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## Development of amorphous $\text{Al}_{65}\text{Cu}_{35-x}\text{Ti}_x$ alloys by mechanical alloying

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### Introduction

Development of high-specific strength structural material is always of great importance to the transportation and aviation industry. It is predicted that the strength of light weight aluminium alloys could be significantly enhanced from about 500–600 MPa in age hardened condition to 1200–1550 MPa level in rapidly quenched glassy/amorphous or nanocrystal dispersed glassy/amorphous matrix aluminium 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 the metallic glasses [2–4]. Furthermore, carefully designed milling routine and/or subsequent heat treatment may enable dispersion of nanocrystalline intermetallic phases in the mechanically alloyed amorphous/glassy matrix precursor [5,6]. Recently, we have demonstrated for the first time that mechanical alloying of the  $\text{Al}_{65}\text{Cu}_{35-x}\text{Ti}_x$  ternary system within a close composition range yields completely or partially amorphous alloy [7]. However, the phase identity and evolution during milling and/or subsequent annealing in this system have not been determined. In the present paper, we shall report the phase evolution sequence during mechanical alloying and subsequent isothermal annealing (at 773 K) of the selected alloys in the  $\text{Al}_{65}\text{Cu}_{35-x}\text{Ti}_x$  ternary system. In addition, we shall also identify an appropriate composition that can yield a completely amorphous microstructure by mechanical alloying.

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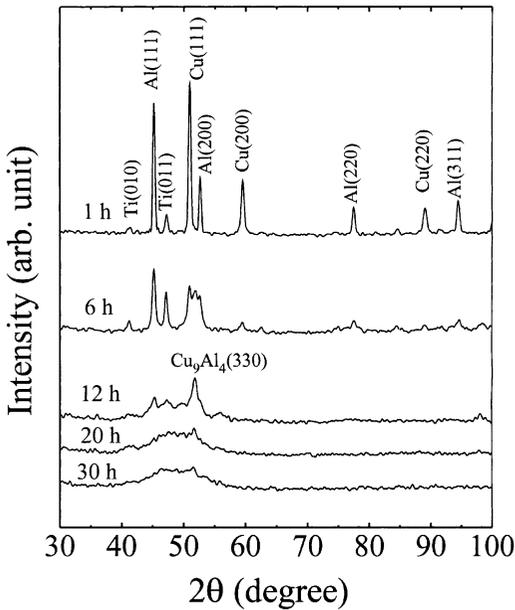
## Experimental

Blends of elemental (>99.5 wt.% purity) Al, Cu, and Ti powders ( $\sim 50$ – $100\ \mu\text{m}$  particle size) having the nominal compositions (in at.%) of  $\text{Al}_{65}\text{Cu}_{35-x}\text{Ti}_x$  ( $x = 5, 10, 15, 20, 25$  and  $30$  at.%) were ball milled in a Fritsch Pulverisette 5 planetary ball mill at 300 rpm and ball to powder weight ratio of 10:1 using WC vial and balls (10 mm diameter) in stages with up to a cumulative milling time of 40 h. The initial composition of the powder blend varied in the range  $x = 5$ – $30$  (at.% Ti) to determine the solid state amorphization range in this system. The identity and phase evolution in different stages of mechanical alloying and subsequent annealing of the ball milled samples were studied by the X-ray diffraction (XRD) analysis using the  $\text{Co-K}_\alpha$  (0.179 nm) radiation in a Philips PW1710 diffractometer. Average grain size was determined from the broadening of the most intense peak of the concerned phases using the Voigt method [8] which allowed judicious elimination of the contributions due to the instrumental and strain effects in the observed peak broadening. For the overlapping peaks, the full width at half intensity maximum and true Bragg angle ( $2\theta$ ) were determined by an appropriate de-convolution exercise.

