Mater.Phys.Mech. 4 (2001) 116-120

DEVELOPMENT OF AMORPHOUS AND NANO-ALUMINIDE DISPERSED Al-MATRIX COMPOSITES BY MECHANICAL ALLOYING

P. Nandi[1], P. P. Chattopadhyay[2], S. K. Pabi[1] and I. Manna[1]

[1]Metallurgical and Materials Engineering Department, I. I. T., Kharagpur 721 302, India
[2]Department of Metallurgy, B. E. College (D.U.), Howrah 711103, India

Received: June 29, 2001

Abstract: Mechanical alloying of $Al_{65}Cu_{35-x}Nb_x$ (x = 5 – 25 at. % Nb) by planetary ball milling yields amorphous and/or nanocrystalline products. Microstructure of the milled product in different stages of milling has been characterized by x-ray diffraction, transmission electron microscopy and differential scanning calorimetry. The results indicate that the present alloys may yield completely/partially amorphous and/or nano-aluminide dispersed Al-rich nanocrystalline or amorphous matrix composites by controlled mechanical alloying.

1. INTRODUCTION

Development of high specific strength structural material is always of considerable interest to the transportation and aviation industry. It is predicted that the strength of light weight aluminum alloys could be significantly enhanced from about 600 MPa in age hardened condition to over 1500 MPa level in rapidly quenched amorphous or nanocrystal dispersed amorphous matrix aluminum based alloys [1]. In the recent times, mechanical alloying has emerged as a convenient solid state synthesis alternative to melt spinning and similar rapid quenching techniques to develop amorphous alloys with metastable microstructures [2-4]. Furthermore, carefully designed heat treatments may enable dispersion of nanocrystalline intermetallic phases in the mechanically alloyed amorphous matrix precursors [5,6]. Earlier, the present authors have demonstrated the possibility of the formation of amorphous matrix composites in Al-Cu-Ti ternary system [7-9]. It has also been indicated that subsequent heat treatment of the mechanically alloyed product allows in-situ dispersion of Cu/Ti-based aluminides in Al-rich nanocrystalline/amorphous alloys. Besides the Cu/Ti-aluminides, the Nb-Al system is also known to yield several high specific strength aluminides useful for structural applications. In the present paper, we shall report the synthesis of aluminum based Al-Cu-Nb ternary amorphous or nanocrystalline alloys by mechanical alloying with varying amount of Nb-aluminides dispersed in the Al-rich matrix. The ternary alloys contain 5-25 at.% Nb to partially substitute Cu in the Al-35 at.% Cu binary alloy known to yield single phase nanocrystalline disordered bcc solid solution by mechanical alloying [7].

2. EXPERIMENTAL

Powder blends of elemental (>99.5 wt. % purity) Al, Cu and Nb powders (< 50 μm grain size) having nominal compositions of $Al_{65}Cu_{30}Nb_5$, $Al_{65}Cu_{20}Nb_{15}$ and $Al_{65}Cu_{10}Nb_{25}$ (in at.%) were ball milled in a Fritsch Pulverisette-5 planetary ball mill in toluene medium at 300 rpm and ball to powder ratio of 10:1 using WC vial and balls (10 mm diameter). The phase evolution in different stages of mechanical alloying was studied by the X-ray diffraction (XRD) analysis using a PHILIPS PW 1710 diffractometer with Co-K_α (0.0179 nm) radiation. Average grain size (d_c) was determined from the broadening of the most intense peak of the concerned phases using Voigt method [10] that allows judicious elimination of the contributions due to instrumental and strain effects in the observed peak broadening. It may be noted that Voigt analysis is based on Scherrer principle of

---

Corresponding author: I.Manna, e-mail: imanna@metal.iitkgp.ernet.in

Table 1. Summary of grain size and enthalpy calculations of 40 h milled samples.

Properties	$Al_{65}Cu_{30}Nb_{05}$	$Al_{65}Cu_{20}Nb_{15}$	$Al_{65}Cu_{10}Nb_{25}$
Peaks analysed	Al_4Cu_9	Nb(CuAl)	Nb(CuAl)
d_c (nm)	2.05	2.54	2.55
Peak width (radian)	1.68	3.82	2.20
Peak area (a.u.)	849.69	293.79	546.73
Peak intensity (a.u.)	403.35	61.30	198.25
Grain size (nm)	11	5	10
Residual strain (%)	1.22	3.58	2.07
ΔH_{chem} (J/mol)	-7540	-9140	-12130
$\Delta H'_{chem}$ as per [12]	3956	4488	4973
$\Delta H = \Delta H_{chem} + \Delta H'_{chem}$ (J/mol)	-3584	-4652	-7157

