ELSEVIER

Materials Science and Engineering A359 (2003) 11–17

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

Solid state synthesis of Al-based amorphous and nanocrystalline Al–Cu–Nb alloys

P. Nandi [a], P.P. Chattopadhyay [b], S.K. Pabi [a], I. Manna [a,*]

[a] *Metallurgical and Materials Engineering Department, Indian Institute of Technology, Kharagpur 721302, India*
[b] *Department of Metallurgy, B. E. College (D.U.), Howrah 711103, India*

Received 18 March 2002; received in revised form 7 January 2003

Abstract

An attempt was made to synthesize amorphous and/or nanocrystalline Al-based alloys from elemental powder blends with the stoichiometry $Al_{65}Cu_{35-x}Nb_x$ ($x = 5$–25 at.% Nb) by high energy planetary ball milling. Microstructure of the milled product at appropriated stages of milling was characterized by X-ray diffraction, transmission electron microscopy and differential scanning calorimetry. The $Al_{65}Cu_{20}Nb_{15}$ powder blend seems most amenable to solid state amorphization. This amorphous alloy was subjected to controlled heat treatment to develop a two-phase or composite microstructure of nano-aluminide dispersion in amorphous matrix. The results indicate that the present ternary system is akin to our previously reported results on Al–Cu–Ti system in developing completely/partially amorphous and/or nano-aluminide dispersed Al-rich nanocrystalline or amorphous matrix composites by controlled mechanical alloying and/or subsequent annealing.

Keywords: Mechanical alloying; Amorphous; Nanocrystals; Aluminides; Aluminum alloys

1. Introduction

Structural materials with high specific strength are always of considerable interest to the transportation and aviation industry. In this connection, developing an Al-based bulk metallic glass is an eagerly awaited technological breakthrough [1]. In the absence of an Al-based bulk amorphous alloy, it is predicted that the strength of light weight aluminum alloys could be significantly enhanced from about 450–600 MPa in age hardened condition to over 1500 MPa level in rapidly quenched amorphous or nanocrystal dispersed amorphous matrix aluminum based alloys [2]. Mechanical alloying is a convenient solid state synthesis alternative to melt spinning and similar rapid quenching techniques to develop amorphous alloys with metastable microstructures [3–5]. Furthermore, subsequent annealing at an appropriate temperature may enable dispersion of nanocrystalline intermetallic phases in the mechanically alloyed amorphous matrix precursors [5,6]. Earlier, the present authors have shown that mechanical alloying yields single phase amorphous or nanocrystalline products in Al-rich Al–Cu–Ti powder blends [7,8]. It has also been demonstrated 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 [9]. In the present paper, we shall report the synthesis of Al-based Al–Cu–Nb ternary amorphous or nanocrystalline alloys by mechanical alloying and nano-aluminide dispersed amorphous/nanocrystalline alloy by controlled annealing of mechanically alloyed product. To justify selecting the present composition range (5–25 at.% Nb), we will first report the results on mechanical alloying of binary Al–Cu blends that yields single phase nanocrystalline disordered bcc solid solution over a wide composition range, and subsequently, enables solid state amorphization by mechanical alloying with appropriate Nb addition.

* Corresponding author. Fax: +91-3222-28-2280.
E-mail address: imanna@metal.iitkgp.ernet.in (I. Manna).

0921-5093/03/$ - see front matter
doi:10.1016/S0921-5093(03)00338-1

2. Experimental

Al+Cu and Al+Cu+Nb elemental powder blends with over 99.5 wt.% purity and about 50–100 μm particle size were subjected to high energy planetary ball milling in Fritsch Pulverisette-5 mill in wet (toluene) medium at 300 rpm and ball to powder ratio of 10:1 using WC vial and balls (10 mm diameter). Milling in toluene prevents agglomeration of powders and welding of Al to the milling media (balls/vial). The initial composition (in at.%) of the powder blends were $Al_{30}Cu_{70}$, $Al_{65}Cu_{35}$ and $Al_{70}Cu_{30}$ (binary), and $Al_{65}Cu_{30}Nb_5$, $Al_{65}Cu_{20}Nb_{15}$ and $Al_{65}Cu_{10}Nb_{25}$ (ternary). To verify reproducibility of the milling product, selected powder blends were subjected to similar wet mechanical alloying in SPEX-8000D shaker mill using hardened steel vial and balls. Milling dynamics, among other factors, depend on the density of the milling media. Thus, comparison of results of mechanical alloying of a given powder blend in planetary and shaker mills using two different milling medium (namely, WC and steel) allowed verification of the results under different milling dynamics. The identity and sequence of phase evolution in different stages of mechanical alloying were studied by X-ray diffraction (XRD) analysis using a PHILIPS PW 1710 diffractometer with Co-Kα (0.179 nm) radiation (for planetary mill products) or Cu-Kα (0.1542 nm) radiation (for shaker mill products). Average grain size (d_c) was determined from 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 crystallite size determination using XRD analysis [11]. The authenticity of the XRD analysis concerning the amorphous phase was verified by transmission electron microscopy (TEM) using a Philips CM-12 TEM instrument. 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 10 °C min^{-1} up to 500 °C. A selected set of mechanically alloyed samples was isothermally annealed in vacuum at 450 C for 2 h. Table 1 presents the relevant XRD analysis data used for determining d_c at an appropriate stage of milling and the thermodynamic data used for calculating the enthalpy of mixing (ΔH_{amor}).

