalline nature of the sample. One of the main characteristics along fivefold symmetry (Fig. 2a) is the presence of the donuts contrast, in which each point is surrounding by ten points as a result of forbidden lattice. The fast Fourier transform (FFT) pattern from the image resemble the fivefold symmetry and have all the characteristics due to the icosahedral structure.

The XRD patterns for the as-milled QC phase with the increment of milling time are shown in Fig. 3. During mechanical milling different structural changes can be observed, for example, for 10 h of milling the principal peaks of QC phase remain stable which

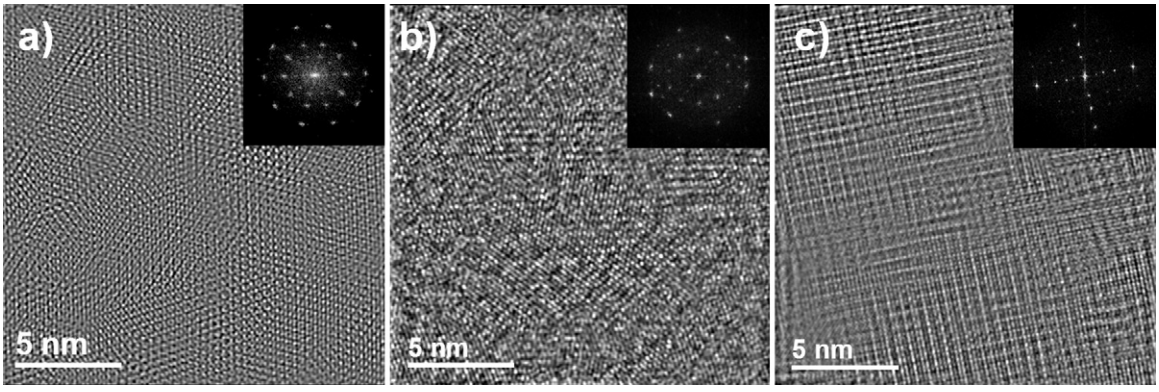

Fig. 2. Different HREM images and its corresponding FFT pattern of as cast sample showing a quasicrystalline phase oriented along (a) fivefold zone axis, (b) twofold and (c) pseudo twofold zone axis.

presume their stability. However, the reflections tend to overlapping. In addition, the relative intensities decrease suggesting finer crystallite size but it is important to mention that this is based on crystals X-ray theories. As the milling time increase up to 20 h, the overlapping continues even more loosely the peaks resolution. At 30 h of milling, the diffraction peaks (indicate by arrows) are related with the β-Al(Cu,Fe) crystalline solid solution and icosahedral phase. These results suggest that, the i-phase transforms gradually with milling time to the β-phase. We can observe that this phase transition begins among 20 and 30 h of milling. Finally, at 50 h of milling the i-phase almost completely transforms to the β-cubic solid solution. However, as the quasicrystal size decreased due to milling effect, the stable phase for this alloys composition is the cubic phase.

During the phase transition, it was observed that, the icosahedral-phase diffraction peaks tend to deviate from their perfect angular positions, for example, the (2 2 1 0 0 1) reflection tends to shift towards lower angles, while the (2 1 1 1 1 1) reflection was shifted towards higher angles. This behavior suggests that the i to β-phase transformation could be related with the i-phase atoms diffusion and confirms the close structural relationship between them [18].

Another important feature of these XRD patterns is the progressive decrease in the intensity of the main reflection of i-phase with the milling time, especially for specimen milled at 40 h. Thus for example, the (2 2 1 0 0 1) diffraction peak (100% peak) decreases in intensity, while the (2 1 1 1 1 1) peak remains unchanging. This peak diminution could be related with an atomic quasicrystal rearrangement that take place after 3 h of MM, where the (2 2 1 0 0 1) peak appear at the first time diminished in intensity in comparison to the (2 1 1 1 1 1) diffraction peak.

