

Devitrification of rapidly quenched Al–Cu–Ti amorphous alloys

D K MISRA, R S TIWARI and O N SRIVASTAVA*

Department of Physics, Banaras Hindu University, Varanasi 221 005, India

MS received 6 January 2003

Abstract. X-ray diffraction, transmission electron microscopy and differential scanning calorimetry were carried out to study the transformation from amorphous to icosahedral/crystalline phases in the rapidly quenched $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ and $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ alloys. In the present investigation, we have studied the formation and stability of amorphous phase in $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ and $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ rapidly quenched alloys. The DSC curve shows a broad complex type of exothermic overlapping peaks (288–550°C) for $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ and a well defined peak around 373°C for $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ alloy. In the case of $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ alloy amorphous to icosahedral phase transformation has been observed after annealing at 280°C for 73 h. Large dendritic growth of icosahedral phase along with α -Al phase has been found. Annealing of $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ alloy at 400°C for 8 h results in formation of Al_3Ti type phase. $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ amorphous alloy is more stable in comparison to $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ alloy and after annealing at 400°C for 8 h it also transforms to Al_3Ti type phase. However, this alloy does not show amorphous to icosahedral phase transformation.

Keywords. Amorphous phase; icosahedral phase; crystallization.

1. Introduction

In recent years there has been spurt of studies relating to amorphous to quasicrystalline transformation due to its scientific as well as technological significance (Greer *et al* 2001; Inoue *et al* 2001). On one hand these studies have been undertaken to throw light on the formation mechanism of the icosahedral phase and the correlation between quasicrystalline phase and local structure of the glassy alloys and on the other hand improved mechanical properties of partially nanoquasicrystalline phase in glassy matrix have aroused considerable interest from application point of view (Fasi *et al* 2001; Aronim *et al* 2001; Li *et al* 2001; Satyanarayana *et al* 2001; Srinivasan and Chattopadhyay 2001; Hambleton *et al* 2001). Large number of alloys exhibiting glass to quasicrystalline transformation have been broadly classified into Zr-based, Ti-based, Hf-based and Al-based alloys. Amongst these alloys Al–Cu–V system has been of special interest because this belongs to Al–Cu–3d–TM series of alloys which have been systematically studied and show chemical dependence of stability of amorphous, icosahedral and decagonal phases (Popescu *et al* 1995). For example, as atomic number of transition metal increases in these alloys, the as quenched alloy exhibits amorphous phase (Al–Cu–V), metastable (Al–Cu–Cr, Al–Cu–Mn) and stable (Al–Cu–Fe) icosahedral phases and stable decagonal phase (Al–Cu–Co).

The Al–Cu–V system which was shown by Tsai *et al* (1999) to form an amorphous phase has been extensively investigated with regard to crystallization and structural similarity between amorphous and quasicrystalline phases (Holzer and Kelton 1991; Tsai *et al* 1999). Upadhyaya and Tiwari (1996) investigated growth of the quasicrystalline and related crystalline phases in $\text{Al}_{65}\text{Cu}_{20}\text{V}_{15}$ alloy and have pointed out the role of electron concentration (e/a) in the stabilization of amorphous and icosahedral phases. Misra *et al* (2001) reported the effect of Fe substitution on the stability and microstructure of icosahedral phase in Al–Cu–V alloy system. Since V and Ti are neighbouring transition metals in periodic table and are very similar in their atomic sizes, therefore, Ti may be chosen as an appropriate substitution element in place of V in Al–Cu–V alloy in order to stabilize amorphous phase. In passing it may be mentioned that the alloy system Al–Ti (in which Cu is absent) exhibits amorphous phase which after subsequent annealing transforms to crystalline phases (Murty *et al* 1992). Also, different crystalline phases in Al–Ti–V alloy system have been recently investigated (Shao *et al* 1995). However, no study pertaining to amorphous to quasicrystalline/crystalline phase transformation in Al–Cu–Ti system has been reported so far. The present work is also important due to the fact that out of various Al–Cu–3d–TM alloys, information regarding the stabilization of quasicrystalline phase in Al–Cu–Ti alloy system is still missing. The aim of the present investigation is to report the results of investigation of formation of amorphous phase and transformation from amorphous to quasicrystalline/crystalline phases in Al–Cu–Ti alloys

*Author for correspondence

employing X-ray diffraction, transmission electron microscopy and differential scanning calorimetry (DSC) techniques. It may be mentioned that the stoichiometry (composition) of the alloys has been chosen, so that the electron concentration (e/a) of the alloy is close to that of $\text{Al}_{75}\text{Cu}_{15}\text{V}_{10}$ which is known to exhibit amorphous phase.