3. Results and discussion

Fig. 1 shows the XRD patterns of the final milled (30 h) binary Al–Cu powder blends in the composition range Al+30–70 at.% Cu. The final milling product of $Al_{70}Cu_{30}$ and $Al_{30}Cu_{70}$ blends consists of a mixture of nanocrystalline bcc and fcc (α-Al or α-Cu) solid solutions with grain size between 10 and 15 nm. In contrast, mechanical alloying of $Al_{65}Cu_{35}$ for 30 h produces a single-phase nanocrystalline ($\sim$8 nm) bcc solid solution. Milling binary powder blends in the composition range Al+35–65 at.% Cu for 25–30 h has always produced a similar single-phase product of bcc solid solution [8]. Thus, $Al_{65}Cu_{35}$ to $Al_{35}Cu_{65}$ is the composition limit in the Al–Cu binary system that yields a single-phase disordered bcc phase by mechanical alloying in the present set up. This result is in agreement with an earlier report that a bcc Bravais lattice is preferred during disordering of equilibrium intermetallic phases in the Cu–Al system [12]. Recently, we have been successful in introducing further disorder in the metastable bcc solid solution by partial substitution of Cu with Ti in $Al_{65}Cu_{35}$ and eventually converting the ternary $Al_{65}Cu_{20}Ti_{15}$ blend into an amorphous product [7,8]. We would now explore if Nb, a similar early transition metal as Ti, could achieve solid state amorphization of $Al_{65}Cu_{35-x}Nb_x$ by mechanical alloying in an identical manner as that in $Al_{65}Cu_{35-x}Ti_x$ [7].

Fig. 2 shows the XRD patterns obtained from the $Al_{65}Cu_{30}Nb_5$ elemental powder blend after different duration of ball milling. It is evident that the elemental constituents undergo mutual dissolution within a few hours of mechanical alloying giving rise to a disordered bcc phase following 10 h of milling. This bcc phase is a disordered Al-rich solid solution with Cu and Nb having a Bravais lattice identical to that of disordered Cu_9Al_4. The remaining peaks belong to α-Al and an unidentified metastable phase (at $2\theta = 43°–45°$ and 55°–57°, Fig. 2) that subsequently disappear at the final stage of milling (30–40 h). The considerable peak broadening of the bcc phase at this stage may be attributed to the effect of 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 constituent peaks/phases (e.g., α-Cu and disordered bcc) in the angular range of overlapping peaks. Consequently, d_c for α-Al and the bcc phase after 10 h of milling was determined as 30 and 42 nm, respectively (as per [10,11]). Continued milling up to 20 h led to further reduction in grain size of the existing phases (evidenced by more broadening of concerned peaks) without any significant change in phase identity and evolution. The XRD pattern of the sample obtained after 40 h of ball milling shows that the nanocrystalline-disordered bcc phase (presumably disordered and alloyed 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 and disordered Cu_9Al_4 alloyed with Nb. Continued milling up to 50 h shows no noticeable change in the identity or size/morphology of the milling product.

