Icosahedral-Phase Formation by Solid-State Interdiffusion

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We have formed the icosahedral phase in $Al_{86}Mn_{14}$, $Al_{82}Mn_{18}$, and $Al_{75.5}Mn_{20}Si_{4.5}$ alloys by the interdiffusion of elemental layers in the solid state. Annealing at 250–425 °C produced the phase in times as short as 1 min with grains up to ~ 14 nm in diameter. Continued annealing transformed the alloy layers into crystalline phases. These results demonstrate that the icosahedral phase nucleates in the solid state in preference to crystalline phases of lower free energy, even though the initial material does not have liquidlike icosahedral short-range order.

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The recent discoveries[1,2] of ordered phases exhibiting long-range icosahedral orientational symmetry have attracted much attention, since this symmetry is inconsistent with lattice periodicity. A variety of experimental techniques are being used to investigate the fundamental properties of these novel phases, which may have unique and useful properties. Forming of the icosahedral phase by methods other than the initially discovered melt-spinning technique has offered insight into the structure and thermodynamics of the phase and the kinetic processes leading to its formation.[3–7] Until now, all the methods have involved either rapid quenching from the melt or ion-beam techniques which produce numerous atomic displacements and point defects.

We have discovered that the icosahedral phase of Al(Mn) can also be formed by solid-state interdiffusion of thin elemental layers annealed at modest temperatures (≥ 250 °C). The method relies on purely thermal processes to intermix the elemental solid layers and form the phase, without the energetic atomic displacements associated with ion irradiation. As we shall show, the phase nucleates readily in preference to other crystalline compounds and forms fine grains (≤ 14 nm), which do not ripen appreciably with further annealing. These findings have important implications for thermodynamic modeling of the phase and for understanding of the kinetic processes leading to its formation. The kinetics of interdiffusion in the solid state favor icosahedral-phase formation, even though the initial material does not uniformly have liquidlike icosahedral short-range order, as is believed to be the case with formation by either liquid quenching[8,9] or annealing of an amorphous alloy.[4–6] The formation of quasicrystalline Al(Mn) from crystalline material is similar to the formation of amorphous phases by solid-state interdiffusion, which has been reported by others.[10] The simplicity of this technique makes it potentially useful for forming icosahedral materials if applications are found for them.

Sequential layers of Al (~ 8 nm thick), Mn (~ 2 nm), and in one sample Si (~ 1 nm) were vapor deposited in a vacuum of 5×10^{-7} Torr at rates of 0.1–0.5 nm/s onto Cu grids covered with a thin Formvar film. Layers with total thicknesses of 43 or 52 nm were produced for observation in the transmission electron microscope (TEM) at 120 kV. Two binary Al alloys with average concentrations of 14 ± 1 and 18 ± 1 at.% Mn were prepared, as well as a ternary Al alloy with 20 ± 2 at.% Mn and 4.5 ± 1 at.% Si. These concentrations were measured with Rutherford backscattering spectrometry and with energy dispersive x-ray spectroscopy in the TEM. Our deposited layers contain some C and O impurities; we measure 2×10^{16} O/cm^2 and 1×10^{16} C/cm^2 with nuclear-reaction analysis in the 18% sample which was 52 nm thick. The O is believed to be mostly in the form of surface oxides, and this level corresponds to a thickness of ~ 3 nm of Al_2O_3. Annealing was performed *in situ* with a heating sample holder in the TEM with a vacuum of $\sim10^{-7}$ Torr and a liquid-nitrogen cold trap around the specimen.