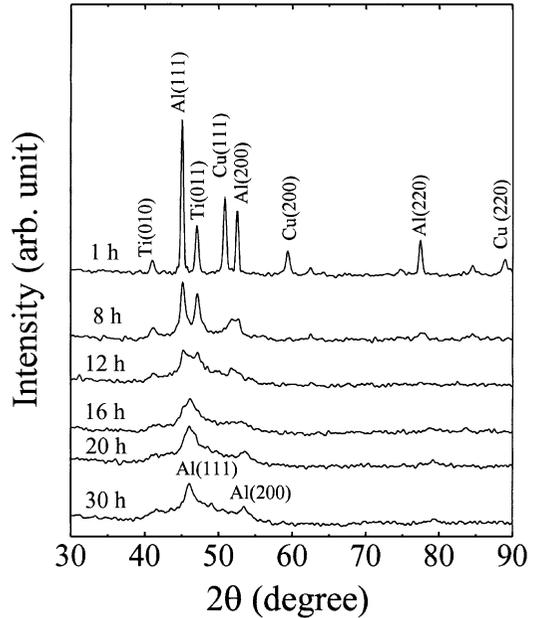
## Results and discussion

### *Mechanical alloying*

Fig. 1 reveals the XRD patterns obtained from the  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$  samples subjected to mechanical alloying for different lengths of milling time. It is apparent that the intensities of the peaks due to the elemental constituents (Al, Cu and Ti) are considerably reduced by 6 h of milling with simultaneous evolution of additional peaks which may be indexed as the disordered  $\text{Cu}_9\text{Al}_4$  phase having a bcc Bravais lattice [9]. In addition to decreasing the intensity, continued ball milling seems to induce considerable grain refinement (reflected by peak broadening) of Al ( $\sim 10$  nm at 12 h from about  $5\ \mu\text{m}$  at 1 h) and Cu ( $\sim 30$  nm at 12 h from about  $15\ \mu\text{m}$  at 1 h). In fact, the apparent grain size of  $\text{Cu}_9\text{Al}_4$  determined from the peak broadening analysis of the (3 3 0) peak as per Ref. [8] is below 15 nm. It is interesting to note that the disordered  $\text{Cu}_9\text{Al}_4$  phase and the remaining Al peaks merge in to a broad peak or a halo beyond 12 h of milling. The exact grain size of Al and disordered  $\text{Cu}_9\text{Al}_4$  could not be determined at this stage of mechanical alloying due to the presence of such a broad halo. The XRD pattern obtained from the sample collected after 20 h of milling indicates that the milled product is now predominantly amorphous without the presence of a significant amount of any crystalline phase in the former. Continued ball milling up to 30 h yields the same single phase amorphous product with a broader halo in the XRD pattern. That prolonged milling of the present powder blend does not lead to evolution of any crystalline phase from the amorphous matrix during continued milling indicates that the amorphous product is stable enough under the present milling condition and heat generated during milling. Thus, Fig. 1 shows that the  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$  ternary alloy is amenable to the complete crystalline to amorphous transition by mechanical alloying. Fig. 1 further



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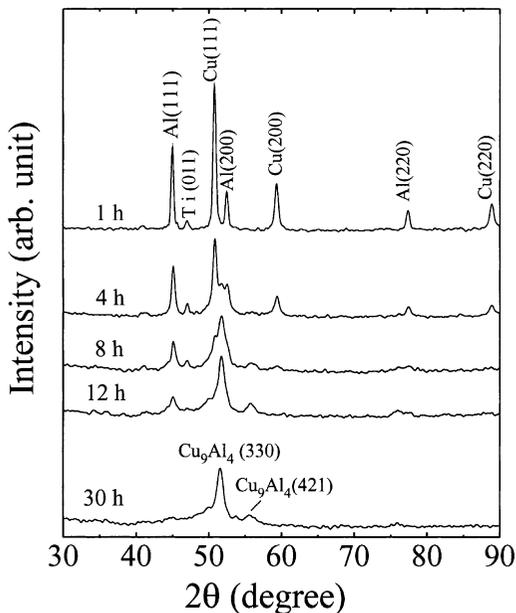
Fig. 1. XRD patterns of  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$  ball milled at 300 rpm for different duration ( $t$ ) of milling. Note that the milled product is completely amorphous (indicated by the broad halo) after 30 h of mechanical alloying.

Fig. 2. XRD patterns of  $\text{Al}_{65}\text{Cu}_{10}\text{Ti}_{25}$  ball milled at 300 rpm for different duration ( $t$ ) of milling. Note that the final milling product is nanocrystalline Al with the entire amount of Cu and Ti dissolved in it.

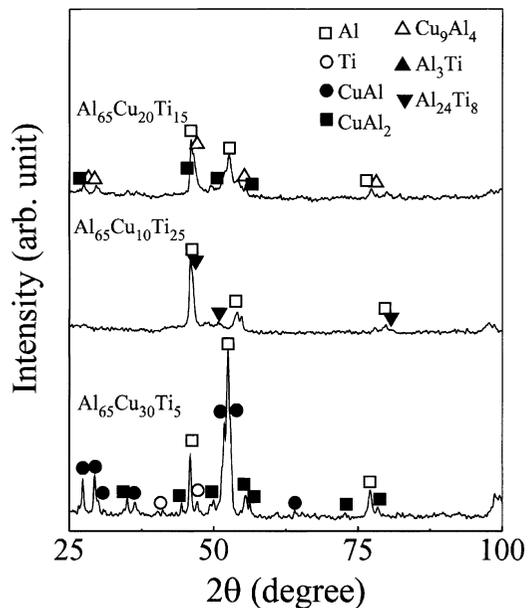
reveals that controlled milling (say, up to 12 h) may develop nanocrystalline intermetallic phases followed by complete solid state amorphization of the same during subsequent milling. Therefore, arresting the milling process at appropriate stages may allow development of an Al-rich composite comprising nanocrystalline and amorphous phases with varying volume fractions.