Table 1
Summary of grain size measurement at appropriate stages and enthalpy calculations of the binary and ternary alloys

Properties	Alloys (peaks analyzed)			
	$Al_{65}Cu_{35}$ (bcc phase)	$Al_{65}Cu_{30}Nb_5$ ($Cu_9Al_{4(330)}$)	$Al_{65}Cu_{20}Nb_{15}$ (bcc phase)	$Al_{65}Cu_{10}Nb_{25}$ ($Nb(CuAl)_{(110)}$)
Milling time stage (h)	30	40	20	40
Peak width (°)	1.46	1.68	2.42	2.20
Grain size (nm) [10,11]	7.8	6.7	4.6	5.1
ΔH_{chem} (J mol^{-1}) [15]	−11 150	−7540	−9140	−12 130
$\Delta H'_{chem}$ (J mol^{-1}) as per [16]	3784	3956	4488	4973
$\Delta H_{amor} = \Delta H_{chem} + \Delta H'_{chem}$ (J mol^{-1})	−7366	−3584	−4652	−7157

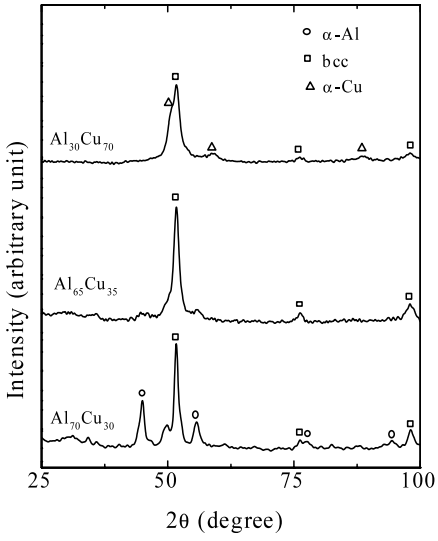


Fig. 1. XRD patterns of selected binary Al–Cu blends following isochronal mechanical alloying for 30 h in a planetary ball mill. Note that the milling product consists of two phases for the terminal compositions but a single phase nanocrystalline disordered bcc solid solution for the Al+35 at.% Cu blend.

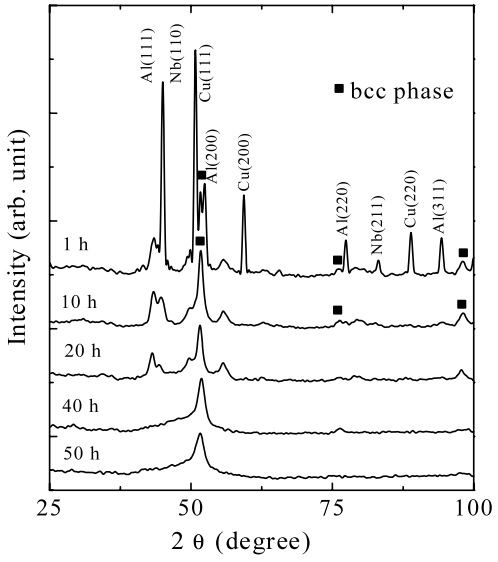


Fig. 2. XRD patterns showing the identity and sequence of phase evolution in the ternary $Al_{65}Cu_{30}Nb_5$ blend at different stages of mechanical alloying in a planetary mill up to 50 h. Note that the final milling product is a single phase disordered bcc solid solution.

Thus, the mechanical alloying product of $Al_{65}Cu_{30}Nb_5$ appears to be a fairly stable but disordered nanocrystalline aluminide that does not undergo any further structural/phase change with continued milling. It is relevant to note that the results on identity and phase evolution during mechanical alloying of $Al_{65}Cu_{30}Nb_5$ are identical with that for $Al_{65}Cu_{30}Ti_5$ [7].

Fig. 3a summarizes the XRD patterns obtained from the $Al_{65}Cu_{20}Nb_{15}$ sample by predetermined periods of mechanical alloying in a planetary ball mill. It is apparent that 10 h of ball milling yields a disordered bcc phase (presumably disordered Cu_9Al_4) with nanometric grain size ($d_c = 12$ nm) along with some unreacted α-Al or Nb ($d_c = 28$–35 nm). Further milling up to 20 h produces a broad halo and adjacent peaks (at $2\theta = 43°$–$45°$ and $55°$–$57°$) due to a nanocrystalline metastable phase with $d_c = 16$ nm. The appearance of this metastable phase was also noted at identical stage of milling of $Al_{65}Cu_{30}Nb_5$ (Fig. 2). In 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 without any other crystalline peak suggesting that the microstructure at this stage may be completely amorphous. Continued milling of this powder blend up to 55 h did not register any noticeable change in the XRD pattern. In order to verify the reproducibility of this result, the same powder blend was subjected to mechanical alloying in a SPEX 8000M mill for up to 50 h. The microstructural evolution during mechanical alloying in the SPEX mill registered exactly identical identity and sequence of phase evolution with the final milling product at 50 h being completely amorphous. Thus, the $Al_{65}Cu_{20}Nb_{15}$ powder blend seems easily amenable to solid state amorphization under both planetary and shaker milling configuration using different milling media (WC and steel). Fig. 3b shows the XRD evidence of the initial (crystalline) and final milling product (amorphous) with about 3–5 at.%

