Measurements of Melting Temperatures of Quasicrystalline Al-Mn Phases

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Melting transformations in metastable quasicrystalline Al-Mn phases have been measured for the first time, by use of a new rapid electron-beam heating technique applied to surface layers with 14.8–20.5 at.% Mn. The melting temperature for icosahedral $Al_{80}Mn_{20}$ is directly measured to be 910 ± 20 °C, and is believed to be near the congruent melting point. The decagonal-phase liquidus at the same concentration is inferred to be 965 ± 20 °C. The melting temperatures of the icosahedral phase are ~30 °C below those of crystalline compounds of the same composition.

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The discovery of metallic phases formed by rapid quenching which exhibit icosahedral or decagonal symmetries in electron diffraction has generated considerable interest in the last two years.[1,2] It is now widely believed that these phases are examples of "quasicrystals," a new form of ordered solid whose nonperiodic structure permits symmetries disallowed for crystalline materials. The best studied system is Al-Mn, which has an icosahedral[1] as well as a decagonal[2] phase. Like most quasicrystals, these phases are metastable,[3] transforming to crystalline phases at modest temperatures (350–400 °C),[1,4] and measurement of their high-temperature thermodynamic properties has been very difficult. Such measurements are needed for a complete understanding of these new materials and as tests for models of these phases.

We report here combining ion-beam mixing and rapid electron-beam heating to provide a new technique for measuring melting temperatures of metastable phases, and apply it to icosahedral and decagonal Al-Mn. The procedure involved first using in-beam mixing to form a smooth, fine-grained surface layer of the icosahedral phase,[4,5] and then treating the layer with an electron beam[6,7] to heat it to a known peak temperature within ~200 μs. Sharp transformations in microstructure, as well as diffusion of an ion-implanted marker, served to delineate the melting transitions. By determining the melting temperatures at several Mn concentrations, we have mapped out a portion of the "T_0" curve, a line in the phase diagram where the free energy of the icosahedral phase equals that of the liquid. At higher peak temperatures, a second transformation maps out the decagonal-phase liquidus. These are the first precise measurements of the melting temperatures of quasicrystalline phases; this approach is generally applicable to other metastable phases as well.

The starting material was prepared by deposition of alternating layers of Al and Mn on a sapphire substrate to a total thickness of 50–100 nm. Sapphire was used because of its high melting point, good thermal conductivity, and inertness. The deposited Al/Mn layers were ion-beam mixed at 150 °C with a 400-keV Xe beam to a total fluence of 1×10^{16} Xe/cm^2. For Mn concentrations of ≈ 15–21 at.%, this treatment formed a single-phase layer of icosahedral Al-Mn with grains 7–30 nm in diameter.[5]

In order to melt the layer without first giving it time to transform in the solid state, we used a line-source electron-beam system to heat it rapidly to a known peak temperature. The *e*-beam system produces a line beam 20 mm long by 1 mm wide, with a measurable and reproducible Gaussian power profile (in the narrow dimension).[7] Different sample areas were exposed to the beam while being swept under it at measured speeds in the range of 300–500 cm/s. Since the *e*-beam parameters and thermal properties of the substrate are accurately known, the temperature history of each treatment may be calculated to within ≈ 10 °C. The thermal properties of the thin overlayer can be neglected for these treatment times; the temperature of the alloy layer tracks that of the sapphire surface to within a fraction of a degree. Figure 1 shows a series of surface-temperature histories calculated for *e*-beam treatments at successively slower sweep speeds with the same beam power profile; the beam dwell times were 241, 249, and 287 μs (full width at half maximum). The peak heating rate of each treatment is $\approx 5\times10^6$ K/s and the subsequent quench rate is $\approx 2\times10^6$ K/s. The beam power used in the calculations was calibrated by our treating a pure Al layer on sapphire with the same beam conditions and finding the dwell time for which the Al melted.

