JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 11, No. 10, October 2009, p. 1460 - 1463

Synthesis of the quasi-crystalline phase in $Al_{63}Cu_{25}Fe_{12}$ powders prepared by mechanical alloying

B. AVAR*, M. GOGEBAKAN
Kahramanmaras Sutcu Imam University, Faculty of Art and Science, Department of Physics, 46100 Kahramanmaras, Turkey

This work investigated the quasicrystalline phase formation during heat treatment in the $Al_{63}Cu_{25}Fe_{12}$ alloy prepared via mechanical alloying, starting from pure elemental powders. The mechanical alloying process was performed at a speed of 300 rpm for times up to 70 hours. The structural evolution of the mechanically alloyed $Al_{63}Cu_{25}Fe_{12}$ powders at different stages of milling was examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The present results showed that mechanical alloying of the $Al_{63}Cu_{25}Fe_{12}$ alloy did not result in the quasicrystalline icosahedral phase (i-phase). The long time milling resulted in the formation of an AlFe(Cu) solid solution identified as the β-phase. In order to examine the structural changes with annealing temperature, the mechanically alloyed powders were heat treated at 600, 700 and 800° C for 4 hours under vacuum. However, the formation of a quasicrystalline phase in the $Al_{63}Cu_{25}Fe_{12}$ alloy was observed after additional annealing at elevated temperature. In the present work, quasicrystalline phase formation in both the as-milled and heat-treated powders is discussed in detail.

(Received November 5, 2008; accepted December 15, 2008)

Keywords: Quasicrystals, Mechanical alloying, Al-Cu-Fe, Heat treatment

1. Introduction

Quasicrystalline (QC) phases have crystal lattices with forbidden symmetry axes, from classical crystallography. The unique features of their atomic structure make them remarkable and attractive materials. They show some excellent properties for commercial applications, such as high hardness and strength, low electrical and thermal conductivities and good corrosion resistance [1-3]. For example, the strength of quasicrystals was measured to be 9-11 and even 13 GPa [4], in comparison to 7-8 GPa for martensitic steels [5]. Also, the Young's modulus of quasicrystals was measured as 110 GPa [6]. This is much higher than for conventional aluminum alloys. Therefore, the QC materials have potential applications in the development of new materials. On the other hand, QC phases with stable and metastable forms have been investigated in several new Al-based binary, ternary and multicomponent metallic systems [7-9]. These alloys can be produced by conventional or rapid solidification, bulk methods of crystal growth, physical vapor deposition, solid-state reactions, mechanical alloying, etc. Among them, the mechanical alloying (MA) technique is necessary to produce quality powders of alloys and compounds with well-controlled microstructures and morphologies [10]. However, MA can access the microstructures which are impossible or difficult to obtain with other techniques. MA can also overcome fabrication difficulties in achieving high solid solubility, mixing of elements with a high vapor pressure and/or a large difference in melting point, as well as to produce amorphous, nanocrystalline and quasicrystalline materials. Furthermore, it should be noted that in many systems, for example in Al-Cu-Fe, the high temperature peritectic transformation prevents the preparation of the icosahedral quasicrystalline phase (i-phase). Because of these advantages, MA has been successfully applied to the Al-Cu-Fe system with the formation of the i-phase [11-16].

One aim of this paper is to use the MA technique to produce the Al-Cu-Fe alloy at compositions close to that of the i-phase. The other aim is to investigate the effects of the MA technique when Al-Cu-Fe alloys are submitted to heat treatment. The microstructural characteristics and morphological features of the mechanically alloyed powders were examined by X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

2. Experimental

As starting materials, pure Al, Cu and Fe powders (99.9%) with particle sizes smaller than 100 μm were mechanically alloyed to produce the $Al_{63}Cu_{25}Fe_{12}$ alloy. MA was performed using planetary ball mills (Fritsch Pulverisette 5). Before the MA process, the elemental powders were mixed inside a glove box under a high purity Ar atmosphere. After that, about 20 g of the elemental mixture was sealed in a 250 ml volume cylindrical stainless steel container together with 9-12 mm diameter stainless steel balls. The powders were alloyed at a ball-to-powder mass ratio of 10:1 at a speed of 300 rpm with intervals of 20 min milling and 20 min rest to prevent the mixture from overheating. The mechanically alloyed powders were annealed at 600, 700 and 800 °C for 4 hours under vacuum. The structural evolutions of the as-milled and heat-treated powders were characterized by X-ray diffraction (XRD) using a Philips X'Pert PRO diffractometer with CuKα radiation (λ=0.154 nm) at 40 kV and 30 mA. The measurements were done in a 2θ scan, ranging from 20° to 120° with a scan rate of 0.02 °/s. The morphological features of the as-milled powders were characterized by scanning electron microscopy (SEM), using a JEOL JSM 5400 microscope at an acceleration voltage of 15 kV.