crystallite size determination using XRD analysis [11]. The thermal stability of the amorphous phase obtained in $Al_{65}Cu_{20}Nb_{15}$ alloy was studied using a Mettler 4000 differential scanning calorimetry (DSC) instrument by heating at the rate of 20 °C/min up to 500 °C. The authenticity of the XRD analysis of the amorphous phase was verified by transmission electron microscopy (TEM) using a Philips CM-20 TEM instrument. Table 1 presents the relevant XRD analysis data used for determining the grain size (d_c) and the thermodynamic data used for calculating the enthalpy of mixing (ΔH).

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns obtained from the powder blends having the nominal composition of $Al_{65}Cu_{30}Nb_5$ after different duration of ball milling. It is evident from Fig. 1 that the elemental constituents undergo mutual dissolution within a few hours of mechanical alloying giving rise to a mixture of several aluminides (Nb_2Al, $NbAl_3$, etc.) following 8 h of milling. The most prominent among the aluminides formed is the disordered bcc solid solution of Cu and Al having a Bravais lattice identical to that of Cu_9Al_4. The considerable peak broadening of this stage may be attributed to grain refinement concomitant with milling. Before carrying out the grain size (d_c) measurement, a careful deconvolution analysis was undertaken to separate out and identify the individual peaks in the angular range of overlapping peaks. Consequently, d_c for Al, the bcc phase and $NbAl_3$ after 8 h of milling was determined as 30 nm, 42 nm and 18 nm, respectively [10,11]. Continued milling up to 24 h yielded no significant change in phase identity and evolution except further reduction in grain size of the existing phases (evidenced by further broadening of concerned peaks). The XRD pattern of the sample obtained after 40 h of ball milling shows that the nanocrystalline disordered bcc phase (presumably Cu_9Al_4) is the principal constituent of the microstructure. Thus, mechanical alloying of $Al_{65}Cu_{30}Nb_5$ by planetary ball milling for 30-40 h may be a potential route for producing monolithic nanocrystalline Cu_9Al_4 alloyed with Nb. Continued milling up to 52 h shows

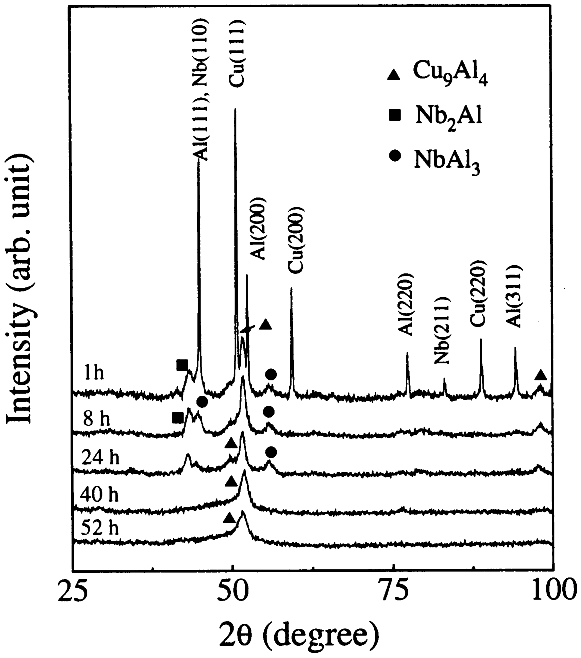

Fig. 1. XRD patterns of $Al_{65}Cu_{30}Nb_5$ following mechanical alloying for varying time.

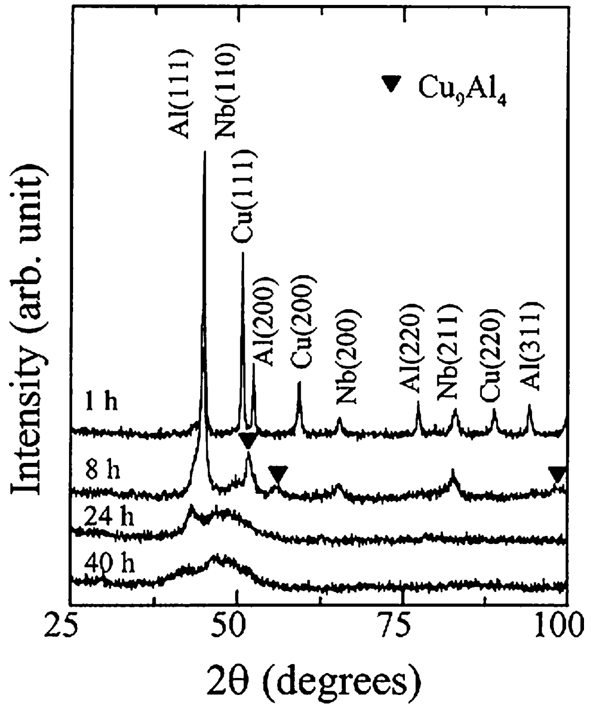

Fig. 2. XRD patterns of $Al_{65}Cu_{20}Nb_{15}$ following mechanical alloying for varying time.

