Proceeding of ICNM - 2009

1st International Conference on Nanostructured Materials and Nanocomposites (6 – 8 April 2009, Kottayam, India)

Published by : Applied Science Innovations Private Limited, India.
http://www.applied-science-innovations.com

****

Effect of mechanical activation on in situ preparation of Cu-Cr-Al_2O_3 nanocomposite

Saeed Sheibani *, A. Ataie, S.Heshmati-Manesh

School of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran.

Abstract :

This paper presents the results of an investigation into processing of Cu-Al_2O_3-Cr nanocomposite with a high fraction of Al_2O_3 and Cr, using a novel approach. Structural evolutions were investigated using X-ray diffraction. The feasibility of synthesizing nanocomposite by ball milling mixture of Cu, Al and Cr_2O_3 and consequent heat treatment was demonstrated. It was shown that in mechanical milling stage, Cu(Al) solid solution and Cu_9Al_4 phase were formed as the intermediate products. Hence, the coarsening of Al_2O_3 particles through combustion reduction reaction of Cr_2O_3 by Al is prevented by decreasing of Al activity as being in the Cu(Al) solid solution or Cu_9Al_4 compound. The subsequent heat treatment carried out under argon atmosphere at 900 °C for 8 hours result in completion of Cr_2O_3 reduction by Al. The results showed that the Al_2O_3 dispersoids are in the nanometer scale.
Keywords: Mechanical activation; Copper; In situ; Nanocomposite

1. Introduction :

Copper matrix composites are promising candidates for application in electrical sliding contacts where good wear resistant properties and high thermal and electrical conductivity are needed. They can be produced by dispersing hard particles like oxides, carbides or nitrides in the copper matrix either by liquid or solid state techniques [1-3]. Mechanical alloying is now an established technique for preparation of nano-structured materials such as alloys, oxide-dispersion-strengthened alloys, amorphous alloys, intermetallic compounds and ceramics [4].

It has been shown that enhanced reaction rates can be achieved and dynamically maintained during milling as a result of microstructural refinement and mixing processes accompanying repeated fracture, welding and deformation of particles during collision events [4,5]. Mechanochemical synthesis using displacement reactions in high energy ball milling has been widely investigated in order to study the changes of reactivity of solids by and after the mechanical milling. When this process is combined with mechanical milling (reactive milling), nano-structured composites with uniform distribution of

* Corresponding author: School of Metallurgy and Materials Engineering, University of Tehran, P.O. Box 14395-553, Tehran, Iran. Tel.: +98 912 1958219; fax: +98 21 88006076. E-mail address: Sheibani_s@engmail.ut.ac.ir.

reinforcement particles are synthesized. Dispersing fine reinforcement particles and nano-structured matrix are beneficial to the mechanical properties of the composite.

On the other hand, solid state reactions with large negative enthalpies may occur with self propagating combustion during ball milling and hence lead to coarse microstructure. In addition, these types of reactions may not be controlled effectively. For example, with an initial powder mixture of Al and Cr_2O_3, alumina based composites are obtained by a displacement reaction induced by reactive ball-milling, which is basically a conventional thermite reaction [6,7]. In this case the following reaction may take place in a combustion manner during milling at room temperature.

$$Cr_2O_3 + Al = Cr + Al_2O_3 \qquad \Delta H = -535 \text{ kJ mol}^{-1} \tag{1}$$

In order to produce composites with the microstructure being at nanometer scale, the self propagating combustion reaction must be avoided during milling and/or subsequent heat treatment [8]. Amongst the various ways that suppress the combustion mechanochemical reactions, the dilution or activity reduction of reductants has been previously studied through solid solution formation of components [9].

In this paper in-situ formation of Cu-Cr-Al_2O_3 nanocomposite by mechanical activation of Cu-Al-Cr_2O_3 powder mixture and consequent heat treatment has been investigated. Particular attention has been paid to the mechanism of this process via the structural evolution during the mechanical milling.

2 Experimental procedure :

Starting materials were commercially pure Cu (99.5%, 10-70 μm), Cr_2O_3 (99.8%, 5-50 μm), Al (99.5%, 10-50 μm) powders and toluene as the process control agent. A mixture of Cu, Cr_2O_3 and Al powders with stoichiometric proportions of Al and Cr_2O_3 according to Eq. (1) have been milled in a high-energy Fritsch P6 type planetary ball mill under a high purity argon gas (>99.999%). Assuming that the Al is completely oxidized by Cr_2O_3, calculations indicate that 10 wt.% Al_2O_3 is generated in the Cu matrix. The ball-to-powder weight ratio was 25:1.