Fig. 2 presents the XRD patterns of the  $\text{Al}_{65}\text{Cu}_{10}\text{Ti}_{25}$  samples as a function of milling time. The observed trend of phase evolution during the initial stage of ball milling (up to 8 h) in Fig. 2 is almost the same as that recorded in the case of  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$  (Fig. 1). However, unlike  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ , the final milling product of  $\text{Al}_{65}\text{Cu}_{10}\text{Ti}_{25}$  is neither completely amorphous nor disordered  $\text{Cu}_9\text{Al}_4$ . Instead, a halo spreading between  $2\theta = 44\text{--}48^\circ$  is noted after 16 h of milling that may arise due to a mixture of amorphous and nanocrystalline phases. A careful de-convolution analysis in the stated  $2\theta$  range indicates that nanocrystalline Al (1 1 1) and Ti (0 1 1) peaks may constitute the halo. But the said halo does not include the (3 3 0) peak of disordered  $\text{Cu}_9\text{Al}_4$  (as noted for  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$  in Fig. 1). It is interesting to note that continued milling up to 30 h yields single phase nano crystalline Al. The considerable shift in the (1 1 1) and (2 0 0) peak of Al at 30 h may be attributed to the influence of grain refinement, strain and dissolution of Cu and Ti in Al. Thus,  $\text{Al}_{65}\text{Cu}_{10}\text{Ti}_{25}$  powder blend is amenable to developing a single-phase nanocrystalline Al alloyed with Cu and Ti by ball milling up to 30 h.

Fig. 3 shows the XRD patterns obtained from samples collected at different stages of ball milling of the  $\text{Al}_{65}\text{Cu}_{30}\text{Ti}_5$  blend. Here too, the intensity of the peaks due to Cu and Al gradually decrease as the milling time increases. In comparison, the intensity of the Ti peak remains nearly unaltered up to 8 h of milling indicating perhaps, the dissolution of Ti is relatively sluggish than that of Cu or Al (though the amount of Ti is minimum among all the blends studied here). By 8–12 h of milling, all these peaks tend to disappear. Furthermore, the elemental constituents, particularly Al and Cu, undergo a considerable amount of grain refinement (evidenced by peak broadening) practically up to the nanometric range (<50 nm) in the course of milling up to 8 h. Perhaps, mechanical alloying is aided by nanocrystallization of the constituent elements. It is interesting to note that Ti is dissolved in the nanocrystalline or glassy matrix much later than Al or Cu in all the powder blends studied in the present investigation. It is relevant to point out that the Wigner–Seitz cell radius of Ti (=1.62 Å) is significantly higher than those of Al (=1.58 Å) and Cu (=1.41 Å) [10]. Though reliable data on volume diffusion of Ti in Cu or Al are not available, it is logical to anticipate that the diffusion rate of the bigger atoms of Ti in Cu or Al (having a smaller atomic size) may be slower. Thus, it is anticipated that Cu and Al may undergo easier and faster dissolution in their counterparts or in Ti, while Ti may undergo a relatively sluggish dissolution either in Cu or Al, as noted in Figs. 1–3.



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Fig. 3. XRD patterns of  $\text{Al}_{65}\text{Cu}_{30}\text{Ti}_5$  ball milled at 300 rpm for different periods of time. Note that the constituent elements undergo complete dissolution and the final product after 30 h of milling is single phase  $\text{Cu}_9\text{Al}_4$ .

Fig. 4. XRD patterns obtained from isothermal treatment of the final milling products of  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ ,  $\text{Al}_{65}\text{Cu}_{10}\text{Ti}_{25}$  and  $\text{Al}_{65}\text{Cu}_{30}\text{Ti}_5$  carried out at 773 K for 1 h.

