On the Structural Evolution of the Amorphous $Al_{75}Cu_{15}V_{10}$ Alloy to the Icosahedral Phase

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The transformations occurring on annealing an as-spun amorphous $Al_{75}Cu_{15}V_{10}$ alloy are studied by X-ray diffraction and transmission electron microscopy (TEM). A continuous growth of icosahedral clusters, which are present already in the as-spun sample, is revealed. The size of the clusters estimated from the diffuse X-ray peak widths is consistent with the size of the modulation observed in the bright field TEM images.

Recently Chen et al. [1] reported a pronounced prepeak and a marked shoulder at the low Q-side of the main peak of the X-ray diffraction profile of amorphous $Al_{66}Si_{20}Mn_{14}$ and attributed these features to icosahedral short-range order clusters in the amorphous phase similar to those in α-$(Al_{77.5}Si_{10.1}Mn_{17.4})$ [2]. Extended X-ray absorption fine structure (EXAFS) measurements showed the similarity of the local atomic structure around a manganese atom in icosahedral and amorphous Al-Mn alloys [3]. Also quantitative analyses of X-ray diffraction profiles of amorphous sputtered $Al_{77.5}Mn_{22.5}$ and as-spun $Al_{56}Si_{30}Mn_{14}$ alloys confirmed the presence of icosahedral clusters resembling those in the α-phase [4]. The composition of the icosahedral and amorphous phases of aluminum alloys recently studied usually varied, and even for the same composition different sample preparation techniques were used. This includes the $Al_{86-x}Si_xMn_{14}$ alloy [5].

On the other hand, the icosahedral phase has recently been found to form as a stable intermediate in Pd-U-Si [6] and Al-Cu-V [7] on annealing the amorphous phase at a temperature below the melting point. Tsai et al. [7] observed an exothermic reaction at 731 K in the differential scanning calorimetry (DSC) curve of amorphous $Al_{75}Cu_{15}V_{10}$ and interpreted it as the formation of the icosahedral phase. However, the structural features of this phase are not yet revealed. The present note provides some interesting results about these features.

A mixture of electrolytic Al, Cu, and V was melted under argon in an arc furnace, and from the alloy amorphous ribbons about 0.02 mm thick and 1 mm wide were prepared by a single roller melt spinning apparatus. Two samples were annealed under argon gas atmosphere for 40 800 sec and 86 400 sec, respectively, at 620 K. The icosahedral phase was prepared by heating the amorphous sample for 300 sec at 820 K. X-ray scattering intensities from powder samples prepared by grinding the ribbons were measured with a molybdenum X-ray tube and a singly-bent pyrolytic graphite monochromator in a diffracted beam. At least 10 000 counts were collected at each scattering angle, so that the counting statistical error was smaller than 1%. Bright field (BF) images of the ribbons and their selected area diffraction patterns (SADP) were obtained by transmission electron microscopy (TEM).

Figure 1 shows BF electron micrographs and their SADPs of the annealed samples. For micrographs of the as-spun sample and the sample heated for 300 sec at 820 K, cf. [7]. The diffraction patterns of the annealed samples show a diffuse halo which proves that they are amorphous. Any macroscopic structural heterogeneity was not detected in the BF images, but they show a very fine modulated structure whose size is about a few nm. In the sample heated at 820 K, the grain size of the icosahedral phase was found to be about 0.7 μm, and its SADP shows the fivefold symmetric pattern of a typical icosahedral structure [7].

The X-ray diffraction profiles of the four samples are shown in Figure 2. As expected from the SADP, the diffraction profile of the as-spun sample indicates a non-crystalline structure. However, there are also some distinct features: a pronounced prepeak at $Q = 16\,\mathrm{nm}^{-1}$, a shoulder on the low-Q side of the main peak and a small hump at $Q = 40\,\mathrm{nm}^{-1}$. Similar features were observed for amorphous $Al_{66}Si_{20}Mn_{14}$ [1], $Al_{56}Si_{30}Mn_{14}$ [4], and $Al_{76}Cu_{14.5}V_7Si_{1.5}Mo_1$ [8]. In general, the prepeak corresponds to the so-called compound forming behavior in non-crystalline systems [9–11], and the prepeak in the amorphous Al-Si-Mn alloy has been interpreted by the presence of chemical short-range order of Mn-Mn pairs positioned at the vertices of the icosahedral clusters [4]. A similar shoulder as mentioned above was observed in as-spun amorphous $Al_{56}Si_{30}Mn_{14}$ [1] and sputtered amor-