These heating times are too short for solid-state transformation to occur, as demonstrated in Figs. 2(a) and 2(b) by results of transmission electron microscopy (TEM) for a treated layer with 19.8 ± 0.4 at.% Mn. In this case the icosahedral layer received the treatment with temperature history *a* shown in Fig. 1, with a peak temperature of 900 °C. Yet the diffraction pattern in Fig. 2(a) and the bright-field image in Fig. 2(b) are indistinguishable from those of the as-mixed icosahedral layer.[5] The diffraction pattern from the layer exhibits only rings from the icosahedral phase, and the grain size

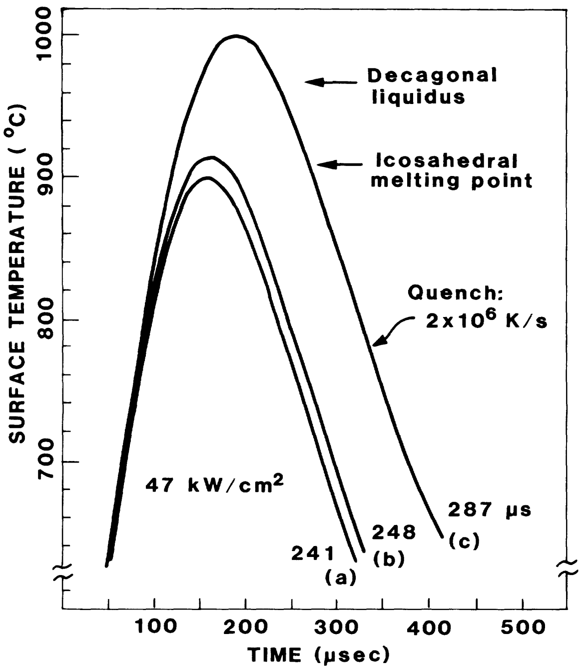

FIG. 1. Surface temperature histories for *e*-beam treatments at three different dwell times. Peak temperatures: curve *a*, 900 °C; curve *b*, 915 °C; and curve *c*, 1000 °C.

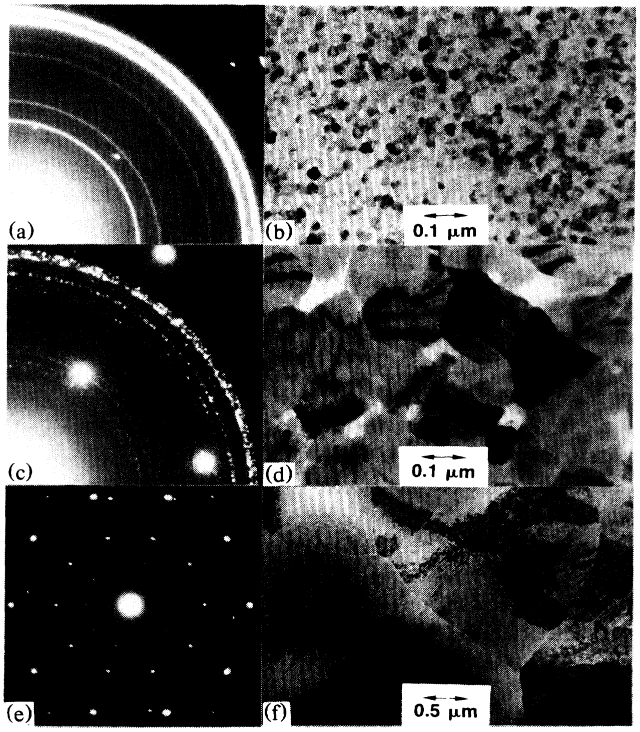

FIG. 2. Diffraction patterns and microstructures of Al-Mn surface layers heated by the *e* beam to (a),(b) 900 °C; (c),(d) 915 °C; and (e),(f) 1000 °C. Spots in (a) and (c) are due to the sapphire substrate.

is unchanged. Optical examination also failed to reveal any change in texture from the smooth starting material.