The peak intensity diminution can be due to a decrease in the efficiency of the XRD scattering. This mean that in the (2 2 1 0 0 1) atomic planes, there are heavy atoms substitution inside the structure by atoms with lower atomic numbers, which is consistent with the variations of *d*-spacings of (2 2 1 0 0 1) and (2 1 1 1 1 1) reflections. In this way, these results suggest atomic diffusion of i-phase during milling and consequently a kind of order–disorder transition in the quasicrystalline material. The order–disorder transition begins within 3 h of MM and continues above 20 h, where the i-phase transforms to β-phase.

On the other hand, XRD pattern of cubic phase (Fig. 3, 50 h of MM) shows, among others the (1 0 0) reflection which corresponds to the resulting crystalline phase. The presence of this reflection suggests the ordered character of the intermetallic phase formed. Therefore, the QC structures suffer an order-disorder transition during the first 20 h of ball-milling. MM processing of i-phase under the present milling conditions can induced gradually point defects, for example, vacancies and antisites atoms which contribute significantly to i-phase disordering. From a thermodynamic point of view the i-phase energy stored after MM, resulting in the formation of point defects which increase the system entropy and induces atoms diffusion. It is important to note that MM process does not induce phase transitions between the quasicrystalline symmetry itself.

Fig. 4 shows the variation of quasicrystal/crystal size with milling time. These measurements were carried out from the (2 2 1 0 0 1) i-phase diffraction peak and the (1 0 0) reflection of the cubic phase. The crystal size was estimate from the Sherrer method which does not consider strain. Thus, we consider only the peak broadening from small diffraction domains. This consideration is based on the low amount of deformation that may have the quasicrystalline material and a peak-Lorentzian profile selection. Due to peaks overlapping the crystal size was only measured

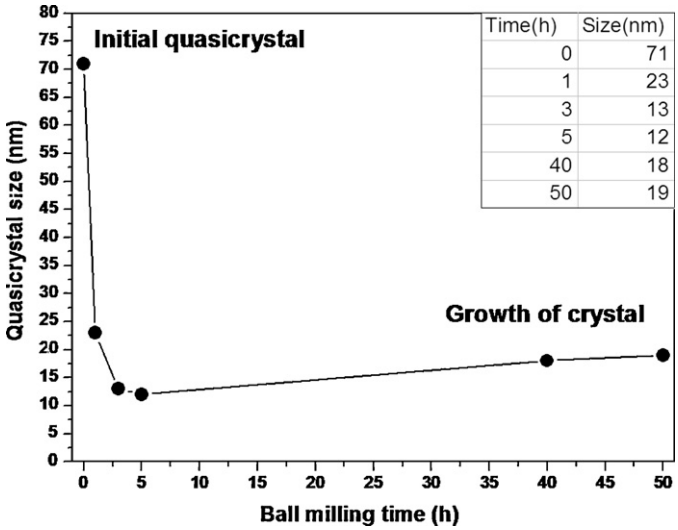

Fig. 4. Quasicrystal/crystal size with the increment of high-energy ball milling.

for 1, 3 and 5 h of milling of the icosahedral phase, while for the crystalline phase was measured in 40 and 50 h of MM. In the case of quasicrystalline phase, the quasicrystal size decreased with the increment of milling time from 1 to 5 h of MM reaching values of 12 nm.

In the same way for the β-phase, the crystal size are increased with milling time, reaching values of 50 nm at 50 h of MM, which is greater than the quasicrystal material because the structure crystallization. As observed from these results, when phase transition begins (after 20 h milling) the disordered QC structure has smaller values of quasicrystal size than 12 nm. This nanometer QC size contributes to the phase transformation. Thus, the complex atomic order of QC phase is lost as the MM process take place, leading first to an internal structure disordering and the subsequent phase transformation from the i-disordered phase to an ordered structure with lower symmetry (cubic).

