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$Mg_{32}(Zn,Al)_{49}$-type icosahedral quasicrystals formed by solid-state reaction and rapid solidification

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Icosahedral quasicrystals of Al-Mg-Zn, Al-Mg-Cu, Al-Li-Zn, and Al-Li-Cu are formed by low-temperature annealing of solid-solution alloys. Comparison is made with icosahedral Al-Mg-Cu, Al-Mg-Zn, and Al-Li-Cu prepared by rapid solidification. The compositions of the icosahedral compounds formed by solid-state reaction are similar to those observed in the rapidly solidified samples. The stability of these new phases is discussed. X-ray line intensities are found to agree well with the computed intensities for a quasicrystalline model based on the (Mg-Zn-Al)-type decoration of the three-dimensional Penrose tiles.

Recently, the synthesis of icosahedral quasicrystals[1,2] by solid-state reaction[3–6] has added impetus to the fundamental studies of formation and stability of this novel class of metallic alloys. Earlier, we reported formation of icosahedral particles via a nucleation and growth process at the grain boundaries of Al-Cu-Li host alloys.[4] Based on the value of the quasilattice constant and the existence of the $Mg_{32}(Al,Zn)_{49}$-type Frank-Kasper phase[7–9] (or the *R* phase according to Hardy and Silcock[10]) in the Al-Li-Cu system, it was suggested that the structure of icosahedral particles belonged to the Mg-Al-Zn class of atomic decoration of the quasilattice.[9]

The structural similarities between the Frank-Kasper phase in the Al-Li-Cu system and corresponding structures found in the systems Al-Li-Zn, Al-Mg-Cu, and Al-Mg-Zn (Ref. 8) raises the question as to whether icosahedral phases are also formed in those host alloys. In fact, a hierarchical Frank-Kasper phase with long-range icosahedral order was discussed by Nelson and Sachdev.[11] Earlier, icosahedral phases were observed in the thin regions of melt-spun Mg_4CuAl_6 (Ref. 12) and $Mg_3Zn_3Al_2$ (Ref. 13) alloy samples. The formation of metastable alloys by rapid solidification and solid-state reaction can involve different thermodynamical driving forces. An example is seen in the area of metallic glasses.[14] It is thus important to compare the compositions of icosahedral phases produced by the two different methods, especially when stoichiometry appears to be important for these new phases.[9,15] From a structural point of view, it is particularly interesting to compare the x-ray diffraction patterns among the various icosahedral phases with different equilibrium Frank-Kasper phases. Recently, Knowles and Stobbs[16] computed x-ray line intensities of quasilattices based on the Al-Mn–type and Mg-Al-Zn–type decorations of the three-dimensional Penrose tiles. These results revealed significant differences in the diffraction patterns of the corresponding icosahedral phases. In this paper, we report new experimental work in the area of solid-state reaction and rapid solidification involving icosahedral phases. Several important issues outlined above will also be addressed.

We prepared three ternary alloys of Al-Mg-Cu, Al-Mg-Zn, and Al-Li-Zn. The compositions are listed in Table I. Results on Al-Li-Cu have been reported in Ref. 4. The ingots were made by casting the melt into a water-cooled copper mold which provided a sufficient cooling rate to produce a compositionally homogeneous crystalline ingot of solid-solution alloy. The ingots were subsequently

TABLE I. Alloy compositions, lattice parameters, and transformation temperatures of icosahedral phases formed by solid-state reaction studied in this work. The ellipsis in column two represents concentration not determined. See text for comparison with melt-spun samples. Quasilattice constants are evaluated following the scheme of V. Elser, Phys. Rev. B **32**, 4892 (1985). In the left column, the numbers are the concentrations of each element in at. %.

Alloys (at. %)	Average composition of I phase	Quasilattice constant (Å)	Transformation (I → FK) temperature (°C)	Lattice parameter (Å) of FK phase
Al–9 Li–1 Cu	$(Al_{5.5}Cu_1)_{100-x}Li_x$	5.07	>500	13.91
Al–8 Li–2 Zn	· · ·	5.24	>400	14.00
Al–5 Mg–1 Cu	$Al_{52}Cu_{12}Mg_{36}$	5.21	~250	14.35
Al–10 Mg–2 Zn	$Al_{52}Zn_{9.5}Mg_{38.5}$	5.28	~250	14.22

annealed at various temperatures (190 °C for 100 h to 460 °C for 24 h) and examined by transmission electron microscopy (TEM). Compositions of elements, except Li, in the icosahedral particles (size 1–10 μm) were determined by energy-dispersive x-ray analysis.