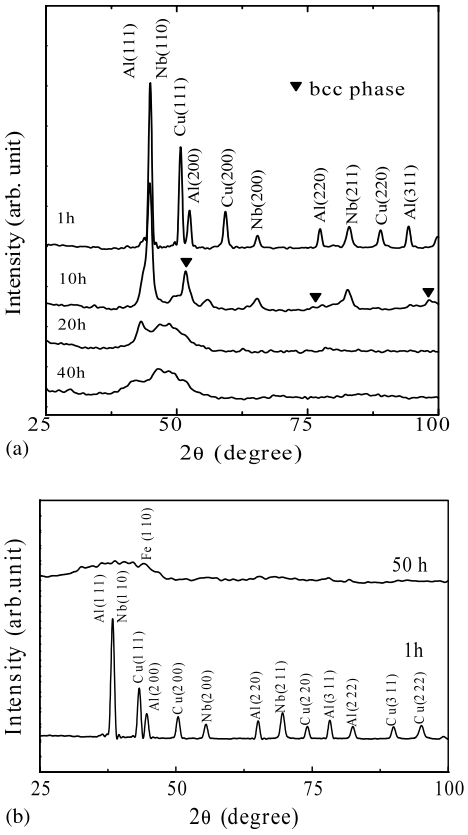


Fig. 3. XRD patterns showing phase evolution in the ternary $Al_{65}Cu_{20}Nb_{15}$ alloy at different stages of mechanical alloying in (a) a planetary ball mill using WC vial and balls, and (b) a shaker mill using steel vial and balls. Note that the final milling product from both the mills is precisely identical (amorphous). XRD patterns of (a) and (b) were obtained using Co-Kα and Cu-Kα radiation, respectively.

Fe impurity picked up from the milling media during milling in the shaker mill. Thus, mechanical alloying of $Al_{65}Cu_{20}Nb_{15}$ in a high-energy mill for an appropriate duration may produce either completely amorphous (after milling over 40 h) or a composite microstructure comprising a nano-aluminide and an amorphous phase (following milling up to 20–35 h).

It is interesting to note that mechanical alloying of $Al_{65}Cu_{20}Ti_{15}$ for 30–40 h under identical milling routine has earlier yielded a completely amorphous product [7,8]. We have earlier shown that substantial amount of defects introduced by milling (manifested by a significant increase in free volume in the true nanometric range of 5–10 nm) may induce appreciable disorder or structural instability in $Nb_{80}Al_{20}$ powder blend [13] or elemental Nb [14] by high energy ball milling. Furthermore, both Nb–Al and Ti–Al systems show a strong negative enthalpy of mixing over a wide composition range. Thus, the structural disorder introduced by high-energy ball milling coupled with a large negative heat of mixing may lead to amorphization in the Al–Cu–Nb system, like that in Al–Cu–Ti, in an appropriate composition range.

In order to investigate the genesis of amorphization in the present alloys, enthalpy of formation (ΔH_{chem}) of binary/ternary amorphous solid solution was calculated as per the Miedema model [15]. Accordingly, ΔH_{chem} for a binary amorphous product may be expressed as

$$\Delta H_{chem} = K[-P(\Delta\phi^*)^2 + Q(\Delta\eta_{ws}^{1/3})^2 - R] \quad (1)$$

where, $\Delta\phi^*$ and $\Delta\eta_{ws}$ are the respective difference in electro-negativity parameter and boundary electron density between components A and B, Q and P are empirical constants such that $Q/P = 9.4$ for all metals, and R is the atomic nearest neighbor factor. Furthermore, the proportionality constant, K and other relevant concentration dependent functions are given by

$$K = 2f(x)(X_A V_A^{2/3} + X_B V_B^{2/3})/[(\eta_{ws}^A)^{-1/3} + (\eta_{ws}^B)^{-1/3}] \quad (2)$$

$$f(x) = X_A^S X_B^S[1 + 5(X_A^S X_B^S)^2] \quad (3)$$

$$X_A^S = [X_A V_A^{2/3}]/(X_A V_A^{2/3} + X_B V_B^{2/3}) \quad (4)$$

and,

$$X_B^S = 1 - X_A^S \quad (5)$$

where, V_A, V_B and X_A, X_B are the respective molar volume and concentrations of A and B, $f(x)$ is a concentration dependent function, and X_A^S and X_B^S are the respective surface concentration terms for components A and B. Since the enthalpy of amorphization of pure metals is only a function of melting temperature (T_i^M) and molar concentration (X_i) of the component i, the same for a single component in a given mixture is estimated [16] as

