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Phase formation in rapidly quenched Cu-based alloys

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Abstract In the present investigation, we report the formation of γ-brass type phase in the rapidly quenched $Cu_{50}Ga_{30}Mg_5Ti_{15}$ and $Cu_{50}Al_{30}Mg_5Ti_{15}$ alloys. Rapid solidification of $Cu_{50}Ga_{30}Mg_5Ti_{15}$ alloy shows the formation of simple cubic γ-brass type phase ($a = 0.863$ nm), which on annealing at 1,023 K for 60 h transforms to disordered type γ-brass phase ($a = 0.879$ nm). It has been observed that intensity modulation of electron diffraction spots corresponding to simple cubic γ-brass phase is similar to the intensity modulation observed in the mirror orientation of icosahedral quasicrystalline phase. Contrary to the crystalline phase formation in Cu–Ga–Mg–Ti alloy, rapid solidification of $Cu_{50}Al_{30}Mg_5Ti_{15}$ shows the formation of amorphous and nanocrystalline bcc γ-brass type phase ($a = 0.870$ nm), which on annealing transforms to ordered γ-brass type phase ($a = 0.872$ nm). The structural and microstructural characterization was done through X-ray diffraction and transmission electron microscopy.

Introduction

Cd-based icosahedral alloys, Cd–Mg–L (L: Lanthanide metals), Cd–Yb, and Cd–Ca have opened a new field of quasicrystal research [1, 2]. In particular, the Cd–Yb and Cd–Ca quasicrystals have drawn great attention because these quasicrystals are the first examples of stable binary quasicrystals, and because they are considered to include a new type of icosahedral shell structure, or atomic cluster, different from either the Bergman-type or the Mackay-type and are known as Tsai type clusters [2]. Subsequently, this type of icosahedral phase was discovered in Zn–Mg–Sc alloy. The Zn–Mg–Sc icosahedral quasicrystalline phase has a structural similarity to the Cd-based icosahedral quasicrystals [3]. Ever since the discovery of icosahedral phase in Cu–Ga–Mg–Sc alloy, which is supposedly derived from Zn-Mg–Sc system, there has been a search for more Cu-based quasicrystalline systems. Such quasicrystalline phases have been reported in quaternary and ternary Cu-based alloys [4, 5].The Cu–Ga–Mg–Sc icosahedral quasicrystal was produced by the substitution of Zn with Cu and Ga in Zn–Mg–Sc alloy system [4]. This Cu-based alloy exhibits formation of stable icosahedral phase with quasilattice parameter 0.69 nm, and it is a new member of the structural type into which Cd-based and Zn–Mg–Sc icosahedral quasicrystals are classified. The substitution studies for Cu–Ga–Mg–Sc alloy have not been done so far.

Therefore, in search for a new quasicrystalline system and their related phases, we have replaced Sc by Ti in Cu–Ga–Mg–Sc alloy system. The reason for replacing Sc by Ti is that both are transition elements and are lying adjacent to each other in the periodic table. The size and valency of Ti and Sc are slightly different. In the present work, we have synthesized the alloy composition $Cu_{50}Ga_{30}Mg_5Ti_{15}$. This composition has been taken due to the reason that the electron concentration per atom (e/a) for this is 2.1, which is quite close to the value for Cu–Ga–Mg–Sc. Also if one considers this alloy as pseudo binary, then size ratio is also close to that of stable binary quasicrystal Cd–Yb [2]. Since Ga and Al are having same valency and comparable atomic radii, one can also do the comparative study between Cu–Ga–Mg–Ti and Cu–Al–Mg–Ti alloys with respect to phase formation and its stability during annealing. In course of our present investigation, we have got a γ-brass type phase.

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It may be mentioned that occurrence of γ-brass phase has been often observed at compositions close to quasiperiodic structures. For instance, this is the case of Al–Cu–Cr [6], Al–Cu [7], Al–Cu–Cr–Fe [7], and Mn–Ga [8] systems. A ternary γ-brass type atomic structure has been reported in Ni–Mn–Ti alloy [9]. Recently, the γ-brass phase has been reported in the Al–Cr–Fe [10] and Al–Cu–Cr [11] systems. The γ-brass phase has also been reported in Cu-based alloys, i.e., $Cu_{40}Mn_{35}Al_{25}$ [12], $Cu_{67.5}Al_{25}Mn_{7.5}$ [13], and $Cu_{81.7}Al_{14.1}Ni_{4.2}$ [14]. Dong [7] has shown that the γ-brass phase is actually approximant of quasicrystals and exhibits orientation relationship with quasicrystals.