The Al-Mg-Zn and Al-Mg-Cu alloys were examined following isothermal annealing at 190 °C/100 h, 250 °C/24 h, and 300 °C/24 h. After 100 h at 190 °C the grain boundaries exhibit a large number of icosahedral (I) particles which are about 1–3 μm in length [Figs. 1(a) and 1(b)]. In the Al-Mg-Cu alloy, the $Mg_{32}(Al,Cu)_{49}$ Frank-Kasper (FK) phase appears as smaller spherical particles at the icosahedral-phase–matrix interface. Isothermal annealing at higher temperatures (~250 °C for 24 h) results only in the formation of the FK particles which exhibit a roughly spherical morphology at the grain boundaries. Such findings suggest that the icosahedral phase is a metastable phase. The transformation temperatures (I→FK) were also determined for the melt-spun samples and were found to be similar to those observed in the solid-solution samples, as will be discussed later. Their values are listed in Table I. The icosahedral phase in the Al-Li-Zn system is observed in two distinct precipitate morphologies, either as long plates which nucleate at high-angle grain boundaries and grow outward into the matrix or as larger, more spherical particles which nucleate and grow on low-angle boundaries. An example of this spherical morphology is shown in Fig. 1(c) for an alloy aged 100 h at 190 °C. Because the icosahedral phase in this system has never been previously reported, Fig. 2 illustrates the five-, three-, and twofold axes using convergent-beam electron diffraction. Higher magnification of the large particle seen in Fig. 1(c) reveals the presence of the Al-Li-Zn FK phase precipitate on the icosahedral-phase–matrix interface.

The phase field of the icosahedral particles in the Al-Mg-Cu alloy is sketched in Fig. 3. That for the Al-Mg-Zn alloy was found to center around $Mg_{38.5}Zn_{9.5}Al_{52}$ with a similar compositional range as in the Al-Mg-Cu system. A reliable estimate of the chemical composition of the Al-Li-Zn icosahedral-phase particles was not possible due to their overlapping with other phases. The Al-Cu ratio for the Al-Li-Cu icosahedral phase is ~5.5/1 (Ref. 4). The quasilattice constants for the I phases and lattice constants for the FK phases determined from electron-diffraction patterns (also from x-ray diffractions for the Al-Mg-Cu, Al-Mg-Zn, and Al-Li-Cu systems) are listed in Table I. The observed trend in quasilattice constants is consistent with the variation in atomic size and composition of the different alloy systems.

Using the compositions determined for I phase particles in Al-Mg-Cu and Al-Mg-Zn, we have prepared melt-spun samples of the two systems over an extended compositional range (Al-Mg-Cu shown in Fig. 3). Structures were examined by TEM and x-ray (Cu $K\alpha$) diffraction. For the Al-Mg-Cu system, samples containing a single I phase can be obtained (Fig. 3). The x-ray diffraction pattern is shown in Fig. 4. It is noteworthy that the compositional range of these samples is similar to that observed in the I phase particles formed by solid-state reaction. For the Al-Mg-Zn system with compositions near $Al_{53}Zn_9Mg_{38}$, samples containing a single I phase cannot be obtained.

(a)

(b)

(c)

FIG. 1. Transmission electron micrograph for (a) Al–10Mg–2Zn, (b) Al–5Mg–1Cu, and (c) Al–8Li–2Zn solid-solution alloys heat treated at 190 °C for 100 h showing icosahedral particles at the grain boundaries. In (b), the Frank-Kasper phase particles formed at the icosahedral particle-matrix interface are arrowed.

We define the best samples as those containing the largest I phase to FK phase volume ratio (~1:1) as determined by TEM and x-ray diffraction. It is found that the I phase and FK phase have the same compositions in these samples, implying that samples containing single I phases can be produced at enhanced cooling rates. These best compositions also fall in the range of those found in solid-state reaction. We have also investigated the Al-Li-Cu system

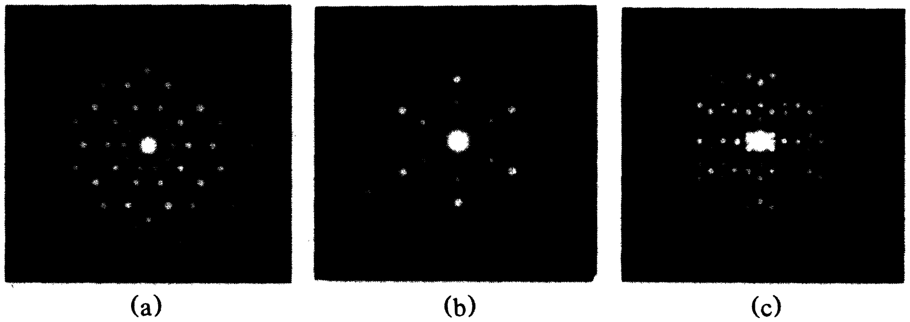

FIG. 2. Electron-diffraction patterns for (a) fivefold axis, (b) threefold axis, and (c) twofold axis of Al-Li-Zn icosahedral particle.

near the composition Al_6CuLi_3. Melt-spun ribbons containing ~85% volume fraction of I phase and ~15% volume fraction of Al were obtained. The I phase crystallites were found to have an Al-Cu ratio of 5.5 to 1, in agreement with our earlier results on icosahedral Al-Li-Cu particles formed by solid-state reaction.[4] The I phase crystallites in all the melt-spun samples are ~0.2–0.5 μm in size.