$$\Delta H'_{chem} = 3.5 \sum X_i \, T_i^M \quad (6)$$

Table 1 summarizes the enthalpy (ΔH) values for the present ternary alloys calculated as per the above models by Miedema et al. [15] and modified by Bakker [16]. It may be noted that all the ΔH_{chem} or ΔH_{amor} values are 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 with the volume fraction of the non-crystalline domains far outnumbering that of isolated nanocrystalline islands. However, initial composition seems crucial in deciding the final microstructure, as the final milling product of $Al_{65}Cu_{10}Nb_{25}$ (having the most negative ΔH_{amor}) is not fully amorphous (Fig. 4), though the same for $Al_{65}Cu_{20}Nb_{15}$ is amorphous. Perhaps, the contribution of plastic strain or strain rate is a composition dependent term that needs to be incorporated into Eqs. (1) and (6) to obtain more realistic values of ΔH_{chem} or ΔH_{amor} in mechanical alloying. We are currently working on this approach of modification of the Miedema model.

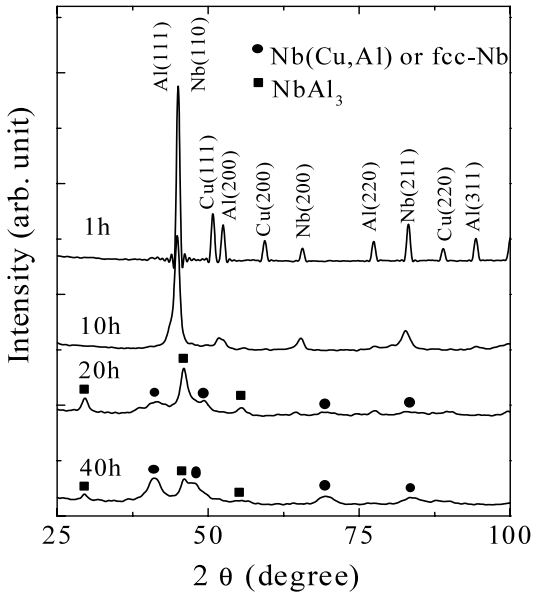


Fig. 4. XRD patterns showing phase evolution in the ternary $Al_{65}Cu_{10}Nb_{25}$ alloy at different stages of mechanical alloying in a planetary mill. Note that the final milling product is a mixture of two nanocrystalline phases ($NbAl_3$ and either Nb(CuAl) or fcc-Nb).

Fig. 4 reveals the phase evolution sequence during ball milling of the powder blend having the initial composition of $Al_{65}Cu_{10}Nb_{25}$. The XRD pattern of the sample obtained after 10 h of ball milling indicates the existence of Al, Cu and Nb rich solid solutions. Due to the occurrence of the most intense Al (1 1 1) and Nb (1 1 0) peaks at almost identical 2θ values, grain sizes of these phases could not be determined with reasonable accuracy. Further milling up to 20 h reveals the presence of ordered $NbAl_3$ phase along with some other new peaks. During continued 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 a fcc solid solution or the rhombohedral Nb(CuAl) phase [17]. It is relevant to point out that we have recently demonstrated that both a $Nb_{80}Al_{20}$ powder blend and elemental Nb undergo a bcc→fcc polymorphic change due to structural instability caused by negative hydrostatic pressure arising out of nanocrystallization during high energy ball milling [13,14]. The appearance of the fcc solid solution phase in the present study may be a consequence of a similar polymorphic change of bcc→fcc-Nb and dissolution of Cu and Al in fcc-Nb. It may be mentioned that the interplanar spacing (d) of the fcc phase in Fig. 4 is in close agreement with the same for the fcc-Nb phase earlier reported by us [13,14]. Further studies are in progress to resolve whether the final milling product of $Al_{65}Cu_{10}Nb_{25}$ (Fig. 4) 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 after appropriate hours of milling. TEM study was conducted along the electron transparent edges of these particles without necessitating microtoming or sectioning. Among the three alloys, $Al_{65}Cu_{20}Nb_{15}$ showed partially and completely amorphous microstructure beyond 20 and 40 h of milling, respectively. Fig. 5 shows the high resolution TEM image of the $Al_{65}Cu_{20}Nb_{15}$ alloy following mechanical alloying in planetary mill for 20 h. The microstructure is predominantly nanocrystalline with grain sizes below 10–15 nm. It is interesting to note that the regions between the nanocrystalline grains seem devoid of crystalline order. However, the corresponding XRD profile does not evidence the presence of amorphous phase yet (Fig. 3a). Investigation along the edges of the powder under TEM indeed showed some regions devoid of crystallinity under different beam orientations. Perhaps, the volume fraction of the amorphous region is too low yet to be detected by the XRD.