2. Experimental

The $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ and $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ alloys were prepared by melting highly pure, Al, Cu and Ti in an induction furnace, in the presence of dry argon atmosphere. The ingots formed were re-melted several times to ensure homogeneity. The homogenized ingots were placed in a quartz nozzle of ~ 1 cm internal diameter with a circular orifice of ~ 1 mm diameter and then melt-spun onto a Copper wheel (~ 14 cm dia) rotating at a speed of about 40 m/s. During melt-spinning, the entire apparatus was enclosed in a steel enclosure through which argon gas was made to flow continuously at an over pressure of 5 MPa so as to prevent oxidation of the ribbons after ejection from the nozzle. The density measurements were performed by archimedean method. A single pan precision balance with sensitivity of 0.001 mg was employed. Samples used weighed about 1 g.

The gross structural characterization was done by employing a X-ray diffractometer (Philips PW-1710) with graphite monochromator and CuK_α radiation. The experimental conditions and parameters (scan speed, cooling speed etc) were kept constant for all diffraction experiments performed on different samples. The ribbons were thinned using an electrolyte, 67% methanol and 33% nitric acid, at -20°C . The samples thus prepared were studied by TEM using a Philips CM-12 electron microscope. The crystallization behaviour of these amorphous alloys has been studied using DSC 2910 (TA Instruments Inc. USA) system in modulated DSC mode.

3. Results and discussion

Figures 1a–b show XRD traces obtained from the as-melt-spun alloys, $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ and $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$. Both the traces show the broad amorphous peak around an angle 43.5° . The subtle differences in the broad peaks (e.g. width of the peak and peak position) corresponding to the two alloys may be noticed. These differences may be due to the different types of short range ordering in these alloys. One of the methods to assess the stability of an amorphous alloy is to use DSC to measure the temperature at which the amorphous phase starts to crystallize. Figure 2 shows the DSC curve taken corresponding to the alloy $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ with the heating rate of $5^\circ\text{C}/\text{min}$. The DSC curve corresponding to this alloy contains a wide exothermic peak extending from 288°C to 550°C . This

wide peak consists of two overlapping maxima at least. The peak temperature of two peaks are 393°C and 440°C , respectively. Figure 3 shows DSC curve corresponding to the alloy $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ with the same heating rate. The DSC curve corresponding to this alloy contains only one exothermic peak at temperature 373°C . The onset of this peak is at relatively higher temperature (347°C) and thus indicates higher stability of this amorphous alloy in comparison to $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$. Figures 4a–b show XRD traces of $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ alloy obtained from isothermal annealing of the sample at 280°C for 73 h and 400°C for 8 h, respectively. The XRD patterns corresponding to $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ amorphous alloy annealed at 280°C shows only peaks which can be identified as a mixture of crystalline α -Al and icosahedral phases. The identification of icosahedral phase was made on the basis of six independent miller indices proposed by Elser (1985). The $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ alloy when annealed at 400°C i.e. near the strong exothermic DSC peak ($\sim 393^\circ\text{C}$) for 8 h, shows only diffraction peaks which have been identified as the Al_3Ti -type tetragonal phase with lattice parameter, $a = 3.84 \text{ \AA}$, $c =$

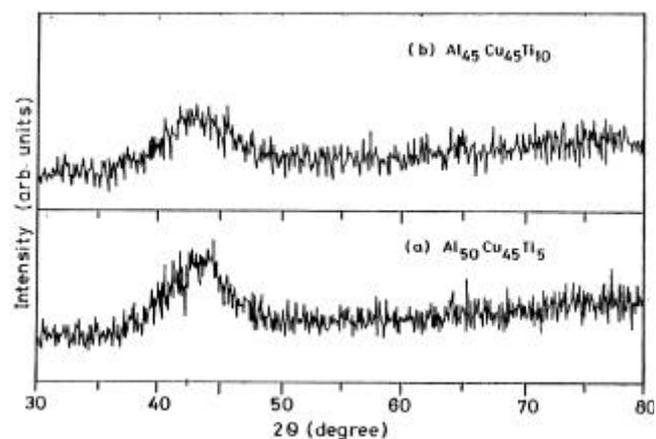


Figure 1. X-ray powder diffraction patterns of the as-quenched (a) $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ and (b) $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ alloys. CuK_α radiation was employed with $\lambda = 0.154$ nm and 2θ scanning rate of $0.05^\circ/\text{s}$.