3. Results and discussion

XRD patterns from $Al_{63}Cu_{25}Fe_{12}$ alloy powders after different milling time intervals are shown in Fig. 1. The XRD patterns show elemental Al, Cu and Fe phases, equivalent to the initial powder peaks for milling times of up to 10 h. After 5 h of MA, the intensities of the Al and Fe peaks decreased, while the Cu peaks disappeared. The elemental powders were getting mixed and refined, as indicated by the decreasing peak intensities and the broadening of the elemental peaks. So, this event revealed that the Cu and Al elements were alloyed, and eventually a tetragonal θ-Al_2Cu phase (θ-phase) was observed at around 2θ = 21° and 2θ = 47°, with a weak peak intensity. At this stage, the XRD patterns also showed a sharp peak at around 2θ = 44.12° corresponding to the formation of a cubic Al(Fe,Cu) solid solution phase (β-phase). However, the θ-phase disappeared after 15 h of MA. Thus, the θ-Al_2Cu phase forms after only short-time milling. Upon continued milling up to 40 h, the XRD patterns showed only the β-phase with dissolution of the other phases. It should be noted that the peak of the β-phase broadened with increasing milling time, indicating a reduction of its crystallite size. No further change occurred with milling up to 80 h, suggesting that the β-phase is the stable one for this composition under the milling conditions studied. From these observations, it could be concluded that no i-phase was observed, and a longer milling time resulted in the formation of the β-phase. On the other hand, the main peak position of the β-phase decreased progressively from 44.30° to 43.15° during MA from 5 h to 70 h. This suggested a change in its composition. These results are in agreement with those recently reported by Barua et al. [13], in which the QC phase was reported as not being obtained directly in $Al_{63}Cu_{25}Fe_{12}$ powder milled for up to 40 h. Also, similar results were reported for $Al_{65}Cu_{20}Fe_{15}$ by Eckert et al. [11] and Yong et al. [15], in which no QC phase was obtained directly. It is suggested that, for the formation of QC powders, inter-diffusion is necessary, in addition to sequential fracturing and welding.

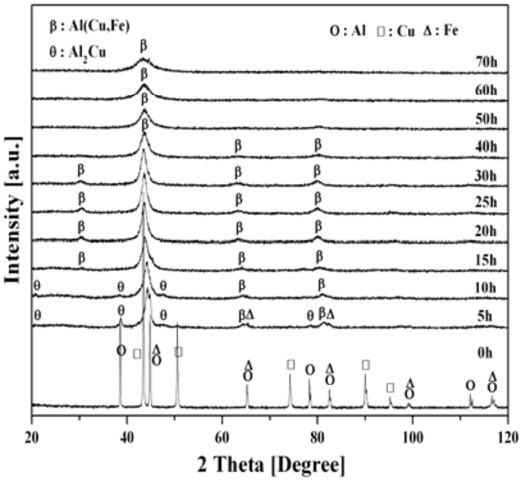

Fig. 1. XRD patterns as a function of milling time for $Al_{63}Cu_{25}Fe_{12}$ powders.

Fig. 2 shows the morphological changes in the $Al_{63}Cu_{25}Fe_{12}$ powders produced at different milling times. It can be seen that the powder particle size is uneven and irregular, with a distribution of very small particles, and also that large agglomerates existed after 10 h of MA. With increasing milling time to 20 h, the size and irregularity of the particles decreased. After 40 h of milling time, the powder particles were nearly spherical in shape. However, at this stage there were still some agglomerates with very small sizes. As seen in Fig. 2, 40 h of MA resulted in the formation of micrometer particles with an average grain size of about 5 μm.

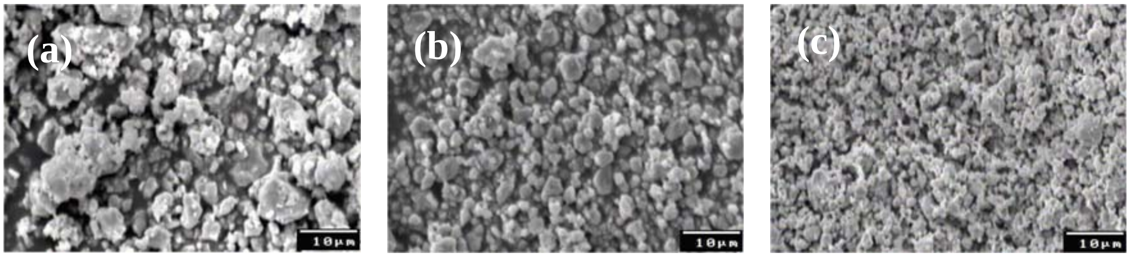

Fig. 2. SEM images of the $Al_{63}Cu_{25}Fe_{12}$ alloy powders milled for: (a) 10 h, (b) 20 h and (c) 40h.