It appears that Ti plays an important role in solid state amorphization of  $\text{Al}_{65}\text{Cu}_{35-x}\text{Ti}_x$  (Figs. 1–3). In  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ , Al and Cu tend to mutually dissolve and form disordered  $\text{Cu}_9\text{Al}_4$  in the early stages (Fig. 1). Continued milling beyond 12 h leads to dissolution of the remnant Ti and formation of the amorphous phase. In  $\text{Al}_{65}\text{Cu}_{10}\text{Ti}_{25}$ , amorphization sets in within 12 h of milling concomitant with nanocrystallization of the constituent elements without necessitating the formation of disordered  $\text{Cu}_9\text{Al}_4$  as a precursor (Fig. 2). Perhaps, the presence of higher amount of Ti in this blend aids the formation of the amorphous phase at an early stage. However, unlike in  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ , amorphization in  $\text{Al}_{65}\text{Cu}_{10}\text{Ti}_{25}$  is incomplete and gives in to single phase nanocrystalline Al as the final milling product. In  $\text{Al}_{65}\text{Cu}_{30}\text{Ti}_5$ , disordered  $\text{Cu}_9\text{Al}_4$  forms through a similar sequence as that in  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ , but does not undergo crystalline to amorphous transition despite dissolving the entire amount of available Ti. Perhaps, the amount of Ti present (=5 at.%) in this blend is inadequate for amorphization (Fig. 3).

In the present study, XRD analysis of a number of samples of  $\text{Al}_{65}\text{Cu}_{35-x}\text{Ti}_x$  ( $x = 5\text{--}30$  at.%) ball milled for up to 40 h shows that a completely single phase amorphous product is obtained only in the  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$  blend. It may be noted that both Al–Ti and Cu–Ti form metallic glasses with up to 90 at.% Ti, respectively [11,12]. An earlier study has shown that partial substitution of Cu with Ti in  $\text{Al}_{65}\text{Cu}_{35}$  is the most potential Al–Cu–Ti glass forming basis [13]. Beyond this ternary composition range with Ti = 10–30 at.%, the microstructure of the milled product is no longer single phase but consists of a number of nanocrystalline metallic/intermetallic phases. However, the precise role of Ti and the threshold amount needed for the formation of the  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$  amorphous alloy by mechanical alloying remains to be determined. Work is in progress to determine the mechanism of solid state amorphization of  $\text{Al}_{65}\text{Cu}_{35-x}\text{Ti}_x$  and thermal stability of the milled product.

#### *Isothermal treatment of the milled product*

Fig. 4 shows the XRD patterns of the samples obtained after isothermal annealing of the final ball milled products of  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ ,  $\text{Al}_{65}\text{Cu}_{10}\text{Ti}_{25}$  and  $\text{Al}_{65}\text{Cu}_{30}\text{Ti}_5$  at 773 K for 1 h. Though annealing was done at different temperatures in the range of 423–773 K, the annealing products of 773 K could only be unambiguously indexed, perhaps, due to considerable grain coarsening (peak sharpening). It is evident that dispersion of nanocrystalline  $\text{CuAl}_2$  and  $\text{Cu}_9\text{Al}_4$  intermetallic phases in the Al matrix replaces the amorphous milling product of  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ .

Similar thermal treatment of the final milled product of  $\text{Al}_{65}\text{Cu}_{10}\text{Ti}_{25}$  has yielded the formation of nanocrystalline  $\text{Al}_{24}\text{Ti}_8$  phase in the Al matrix. In isothermal annealing of  $\text{Al}_{65}\text{Cu}_{30}\text{Ti}_5$ , the milling product of the disordered bcc phase is substituted with several equilibrium phases like Al, Ti, CuAl, and  $\text{CuAl}_2$ . It is interesting to note that peaks of the constituent phases/compounds remain noticeably wide even after annealing at 773 K indicating perhaps, some of the phases/compounds could still be considerably fine, if not nanocrystalline. Thus, isothermal annealing of the present range of Al–Cu–Ti ternary alloys may develop an in situ composite microstructure of dispersion of one or more nanocrystalline intermetallic phases in the amorphous or nanocrystalline matrix.

A detailed study on the microstructural evolution during isothermal annealing at different temperatures is in progress.

## Conclusion

Mechanical alloying of  $\text{Al}_{65}\text{Cu}_{35-x}\text{Ti}_x$  ( $10 < \text{Ti} < 25$  at.%) by planetary ball milling up to 30 h leads to the formation of a single phase amorphous or nanocrystalline product. Controlled milling up to (or arresting the milling at) the appropriate stage may develop an in situ composite microstructure comprising amorphous (to a varying degree) and nanocrystalline metallic/intermetallic phases. Ti plays a crucial role in solid state amorphization of  $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ . Subsequent isothermal annealing of the milled product at 673 K for 1 h enables precipitation of nanocrystalline intermetallic phases in Al-rich matrix. With less than 10 at.% Ti in  $\text{Al}_{65}\text{Cu}_{35-x}\text{Ti}_x$ , say in  $\text{Al}_{65}\text{Cu}_{30}\text{Ti}_5$ , mechanical alloying leads to the formation of a single phase nanocrystalline disordered  $\text{Cu}_9\text{Al}_4$  powder which upon annealing at 773 K transforms into an in situ composite comprising a number of nanocrystalline aluminides in Al-rich matrix.

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