The purpose of the present study is to investigate the phase formation in the rapidly quenched $Cu_{50}Ga_{30}Mg_5Ti_{15}$ and $Cu_{50}Al_{30}Mg_5Ti_{15}$ alloys and its stability during subsequent annealing. The X-ray diffraction and transmission electron microscopy (TEM) techniques were employed for characterization of the samples.

Experimental

The $Cu_{50}Ga_{30}Mg_5Ti_{15}$ and $Cu_{50}Al_{30}Mg_5Ti_{15}$ alloys were prepared by melting highly pure Cu, Ga, Al, Mg, and Ti in an induction furnace in argon ambience. The ingots so formed were remelted several times to ensure homogeneity. To convert the as-formed ingots into ribbons, they were placed in a silica nozzle tube with a circular orifice of $\sim$1 mm diameter. The alloys were then melt spun onto a copper wheel ($\sim$14 cm diameter) rotating at a speed of 25 m/s. During melt spinning, the entire apparatus was enclosed in a steel enclosure through which argon gas was made to flow continuously so as to prevent oxidation of the ribbons after ejection from the nozzle. After melt-spinning, ribbons were formed. The length and thickness of the ribbons were $\sim$1–3 cm and $\sim$40 μm, respectively. These ribbons of Cu–Ga–Mg–Ti and Cu–Al–Mg–Ti were then packaged in the Ta foil, which was sealed in a silica ampoule under an argon atmosphere for annealing experiment.

The gross structural characterization was done by employing an X-ray diffractometer (X'Pert PRO PANalytical diffractometer) with CuK_α radiation. The experimental conditions and parameters (scan speed, etc.) were kept the same for all diffraction experiments performed on different samples. The ribbons were thinned using an electrolyte, 70% methanol and 30% nitric acid at –20 °C. The optimum voltage and current employed for the thinning of the ribbons were found to be 8 V and 40 mA, respectively. In order to further characterize the as-grown ribbons, TEM explorations of the ribbons were carried out. The samples were studied by TEM using Philips CM-12 and FEI, Technai $20G^2$ electron microscope. An energy dispersive X-ray analysis (EDAX) coupled with Technai $20G^2$ electron microscope was employed for the compositional analysis.

Results and discussion

Structural/microstructural characterization of Cu–Ga–Mg–Ti alloy

Figure 1a shows the X-ray diffraction (XRD) profile obtained from the as-melt spun alloy, $Cu_{50}Ga_{30}Mg_5Ti_{15}$. Detailed XRD characterization of the as-grown ribbons revealed the presence of γ-brass phase of Cu_9Ga_4 type with lattice parameter $a = 0.863 \pm 0.003$ nm. The profile shows the maximum intensity peak around an angle $2\Theta = 44.04$ with d-value 2.06 Å, which corresponds to (330) reflection. The presence of (300) peak along with the other peaks in the XRD pattern reveals that the crystal structure of this alloy is not a common bcc γ-brass structure unlike Cu–Zn system [15], rather it is a simple cubic structure with a lattice parameter of $a = 0.863$ nm. Thus, the as-grown ribbons revealed the presence of γ-brass phase of Cu_9Ga_4 type [16].

In order to explore the possibility of phase transformation including the search for the possible occurrence of quasicrystalline phase, the ribbons were annealed in argon ambience at 1,023 K for a duration of 60 h. The XRD of the annealed ribbons shown in Fig. 1b exhibits a significantly different peak pattern. Detailed analysis showed that on annealing the as-grown sample Cu_9Ga_4 type phase undergoes a phase transformation to bcc, which was evidenced by the specific extinction condition. Disappearances of some peaks such as (300), (410), etc. is due to

