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Crystallization of icosahedral phase from glassy Pd-U-Si alloys

Y. Shen and S. J. Poon
Department of Physics, University of Virginia, Charlottesville, Virginia 22901

G. J. Shiflet
Department of Materials Science, University of Virginia, Charlottesville, Virginia 22901
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The glassy-to-icosahedral phase transformation in Pd-U-Si alloys is studied by using x-ray and transmission electron diffraction. It is found that the transformation is polymorphous and it proceeds via a nucleation and growth process. The nucleation is homogeneous, and a large number of nuclei ($\simeq 10^{18}$ cm^{-3}) are found in the early stage of transformation which can be explained by the existence of short-range icosahedral order in the corresponding glassy phase. It appears that the icosahedral particles grow by atomic attachment at the particle interphase boundary. Some particles are in pentagonal or hexagonal shape, which reflects the internal symmetry of icosahedral phase. Coarsening is believed to occur during the growth process. A picture of the transformation is presented and comparisons are made with other results on glassy-to-icosahedral phase transformations.

The quasicrystalline phase is characterized by global orientational order and the lack of long-range periodic translational order. Since the discovery[1] of the icosahedral phase in Al-Mn alloys, various structural models[2-6] have been proposed. From Landau theory,[7-10] it is shown that the formation of the icosahedral phase is favored in some region of a phase diagram. However, the details of atomic structures in icosahedral phases are still far from clear.[8] Study of the glass-to-quasicrystal phase transformation would certainly help us to understand the structure of icosahedral phases and the kinetics of their formation. A number of studies[11,12] have been carried out on the glass-to-quasicrystal phase transformation of Al-Mn alloys mainly by direct energy processes. However, the mechanism of transformation has not been investigated systematically because either the transformation process is too rapid to be controlled or it is interfered with by the existence of undesired phases.

The recently discovered Pd-U-Si system[13] is appropriate for studying the glass-to-quasicrystal phase transformation because (1) the as-quenched ribbons are in the glassy state, and (2) upon annealing, the glassy phase of $Pd_{58.8}U_{20.6}Si_{20.6}$ is gradually transformed to a complete icosahedral phase. In this Rapid Communication, we present the first detailed study of glass-to-quasicrystal phase transformation by using x-ray and electron diffraction techniques. A mechanism for the transformation will be proposed.

The method of sample preparation is the same as that described in Ref. 13. The melt-spun ribbons were examined by x-ray diffraction (Cu $K\alpha$ radiation). Transmission electron microscopy (TEM) studies were performed with a Philips 400T microscope at 120 keV. The inset in Fig. 1 gives the differential scanning calorimetric (DSC) thermogram obtained on heating the glassy Pd-U-Si ribbons at a heating rate of 10 °C/min. The first peak ($T1$) corresponds to the transformation from the glassy phase to the icosahedral phase. The second peak is associated with the transformation from the icosahedral phase to the crystalline phases. Upon isothermal annealing below $T1$, the glassy phase is gradually transformed to the icosahedral phase. The evolution of the transformation in Fig. 1 is obtained at an annealing temperature below the first transformation peak $T1$ in the thermogram. The indexing of diffraction peaks in Fig. 1 is the same as that in Ref. 13. Annealing beyond the fully transformed quasicrystalline state results in crystalline phases, of which the compound Pd_3U is dominant. Transformation was very fast upon annealing near $T1$. It took four minutes for a complete quasicrystalline transformation at 540 °C. In our experiments, we restrict the annealing temperature below $T1$ so that better control of the transformation can be achieved.

At the composition of Pd–20.6 at.% U–20.6 at.% Si, the samples contain essentially only icosahedral grains in the glassy matrix upon annealing below $T1$. From energy-dispersive x-ray analysis, it is found that the composition of these grains is the same as the glassy matrix, indicating a polymorphous transformation. Polymorphous crystallization can usually occur only near the composition of intermetallic compounds.[14] If the composition of Pd-U-Si varied by 1 at.% of the ideal composition, other crystalline phases appeared and a completely transformed icosahedral phase could not be produced. On the other hand, a relatively broad composition range was found[13] to form glassy ribbons of Pd-U-Si. It was suggested that[13] a strong chemical order exists in Pd-U-Si icosahedral phase.