The milling products were compacted and then heat treated under flowing argon at heating rate of 25 °C/min at 900 °C for 8 hours.

The microstructure was evaluated by CamScan MV2300 scanning electron microscopy (SEM). The phase identification of the products was examined by Philips PW-3710 X-ray diffraction (XRD) using Co K_α radiation. The crystallite size and internal strains of copper particles were determined according to the Williamson-Hall plot [10]. The line broadening due to the instrument was calculated from Warren's method [11,12].

3. Results and discussion :

Fig. 1 shows XRD patterns of Cu-Al-Cr_2O_3 powder mixture after different milling times. The Cu peaks tend to broaden as the milling time increases and their intensities decrease with increased milling time. This is known to be due to mechanical deformation, crystallite refinement and storage of the lattice strain in powder particles. While Al peaks disappeared rapidly in the first 10 hours of milling, the decrement of Cr_2O_3 peaks intensities was much slower. Furthermore, it could be seen that with increased milling time, the Cu peaks shift to lower angles. However between 30-40 hours of milling the Cu peaks shift to higher angles. This gradual shift in peaks location may be attributed to the solid state dissolution of Al in Cu. Similar observation was also reported in the previous work by Ying and Zhang [13] during mechanical alloying in an Al - Cu system.

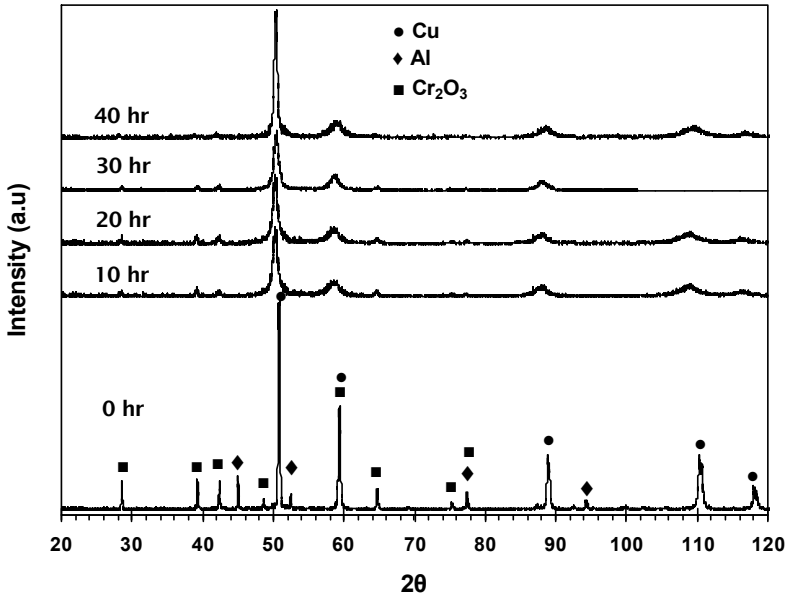

Figure (1) : XRD patterns of the powder mixture after different milling time.

To investigate the structural evolution in more detail, the partial XRD pattern of the sample milled for 40 hours is shown separately in Fig. 2 within the diffraction angle range of $2\theta=25\text{-}55^{\circ}$. This pattern shows that Cr_2O_3 peaks are still present. However, decreased intensity of the Cr_2O_3 peaks could be attributed to the very small size Cr_2O_3 particles distributed within the Cu matrix and therefore, it was partially detectable by XRD.

It is worth noting that, the new peaks between $2\theta=25°$ to 55° could be identified as the diffraction peaks of Cu_9Al_4 phase. The formation of Cu_9Al_4 during ball milling is in agreement with previous study on mechanical alloying of Cu an Al [9].