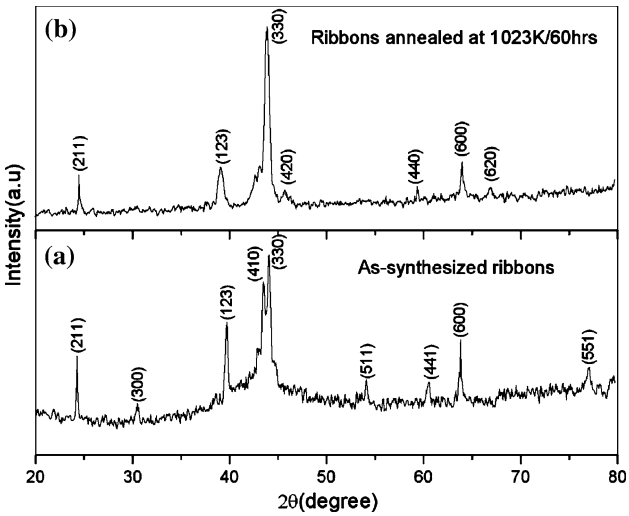

Fig. 1 XRD pattern of rapidly quenched Cu–Ga–Mg–Ti alloy. **a** As-synthesized ribbons and **b** Ribbons annealed at 1,023 K for 60 h

transformation of the as-synthesized simple cubic to bcc in the annealed sample of melt spun alloy. The XRD pattern of the annealed ribbons revealed the presence of body centered cubic structure with lattice parameter $a = 0.879 \pm 0.004$ nm. This shows that on annealing the ordered structure transforms to disordered structure.

Further characterization of the as-grown as well as annealed sample was carried out through TEM. The selected area diffraction pattern (SADP) of the as-grown ribbons is shown in Fig. 2a, b. Whereas Fig. 2a shows the expected $[\bar{1}10]$ diffraction pattern from the γ-brass phase, Fig. 2b shows the [001] diffraction pattern. A curious feature exhibited by Fig. 2b is the intensity modulation along [110] direction. The intensity modulated spots are marked by arrows in Fig. 2b. This intensity modulation is similar to the intensity modulation observed in the mirror orientation of icosahedral phase [17]. It may be noted that such an intensity modulation in γ-brass phase has also been observed earlier [18, 19]. As can be seen in the SADP of mirror orientation of icosahedral phase, the intensity variations correspond to long–short type arrangement. In the present case, the arrangement of spots is periodic but the intensity variations are similar to that of icosahedral phase. In particular, the [001] zone shows square diffraction pattern. In this orientation, the most intense spots correspond to the {330} planes. This feature is related to the fact that this phase is a superstructure of a CsCl phase having a lattice parameter three times smaller. Such a long period superlattice was previously described in Cu–Al alloy system [20]. The SADP of the annealed melt spun alloy are shown in Fig. 3a, b along [111] and $[\bar{1}10]$ zone axis. We have observed a body centered cubic structure in the annealed alloy with the lattice parameter $a = 0.879$ nm.

For the composition determination, a quantitative EDAX was performed. The quantitative analysis for the as-cast alloy results in a Cu:Ga:Mg:Ti atomic percentage ratio of 50.73:29.37:5.77:14.13, which indicates a slight enrichment in Cu and deficiency in Ga and Ti when compared with the nominal stoichiometry 50:30:5:15 of the alloy under consideration.

Structural/microstructural characterization of Cu–Al–Mg–Ti alloy

Figure 4a shows the XRD profile obtained from the as-melt spun alloy, $Cu_{50}Al_{30}Mg_5Ti_{15}$. Detailed XRD characterization of the as-grown ribbons revealed the presence of nanocrystalline bcc γ-brass phase of Al_4Cu_9 type with lattice parameter $a = 0.870 \pm 0.022$ nm. The profile shows the maximum intensity peak around the same angle as observed in the as-melt spun alloy of Cu–Ga–Mg–Ti, which corresponds to (330) reflection. As it can be seen from the XRD profile that some amount of amorphous phase overlapping with the broadened (330) peak of

