



A MEASURE OF ENHANCED DIFFUSION KINETICS IN MECHANICAL ALLOYING OF Cu-18 at.% Al BY PLANETARY BALL MILLING

D. Das, P.P. Chatterjee, I. Manna and S.K. Pabi

Metallurgical and Materials Engineering Department, Indian Institute of Technology,
Kharagpur 721 302 (W.B.), India

(Received January 7, 1999)

(Accepted in revised form May 21, 1999)

Keywords: Mechanical alloying; Diffusion; Kinetics; X-ray diffraction; Mathematical modeling

Introduction

Mechanical alloying (MA) by high energy ball milling has established itself as a versatile solid state processing route for producing metals, alloys and intermetallics in the nanocrystalline state [1]. In MA of ductile metals, powder particles trapped between the colliding balls and vial undergo repeated deformation, fragmentation and cold welding resulting into agglomerates of multilayered structures with clean interfaces [2,3]. Intermixing in such an aggregate during MA is actuated by the deformation process [1]. Indeed, it is well known over three decades that mechanical deformation enhances the diffusion rate and the process has been termed as mechanical interdiffusion by Balluffi and Rouff [4]. Gleiter [5] has shown that a large potential gradient leads to high rate of diffusion in the vicinity of a dislocation even at a temperature where self diffusion is practically negligible. In analogy to the mass transport in ion irradiation, Martin and Gaffet [6] have suggested that ballistic diffusion, which is independent of temperature, may account for the enhanced rate of intermixing during MA. Similarly, Bellon and Averback [7] have considered shear along randomly selected glide planes as one of the possible mechanisms of intermixing that accompanies MA during ball milling. In a recent work, Pabi *et al.* [8] have developed a rigorous mathematical model of MA by means of the modified *iso*-concentration contour migration (MICCM) method to estimate the effective intermixing rate during MA, which is equivalent to volume diffusion at an elevated temperature (T_{eff}). Application of this analysis to the experimental data of MA kinetics in the Cu-Ni and Cu-Zn systems showed that the intermixing rate could be correlated with the liquidus temperature (T_L) of the system (*i.e.*, $T_{eff}/T_L = 0.4-0.5$). The results have further revealed that T_{eff} is unlikely to have any direct correlation with the temperature at the point of ball powder collision and varies marginally with the milling speed (200–300 rpm). Earlier, Dallimore and McCormick [9] investigated the mechanism of MA and compared the predicted results with the experimental kinetics determined from the reaction synthesis of nanosized NiO dispersed in the Cu-matrix. It was demonstrated that the distribution of impact collision energies does not significantly affect the reaction propagation over the range of speed investigated (*i.e.*, 240 to 330 rpm). The experimental results of Li *et al.* [10] for MA in the Cu-Al system have indicated that solubility of Al in Cu does not exhibit any extension beyond the equilibrium value (*i.e.*, 18 at.% Al

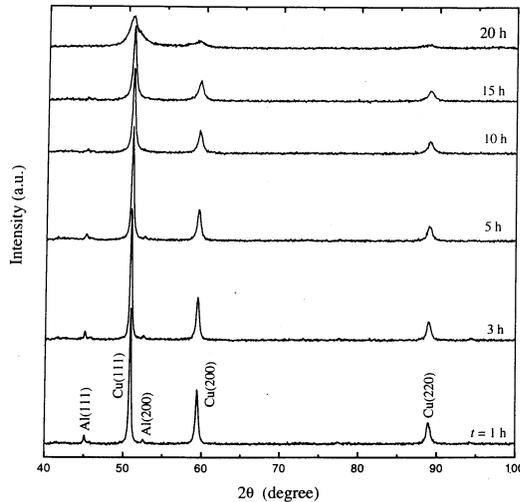


Figure 1. XRD patterns of $\text{Cu}_{82}\text{Al}_{18}$ ball milled at 300 rpm. Samples were collected at different stages (t) of milling.

[11]). Moreover, taking the mechanisms of intermixing during MA proposed by Pabi *et al.* [12] into account, it appears that the heat of formation for $\text{Cu}_{82}\text{Al}_{18}$ (≈ -8 kJ/mol [13]) is conducive for continuous diffusive mixing rather than discontinuous additive mixing for the given composition. Therefore, considering both the absence of extension of solid solubility as well as possibility of continuous diffusive mode of intermixing in $\text{Cu}_{82}\text{Al}_{18}$, the present study aims to obtain the T_{eff}/T_L value for the $\text{Cu}_{82}\text{Al}_{18}$ composition using the MICCM model [8], analyze the relevant experimental result and compare the latter with that for the Cu-Zn and Cu-Ni systems obtained from Ref. 8.