High-resolution electron microscopy has been used to examine the XRD results obtained and evaluate the i-phase stability. Fig. 5(a) shows HREM images and the corresponding FFT pattern (inset) of the milled sample for 10 h. The presence of nanoquasicrystalline regions as small as 15 nm has been observed here. HREM analysis of crystallite size and structure is in good agreement with XRD results. The FFT pattern confirms the superlattice character of the structure and the aperiodic order with fivefold axis of symmetry.

Fig. 5(b) shows HREM image of the alloy milled by 30 h. With increasing ball-milling time the quasicrystalline regions reduce in size. In this image nanophase quasicrystalline region of less than 10 nm surrounded by several deformed crystalline planes can be observed. The interplanar distances of the periodic structure were measurements which approximately correspond to 2.05 Å of the (1 1 0) planes of BCC structure. The presence of both phases can also be seen from the FFT pattern, where the points which correspond to the periodic distances are marked. In here, the points which correspond to the periodic distances and a distorted icosahedral symmetry due to the mechanical milling are also illustrated. However, the quasiperiodic super-reflections almost disappear at this time of milling. These results are in agreement of XRD results for 30 h of milling, where the XRD pattern illustrate a mixture of phases (i and β phases).

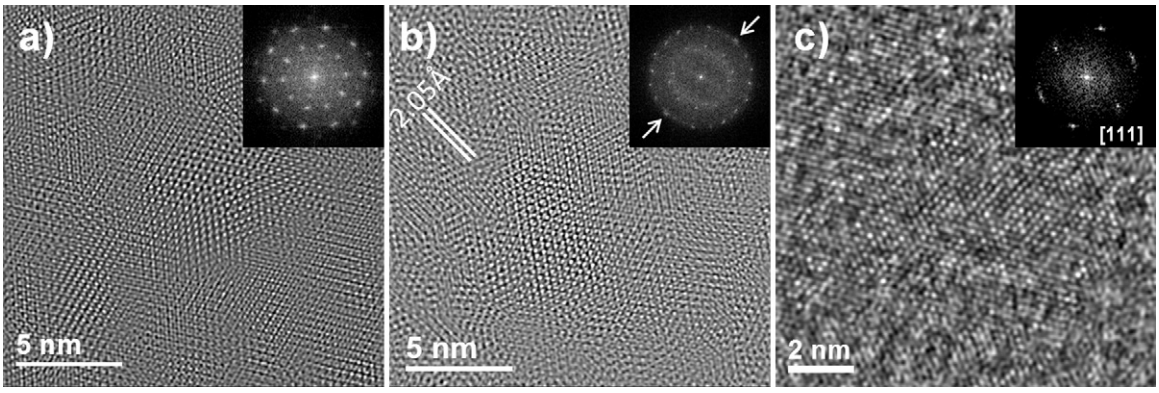

Fig. 5. HREM images of ball-milled powders: (a) 10 h, it can observe the typical fivefold symmetry which correspond to the i-phase, (b) 30 h of milling, QC nanoregions coexisting with nanocrystals that correspond to β cubic phase, (c) HREM image which correspond to milled specimen by 50 h, can clearly observed the presence of β-phase as a single phase along [1 1 1] zone axis.

Fig. 5(c) shows HREM images of the alloy milled by 50 h. In this image we observe crystalline region, in this case from the [1 1 1] direction of the BCC structure, the interplanar distances were 2.06 Å which correspond to (1 1 0) planes of B2 structure. These crystalline regions coexist with small non-crystallized regions. Previous investigations have found that the i-phase is formed from a peritectic reaction [20]. The β-solid solution reacts with the liquid to form i-phase. According to the present results partially amorphous regions are observed and are justified from the kinetic behavior of the i-phase formation on the solidification of this alloy composition. Therefore, amorphous regions are necessary for the decomposition of i-phase. Thus, this result suggests that the i-phase tends to transforms to the amorphous phase and after this, a crystallization phenomena conduct to the β-phase formation.