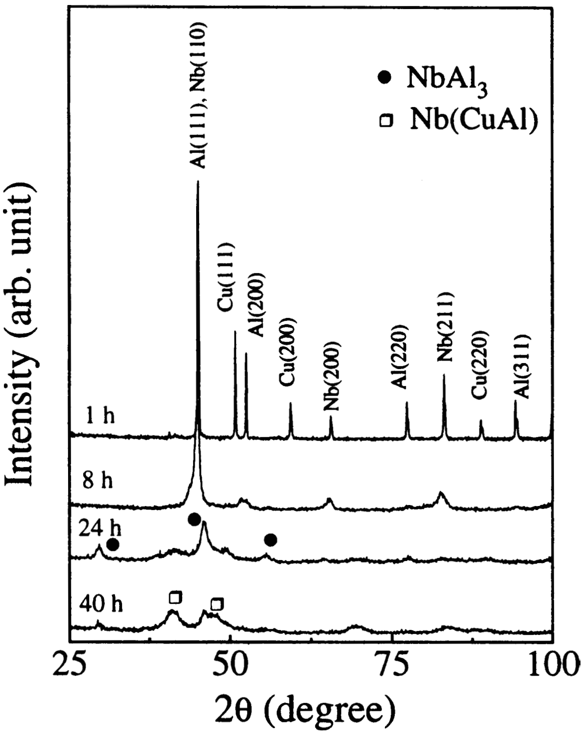

Fig. 3. XRD patterns of $Al_{65}Cu_{10}Nb_{25}$ following mechanical alloying for varying time.

no noticeable change in the identity or size/morphology of the milling product. Thus, the mechanical alloying product of $Al_{65}Cu_{30}Nb_5$ appears to be a fairly stable nanocrystalline aluminide.

Fig. 2 reveals the XRD patterns obtained from the $Al_{65}Cu_{20}Nb_{15}$ sample after different stages of ball milling. It is apparent that 8 h of ball milling yields a disordered bcc phase (presumably Cu_9Al_4) with nanometric grain size (d_c = 12 nm) along with some unreacted Al or Nb (d_c = 28 nm). Further milling up to 24 h results into the formation of a broad halo and an adjacent peak due to nanocrystalline Nb_2Al with d_c = 16 nm. At this stage, the volume fraction of the bcc phase is significantly reduced. Continued milling up to 40 h leads to the extension of the breadth of the halo suggesting that the microstructure at this stage may be completely amorphous. Furthermore, milling of this powder blend for an appropriate duration may produce a composite microstructure comprising a nano-aluminide and an amorphous phase.

It is interesting to note that a similar ball milling of $Al_{65}Cu_{20}Ti_{15}$ for 30-40 h has earlier yielded a completely amorphous product [7,8]. The substantial amount of defects introduced by milling (manifested by a significant increase in free volume in the true nanometric (5-10 nm) range) may induce appreciable disorder in the milled product [12,13]. Furthermore, the binary Nb-Al and Ti-Al systems have strong negative enthalpy of mixing. Table 1 shows that the enthalpy values for the present ternary alloys calculated, as per Miedemma and Bakker model [14,15] is strongly negative. Perhaps, the stable ternary solid solution is further stabilized by the entropy contribution due to the disorder and free volume expansion introduced by milling. The latter influence may ultimately convert the crystalline mass into a highly disordered amorphous aggregate.

Fig. 3 demonstrates the phase evolution sequence during ball milling of the powder blend having the nominal composition of $Al_{65}Cu_{10}Nb_{25}$. The XRD pattern of the sample obtained after 8 h of ball milling indicates the existence of Al, Cu and Nb phases. Due to the occurrence of the most intense Al (111) and Nb (110) peak at almost identical 2θ values, grain sizes of these phases could not be determined with reasonable accuracy. Further milling up to 24 h reveals the presence of ordered $NbAl_3$ phase along with some other new peaks. During further milling up to 40 h, the increase in the intensities of the peaks related to the new phase and concurrent reduction in the intensity of the $NbAl_3$ peaks allowed indexing of the former one as an Nb(CuAl) solid solution phase. The appearance of

Fig. 4. Amorphous halo in the TEM dark filed image of the $Al_{65}Cu_{20}Nb_{15}$ alloy following mechanical alloying for 40 h.