Annealing of the two binary alloys at 250 °C produced detectable diffraction rings which matched those of the icosahedral phase within 5 min; with annealing at 300 °C such rings were observed within 1 min. These observations show that our samples respond quickly at the center of the grid to changes in the heater current, and that the phase nucleates readily at these temperatures. Results are shown for these two alloys in Fig. 1; Fig. 1(a) is a diffraction pattern from the unannealed layers of the 14% sample for reference. After 80 min at 250 °C, the 14% alloy exhibited the ring pattern shown in Fig. 1(b); the sharp rings are fcc Al and are also seen in Fig. 1(a), while the five more diffuse rings noted with arrows match the five most intense x-ray reflections from the icosahedral phase[11] to within about ±1%, with the qualification that the brightest ring is actually an unresolved doublet. These additional rings are not seen in Fig. 1(a). Two of the rings marked in Fig. 1(b) are not seen in amorphous Al(Mn),[4] and are detected early in the anneal sequence. Thus the elemental layers apparently transform directly to the icosahedral phase without first

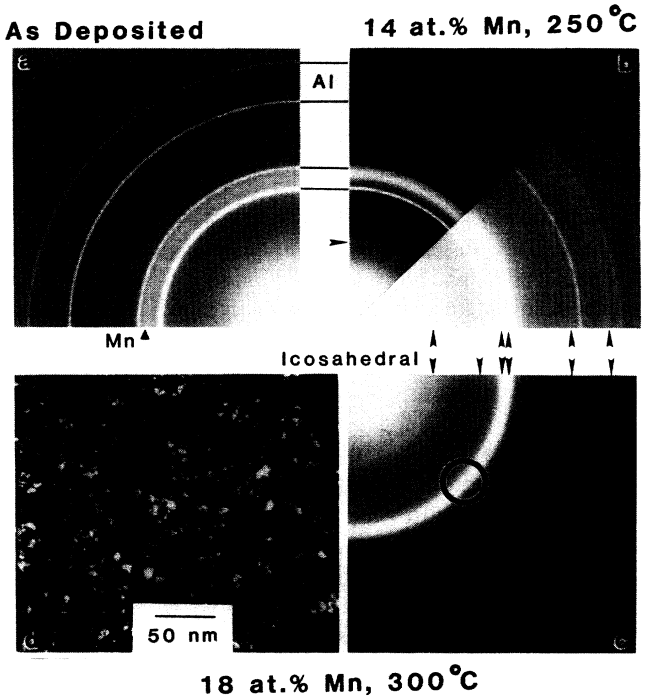

FIG. 1. TEM results for Al(Mn) layered alloys. Diffraction patterns: (a) as deposited, 14% Mn; (b) 14% sample after 80 min at 250 °C (two exposures); and (c) 18% sample after 15 min at 300 °C. (d) Dark-field image of icosahedral grains ≤ 10 nm in diameter obtained by use of the brightest rings in (c).