In order to understand the effect of annealing on the un-milled and as-milled powders, different heat treatments were applied to the mechanically alloyed $Al_{63}Cu_{25}Fe_{12}$ powders. XRD patterns from $Al_{63}Cu_{25}Fe_{12}$ alloy powders annealed at 600 °C for 4 h are shown in Fig. 3. The un-milled powder shows the presence of the tetragonal

Al_7Cu_2Fe phase (ω-phase), with a small amount of elemental Al and Fe peaks. So, this indicates that the dissolution of Al and Fe in the θ-Al_2Cu phase produces the inter-metallic ω-Al_7Cu_2Fe phase. The annealed powder after 5 h of MA resulted in the formation of new peaks which were indexed to the i-phase. Also, the resultant product was almost composed of a single i-phase. This indicates that the i-phase forms from the θ- and β-phases. After 10 h of MA, the i-phase completely transformed into the β-phase. This suggests that the i-phase forms only after a short-time of MA and subsequent annealing of the $Al_{63}Cu_{25}Fe_{12}$ alloy under the milling conditions studied. After annealing, 30 h of MA showed only a single β-phase, with the sharpening of the individual X-ray lines due to the grain growth. However, from 40 to 70 h, milled samples consisted of the β-phase plus the monoclinic λ-Al_3Fe phase (λ-phase), suggesting that these phases are stable ones.

XRD patterns from $Al_{63}Cu_{25}Fe_{12}$ alloy powders annealed at 700 °C for 4 h are shown in Fig. 4. The results are similar to those shown for the powders annealed at 600 °C for 4h. Unlike the results for the powders annealed at 600 °C, the i-phase was observed with the β-phase, after 5 h of MA. Then, the i-phase transformed to the β-phase and the intensity of the β-phase increased with increasing milling time. This indicates that the β-phase becomes stabilized with increasing milling time and hampers the formation of the i-phase once it forms. After annealing of 20 h milling, the diffraction pattern showed the formation of an almost single β-phase. Upon further milling up to 70 h, XRD patterns showed that the λ-phase was the major one, plus a small amount of the β-phase.

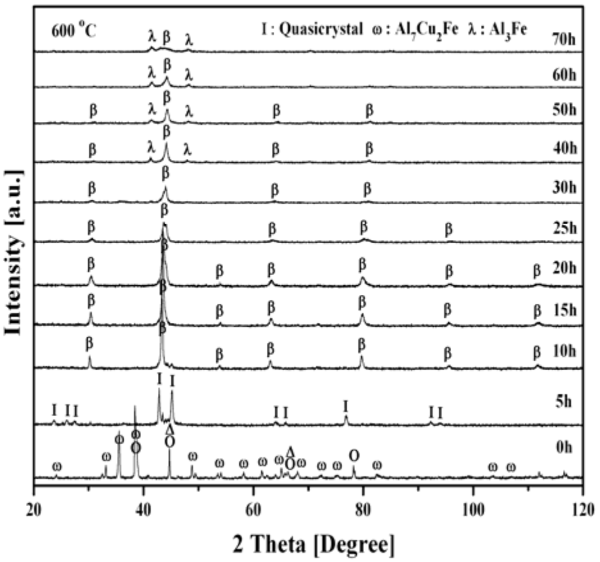

Fig. 3. XRD patterns of $Al_{63}Cu_{25}Fe_{12}$ powders annealed for 4 h at 600 °C.

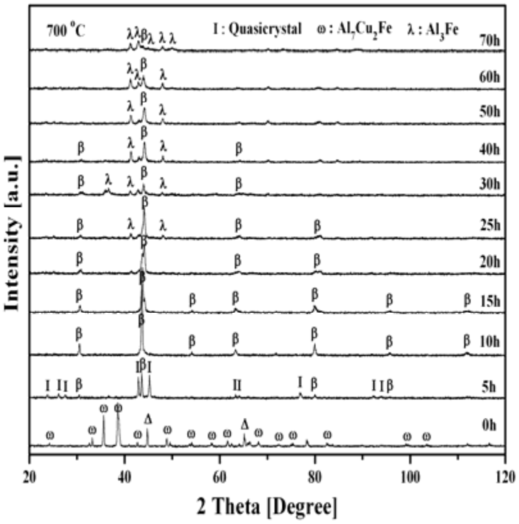

Fig. 4. XRD patterns of $Al_{63}Cu_{25}Fe_{12}$ powders annealed for 4 h at 700 °C.