Fig. 6a shows the high resolution TEM image of the $Al_{65}Cu_{20}Nb_{15}$ powder blend following mechanical alloying in shaker mill for 50 h. The microstructure is completely amorphous at this stage of mechanical alloying. Corresponding energy dispersive X-ray analysis showed a fairly homogeneous composition of the powder particles (close to the initial composition) and negligible amount of W or Fe contamination in samples taken from either planetary or shaker mill. Fig. 6b shows a typical single-order amorphous halo with

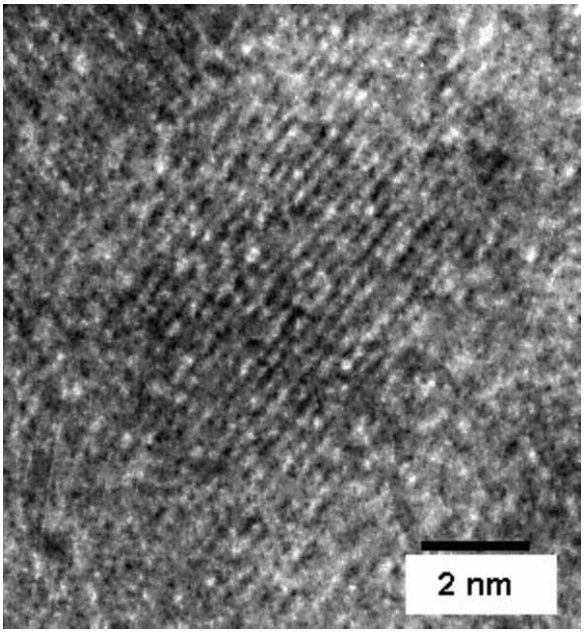
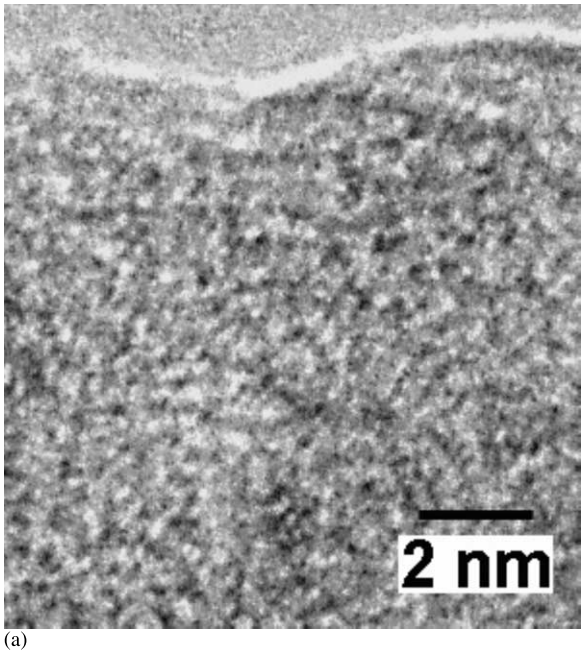
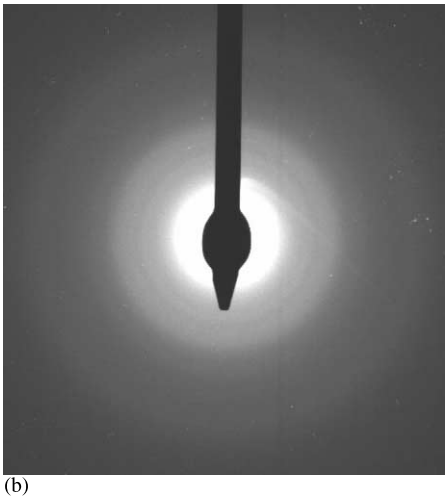


Fig. 5. High resolution TEM image of $Al_{65}Cu_{20}Nb_{15}$ following mechanical alloying in a planetary mill for 20 h. Note that the microstructure is nanocrystalline with some intervening regions being amorphous with no well defined crystallinity or lattice fringes.