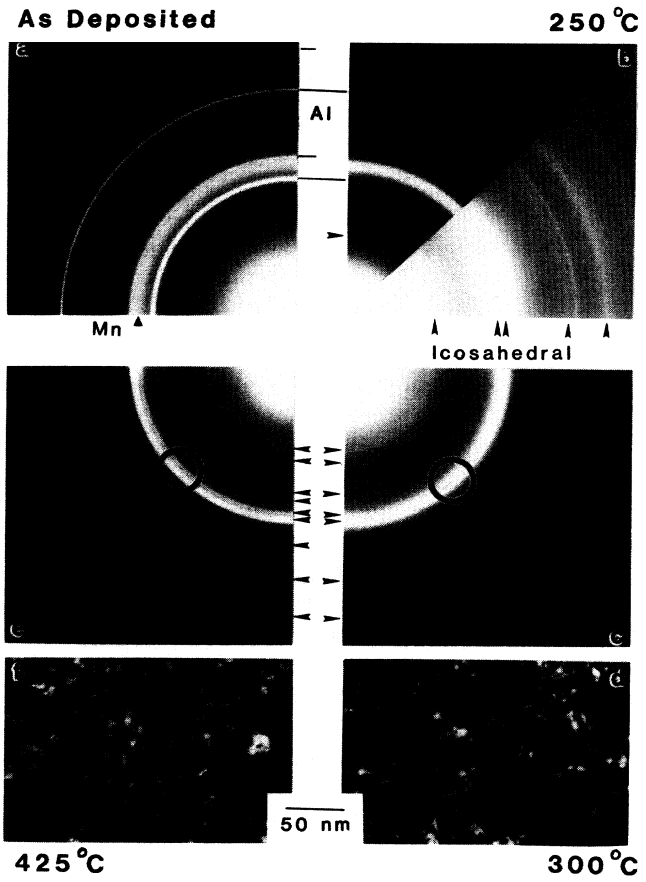

FIG. 2. TEM results for Al(Mn,Si) layered alloy with 20% Mn and 4.5% Si. Diffraction patterns: (a) as deposited; (b) after 60 min at 250 °C (two exposures); (c) after 15 min at 300 °C; and (e) after 15 min at 425 °C. Dark-field images of icosahedral grains obtained by use of the brightest rings: (d) after 15 min at 300 °C, ≤ 10 nm in diameter; and (f) after 15 min at 425 °C, ≤ 14 nm in diameter.

forming an amorphous intermediate state. The ring pattern changed little during the anneal after the first 20 min. Annealing of a new sample with the same deposited layers but at 300 °C initially showed similar rings; however, within 2 min the crystalline phase Al_6Mn formed, and the layer was converted into this phase within 12 min.

Similar results were obtained with layers deposited on an Al substrate which was subsequently removed by electropolishing prior to annealing.[4] The free-standing layers with average concentration 16 ± 1 at.% Mn first formed the icosahedral phase during annealing at 250 °C, and then crystallized to Al_6Mn with further annealing at 350 °C. This result shows that the nucleation of icosahedral Al(Mn) is not due to the presence of the Cu grid.

Annealing of the 18% sample at 250 °C produced a ring pattern similar to that in Fig. 1(b), but the residual fcc-Al rings were less intense. Subsequent annealing for 15 min at 300 °C sharpened the icosahedral-phase rings slightly, as shown in Fig. 1(c). The Al rings are absent after the 300 °C anneal, indicating that a single-phase sample of the icosahedral phase has been produced with this higher Mn concentration. Dark-field imaging with the brightest ring illuminated icosahedral grains up to ~ 10 nm in diameter, as shown in Fig. 1(d). Annealing at 350 °C produced a new phase not yet identified.

We chose to examine Al/Mn/Si alloy layers as well because Si has been found to stabilize the icosahedral phase and to relieve strains to produce sharper diffraction.[12] In addition, structural modeling suggests that the ternary phase α-(AlMnSi) is closely related to the icosahedral phase.[13,14] Annealing of this ternary layered alloy for 1 h at 250 °C and then for 15 min at successively higher temperatures produced the results shown in Fig. 2. The ring pattern in Fig. 2(b) obtained after the 250 °C anneal shows two weak rings from residual Al [see the as-deposited reference pattern in Fig. 2(a)] and broader rings (arrowed) indexing to the icosahedral phase. At 300 °C the Al rings disappeared as shown in Fig. 2(c); the icosahedral grain sizes were generally in the range of 3–10 nm with an average of 6 nm, as seen in the dark-field image in Fig. 2(d). Annealing at 350 °C produced particles of the hexagonal phase β-Al_9Mn_3Si,[15,16] however, these did not occupy the entire layer area and grew slowly enough that the

anneal sequence could be extended to higher temperatures by examining the icosahedral phase in areas between the particles. The ring pattern sharpened and additional rings appeared, eventually giving the pattern in Fig. 2(e), with twelve rings indexing to the icosahedral phase observed after annealing 15 min at 425 °C. Dark-field imaging [see Fig. 2(f)] after this anneal shows grains 3–14 nm in diameter with an average size of 8 nm. Although the ring pattern has sharpened (the doublet is now resolved) and more rings are present after this anneal, the average grain size has changed very little and the structure thus exhibits only a minimal ripening effect. The sharpening of the rings may therefore also reflect an increase in atomic order within the grains obtained by removal of defects with annealing at 425 °C. Annealing at 450 °C produced numerous additional crystalline particles and perhaps another phase, thus ending the anneal sequence.