In sharp contrast, the microstructure for a peak temperature of 915 °C is very different from the starting material. Temperature history *b* in Fig. 1 produced the TEM results in Figs. 2(c) and 2(d). The grains in the bright-field image are an order of magnitude larger (100–200 nm) and diffraction reveals that the layer is now composed mostly of the decagonal phase of Al-Mn, along with a small amount of fcc Al (<3%). Optical microscopy also showed an abrupt change from the smooth as-mixed surface to a rougher topography. Such a dramatic change in microstructure for a change in peak temperature of just 15° appears to indicate melting of the original icosahedral phase followed by nucleation and growth of the decagonal phase. To confirm that the layer melted, a similar sample was implanted at 150 °C with 2×10^{15} Xe/cm^2 at 50 keV to provide a diffusion marker within the layer. Broadening of the Xe profile within the layer, as measured by Rutherford backscattering, was observed only after treatments which produced the above microstructure transition. Such an abrupt increase in Xe diffusivity indicates that the microstructure transformation is indeed due to melting of the icosahedral phase. Using several such treatments, we deduce a melting temperature for icosahedral $Al_{80}Mn_{20}$ of 910 ± 20 °C, where we have included the uncertainties in the measurements and calculations.

One possible concern is that this experiment has measured a melting temperature unique to the fine-grained, ion-mixed layers. We checked this by first treating some samples to higher temperatures (1000 °C) to form a single-phase icosahedral layer with much larger grains (up to 5 μm in diameter; see below), and then repeating the lower temperature treatments to delineate the melting temperature. The same melting temperature was observed for the large grains as for the fine-grained layer.

Previous work indicates that the minimum quench rate required to form the icosahedral phase from a liquid is $\approx 1\times10^6$ K/s, with the decagonal phase forming only at slower quenching rates.[6,8] Yet in the layer heated to 915 °C the decagonal phase has formed, even though the quench rate reaches $\approx 2\times10^6$ K/s, sufficient to favor formation of the icosahedral phase. Furthermore, heating the layer to an even higher peak temperature *does* result in reformation of the icosahedral phase; Figs. 2(e) and 2(f) show the TEM results for temperature history *c* in Fig. 1, with a peak temperature of 1000 °C. The layer has again melted and undergone a dramatic change in microstructure, but instead of resolidifying as the decagonal phase, the thin surface layer is now composed of icosahedral grains as large as 5 μm in diameter, with no fcc Al present. Figure 2(e) shows a diffraction pattern obtained from a fivefold axis of one of these grains.

The resolution of this apparent inconsistency leads to an inference of the liquidus temperature for the decagonal phase. For treatment *b* in Fig. 1, the icosahedral layer begins melting when the temperature rises above its melting temperature, but then the temperature rises only a few degrees higher to 915 °C. Our observation of fcc Al with the decagonal phase indicates that the melt entered a two-phase regime of decagonal phase and Al-rich liquid. This further implies that the congruent melting point of the decagonal phase must be at higher Mn content and higher temperature. In other rapid quenching experiments[8] the decagonal phase is observed to nucleate more slowly than the icosahedral phase, and may even nucleate only on existing icosahedral grains.[9] The molten surface layer spends 30–40 μs in the two-phase regime, but above the melting temperature of the icosahedral phase. There is evidently sufficient time to nucleate and grow the decagonal phase within the liquid before the temperature falls sufficiently for the icosahedral phase to form; the melting icosahedral grains may act as nuclei for the decagonal phase.