In the study of the glass-to-quasicrystal phase transformation of the Al-Mn alloy, different mechanisms of the transformation were suggested.[11,12,16] Lilienfeld *et al.*[12] proposed that the transformation was due to either a nucleation and growth process or continuous transformation. Knapp and Follstaedt[11,15] explained the formation of the icosahedral phase from the glassy phase using the Stephens-Goldman model,[6] in which the formation of the icosahedral phase is considered as packing small icosahedral units while maintaining an orientational order.

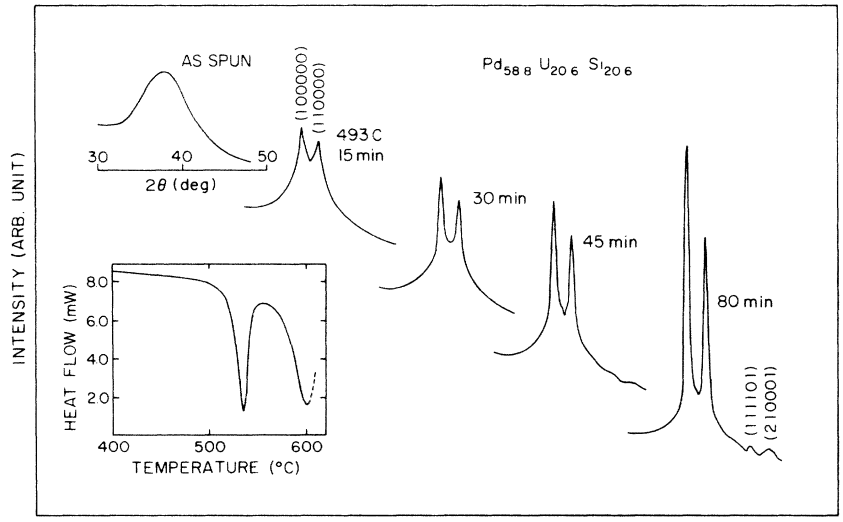

FIG. 1. X-ray diffraction pattern showing the evolution of the glassy phase into the icosahedral phase as a function of time at 493 °C. Inset shows the thermal trace obtained in a differential scanning calorimetry measurement. The dashed line is extrapolated from results for the composition $Pd_{60}U_{20}Si_{20}$ (Ref. 13).

That is, the transformation in Al-Mn comes from the reordering of small icosahedral units preexisting in the liquid state. In their experiment, since the transformation took place within a short time (less than 900 ns), a reordering mechanism was proposed. From TEM and x-ray data, we believe that the glass-to-quasicrystal phase transformation in Pd-U-Si consists of a nucleation and growth process. Micrographs in Fig. 2 describe the evolution of the glassy phase to the icosahedral phase with annealing time at 493 °C. Figure 2(a) is the early stage of transformation. The black dots, which are shown to be small icosahedral particles about 100 Å in size, are uniformly distributed in the micrograph. This coupled with their high density indicates that the nucleation is homogeneous. An intermediate stage of growth is shown in Fig. 2(b) and the totally transformed microstructure in Fig. 2(c), where the particles have impinged. Homogeneous nucleation was also found[16] in submicron droplets in Al-Mn rapidly solidified particles produced by the electrohydrodynamic atomization technique.

Combining x-ray and TEM data, we estimated the volume fraction of the icosahedral phase, in the ribbons as shown in Fig. 3. When the volume fraction is 20%, all of