The formation of the icosahedral phase by solid-state reaction is similar to the formation of metastable amorphous alloys by interdiffusion of elemental metals.[10,17] In both cases, the structure is known to be metastable with respect to crystalline structures and was first produced by rapid quenching of a liquid; yet amorphous and quasicrystalline phases can be formed from crystalline material by heating to increase atomic mobility. The essential requirements for forming both structures in the solid state are that the free energy of the binary system is lowered by alloying, and that the metastable structure forms more readily than crystalline phases. The driving force for interdiffusion and amorphous alloy formation is believed to be the large negative heat of mixing between the two elements, such as Ni and Zr for which Miedema[18] gives $H_m = -71$ kJ/g-at. For Al and Mn this parameter is also negative but smaller in magnitude, -43 kJ/g-at. Solid-state formation of amorphous metals has been suggested to require a high diffusivity of one element into the other[10,17]; however, questions have been raised concerning how the interdiffusion takes place between the two metals and through the amorphous phase.[19] The available diffusivity measurements[20] of Mn in Al at higher temperatures do not suggest that Mn will diffuse rapidly in Al at 250 °C; grain boundaries may therefore have provided the fast diffusion paths needed for the reaction to occur.

Icosahedral phase formation requires that kinetic processes allow the phase to nucleate and grow more rapidly than the possible crystalline phases. Melt-spinning results[1,2] showed that kinetics favor the formation of the icosahedral phase during quenching from the liquid, which has recently been demonstrated to occur within ≤ 20 ns at 660 °C.[4] The results presented here show that kinetics favor formation of this phase during low-temperature, solid-phase reactions as well. There is an important distinction between these two processes: With liquid quenching, as well as with annealing of amorphous alloys,[4] the icosahedral phase forms from a compositionally uniform medium believed to have short-range icosahedral order,[5,8,9] which might favor its nucleation over other phases. However, the Al/Mn/Si layers do not uniformly have such order, although icosahedral atomic configurations are present[15] within the unit cell of α-Mn and might also be present at grain boundaries in the layers. The ready formation of the icosahedral phase in the solid state demonstrates that an initial liquidlike structure with uniform icosahedral short-range order is *not* a prerequisite for nucleation and growth of the phase. The icosahedral-phase precipitates observed after solid-state heat treatment of Al(Li,Cu,Mg) alloys may be a similar example of formation in the solid state.[21,22]

The eventual transformation to crystalline phases indicates that they are lower in free energy than the icosahedral phase, certainly for temperatures at or above the transformation temperature, and probably also below. However, the free-energy difference is apparently not sufficient to overcome kinetic limitations on formation of the possible crystalline phases before the icosahedral phase forms. Nucleation of the crystalline phases may be difficult because their unit cells are relatively large and complex.[13,15] These phases can often be described as ordered stackings of icosahedral structural units. Recent models of the icosahedral phase utilize alternate stackings of the same structural units, but with less stringent ordering requirements than those of crystalline structures.[13,14,23] Even very disordered stackings of such units with only simple attachment rules have been shown to exhibit sharp diffraction patterns with icosahedral symmetry.[24–26] If such structural considerations are correct, the icosahedral phase might be expected to nucleate more easily than the more ordered crystalline phases, in agreement with observations.

Two effects of alloy concentration are apparent in our results. First, when the concentration is correct, this method can produce single-phase alloy layers as evidenced by the loss of the excess Al on going from 14% to 18% Mn [see Figs. 1(b) and 1(c)]. Second, changing the concentration can inhibit the formation of competing crystalline phases; with 18% Mn the formation of Al_6Mn was suppressed, and a crystalline phase did not form until 350 °C. With the addition of Si, a different phase formed at 350 °C which grew more slowly.