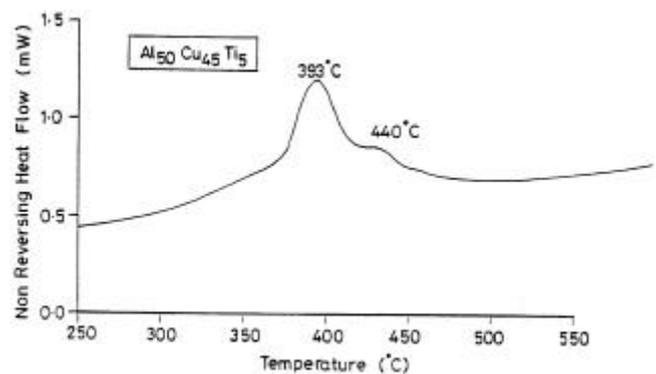


Figure 2. Differential scanning calorimeter curve of $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ amorphous alloy at scanning rate $5^\circ\text{C}/\text{min}$.

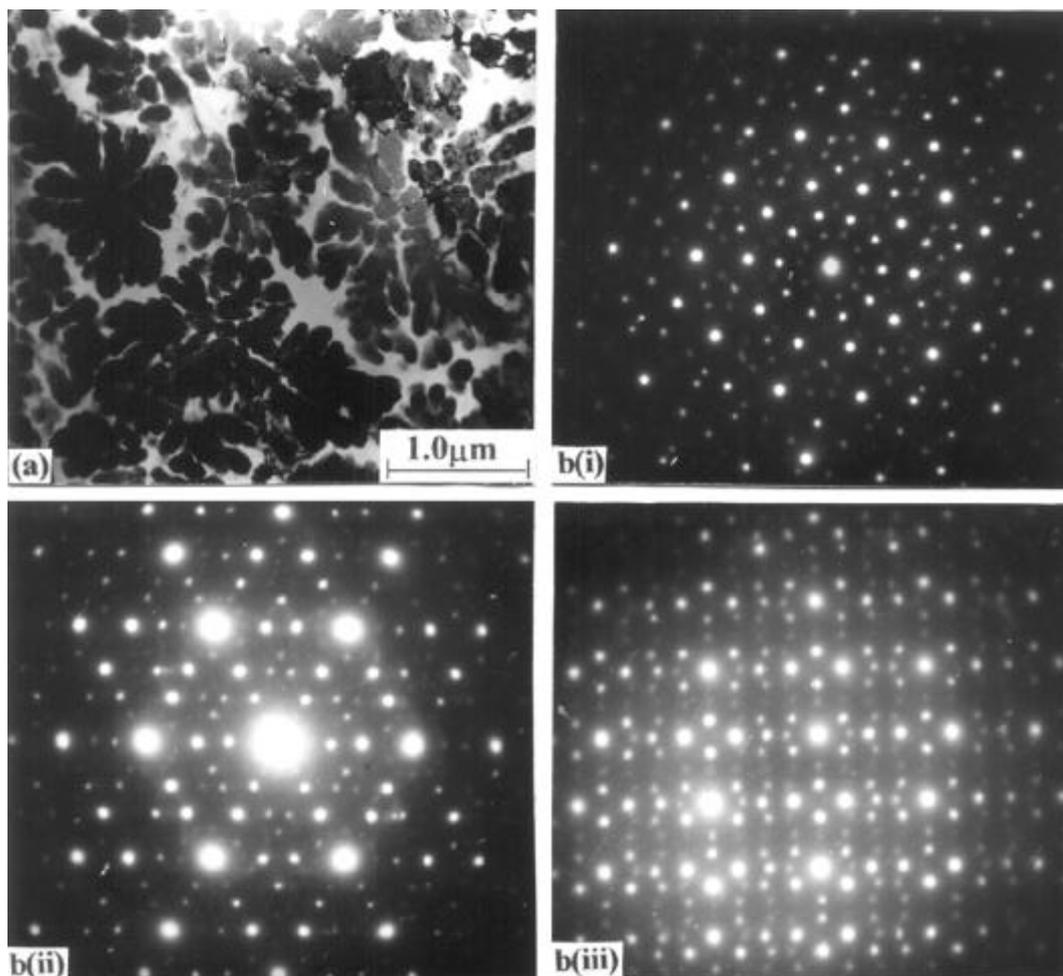


Figure 5. (a) Electron micrograph showing large dendritic icosahedral grains and (b) selected area diffraction (SAD) patterns exhibiting (i) five-fold, (ii) three-fold and (iii) two-fold axes parallel to electron beam corresponding to large dendritic grains.