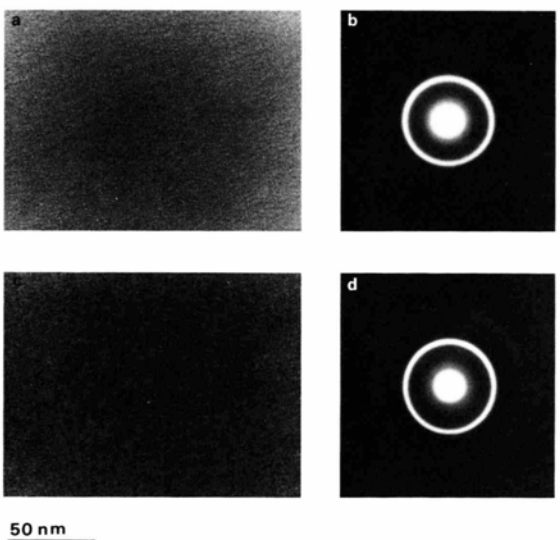

Fig. 1. Bright field electron micrographs (a, c), and selected area diffraction patterns (b, d) of an amorphous $Al_{75}Cu_{15}V_{10}$ alloy aged for 40 800 sec (a, b) and 86 400 sec (c, d) at 620 K.

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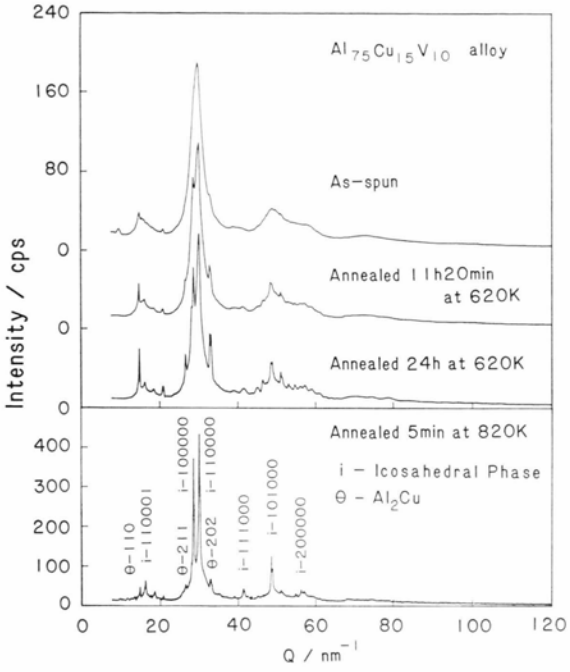

Fig. 2. X-ray diffraction profiles of $Al_{75}Cu_{15}V_{10}$ as-spun, annealed for 40 800 sec, and 86 400 sec at 620 K, and heated for 300 sec at 820 K.

phous $Al_{77.5}Mn_{22.5}$ [4] and was attributed to the presence of icosahedral clusters resembling to the α-phase. In Fig. 2 it is also found that a small amount of crystalline Al_2Cu did already exist in the as-spun sample and that this crystalline phase grows on annealing at 620 K although the sample mainly transforms into the icosahedral phase as seen in the intensity profile at the bottom of Figure 2.

On annealing the sample, the main peak and its shoulder separate into the two icosahedral peaks, which are 100000 and 110000 according to the indexing scheme of Bancel et al. [12]. Similarly, the prepeak, the small hump around $Q = 40\,nm^{-1}$, the second peak and its shoulder sharpen and grow into the icosahedral peaks 110001, 111000, and 200000, respectively. On assuming that the first peak consists of the two peaks whose shapes are Gaussian even for the as-spun sample, it may be fitted to estimate the size of the icosahedral clusters, L, from the half width at half maximum (HWHM), ΔQ, using a relation $L = \pi/\Delta Q$. The peak position was determined from the position of the apex of the fitted curves. The results are summarized in Table 1. The positions of the two peaks do not change much on annealing and rather surprisingly show good agreement with those for the grown icosahedral phase. The peak profile of the as-spun sample quickly sharpens by annealing, and the decrease in the widths appears to slow down on further annealing, which is often seen in the usual diffusion-controlled precipitation growth of as-quenched super-saturated alloys. The HWHM of the icosahedral phase shows the same order of magnitude as those determined in AlSiMn [1] and AlMn [13]. The difference between the sizes of the icosahedral clusters observed by TEM and that estimated from the peak widths may be interpreted by the harmony of the frozen-in phason strain or random icosahedral packing [13], because defects in the grown icosahedral phase were found by TEM observations [7]. Anyway, the cluster size estimated from the HWHM values is of the same order as the modulations observed in the BF images. Further structural investigations are required to explain this particular transformation mechanism in more detail.

Table 1. Positions and half widths at half maximum (HWHMs) of the two main icosahedral peaks determined from the fitting, and the size of the icosahedral chemical short-range order clusters estimated from the HWHMs in $Al_{75}Cu_{15}V_{10}$.

	Q [nm^{-1}]	HWHM [nm^{-1}]	L [nm]
As-spun	28.3	1.8	1.75
	29.7	1.6	1.96
Annealed for 40 800 sec	28.6	0.6	5.24
at 620 K	29.9	0.7	4.49
Annealed for 86 400 sec	28.5	0.55	5.71
at 620 K	29.9	0.6	5.24
Heated for 300 sec	28.55	0.17	18.5
at 820 K	30.0	0.17	18.5

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