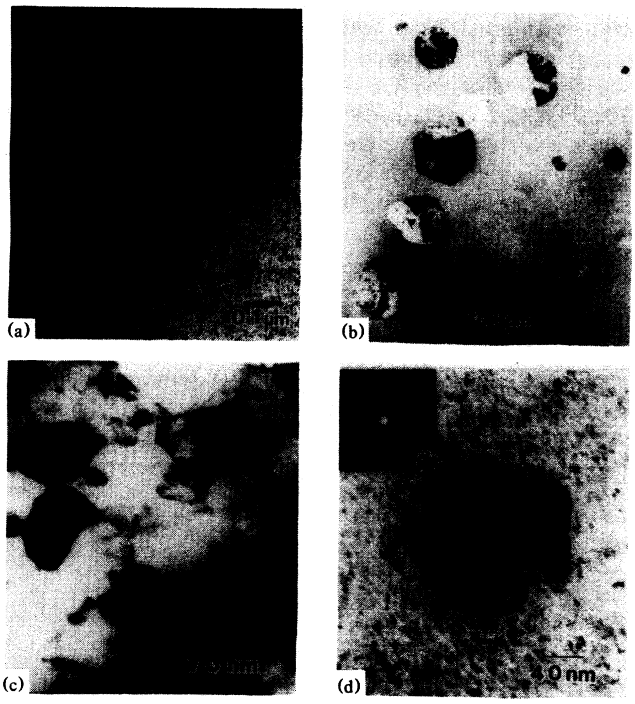

FIG. 2. Electron micrographs showing different stages of the glassy-to-icosahedral phase transformation. The inset in (d) shows the diffraction pattern taken at the fivefold axis of an icosahedral particle. This axis is not necessarily normal to the pentagonal plane because a pentagonal image can be formed over a rather wide angle of view in a thinned sample ($\lesssim$1000 Å). The diffuse ring is due to the matrix.

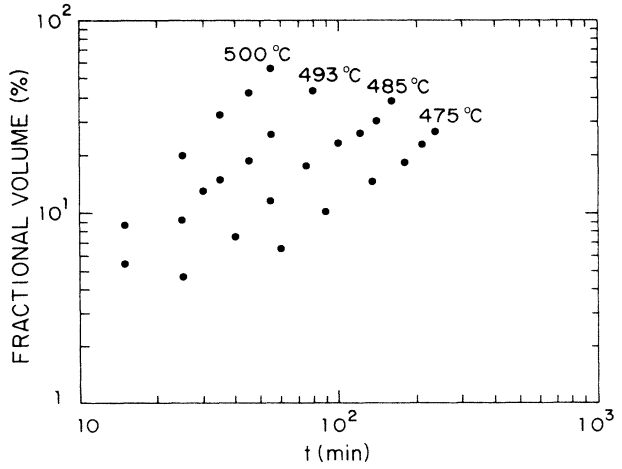

FIG. 3. Fractional volume of icosahedral phase in glassy matrix obtained as a function of annealing time (log scale) at different annealing temperatures.

the icosahedral grains are smaller than 100 Å. The average size is about 50 Å. Therefore, the density of nucleation sites is approximately equal to $0.2/(50\ \text{Å})^3 \simeq 10^{18}$ cm^{-3}. This copious nucleation of the icosahedral phase in the early stages of the transformation originates from the existence of the short-range icosahedral order (10 Å) in the glassy state of Pd-U-Si, which is observed with high resolution x-ray studies.[17]

At low magnification in the TEM the icosahedral particles are regularly faceted at the interface between the particle and glassy matrix into which it is growing. Some appear as either pentagonal or hexagonal shape [Figs. 2(b) and 2(d)]. This is clearly due to the internal symmetry of the structure and occurs by atomic attachment at the interface. Because the transformation is polymorphic, there are no long-range diffusion fields and growth is achieved by atomic jumps over the relatively short distance at the interphase-interface boundary. At high magnifications, however, the facets are characterized as not planar but atomistically rough [Figs. 2(b) and 2(d)]. This is due to there not being strong interface stabilizing forces, because of growth into a glassy matrix or weak molecular binding on the surface of icosahedral particles. When there are no strong forces acting to shape the interface of the growing particle, surface perturbations develop which can become stable and lead to deviations from the original morphology.[18] It should be noted that in this solid-state polymorphic transformation, there still exist short-range diffusion fields and a thermal gradient. The latter is due to the difference in enthalpies of the two phases (inset of Fig. 1).