Experimental

A powder blend of pure (>99.5 wt.%) Cu and Al of -325 mesh size having a nominal composition of $\text{Cu}_{82}\text{Al}_{18}$ was milled in a FRITSCH P5 planetary ball mill using WC vial and 10 mm diameter WC coated balls with a ball to powder weight ratio of 10:1. The samples collected at different stages of milling were characterized by x-ray diffraction (XRD) analysis using a Philips PW 1710 diffractometer and $\text{Co-K}\alpha$ (0.1789 nm) radiation. Amount of Al dissolved into Cu (Cu_{Al}) was determined through the peak shift analysis of Cu peaks with respect to the standard data of the same available in the literature [14]. The variation of the crystallite size (d_c) and relative strain (e) with milling time (t) were calculated from the standard peak broadening analysis using the Voigt function [15]. Here the contribution of the instrumental factor to peak broadening was eliminated using the observed broadening in the standard sample ($\text{Cu}_{82}\text{Al}_{18}$ sample annealed at 700°C for 4 h under vacuum). Finally, the microstructural evolution of the milled product at appropriate stages was monitored by the scanning electron microscopy (SEM).

Results and Discussion

Figure 1 shows a series of XRD patterns for the samples collected at different stages of ball milling. It is evident that the (111) peak of Cu shifts towards higher angles with the progress of milling. This gradual shift may be attributed to the solid state dissolution of Al in Cu as the atomic diameter of the

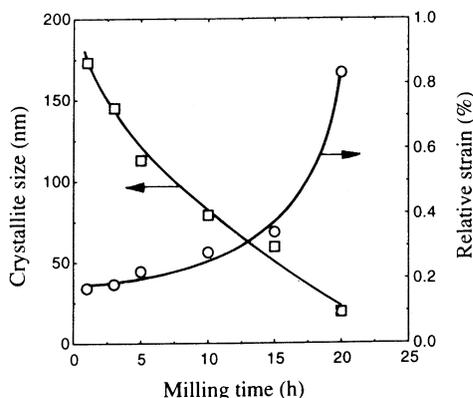


Figure 2. Variation of crystallite size and relative strain of Cu in the $\text{Cu}_{82}\text{Al}_{18}$ blend with milling time.

former (0.2886 nm) is greater than that of the latter (0.2556 nm) [14]. It may be noted that earlier studies have investigated the effect of d_c on the change in lattice parameter during MA [16,17]. However most of the experimental results indicate that the said effect is pronounced at $d_c < 15$ nm [18]. In the present investigation, the lower limit of d_c is estimated to be ~ 20 nm after 20 h of ball milling (*cf.* Fig. 2). Thus, the determination of Cu_{Al} from the XRD peak shift analysis (Fig. 1) seems quite appropriate. Variation of d_c of Cu solid solution as a function of t , obtained from the XRD peak broadening analysis, is shown in Fig. 2. It is apparent that the lower limit of d_c ($\cong 20$ nm) is attained after 20 h of milling. Fig. 2 also demonstrates that in Cu-Al system e increases monotonically with milling time t up to $d_c \cong 20$ nm.

Figure 3 displays an alternate lamellar arrangement of particles obtained after 3 h of milling. It may be noted that the kinetic model of Pabi *et al.* [8] based on the MICCM method envisages that such a lamellar structure is essential for the continuous diffusive intermixing of solute atoms in the course of MA. The effect of continuous change in d_c on the time-modulated concentration profiles during the MA process has been duly considered in the present analysis. In this regard, it may be noted that effect of d_c on concentration gradient has earlier been investigated by Desre [19] and Desre and Yavari [20] to explain the kinetics of amorphization by solid state diffusive intermixing in a multilayered diffusion couple. Experimental results of d_c as a function of t (*cf.* Fig. 2) and volume diffusivity (D_v) as a function of temperature (T) for the Cu-Al alloys [21] have been used as input data to predict the alloying kinetics

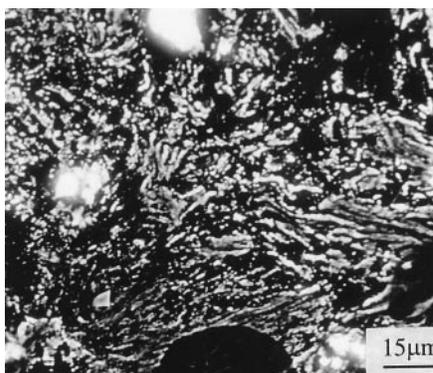


Figure 3. A typical lamellar microstructure developed in ball milling of $\text{Cu}_{82}\text{Al}_{18}$ after 3 h.