4. Conclusions

After the mechanical milling of icosahedral single-phase, a decrease in the quasicrystal size reaching values of about 12 nm for a period of time ranging from about 3 to 20 h was obtained. The results indicate that point defects are induced during this period of milling time leading to atomic diffusion. Consequently, an order–disorder quasicrystal transition was obtained. Increasing the milling time over the range 20–30 h, the results indicate that the i-phase begins to transform to the β-phase until at 50 h, when widely completed the phase transition. This transformation confirms the structural relationships between both types of structures; due to this mechanism is approximately the same mechanism for which the i-phase is formed on cooling in equilibrium at 700 °C. The highly ordered i-phase of high symmetry transforms to a crystalline phase with intermetallic character and lowest symmetry.

Acknowledgement

G. Rosas would like to thank the financial support received from the National Council for Science and Technology of Mexico (CONACYT) under the Grant 48716-25535.

References

[1] D.J. Sordelet, J.M. Dubois, MRS Bull. 22 (1997) 34.
[2] J.M. Dubois, S.S. Kang, J. Von Stebut, J. Mater. Sci. Lett. 10 (1991) 537.
[3] S.S. Kang, J.M. Dubois, J. Von Stebut, J. Mater. Res. 8 (1993) 2471.
[4] C. Patiño-Carachure, E. García-De León, C. Angeles-Chávez, R. Esparza, G. Rosas-Trejo, J. Non-Cryst. Solids 355 (2009) 1713.
[5] M. Sherif El-Eskandarany, A. Inoue, Phys. Rev. B 75 (2007) 224109.
[6] Q.Z. Chen, A.H.W. Ngan, B.J. Duggan, Materials Research Society Symposium Proceedings, vol. 481, Boston, MA, USA, 1–5 December, 1997, p. 225.
[7] S.M. Cotes, A.F. Cabrera, L.C. Damonte, R.C. Mercader, J. Desimoni, Hyperfine Interact. 141/142 (2002) 409.
[8] S.V. Starenchenko And, V.A. Starenchenko, Russ. Phys. J. 49 (1) (2006) 5.
[9] P. Barua, B.S. Murty, V. Srinivas, Mater. Sci. Eng. A 304–306 (2001) 863.
[10] A.I. Salimon, A.M. Korsunsky, E.V. Shelekhov, T.A. Sviridova, S.D. Kaloshkin, V.S. Tcherdyntsev, Y.V. Baldokhin, Acta Mater. 49 (2001) 1821.
[11] X. Yong, I.T. Chang, I.P. Jones, J. Alloys Compd. 387 (2005) 128.
[12] S.D. Kaloshkin, V.V. Tcherdyntsev, V.D. Danilov, Crystallogr. Rep. 52 (2007) 953.
[13] P. Barua, B.S. Murty, B.K. Mathur, V. Srinivas, J. Appl. Phys. 91 (2002) 5353.
[14] R.S. Tiwari, T.P. Yadav, N.K. Mukhopadhyay, M.A. Shaz, O.N. Srivastava, Z. Kristallogr. 224 (2009) 26.
[15] A.J. Bradley, H.J. Goldschmidt, J. Inst. Met. 65 (1939) 403.
[16] C. Dong, J.M. Dubois, M.D. Boissieu, C. Janot, J. Phys. Condens. Matter 2 (1990) 6339.
[17] F. Faudot, A. Quivy, Y. Cavayrac, D. Gratias, M. Harmelin, Mater. Sci. Eng. A 133 (1991) 383.
[18] G. Rosas, R. Pérez, Mater. Lett. 36 (1998) 229.
[19] J.W. Cahn, D. Shechtman, D. Gratias, J. Mater. Res. 1 (1986) 13.
[20] V.V. Tcherdyntsev, S.D. Kaloshkin, A.I. Salimon, E.A. Leonova, I.A. Tomilin, J. Eckert, F. Schurack, V.D. Rogozin, S.P. Pisarev, Y.P. Trykov, Mater. Manuf. Processes 17 (2002) 825.