To understand the kinetics of crystallization of the icosahedral phase from the glassy phase, we show the Johnson-Mehl-Avrammi plot in Fig. 4, where X is the volume fraction of the icosahedral phase and t is annealing time. In the plot, the slope, defined as n, is almost equal to 1 at a relatively low annealing temperature, and increases from 1 to 2 when the annealing temperature changes from 475 °C to 500 °C. It is known that[19] n is between 3 and 4 for most glass-to-crystal phase transformations. In these cases, crystalline phases grow from quenched-in nuclei or thermally created nuclei without interference among them. In the crystallization of the icosahedral phase from glassy Pd-U-Si, we believe that the low n values come from the interference among neighboring grains during growth. Based on these findings, a picture of the transformation is suggested. In the early stage of annealing, homogeneous nucleation is dominant because of local icosahedral order in the glassy phase. A small number of larger icosahedral clusters may have already been formed during quenching. Only those with particle size larger than some critical radius grow at the expense of neighboring small icosahedral particles so as to reduce the total surface energy coupled with a decrease in the Gibbs free energy due to the transformation itself. This explains why only a small number of sites can grow into bigger particles despite the presence of a large number of nuclei. The suggested coarsening process during growth is consistent with a relatively high activation energy (> 4.6 eV) involved in the transformation estimated from differential scanning calorimetry measurements.[20] This activation energy is of the order of those observed in crystal-to-crystal phase transformation in contrast to the relatively low activation energy involved in glass-to-crystal phase transformation.[19] To further our understanding of the transformation, we are going to investigate in detail the interphase boundary between icosahedral and glassy phases during the crystallization reaction.

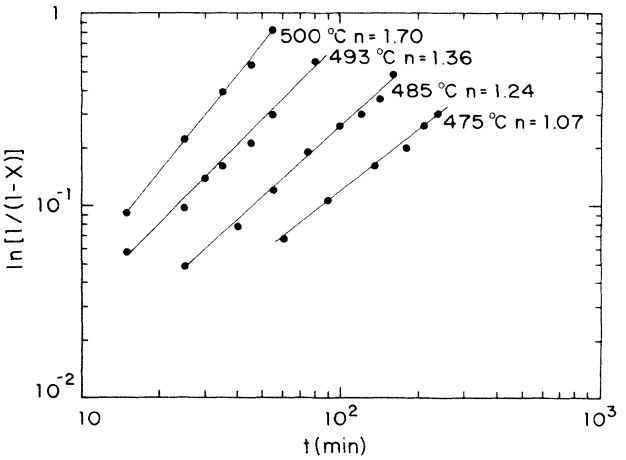

FIG. 4. Johnson-Mehl-Avrammi plot of data depicted in Fig. 2.

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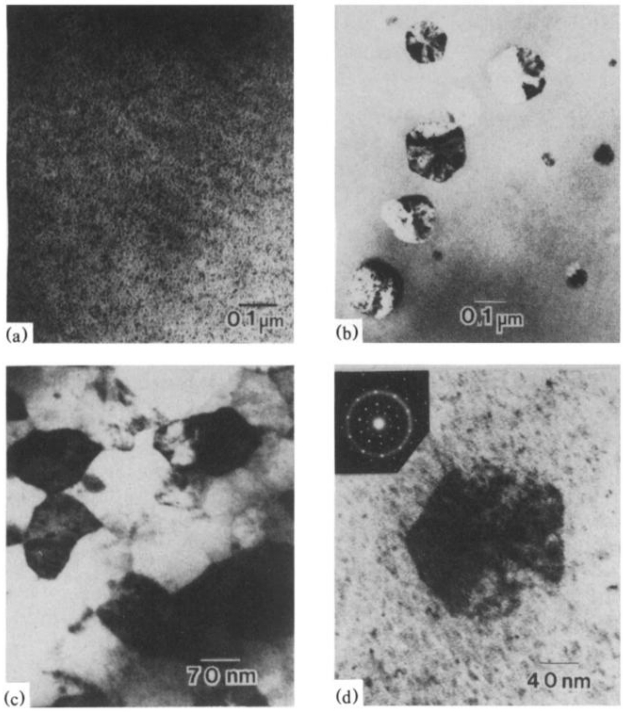

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