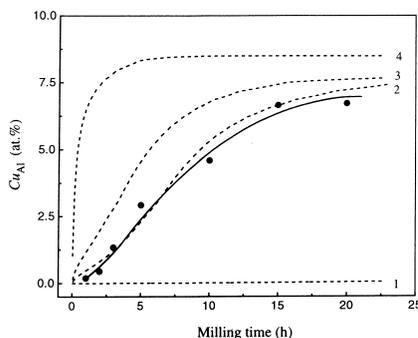


Figure 4. Variation of Al-content in Cu-solid solution (Cu_{Al}) with milling time (t) for $Cu_{82}Al_{18}$ milled at 300 rpm. The curve with continuous line represents the experimental data and the curves with broken lines refer to the computed MA kinetics obtained for D_v at $T = 473$ K (curve 1), for D_v at $T_{eff} = 675$ K (curve 2), for D_v at $T = 725$ K (curve 3), and for D_b at $T = 303$ K (curve 4), respectively.

by the MICCM method [8] during MA. Figure 4 presents the variation of Cu_{Al} as a function of t obtained from the experimental results (firm line) along with the predicted kinetics of MA under varying diffusion conditions (broken lines). It is apparent from Figs. 2 and 4 that diffusion in the course of MA is accelerated after the attainment of nanometric grain size (say, < 100 nm obtained after 2.5 h of milling). This accelerated diffusion may be facilitated by the fine scale multilayered sandwich configuration of the power particles as seen in the secondary electron SEM image in Fig. 3.

The predicted results in Fig. 4 are obtained from the calculations carried out under the following conditions: diffusion occurs by volume diffusion at a temperature attainable during MA, *i.e.*, 473 K [22] (curve 1 in Fig. 4), diffusion occurs by volume diffusion at 675 K (curve 2 in Fig. 4) and 875 K (curve 3 in Fig. 4), and diffusion rate becomes as high as grain boundary diffusivity (D_b) at room temperature, *i.e.*, 303 K (curve 4 in Fig. 4). Here, D_b of Al in Cu-Al at 303 K is obtained from the Ref. 23. It is evident from Fig. 4 that the results on alloying kinetics obtained in the last case (D_b controlled kinetics) is more than one order of magnitude higher than the concerned experimental results. On the other hand, the same obtained by assuming solute transport by volume diffusion at 473 K is lower by two orders of magnitude than the experimental results. It is interesting to note that a remarkable match of the theoretically predicted and experimentally determined results is registered in the case where the effective intermixing rate is equivalent to that by volume diffusion at 675 K (curve 2). Hence, 675 K is the T_{eff} of the $Cu_{82}Al_{18}$ composition in the given milling condition as per the definition of T_{eff} in [8]. It is interesting to note that the ratio of T_{eff} to the corresponding liquidus temperature ($T_L = 1320$ K) at the given composition ($Cu_{82}Al_{18}$) is 0.51, which is in good agreement to the values obtained by Pabi *et al.* [8] for the Cu-Ni and Cu-Zn systems. Thus, the enhanced rate of diffusion operative in MA seems to be related to T_L .

For comparison, the equation proposed by Martin [24] to predict the temperature equivalence for enhancement in diffusivity due to ballistic effect has also been considered here to examine its applicability to the MA process in the present system. It may be noted that the value Cu_{Al} (< 10 at. %, *cf.* Fig. 3) after 20 h of ball milling is lower than the concerned equilibrium solubility limit (~ 18 at. % [11]). However, substitution of T' by T_{eff} ($= 675$ K) and considering $T = 473$ K (a typical measure of the temperature at the point of ball-vial contact [22]) in the said equation can not account for the order of magnitude enhancement in volume diffusivity as evidenced in the present experimental kinetic data. Nevertheless, the encouraging agreement in the value of T_{eff}/T_L for Cu-Al obtained in the present investigation with that for Cu-Ni and Cu-Zn obtained by Pabi *et al.* [8] suggests that a deformation induced mechanism is responsible for an enhanced mechanical interdiffusion, which also seems to be

related to T_L in the chosen systems. In this respect, it may be pointed out that the presence of shear bands populated with dislocations are expected in the course of MA process [25], and Gleiter [5] has earlier demonstrated that a high rate of diffusion occurs in the vicinity of dislocations even at low temperatures.