Fig. 3 shows the calculated lattice parameter of the milled Cu as a function of milling time. The lattice parameter first increased with increasing the milling time, reaching to a maximum value at about 0.36378 nm after 30 hours of milling and decreased during further milling. The increase of lattice parameter is related to the dissolution of Al in Cu. Based on the XRD pattern of 40 hours milled powder in Fig. 2, the reduction of Cu lattice parameter after 30 hours of milling should be related to the Cu_9Al_4 formation. In fact, by formation of this phase, Al solute atoms come out of the solid solution. In relation to this phenomenon, Dong et al. [14] have also reported the same drop in the lattice parameter of Cu by precipitation of a Cu-Ti compound during mechanical alloying.

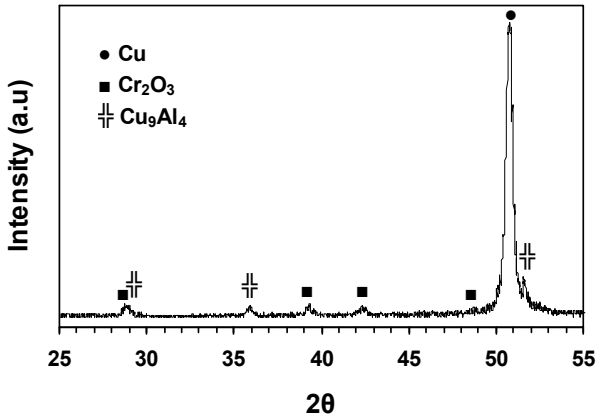

Figure (2) : XRD pattern of the powder mixture after 40 hours milling time.

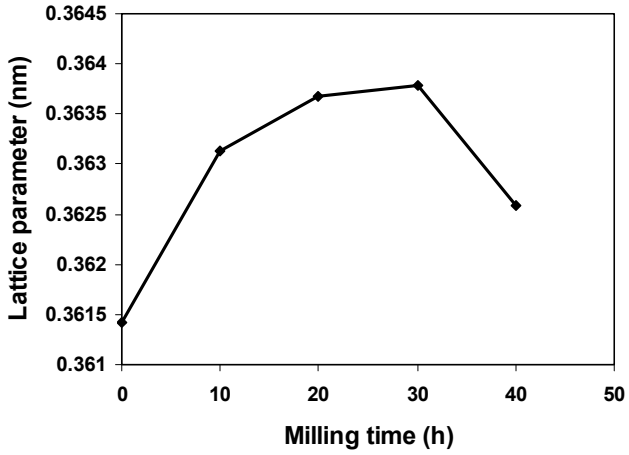

Figure (3) : The Cu lattice parameter of Cu-Al-Cr_2O_3 mixture versus milling time.

XRD patterns in Fig. 1 shows a progress of peak broadening with milling time, as a result of microstructural refinement and increased stored strain energy. Therefore, the crystallite size and lattice strain were estimated from Williamson-Hall plot. These results are shown in Fig. 4. It can be seen that the crystallite size decreased rapidly at the very beginning of the milling process, and then continued to decrease slowly with the prolonged milling. Therefore, the most intensive refinement occurs in the early stages of milling, when the crystallite size abruptly decreases from 659 nm to 83 nm. As can be seen, mechanical alloying reduces the Cu crystallite size to the nanometre range. It is interesting to note the correlation between the changes in internal strain in Fig.4 and the lattice parameter (see Fig. 3). It means that the lattice strain increase abruptly up to 30 hours of milling, while it decrease with further milling. This result does also support the Cu_9Al_4 formation after 30 hours of milling. The diffusion in the course of mechanical alloying is accelerated after the attainment of nanometric crystallite size [15]. Gleiter [16] has also earlier demonstrated that a high rate of diffusion occurs in the vicinity of dislocations even at low temperatures. This accelerated diffusion may lead to the Cu_9Al_4 phase formation during the milling operation.

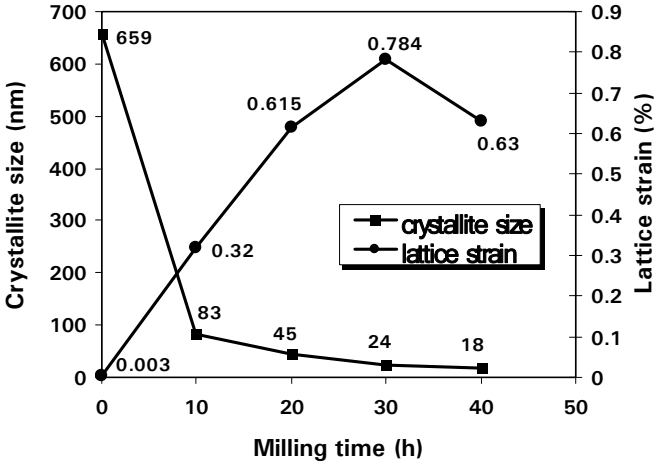

Figure (4) : Cu mean crystallite size and lattice strain against milling time for Cu-Al-Cr_2O_3.