For treatment *c* in Fig. 1, the temperature of the surface rises to 1000 °C, which is above the liquidus for the decagonal phase, and the layer melts to a homogeneous, single-phase liquid. As the molten layer cools, the quench rate reaches 1.5×10^6 K/s before the temperature has fallen below 980 °C; this quench rate does not allow sufficient time below the decagonal liquidus for significant formation of this phase[8] before the temperature drops below the melting temperature of the icosahedral phase, which then readily nucleates and consumes the layer. Furthermore, no residual icosahedral grains are present in the liquid to nucleate the decagonal phase. Cooling at the high quench rate from 1000 °C accordingly results in solidification of the layer as large grains of the icosahedral phase. Other heat treatments with peak temperatures intermediate between 915 and 960 °C result in decagonal plus fcc Al layers similar to that of Fig. 2(d); a sharp transition to the large-grained icosahedral layer is observed for peak temperature near 965 °C. With the above interpretation, the decagonal phase is lost when its liquidus is exceeded; our results then place this liquidus at 965 ± 20 °C for 20 at.% Mn.

We have applied the same technique to layers prepared with other Mn concentrations, all within or at the edge of the range for which ion-beam mixing produce a single-phase icosahedral alloy. The same two abrupt transitions were observed, and Fig. 3 shows their temperatures plotted versus Mn concentration. The melting temperatures for the icosahedral phase are largest at 20 at.% Mn, which several studies indicate to be at or near the central composition for the phase.[8,10] Thus the melting temperature of 910 ± 20 °C is taken to be near the congruent melting point of the icosahedral phase. Less is known about composition bounds for the decagonal phase, but the presence of some fcc Al with the decagonal phase in our experiments indicates that the congruent melting point is at greater than 20 at.% Mn and above 965 °C. The melting temperatures of both phases are below the equilibrium liquidus of the recently reevaluated Al-Mn phase diagram,[11] shown as a dot-dashed line in Fig. 3.

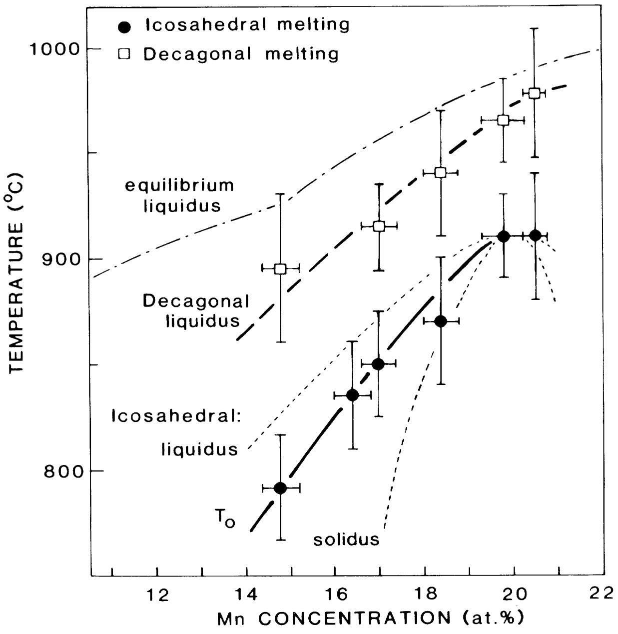

FIG. 3. Melting transformations vs Mn concentration.

Since the congruent melting point for the icosahedral phase is believed to be at 20 at.% Mn, the lower concentrations in Fig. 3 fall within a two-phase field at elevated temperatures (liquid plus icosahedral). An indication of where such phase boundaries may lie for the icosahedral phase is shown by dotted lines in Fig. 3. For sufficiently slow heating rates these alloys would undergo segregation into an Al-rich liquid and Mn-rich icosahedral solid over the temperature interval between the liquidus and solidus before complete melting is achieved. Heating at our rapid rates ($\approx 5\times10^6$ K/s) apparently does not allow time for Mn segregation in the solid state, as indicated by the abruptness of the microstructure change with increasing temperature and the absence of quenched-in fcc Al below the first transition. Rather, the alloy remains single phase until it reaches the icosahedral T_0 curve, where the free energy of the liquid equals the free energy of the single-phase solid, and partitionless melting can occur without solute segregation. The solid line traced out by the lower-temperature transitions in Fig. 3 is then the T_0 curve for the liquid and icosahedral phases. The presence of fcc Al for higher peak temperatures indicates that phase separation does occur in the liquid state, as discussed above. Accordingly, the dashed line traced out by the higher-temperature transitions is the decagonal-phase liquidus.