As seen in Fig. 5, XRD results for the un-milled and as-milled powders annealed at 800 °C were quite similar to those for powders annealed at 600 and 700 °C. The difference, in both cases, is that the un-milled powders were composed of a majority of ω-phase. In the powder milled for 5 h, the β-phase was observed with a small amount of i-phase. After annealing, the 10 h milled sample showed the disappearance of the i-phase. In the latter stages, XRD patterns showed the presence of the λ-phase with an increasing amount depending on the milling time. However, no new phase formation was observed continuing up to the last stage of MA.

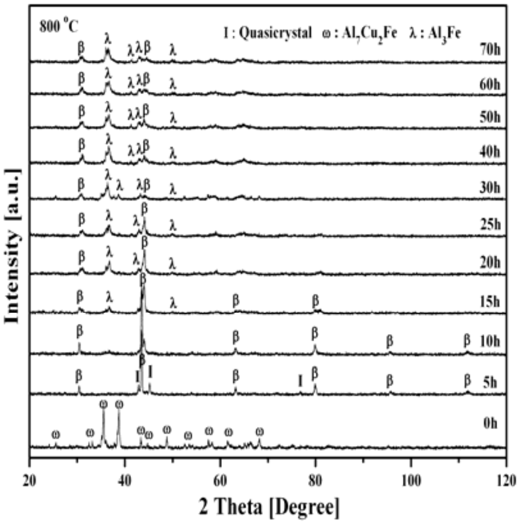

Fig. 5. XRD patterns of $Al_{63}Cu_{25}Fe_{12}$ powders annealed for 4 h at 800 °C.

The present investigation showed that MA assisted by heat treatment can be an effective route for i-phase formation; even though it couldn't be formed directly by MA for a long time. Therefore, a good way to obtain a large amount of quasicrystalline powders is by using a combination of short-time MA and subsequent annealing. Also, it was observed that the i-phase was partially transformed into the β-phase. These results are in agreement with others [13,15,16].

4. Conclusions

The formation of the i-phase in $Al_{63}Cu_{25}Fe_{12}$ alloy powders during heat treatment by MA was examined. It was found that the i-phase does not form directly by MA, but only after additional annealing at elevated temperatures. However, long time MA resulted in the formation of the β-phase, while short time MA resulted in the formation of the θ-phase. Also, the SEM results showed the formation of micrometer sized particles with an average grain size of about 5 μm after 40 h of MA.

Acknowledgements

This work was supported by the Scientific and Technological Research Council of Turkey (TUBITAK), Project No: 106 T 701.

References

[1] E. Huttunen-Saarivirta, J. Alloys and Comp. **363**, 150 (2004).
[2] O. Rapp, Mater. Sci. Eng. A **294-296**, 458 (2000).
[3] S. L. Chang, W. B. Chin, C. M. Zhang, C. J. Jenks, P. A. Thiel, Surf. Sci. **337**, 135 (1995).
[4] K. Urban, M. Feuerbacher, M. Wollgarten, Mater. Res. Soc. Bull. **22**, 65 (1997).
[5] S. D. Kaloshkin, V. V. Tcherdyntsev, V. D. Danilov, Cryst. Reports **52**, 953 (2007).
[6] U. Koster, W. Liu, H. Liebertz, M. Michel, J. Non-Cryst. Solids **153-154**, 446 (1993).
[7] A. Inoue, H. M. Kimura, T. Matsumoto, J. Mater. Sci. **22**, 1758 (1987).
[8] A. P. Tsai, A. Inoue, T. Matsumoto, Mater. Trans. JIM **40**, 666 (1989).
[9] G. S. Song, E. Fleury, S. H. Kim, W. T. Kim, D. H. Kim, J. Alloys and Comp. **342**, 251 (2002).
[10] C. Suryanarayana, Prog. Mater. Sci. **46**, 1 (2001).
[11] J. Eckert, L. Schultz, K. Urban, Acta Metall. Mater. **39**, 1497 (1991).
[12] N. Asahi, T. Maki, T. Matsumoto, T. Sawai, Mater. Sci. Eng. A **181-182**, 841 (1994).
[13] P. Barua, V. Srinivas, B. S. Murty, Philos. Mag. A **80**, 1207 (2000).
[14] F. Schurack, J. Eckert, L. Schultz, Philos. Mag. **83**, 1287 (2003).
[15] X. Yong, I. T. Chang, I. P. Jones, J. Alloys and Comp. **387**, 128 (2005).
[16] S. Yin, Z. Xie, Q. Bian, B. He, Z. Pan, Z. Sun, Z. Wei, L. Qian, S. Wei, J. Alloys and Comp. **455**, 314 (2008).

---

[*] Corresponding author: barisavar@gmail.com