The reciprocal vectors corresponding to the maximum peak intensity for amorphous phase in $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ and $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ alloys as determined from XRD are 30.7 and 29.70 nm^{-1} , respectively. The parameters used to calculate $k_p/2k_F$ for amorphous is given in table 1. It can easily be discerned that for these two alloys the ratio $k_p/2k_F$ remains nearly equal to unity and consequently amorphous phase gets stabilized. However, it is quite intriguing that unlike $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ amorphous alloy which directly transforms to Al_3Ti -type phase, $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ amorphous alloy initially transforms to icosahedral phase. At this stage it is not clear why these two alloys which have nearly same electron concentration, e/a (table 1), behave differently in regard to amorphous to icosahedral phase transformation. A plausible explanation may be given in terms of hindrance of nucleation of icosahedral phase in $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ alloy. Even in $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ alloy, large size of icosahedral grains (figure 5a) indicates that nucleation rate is low thus allowing the growth of icosahedral grains before impingement. However, with slight

variation in stoichiometry (e.g. in $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$), the nucleation rate of icosahedral phase might be considerably reduced. This would result in the transformation of amorphous phase in $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ alloy to Al_3Ti -type phase. Further investigations would be required to get insight of the factors which govern the nucleation of icosahedral phase in these amorphous alloys. It should be mentioned that as in the case of Al-Cu-V alloy, Al-Cu-Ti alloy also exhibits amorphous to icosahedral phase transformation. In comparison to Al-Cu-V , however, the morphology of icosahedral phase in the present case is more dendritic in nature. The present investigation also indicates that the stability of icosahedral phase in Al-Cu-3d-TM alloy series increases with increasing atomic number of transition metal as has been pointed out earlier for $\text{TM} = \text{V, Cr, Mn, Fe}$ (Popescu *et al* 1995). Thus the chemical dependence of the stability of icosahedral phase in Al-Cu-3d-TM series becomes further evident from the present work.

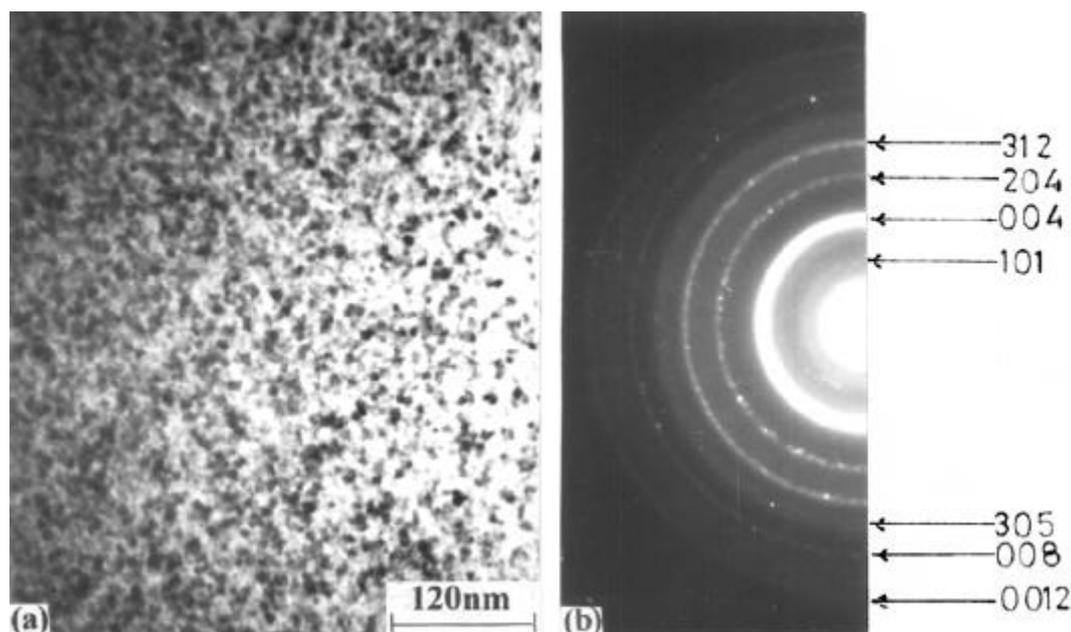


Figure 6. (a) Nano-sized electron micrograph corresponding to Al_3Ti -type tetragonal phase and (b) powder ring corresponding to nano-sized grain which has been indexed with Al_3Ti -type tetragonal phase.