XRD pattern of the sample milled for 40 hours heat treated at 900 °C for 8 hours shows that Cr_2O_3 and Cu_9Al_4 peaks were disappeared (Fig. 5). Also, the decrease in the lattice parameter to 0.36143 nm

(approximately same as that of pure Cu) is assumed to be due to the oxidation of dissolved Al by Cr_2O_3, which forms Al_2O_3 dispersoids. Furthermore, the diffraction peak at around 52° has been detected clearly, which is the characteristic peak of Cr. These results could be attributed to the completion of reduction process. We notice that, in fact the homogeneous existence of Cu_9Al_4 phase and dissolved Al in Cu in the 40 hours milled sample supplies the accessible necessary reductant around each Cr_2O_3 fine particle in Cu matrix. Therefore oxidation and reduction reactions occur at the interfaces and nanoscale Al_2O_3 particles are formed. It may be concluded that Cu_9Al_4 and Cu(Al) solid solutions are intermediate products which appear during milling operation. Following reaction may be considered in this novel process for Cu-Cr-Al_2O_3 production.

$$Cu+Al+Cr_2O_3 \xrightarrow{\text{Mechanical alloying}} Cu(Al)/Cu_9Al_4 + Cr_2O_3 \xrightarrow{\text{Heat treatment}} Cu+Cr+Al_2O_3 \qquad (2)$$

Hence, the coarsening of Al_2O_3 particles through combustion reduction reaction of Cr_2O_3 by Al is prevented by decreasing of Al activity as being in the Cu(Al) solid solution or Cu_9Al_4 compound.

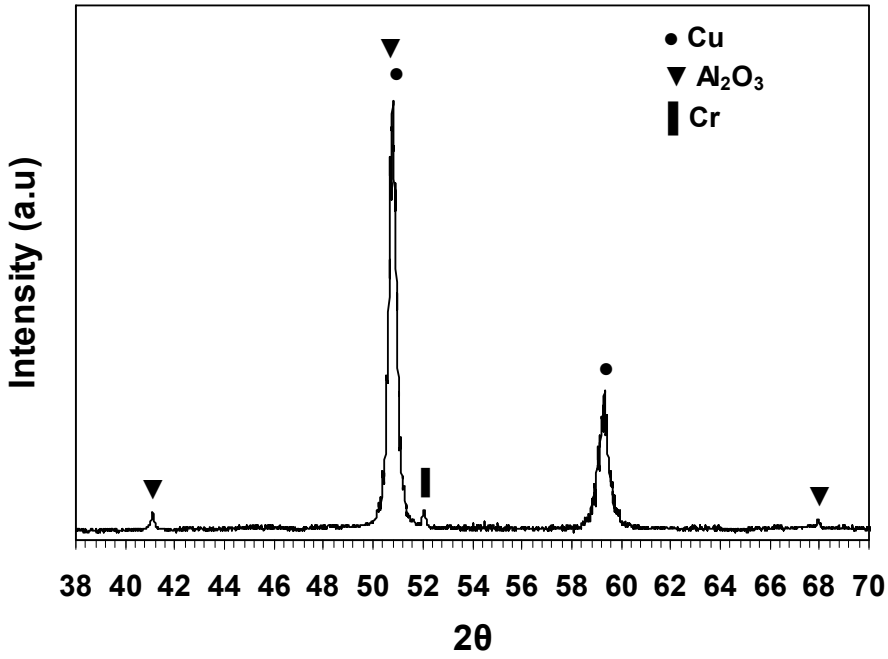

Figure (5) : XRD pattern of 40 hours milled powder heat treated at 900 °C for 8 hours.