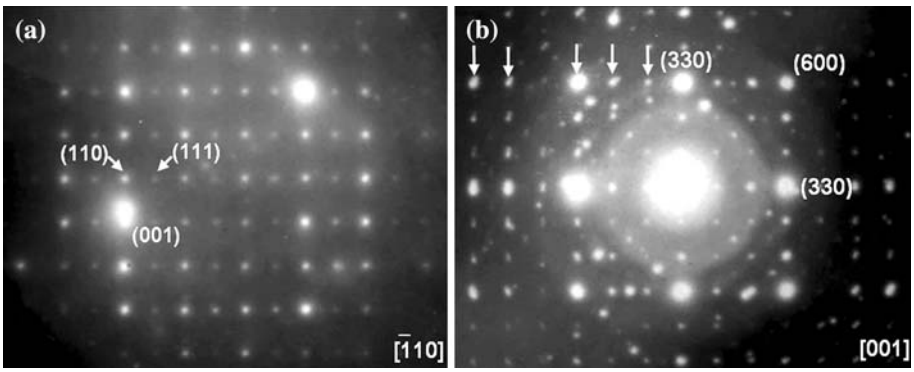

Fig. 2 **a** Selected area diffraction pattern (SADP) of the cubic γ-brass phase along the $[\bar{1}10]$ zone axis. **b** SADP along the [001] zone axis. The *arrow marks* shows the intensity modulation similar to the intensity modulation observed in the mirror orientation of icosahedral phase

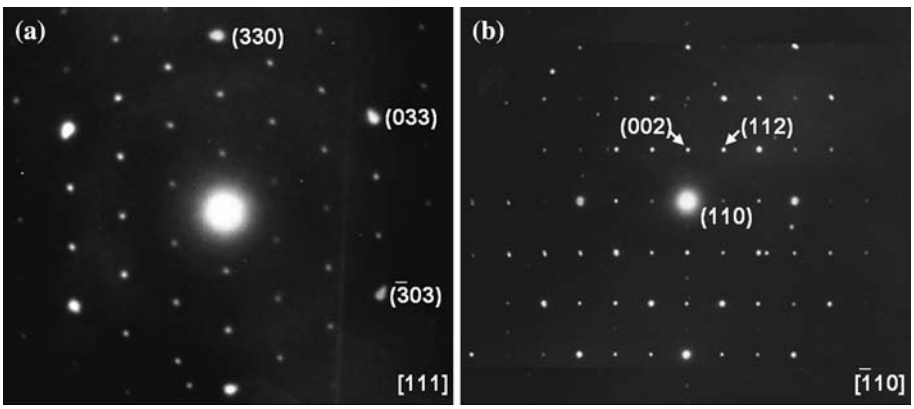

Fig. 3 **a** SADP of the γ-brass phase along the [111] zone axis. **b** SADP along the $[\bar{1}10]$ zone axis

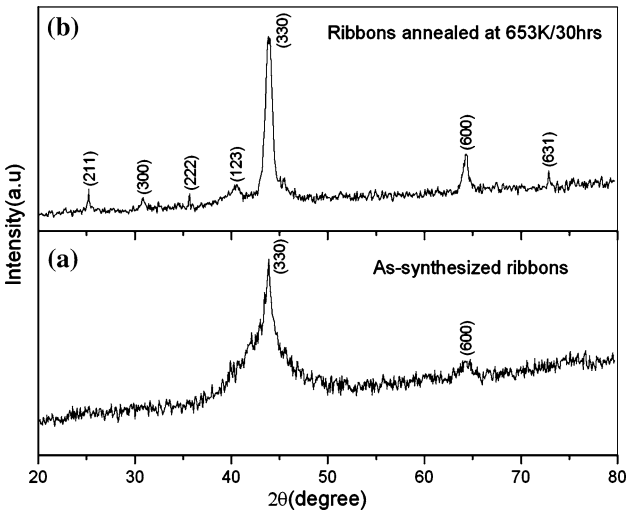

Fig. 4 XRD pattern of rapidly quenched Cu–Al–Mg–Ti alloy. **a** As-synthesized ribbons. **b** Ribbons annealed at 653 K for 30 h