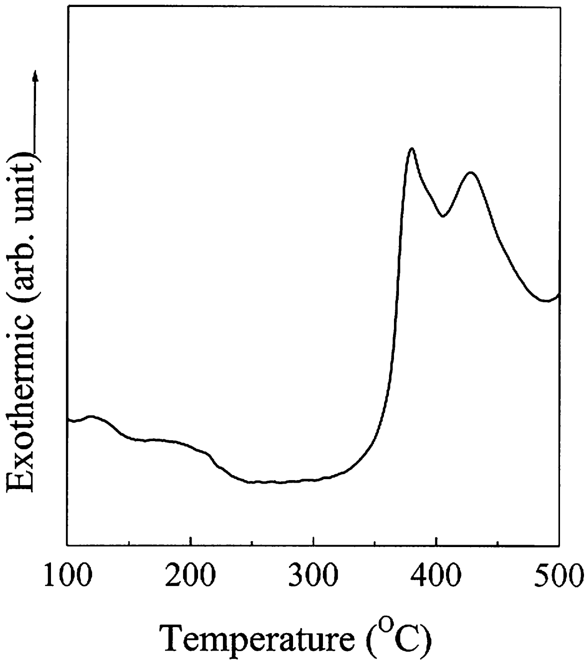

Fig. 5. DSC thermogram of the $Al_{65}Cu_{20}Nb_{15}$ alloy following mechanical alloying for 40 h showing overlapping double crystallization peaks before melting.

the fcc-Nb solid solution phase is in accordance with the results of the $Al_{65}Cu_{20}Nb_{15}$ (Fig. 2) and an earlier study [12,13]. It may be mentioned that the interplanar spacing (*d*) of the Nb(CuAl) phase in Fig. 3 are in close agreement with the same for the fcc-Nb phase earlier reported by us [12,13]. Further studies are in progress to resolve whether the final milling product of $Al_{65}Cu_{10}Nb_{25}$ (Fig. 3) is Cu and Al alloyed nanocrystalline fcc-Nb solid solution or a non-stoichiometric Nb(CuAl) intermetallic phase.

In order to verify the XRD results, a selected numbers of samples were examined under the TEM for microstructural study and phase identification. Among the three alloys, $Al_{65}Cu_{20}Nb_{15}$ showed a predominantly amorphous product beyond 30 h of milling. Fig. 4 shows the amorphous halo from the dark field image of an $Al_{65}Cu_{20}Nb_{15}$ sample milled for 40 h. Similar studies with the other two alloys following under identical milling routines revealed the presence of nanocrystalline (10-20 nm) bcc and fcc phases dispersed with amorphous regions in the $Al_{65}Cu_{30}Nb_5$ and $Al_{65}Cu_{10}Nb_{25}$ alloys, respectively. However, TEM investigation with samples from all the powder blends milled up to an intermediate stage (say, 15 h) shows a composite microstructure comprising a bcc or fcc phase along with varying amounts of the Al-rich amorphous regions. Thus, TEM studies essentially substantiated the results of XRD investigation that the $Al_{65}Cu_{20}Nb_{15}$ alloy is most appropriate for solid state amorphization of Al-Cu-Nb by mechanical alloying.

Fig. 5 shows the DSC thermogram obtained from the 40 h ball milled sample of the $Al_{65}Cu_{20}Nb_{15}$ alloy. The plot clearly reveals the appearance of two exothermic peaks at 380 and 428 °C indicating the occurrence of two-stage crystallization process during the heating experiment. It may be noted mentioned that similar overlapping two-stage crystallization behavior has earlier been observed in the DSC analysis of the $Zr_{50-x}Al_{12}Ti_xNi_{10}Cu_{20}$ amorphous alloy containing various amount of Ti [16]. It is also interesting to note that the crystallization process is preceded by an endothermic change in curvature in the temperature range of 200-350 °C which bears a close resemblance to the glass transition phenomena commonly observed in glass forming metallic alloys. However, it is premature to attribute the above-mentioned change in curvature to glass transition without supporting evidence of the relevant thermophysical data. Studies to determine the thermophysical properties of the $Al_{65}Cu_{20}Nb_{15}$ alloy are under progress.