The fine grains of the icosahedral phase show little ripening after their formation, even when annealed at a significantly higher temperature than their formation temperature (see Fig. 2). This absence of grain growth has been found by others as well.[27] Either the surface

energy of their grain boundaries is not sufficiently large to promote ripening, or the diffusion of atoms between icosahedral-phase grains is too slow. The sharpening of the rings in the diffraction pattern with annealing up to 424 °C suggests that defects can be removed from quasicrystals by annealing at time/temperature combinations which do not permit crystalline phases to nucleate. Such defect evolution may be associated with the relaxation processes recently reported to have been observed in calorimetry and Young's modulus measurements during annealing of icosahedral Al(Mn).[28]

The formation of the icosahedral phase by interdiffusion of elemental solid layers not only provides information on solid-state kinetic processes, but is also a relatively simple process requiring only modest temperatures (250 °C). Materials with this new form of atomic order and unique symmetry may be found to have beneficial physical properties, and to be useful in components. If applications are discovered for icosahedral phases, this method may provide an easy way to produce the material.

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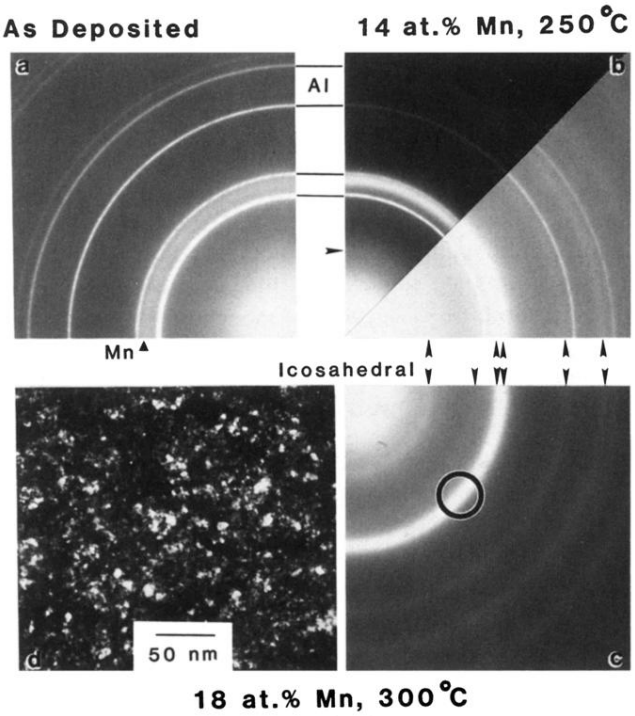

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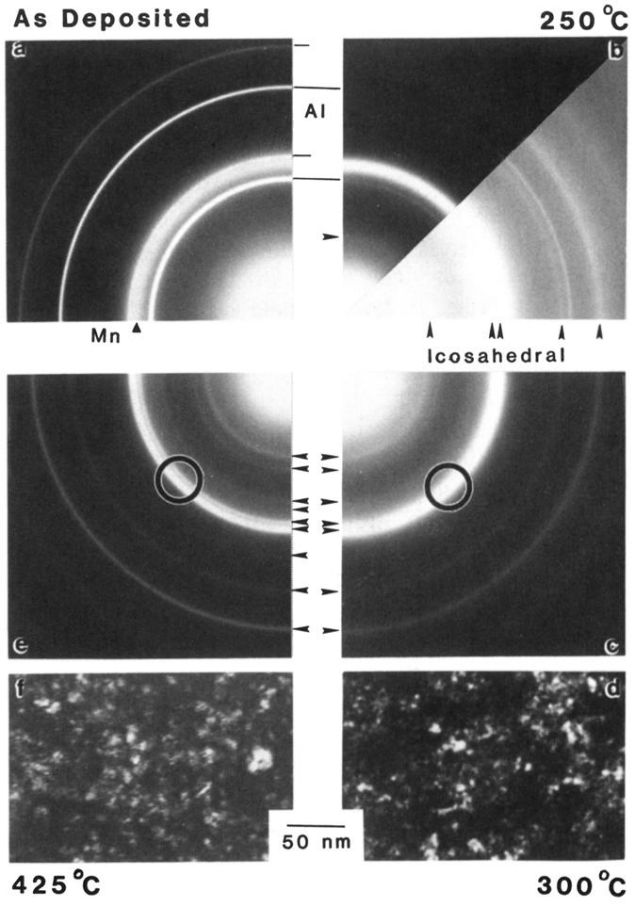

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