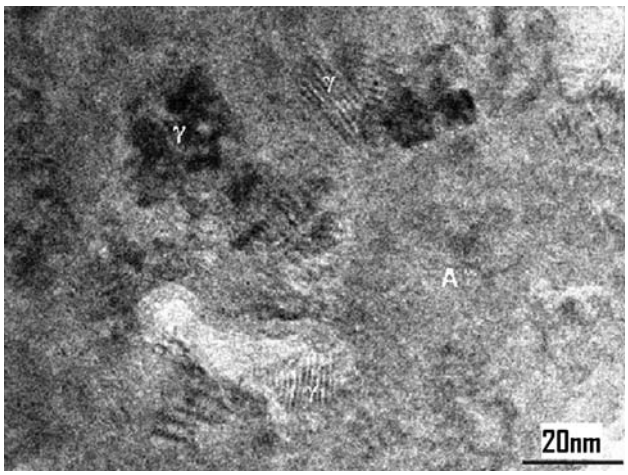

Fig. 6 A high-resolution TEM image, which shows the formation and co-existence of amorphous phase (A) as well as nanocrystalline phase (γ)

nanocrystalline phase can co-exit, and this has been further confirmed during TEM/HREM investigation. Figure 4b shows the XRD profile of the ribbons annealed at 653 K for 30 h, respectively. In Fig. 4b, the appearance of (300) peak (odd $h^2 + k^2 + l^2$ value) along with the other peaks in the XRD pattern shows that this phase resembles the structure of the ordered γ-brass phase of Al_4Cu_9 type with lattice parameter $a = 0.872 \pm .027$ nm.

Further characterizations of the as-grown and annealed ribbons were carried out through TEM. Figure 5 shows the TEM images of the as-grown ribbons. The microstructure at this stage seems to be predominantly nanocrystalline with traces of the remnant amorphous phase. The size of the particles is in the range of 10–20 nm. The corresponding SADP shows diffuse rings with several spots coinciding with the rings, which confirm that the as-grown ribbons are mixture of nanocrystalline and amorphous phases. The d-values obtained after indexing of the ring pattern were compared with the values obtained by X-ray analysis. The two sets of values match with each other, which confirm the presence of γ-brass type phase. It has been analyzed from the SADP that particles at this stage consist of disordered nanocrystalline single phase materials with lattice parameter of 0.870 nm. Figure 6 shows the high-resolution TEM image of the as-melt spun alloy. It shows traces of fringe-like pattern, which corresponds to crystalline phase. The spacing between the fringes is nearly $\sim$0.870 nm, which corresponds to the {100} plane of the γ-brass phase. The HREM of the ribbon sample confirms the formation and co-existence of amorphous phase as well as nanocrystalline phase.

The SADP of the annealed melt-spun alloy are shown in Fig. 7a, b along $[\bar{1}10]$ and [001] zone axis. We have observed a simple cubic structure in the annealed melt-spun alloy with the lattice parameter $a = 0.872$ nm. The EDAX analysis for the as-cast alloy results in a Cu:Al:Mg:Ti atomic percentage ratio of 51.03:28.87:5.77:14.33.

Based on the results described above, it can be said that Cu–Ga–Mg–Ti and Cu–Al–Mg–Ti both show the formation of γ-brass type phase. In the case of Cu–Ga–Mg–Ti

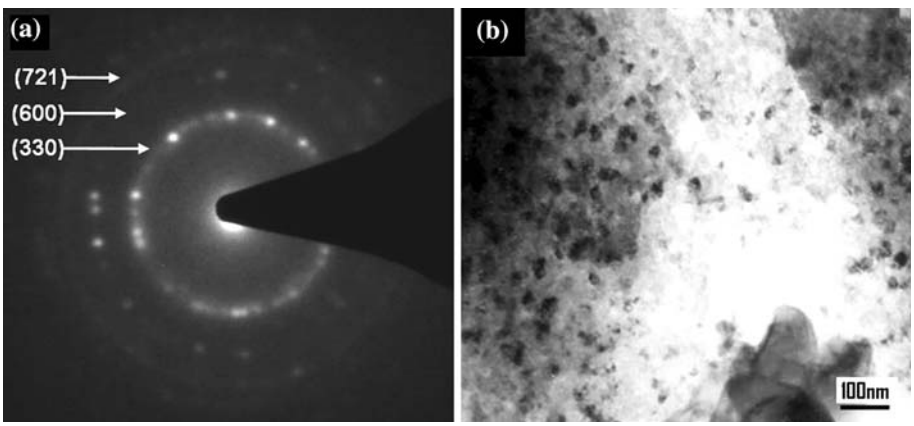

Fig. 5 **a** SADP of γ-brass phase showing a number of diffuse rings with several diffraction spots coinciding with the rings. **b** The corresponding microstructure showing nanocrystalline and amorphous phase