Conclusions

The important conclusions emerging from the present study on the kinetics of mechanical alloying in $\text{Cu}_{82}\text{Al}_{18}$ are as follows:

1. Mechanical alloying in Cu-Al takes place by continuous diffusive intermixing at an appreciable rate only after the grain size is reduced to a level below 100 nm. Furthermore, the sandwich lamellar structure, that arises in the early stage of mechanical alloying, is conducive for the said mechanism of intermixing.
2. The observed mechanical alloying kinetics in Cu-Al is compared with the rate predicted by the modified *iso*-concentration contour migration model of Pabi *et al.* [8] to yield the effective mass transport rate to be equivalent to that by volume diffusion at $T_{eff} = 675$ K.
3. Thus, the ratio between T_{eff} and the concerned liquidus temperature (=1320 K) for the $\text{Cu}_{82}\text{Al}_{18}$ composition under the present milling condition is 0.51, which agree well with the concerned results of the Cu-Ni and Cu-Zn systems [8].

Acknowledgment

Equipment support from the D.S.T. New Delhi (grant no.: III.4(23) 92 - ET) is thankfully acknowledged. PPC is grateful to the Q.I.P. scheme of financial support of the A.I.C.T.E., New Delhi.

References

1. C. C. Koch, in Processing of Metals and Alloys, ed. R. W. Cahn, P. Haasen, and E. J. Kramer, vol. 15, p. 193, VCH Publishers, Weinheim (1991).
2. J. S. Benjamin, *Sci. Am.* 40, 234 (1976).
3. F. Cardellini, G. Mazzone, A. Montone, and M. V. Antisari, *Acta Metall. Mater.* 42, 2445 (1994).
4. R. W. Balluffi and A. L. Rouff, *Appl. Phys. Lett.* 1, 59 (1962).
5. H. Gleiter, *Acta Metall. Mater.* 16, 455 (1967).
6. G. Martin and E. Gaffet, *J. Phys. (Colloque)*. C4-71, 51 (1990).
7. P. Bellon and R. S. Averback, *Phys. Rev. Lett.* 74, 1819 (1995).
8. S. K. Pabi, D. Das, T. K. Mahapatra, and I. Manna, *Acta Mater.* 46, 3501 (1998).
9. M. P. Dallimore and P. G. McCormick, *Mater. Trans. JIM.* 7, 1091 (1996).
10. F. Li, K. N. Ishihara, and P. H. Shingu, *Metall. Trans.* 22A, 2849 (1991).
11. J. L. Murray, in Binary Alloy Phase Diagrams, 2nd edn., ed. T. B. Massalski, vol. 1, p. 142, ASM International, Materials Park, OH (1990).
12. S. K. Pabi, J. Joarder, I. Manna, and B. S. Murty, *Nanostruct. Mater.* 9, 149 (1997).
13. N. G. Ageev, *Handbook of Binary System*, vol. 1, p. 90, Israel Program for Scientific Translation, Jerusalem (1967).
14. B. R. Coles, in *A Handbook of Lattice Spacing and Structures of Metals and Alloys*, ed. W. B. Pearson, p. 598, Pergamon Press, London (1958).
15. Th. H. De Keijser, J. I. Langford, E. J. Mittemeijer, and A. B. P. Vogels, *J. Appl. Crystallogr.* 15, 308 (1982).
16. E. Gaffet, N. Malhouroux, and M. Abdellaoui, *J. All. Comp.* 194, 339 (1993).
17. E. Gaffet, *Mater. Sci. Eng.* A136, 161 (1991).
18. X. D. Liu, M. Magnmo, and M. Vmemoto, *Mater. Trans. JIM.* 38, 1033 (1997).
19. P. J. Desre, *Acta Mater. Mater.* 39, 2309 (1991).

20. P. J. Desre and A. R. Yavari, *Phys. Rev. Lett.* 64, 1533 (1990).
21. N. Matsuno and H. Oikawa, *Metall. Trans. A*, 6, 2191 (1975).
22. M. R. Davis, B. T. McDermott, and C. C. Koch, *Metall. Trans.* 19A, 2867 (1988).
23. I. Kaur, W. Gust, and L. Kozma, *Handbook of Grain and Interphase Boundary Diffusion Data*, Vol. 1, p. 187, Ziegler Press, Stuttgart (1989).
24. G. Martin, *Phys. Rev.* 30B, 1424 (1984).
25. H. J. Fecht, *Nanostruct. Mater.* 1, 125 (1992).