(a)



(b)

Fig. 6. (a) High resolution TEM image of $Al_{65}Cu_{20}Nb_{15}$ following by mechanical alloying in a shaker mill for 50 h showing a complete amorphous microstructure, and (b) SAD pattern of the same sample showing a diffused halo of the amorphous matrix.

diffused intensity from the dark field image of the same $Al_{65}Cu_{20}Nb_{15}$ sample milled for 50 h. Careful diffraction study along the fringes and center of the same powders did not show any crystallinity at all. It may be noted that the same $Al_{65}Cu_{20}Nb_{15}$ powder blend after identical hours of milling in the planetary mill failed to show lattice image or crystallinity under different beam orientations. The results from two different mills are shown here only for the $Al_{65}Cu_{20}Nb_{15}$ alloy to highlight that the microstructural evolution was identical in the samples milled under comparable conditions of milling in either of the mills. Thus, Fig. 6 substantiates the corresponding XRD results presented in Fig. 3. Furthermore, comparison of the TEM and XRD results essentially indicates that the $Al_{65}Cu_{20}Nb_{15}$ alloy, among the three Al–Cu–Nb alloys investigated here, is most appropriate for solid state amorphization by mechanical alloying.

Fig. 7 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 mentioned that similar overlapping two-stage crystallization behavior has earlier been observed in the DSC analysis of the $Zr_{58-x}Al_{12}Ti_xNi_{10}Cu_{20}$ amorphous alloy containing various amount of Ti [18]. However, the present alloy does not record any distinct glass transition behavior.

Fig. 8 shows the XRD analysis of the products of isothermal annealing of amorphous $Al_{65}Cu_{20}Nb_{15}$ at 450 °C for 2 h in vacuum following mechanical alloying for 40 h. Since annealing was done well above the crystallization temperature of the alloy, Fig. 8 shows that isothermal annealing of $Al_{65}Cu_{20}Nb_{15}$ yields a composite microstructure comprising two nano-aluminides, namely $CuAl_2$ and $NbAl_3$. It may be noted that both the aluminides possess high specific strength. Thus, the present alloy is amenable to developing either completely amorphous (by mechanical alloying) or nanocrystalline aluminide products (by mechanical alloying and annealing) with the same initial composition.

It is relevant to mention that the exactly identical products of nanocrystalline 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 [7]. The striking

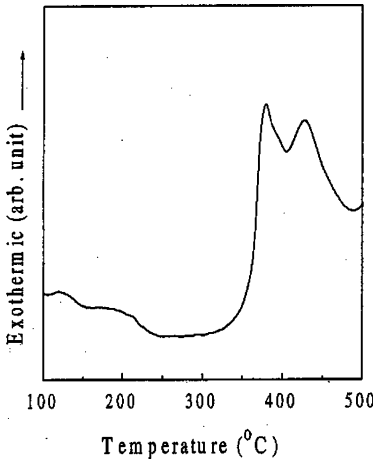


Fig. 7. DSC thermogram of the $Al_{65}Cu_{20}Nb_{15}$ alloy measured in Ar atmosphere at 20 °C min^{-1} heating rate following mechanical alloying in a planetary mill for 40 h showing overlapping double crystallization peaks approximately at 380 and 428 °C, respectively.

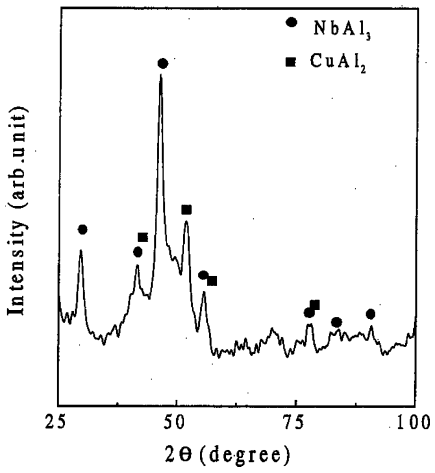


Fig. 8. XRD pattern of the ternary $Al_{65}Cu_{20}Nb_{15}$ alloy following mechanical alloying in a planetary mill for 40 h and subsequent isothermal annealing at 450 °C for 2 h in vacuum. Note that the annealed microstructure comprises nanocrystalline $NbAl_3$ and $CuAl_2$.

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 or Nb 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. [12] as well as by ourselves [19,20] have indicated that mechanical alloying of Al–Cu yields a metastable bcc solid solution in the composition range Al−35-65 at.% Cu that does not turn amorphous even after extended hours of milling under identical condition. Thus, the present investigation substantiates the above hypothesis on the role of Nb or a similar early transition metal in solid state amorphization of $Al_{65}Cu_{35-x}Nb_x$ by introducing further disorder in $Al_{65}Cu_{35}$.