Table 1. Density, r , electron concentration e/a , Fermi wave vector, k_F , and reciprocal vector, k_p , for amorphous phase.

Alloy phase	$\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ (amorphous)	$\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ (amorphous)
r (g/cm^3)	3.84	3.56
e/a	2.15	2.20
$2k_F$ (nm^{-1})	29.74	29.05
k_p (nm^{-1})	30.7	29.7
$k_p/2k_F$	1.03	1.02

4. Conclusions

In the present investigation, we have studied the formation and stability of amorphous phase in $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ and $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ rapidly quenched alloys. The DSC curve shows a broad complex type of exothermic peak (288–550°C) for $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ and a well defined peak around 373°C for $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ alloy. In the case of $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ alloy, amorphous to icosahedral phase transformation has been observed after annealing at 280°C for 73 h. Large dendritic growth of icosahedral phase along with α -Al phase have been found. Annealing of $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ alloy at 400°C for 8 h results in formation of Al_3Ti type phase. $\text{Al}_{45}\text{Cu}_{45}\text{Ti}_{10}$ amorphous alloy is more stable in comparison to $\text{Al}_{50}\text{Cu}_{45}\text{Ti}_5$ alloy and after annealing at 400°C for 8 h, it also transforms to Al_3Ti type phase. However, this alloy does not show amorphous to icosahedral phase transformation.

Acknowledgements

The authors are grateful to the Ministry of Non-Conventional Energy Sources and the Department of Science and Technology, for providing the financial support. Authors are also thankful to Dr A M Awasthi, Inter University Consortium, Indore, for useful discussions and providing DSC facilities for the present work. One of the authors (DKM) gratefully acknowledges the financial support provided by the Council of Scientific and Industrial Research (CSIR).

References

- Aronim A S, Abrosimove G E, Gurov A F, Yu and Kornova V 2001 *Mater. Sci. & Eng.* **A304–306** 375
- Elser V 1985 *Phys. Rev.* **B328** 4892
- Fasi T K, Zhang T, Inoue A, Yang Y S, Kim I B and Kim V H 2001 *Mater. Sci. & Eng.* **A304–306** 892
- Greer A L 2001 *Mater. Sci. & Eng.* **A304–306** 68
- Hambleton R, Jones H and Rainforth W M 2001 *Mater. Sci. & Eng.* **A304–306** 524
- Holzer J C and Kelton K 1991 *Acta Metallogr.* **39** 1833
- Inoue A 2001 *Mater. Sci. & Eng.* **A304–306** 1
- Li C, Saida J, Matsusheta M and Inoue A 2001 *Mater. Sci. & Eng.* **A304–306** 308
- Misra D K, Tiwari R S and Srivastava O N 2001 *Cryst. Res. Technol.* **36** 419
- Murty B S, Naik M O, Mohan M Rao and Ranganathan S 1992 *Mater. Forum* **16** 19

- Popescu R, Jianu A, Manciu M, Nicula R and Manaila R 1995 *J. Alloys & Compounds* **221** 240
- Raynor G V 1994 *Progr. Metal. Phys.* **1** 1
- Satyanarayana K G, Ojha S N, Naresh Nath Kumar D and Shastry G V S 2001 *Mater. Sci. & Eng.* **A304–306** 627
- Shao G, Tsai P, Kiropoulos and Miodownik A P 1995 *Int. J. Rapid Solidification* **9** 13
- Smith J F and Ray A E 1957 *Acta Crystallogr.* **10** 169
- Srinivasan D and Chattopadhyay K 2001 *Mater. Sci. & Eng.* **A304–306** 534
- Tsai A P, Hiranga K, Inoue A, Masumoto T and Chen H S 1999 *Phys. Rev.* **B44** 3569
- Upadhya R and Tiwari R S 1996 *Phys. Status Solidi (a)* **156** 39