Precipitation of Icosahedral Al–Mn during pulsed laser melting

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The icosahedral phase has been produced by pulsed laser melting of thin films of Mn-implanted Al. With increasing laser intensity, we observe a mixture of icosahedral and fcc phases followed by a single phase fcc region. Grains as large as 1 μm in diameter have been observed in 0.1 μm thick films. Electron diffraction studies of individual icosahedral grains indicate that the rapid growth direction from the melt is along the threefold symmetry axis.

The discovery of a metallic phase possessing both long-range icosahedral orientational order and sharp diffraction peaks has been reported in experiments on rapidly quenched Al–Mn alloys. Since fivefold rotational symmetry precludes translational periodicity, this observation has stimulated a tremendous amount of work on the nature of the atomic ordering in such structures. It has been pointed out that the aperiodic two-dimensional Penrose tiling and its three-dimensional quasicrystal generalization, which possess long-range orientational order, yield diffraction patterns very similar to those observed in the Al–Mn alloys.

Materials exhibiting metastable quasicrystalline order have been produced by melt-spinning, ion mixing, ion implantation, precipitation from the amorphous solid phase, solid-state reaction of thin crystalline layers, e-beam melting, and by pulsed laser melting. Despite the numerous studies undertaken, however, methods have not been found to produce individual icosahedral grains sufficiently large to allow the use of “single crystal” x-ray diffraction techniques to establish the atomic locations in a quasicrystal structure.

In this Rapid Communication we report the use of pulsed laser melting in the formation of icosahedral Al–Mn with grain sizes of up to 1 μm. This technique is similar to melt spinning and e-beam melting in that they both create metastable phases from a rapidly cooled liquid. Pulsed laser melting, however, can be used to create highly uniform plane-front one-dimensional interface motion, allowing important quantities such as temperature and composition profiles, and interface position and velocities to be calculated and even measured. It also allows one to use the unmelted portion of the sample as a seed for liquid phase epitaxy of a desired phase. In general the quench rates attained with this technique are significantly greater than are those attained by melt spinning. An independent study of laser melted Al–Mn films on metal substrates found that icosahedral grains ~2 nm in diameter could be formed. In the present study large grains of the quasicrystal phase were created by deliberately reducing the quench rate by using high laser-pulse energy densities on thin films on an insulating substrate.

Thin film samples were prepared by vacuum deposition of approximately 0.1 μm Al films onto cleaved (100) NaCl substrates at room temperature. The Al films were then implanted with 56Mn+ ions at two energies (35 and 75 keV) in order to produce roughly uniform Mn concentrations measured by Rutherford backscattering analysis to be typically in the range of 10–18 at. % near the center of the films. Implantation at substrate temperatures of 20, 150, and 275 °C resulted in amorphous, icosahedral, and crystalline phases, respectively. These three different types of samples, described in more detail in Ref. 7, were used as starting material for the pulsed laser experiments.

The samples were irradiated using a pulsed KrF+ excimer laser (pulse duration 25 ns FWHM, wavelength 248 nm). The beam is usually uniform over several mm in spatial extent. However, in order to cover the entire range of pertinent pulse energy densities, in this case we focused the beam to a small spot on the sample. The beam thus blew away the film under the central portion of the laser spot. We estimate that the pulse energy density on the remaining material along the edge of the hole was ~3 J/cm². The metal films were removed from the NaCl substrate by placing the samples in distilled water and then mounted on TEM grids. Preparing samples in this manner allowed us to study the formation of various alloy phases as a function of distance from the center of the laser beam and hence over a continuous range of cooling rates in a single sample.