Comparison of these measured melting temperatures to those of stable compounds indicates the relative thermodynamic stabilities of crystalline and quasicrystalline states of Al-Mn at high temperature. Recent thermodynamic modeling[11] of the Al-Mn phase diagram gives the melting points for two crystalline compounds: λ(17 at.% Mn, 875 °C) and μ (20 at.% Mn, 940 °C). These temperatures are $\sim 30\,^{\circ}\mathrm{C}$ higher than those of the icosahedral phase at the same concentrations; thus, the icosahedral phase is clearly metastable near its melting temperature. The free energy of crystalline compounds relative to the liquid is closely approximated by $\Delta G = S_f(T - T_m)$, where S_f is the entropy change upon melting. We use values for the pure metals to estimate[12] $S_f = 15.3$ J/K g-at. for the ordered compound μ with 20 at.% Mn. The free energy of the icosahedral phase is then ~ 460 J/g at. higher than that of μ, or $\approx 3\%$ of the heat of fusion. Our experiments indicate that the decagonal phase congruent melting point is at least as high as 965 °C. This melting point is comparable to the melting point of μ as well as another crystalline phase at higher concentration, ϕ (23 at.% Mn, 950 °C).[11]

These measurements also have implications for structural modeling. A recent paper[13] proposes that icosahedral and decagonal Al-Mn are two different configurations of twinned crystals of the same cubic phase; our observations clearly show that the icosahedral and decagonal structures are distinct phases with different melting points.

A more complete metastable phase diagram for the icosahedral, liquid, and fcc Al phases will be given elsewhere, with use of information from several of our experimental techniques. We emphasize here that it is the use of controlled *e*-beam treatments with rapid heating and cooling and a precise knowledge of the temperature histories which has allowed us to obtain high-temperature thermodynamic information about these metastable quasicrystalline materials. This approach should be applicable to other metastable systems as well; an analogous result, the melting point of amorphous Si, has been obtained by a different technique.[14]

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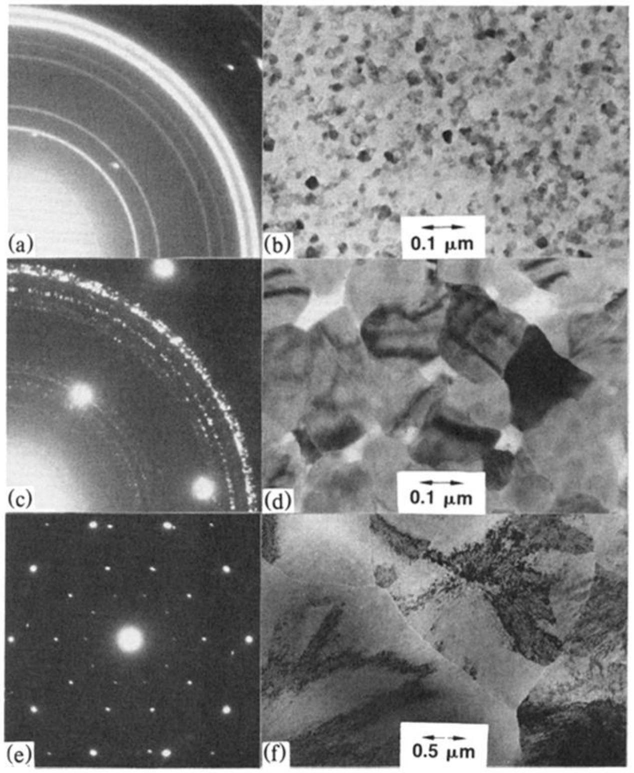

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