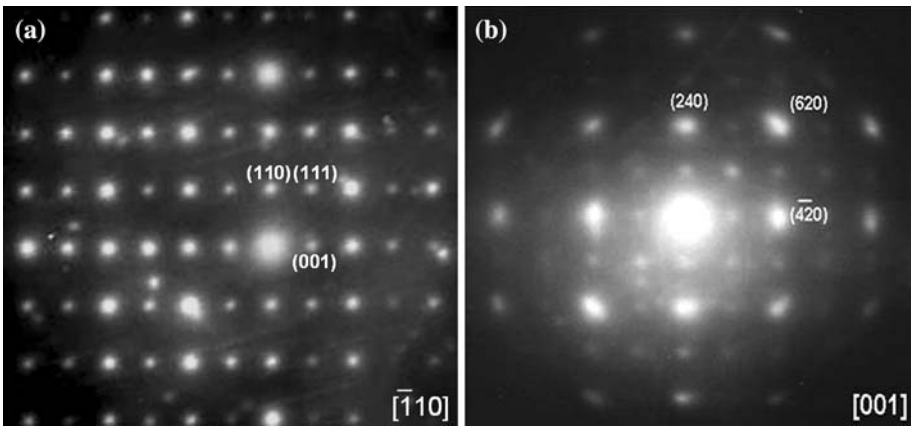

Fig. 7 SADP of the γ-brass phase along different zone axis: **a** [$\bar{1}$10] and **b** [001]

alloy, on annealing the ordered structure transforms to disordered variant, while in the case of Cu–Al–Mg–Ti alloy the disordered structure transforms to ordered one. The reason for such transformations in the two alloys is not clear at present. However, it is an interesting observation that may embody fine scale inter and/or intra cluster interactions present in γ-brass type structure [16] and needs further exploration. One important observation in the present work is that Ti in place of Sc in Cu-based alloys is stabilizing γ-brass type phase only instead of icosahedral phase inspite of the fact that the two studied alloys have *e/a* values and pseudo binary size ratio quite close to Cu–Ga–Mg–Sc quasicrystalline alloy. On the basis of above observation, it may be said that the role of Sc in Cu–Ga–Mg–Sc alloy seems to be very crucial for the stabilization of icosahedral phase. The difference in the size and valency of Ti from Sc leads to the formation of γ-brass type phase, which has been identified as an approximant phase by Dong [7]. If the difference in size and valency can be compensated for these two elements, the γ-brass structure may be destabilized. At this juncture, it would be intriguing to substitute partially neighboring atoms of Sc at Ti sites and see if icosahedral phase gets stabilized.

It is of interest to mention that one of the advantages of formation of nanocrystalline or amorphous state in the rapidly solidified Cu–Al–Mg–Ti alloy is that it may enhance the ductility and toughness [21–25]. Hence it has a possibility for use as a coating material. Keeping in view the fact that the size distribution and volume fraction of fine scale nanophase can significantly alter the physical and mechanical properties of brittle intermetallics [26], further investigation of these alloys would be worth pursuing.

Conclusions

On the basis of present investigation, it may be concluded that after rapid solidification, Cu–Ga–Mg–Ti and Cu–Al–Mg–Ti alloys exhibit the formation of γ-brass type phase. Rapid solidification of Cu–Ga–Mg–Ti alloy shows the formation of simple cubic γ-brass type phase, which on annealing at 1,023 K for 60 h transforms to disordered type γ-brass phase. Electron diffraction patterns have been found to show a close structural similarity with the icosahedral phase. The SADP along [001] zone axis shows the intensity modulation of spots, which is similar to the intensity modulation observed in the mirror orientation of icosahedral quasicrystalline phase. Contrary to the crystalline phase formation in Cu–Ga–Mg–Ti alloy, rapid solidification of Cu–Al–Mg–Ti leads to the formation of amorphous and nanocrystalline bcc γ-brass phase with 10–20 nm particle size. Long-term annealing of these ribbons reveals the formation of ordered γ-brass type phase.

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