The homogeneous distribution of nanometric dispersoids can be seen in the SEM image of the heat treated sample at 900 °C for 8 hours (Fig. 6).It may be assumed that presence of Al_2O_3 and Cr prevents Cu matrix microstructure growth during the course of heat treatment and nanocomposite formation via this process becomes more feasible. Retained microstructure in nanometric scale during high temperature exposure is an indication of relatively high thermal stability of nanocomposite. However, this issue needs to be investigated in higher magnification such as transmission electron microscopy. More work remains to be done in order to characterize both the Al_2O_3 and Cr phases in more details. It is expected that formation of 10 wt. % of the Al_2O_3 dispersoids and 10 wt. % of Cr containing precipitates formed during the course of this process can lead to a strong hardening effect. Moreover, other consolidation routes of milled powders such as hot pressing or hot extrusion seem to be more suitable because of higher attainable density. Therefore, the mechanical properties of such nanocomposite are beyond the scope of the present paper and will be published in near future.

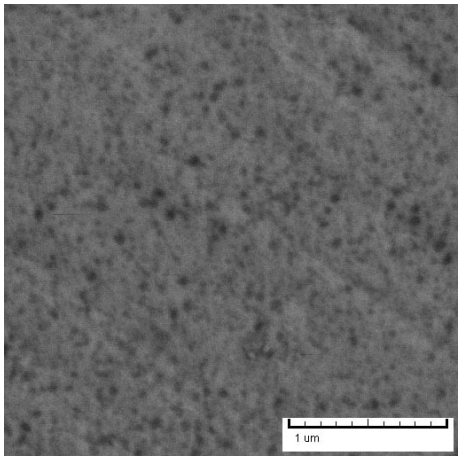

Figure (6) : SEM image of 40 hours milled powder heat treated at 900 °C for 480 min.

4- Conclusion :

In this work, the formation of a Cu-10 wt. % Cr-10 wt. % Al_2O_3 nanocomposite by mechanical alloying and subsequent heat treatment has been investigated. The results showed the solubility of Al in Cu during mechanical alloying, which resulted in an increased Cu lattice parameter. The formation of Cu_9Al_4 during milling decreased the Cu lattice expansion and, hence, the internal strain, which was caused by the dissolution of Al into Cu. Subsequent heat treatment of the sample milled for 40 hours showed that the in-situ formation of Al_2O_3 occurred at 900 °C after 8 hours, which is believed to result from a reaction between Cu(Al) solid solution and Cu_9Al_4 with Cr_2O_3. The mechanism of the in-situ formation of Al_2O_3 particles in the copper composite was also discussed as a two stage process.

References :

[1] S.C. Tjong, K.C. Lau, Mater. Sci. Eng. A 282 (2000) 183-6.
[2] J. Lee, J.Y. Jung, E.-S. Lee, W.J. Park, S. Ahn, N.J. Kim, Mater. Sci. Eng. A 277 (2000) 274.
[3] Y. F. Lee, S. L. Lee, Scripta Mater. 7 (1999) 773.
[4] C. Suryanarayana: Prog. Mater. Sci. 46 (2001) 1
[5] G. B. Schaffer and P. G. McCormick, Metall. Trans. 22A (1991) 3019.
[6] P. Matteazzi, G. Le Caer, J. Am. Ceram. Soc. 75(1992) 2749.
[7] J. L. Guichard, 0. Tillement and A. Mocellin, J. Eur. Ceram. Soci. 18 (1998) 1143.
[8] L. Takacs, Prog. Mater. Sci. 47 (2002) 355.
[9] D.Y. Ying, D.L. Zhang, Mater. Sci. Eng. A 361 (2003) 321.
[10] G.K. Williamson, W.H. Hall, Acta. Metall. 1 (1953) 22.
[11] B.D. Cullity, S.R. Stock, Elements of X-ray Diffraction, third ed., Prentice Hall, Upper Saddle River, NJ, 2001, p. 399.
[12] H. Lipson, H. Steeple, Interpretation of X-ray Powder Diffraction Patterns, Macmillan, London, 1970.
[13] D.Y. Ying, D.L. Zhang, Mater. Sci. Eng. A 286 (2000) 152.
[14] S.J. Dong, Y. Zhou, Y.W. Shi, B.H. Chang, Metall. Mat. Trans. 33A (2002) 1275.
[15] D. Das, P.P. Chatterjee, I. Manna, S.K. Pabi, Scrip. Mater. 41 (1999) 861.
[16] H. Gleiter, Acta Metall. Mater. 16 (1967) 455.