We show in Fig. 1 the result of pulsed laser melting of an amorphous film. Region “a,” farthest from the hole produced by the laser, is still amorphous. As we approach the center of the laser spot, encountering regions that were irradiated with continuously increasing laser intensity, we find a two-phase region (“b”) of fcc Al and icosahedral precipitates of increasing size. A sec-
ond transition occurs to region "c," single phase fcc Al supersaturated with Mn. The Al grain boundaries can be traced across regions b and c, indicating lateral growth inward of this phase. X-ray fluorescence shows that the average Mn concentration is the same in the three different regions. The abrupt disappearance of quasicrystals can be explained by diffusive liquid-phase broadening of the as-implanted Mn profile. The peak of the implanted Mn profile is estimated to be 18 at. % Mn, but if liquid phase diffusion were to average out the composition throughout the thickness of the film, we would be left with a composition of only ~7 at. % Mn. The structure in region b of Fig. 1 is consistent with nucleation of quasicrystals before significant broadening can occur in the liquid phase, whereas region c, which was irradiated with a greater laser intensity, may have been at temperatures above the quasicrystal melting point for periods of time long enough to reduce the peak Mn concentration below that required for easy icosahedral phase nucleation. The larger quasicrystalline grain size observed in region b near the border with region c might be due to either quasicrystal coarsening while surrounded by liquid Al or preferential melting of the smallest icosahedral grains, which are destablized by capillarity effects.

We show in Fig. 2 a higher magnification of a region containing two star-shaped quasicrystal grains formed by pulsed laser treatment of a sample that was originally a two-phase mixture of fcc and Al₃Mn. Convergent beam electron diffraction patterns showing the icosahedral symmetry axes are given in Fig. 3. From the relationship between the diffraction patterns and morphology of these and other grains with other symmetry axes near to the film normal, we conclude that the most rapid growth direction (i.e., the "point" on the stars) are the threefold symmetry axes of the icosahedral structure. In general, the "points" correspond to projections of these axes into the plane of the film. This observation rules out the model of Hilbert for rapid growth along the fivefold axis and corroborates those of Schaefer et al.⁷ Note that the grain size here of 0.2–0.3 μm is significantly larger than the film thickness. On either side of these icosahedral "stars" are brick-shaped grains that were identified as crystalline Al₃Mn by microdiffraction. It is likely that these Al₃Mn crystals, which do not readily nucleate, never melted, since in regions of higher laser intensity only icosahedral and fcc phases were found. Further evidence that they never melted is the observation that the Al₃Mn grains were not found in samples that did not contain this phase before pulsed laser melting. The region between the icosahedral and Al₃Mn grains is fcc Al, which contains some Mn in solid solution. The x-ray fluorescence indicates that the ratio of Mn compositions of the icosahedral, fcc, and Al₃Mn phases in this region is 15:14:40, respectively. If we assume the Al₃Mn is near stoichiometry (14.2 at. % Mn), we find an icosahedral composition in this region of 13 at. % Mn and an fcc composition of 4 at. % Mn. During cooling, the icosahedral phase apparently nucleates first, rejecting Al as it grows, whereupon fcc Al subsequently nucleates. However, unlike the as-implanted samples, no unique orientation relationship between the fcc and icosahedral precipitates was found in this case. Perhaps it is no surprise that less texturing is observed in this case since the precipitating fcc phase is surrounded only partially by the quasicrystal and the
rest by liquid. The orientation dependence of the surface-free energy term in the expression for the free energy of the micrographs obtained by Schaefer et al. from melt-spun icosahedral samples. The size of the grains allows us to estimate the melt duration, assuming that growth with solute partitioning requires diffusion-controlled kinetics. With a liquid-phase diffusivity assumed to be $10^{-7} - 10^{-5}$ cm$^2$/s, the time necessary for 0.5 $\mu$m radial growth is of the order 100 $\mu$s. Pulsed laser melting of metals and semiconductors typically produces melt durations of 0.1–1 $\mu$s. Large grains of the icosahedral phase thus can only be produced by pulsed laser melting if steps are taken to reduce the quench rate, such as by utilizing insulating substrates.

The growth of materials with icosahedral symmetry can be achieved with pulsed laser melting under well-controlled experimental conditions. This simple technique should prove quite useful by making larger grain sizes possible as well as by providing information concerning the thermodynamics and formation kinetics of these novel structures.

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