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 appropriate time (30–50 h) in a planetary or shaker mill results into the formation of a single phase nanocrystalline disordered metallic phase, an amorphous alloy and a nano-aluminide mixture of $NbAl_3$, and fcc-Nb solid solution or Nb(CuAl), respectively. The nanocrystalline Nb(CuAl) may be an extended solid solution of fcc-Nb (polymorph of bcc-Nb) or a non-stoichiometric intermetallic phase. Presence of Nb in appropriate amount is crucial for introducing adequate disorder and solid state amorphization of the present ternary system. The $Al_{65}Cu_{20}Nb_{15}$ powder blend is most prone to solid state amorphization. The amorphous product of $Al_{65}Cu_{20}Nb_{15}$ undergoes thermally activated crystallization transformation at 380 and 428 °C without any distinct glass transition prior to that. Thus, mechanical alloying may be a potential route of synthesizing Al-based nanocrystalline or amorphous matrix Al–Cu–Nb alloy powders/composites for applications below 350 °C.

Acknowledgements

Partial financial support from the Department of Science and Technology, New Delhi (Grant no.: SP/S2/K-17/98) is gratefully acknowledged. Useful technical discussion with Prof. Dr H.-J. Fecht and Dr F. Banhart are greatly appreciated. One of the author (I.M.) is grateful to Alexander von Humboldt Foundation, Bonn for financial support during the preparation of the manuscript.

References

[1] C.S. Kiminami, N.D. Basim, M.J. Kaufman, M.F. Amateau, T.J. Eden, G.J. Galbraith, Key Eng. Mater. 189–191 (2001) 503.
[2] T. Masumoto, Mater. Sci. Eng. A 179/180 (1994) 8.
[3] C.C. Koch, in: R.W. Cahn, P. Haasen, E.J. Kramer (Eds.), Processing of Metals and Alloys, vol. 15, VCH Publication, Weinheim, 1991, p. 193.
[4] C. Suryanarayana, Prog. Mater. Sci. 46 (2001) 1.
[5] M.S. El-Eskandarany, K. Aoki, K. Suzuki, Scripta Metall. Mater. 36 (1997) 1001.
[6] J. Eckert, L. Schultz, K. Urban, Appl. Phys. Lett. 55 (1989) 117.
[7] P.P. Chattopadhyay, R.N.R. Gannabattula, S.K. Pabi, I. Manna, Scripta Mater. 45 (2001) 1191.
[8] P.P. Chattopadhyay, S.K. Pabi, I. Manna, An application for Indian patent (355/Cal/2000) filed in June 2000.
[9] T.B. Massalski (Ed.), Binary Alloys Phase Diagram, vol. 1, second ed., ASM International, Materials Park, OH, 1990, p. 179.
[10] T.H. Keijser, I.L. Langford, E.J. Mittemeijer, B.P. Vogel, J. Appl. Cryst. 15 (1982) 308.
[11] H.P. Klug, L.E. Alexander, X-ray Diffraction Procedures, Wiley, New York, 1967, p. 491.
[12] F. Li, K.N. Ishihara, P.H. Shingu, Metall. Trans. A22 (1991) 2894.
[13] P.P. Chatterjee, S.K. Pabi, I. Manna, J. Appl. Phys. 86 (1999) 409.
[14] P.P. Chattopadhyay, P.M.G. Nambissan, S.K. Pabi, I. Manna, Phys. Rev. B 63 (2001) 54107.
[15] A.R. Miedema, P.F. de Chatel, F.R.D. Boer, Physica B 100 (1980) 1.
[16] H. Bakker, Enthalpies in Alloys, vol. 1, Trans Tech Publication, 1998.
[17] JCPDS file no. 18–12.
[18] A. Inoue, Acta Mater. 48 (2000) 279.
[19] P. Nandi, P.P. Chattopadhyay, S.K. Pabi, I. Manna, Mater. Phys. Mech. 4 (2002) 116.
[20] I. Manna, P. Nandi, P.P. Chattopadhyay, S.K. Pabi, F. Banhart, H.-J. Fecht, In: N. Chakraborti, U.K. Chatterjee, (Eds.) Advances in Materials and Material Processing (Conference Proceeding), Tata McGraw Hill Pub. Company Ltd., New Delhi (2002) pp. 410–414.