It is relevant to mention that the exactly identical products of nanocrstalline aluminides, amorphous alloy and nano-aluminide dispersed amorphous matrix characterized the respective microstructure of $Al_{65}Cu_{30}Ti_5$, $Al_{65}Cu_{20}Ti_{15}$ and $Al_{65}Cu_{10}Ti_{25}$ alloys following mechanical alloying in an earlier investigation by us with selected Al-Cu-Ti ternary alloys [8]. The striking similarity of the results of mechanical alloying of $Al_{65}Cu_{35-x}TM_x$ (TM = early transition metal like Ti or Nb) suggests that appropriate substitution of Cu with Ti, Nb or a similar-TM may introduce adequate disorder in $Al_{65}Cu_{35}$ metastable solid solution and eventually convert the crystalline aggregate into an amorphous product. Earlier studies by Li *et al*. [17] as well as by ourselves [7] have indicated that mechanical alloying yields a metastable bcc solid solution in the composition range of Al – 35 to 65 at. % Cu. The present investigation was, thus, aimed at probing the above hypothesis and exploring if Nb could achieve solid state amorphization of $Al_{65}Cu_{35-x}Nb_x$ (by further disordering $Al_{65}Cu_{35}$) as in case of $Al_{65}Cu_{35-x}Ti_x$ [8] by mechanical alloying. Detail studies on the glass forming ability and glass forming range of the present alloys, if any, are in progress.

4. CONCLUSIONS

It may be concluded that mechanical alloying of $Al_{65}Cu_{30}Nb_5$, $Al_{65}Cu_{20}Nb_{15}$ and $Al_{65}Cu_{10}Nb_{25}$ powder blends for up to 40 hours in a planetary mill results into the formation of a nanocrystalline disordered intermetallic phase mixture, an amorphous and single phase nanocrystalline Nb(CuAl), respectively. The nanocrystalline Nb(CuAl) may be an extended solid solution of fcc-Nb (metastable polymorphic) or an intermetallic phase. In any case, mechanical alloying may be a potential route of synthesizing Al-based high specific strength nanocrystalline or amorphous matrix Al-Cu-Nb alloy powders/composites.

ACKNOWLEDGEMENTS

Partial financial support from the Department of Science and Technology, New Delhi (Grant no.: III.4 (23) 92 – ET-1999) is gratefully acknowledged.

REFERENCES

[1] T. Masumoto // *Mater. Sci. Eng. A* **179/180** (1994) 8.

[2] C. C. Koch, O. B. Cavin, C. G. Mckamey and J. O. Scorbrough // *Appl. Phys. Lett.* **43** (1983) 1017.

[3] E. Gaffet, W. Mark, G. Martin and J. Birgor // *J. Less Common Mat.* **145** (1988) 251.

[4] M. S. El-Eskandarany, K. Aoki and K. Suzuki // *Scripta Metall. Mater*. **36** (1997) 1001.

[5] J. Eckert, L. Schultz and K. Urban // *Appl. Phys. Lett.* **55** (1997) 1001.

[6] C. C. Koch, In: *Processing of Metals and Alloys*, ed. by R. W. Cahn, P. Hassan and E. J. Kramer (VCH Publication, Weinheim, 1991), Vol. 15, p. 193.

[7] P. P. Chattopadhyay, *Ph.D thesis*, Indian Institute of Technology, Kharagpur, India, 1999.

[8] P. P. Chattopadhyay, R. N. R. Gannabattula, S. K. Pabi and I. Manna // *Scripta Mater.* **45** (2001) 1191.

[9] P. P. Chattopadhyay, S. K. Pabi and I. Manna, *An application for Indian patent* (355/Cal/2000) filed in June 2000.

[10] T. H. Keijser, I. L. Langford, E. J. Mittemeijer and B. P.Vogel // *J. Appl. Cryst.* **15** (1982) 308.

[11] H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures* (John Wiley & Sons, Inc. New York, 1967), p. 491.

[12] P. P. Chatterjee, S. K. Pabi and I. Manna // *J. Appl. Phys.* **86** (1999) 409.

[13] P. P. Chattopadhyay, P. M. G. Nambissan, S. K. Pabi and I. Manna // *Physical Review B* **63** (2001) 54107.

[14] C. Suryanarayana // *Progress in Material Science* **46** (2001) 1.

[15] H. Bakker, *Enthalpies in Alloys* (Trans Tech Publication, 1998) Vol. 1.

[16] A. Inoue // *Acta Mater*. **48** (2000) 279.

[17] F. Li, K. N. Ishihara and P. H. Shingu // *Metall. Trans. A* **22** (1991) 2894.