For metallic glasses synthesized by the two methods discussed here, different compositional ranges of glass formation were usually noted.[14] This is due to the fact that in solid-state reaction, the lowering of the free energy of the glass with respect to the unreacted components provides the driving force for glass formation. On the other hand, glass formation by rapid solidification is determined by the degree of undercooling which is maximized near the eutectic composition. In view of the present results, it appears that the formation of icosahedral phases is mainly determined by the free energy of the quasicrystalline structures. Despite the fact that Cu and Zn can easily substitute Al, the phase fields of icosahedral quasicrystals are narrow in comparison with those of metallic glasses. This suggests that the shape of the free energy curve of the I phase may resemble that of an intermetallic compound.

The x-ray line intensities for icosahedral $Al_{51}Cu_{12.5}$-$Mg_{36.5}$ (Fig. 4) are significantly different from those of icosahedral Al-Mn (Ref. 17) and Pd-U-Si (Ref. 15). Here, we use the indexing scheme of Ref. 17. Then, most noticeably, the strongest peak is now at (110000) instead of (100000). The (111101) peak which barely shows up in other I phases is now quite strong. The x-ray pattern for icosahedral Al-Li-Cu shows similar features. Knowles and Stobbs[16] have recently computed intensities of the diffracted beams of kinematic electron diffraction patterns of modeled quasicrystals with different atomic decoration of the Penrose tiles. The intensities which are computed for different symmetry axes are more appropriate for comparison with x-ray diffraction experiment since multiple diffraction can alter the relative intensities of electron-diffraction peaks. Different results are obtained for the different quasicrystalline models.[9] The strongest peaks are at (100000) and (110000) for icosahedral Al-Mn and Al-Mg-Zn, respectively. The (111101) peak is also predicted to be quite strong for the Al-Mg-Zn–type decoration of

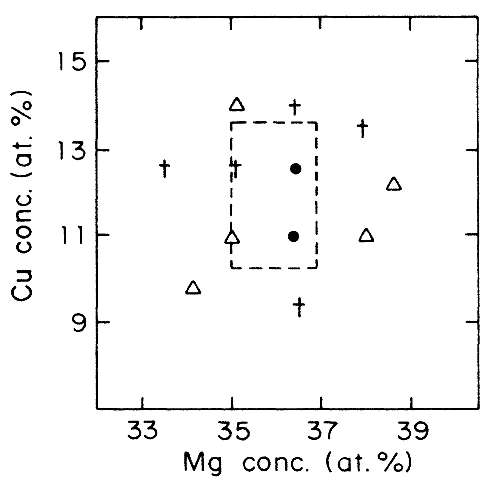

FIG. 3. Region enclosed by dashed borderline represents compositional range of Al-Mg-Cu I-phase particles formed by solid-state reaction. Compositions of melt-spun samples containing I phase are represented by ● for samples containing single I phase, + for those containing ~5% volume fraction FK phase, and Δ for those containing ~10% volume fraction FK phase.

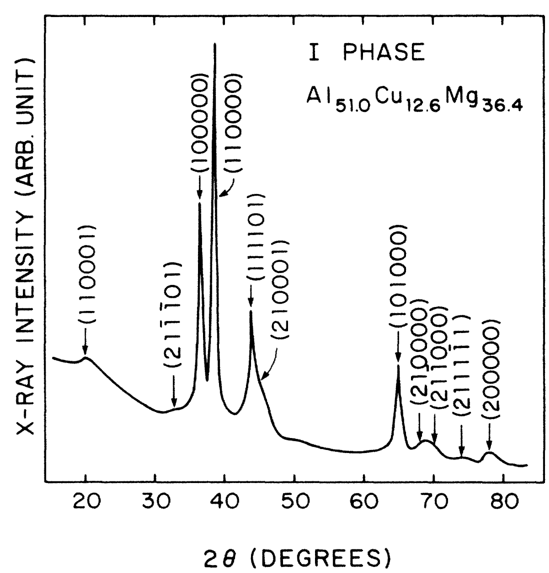

FIG. 4. X-ray diffraction pattern of I-phase $Al_{51.0}Cu_{12.6}$-$Mg_{36.4}$.

quasilattice. The computed results [available only up to the (101000) peak] are compared with experiment as shown in Fig. 4. Qualitative agreement is achieved except for the (110001) peak, where the computed intensities are found to be stronger than those observed in all I phases studied so far.

In summary, it is found that the $Mg_{32}(Al,Zn)_{49}$-type icosahedral quasicrystals can be synthesized by solid-state reaction and rapid solidification. The systems chosen for this study are Al-Li-Cu, Al-Li-Zn, Al-Mg-Cu, and Al-Mg-Zn. The compositions of the icosahedral phases prepared by the two methods are found to be similar. This, together with the relatively narrow phase fields as compared with metallic glasses lends support to the notion that stoichiometry plays an important role in the formation of icosahedral quasicrystals. The x-ray line intensities compare favorably with computed results based on the Al-Mg-Zn-type decoration of the quasilattice.

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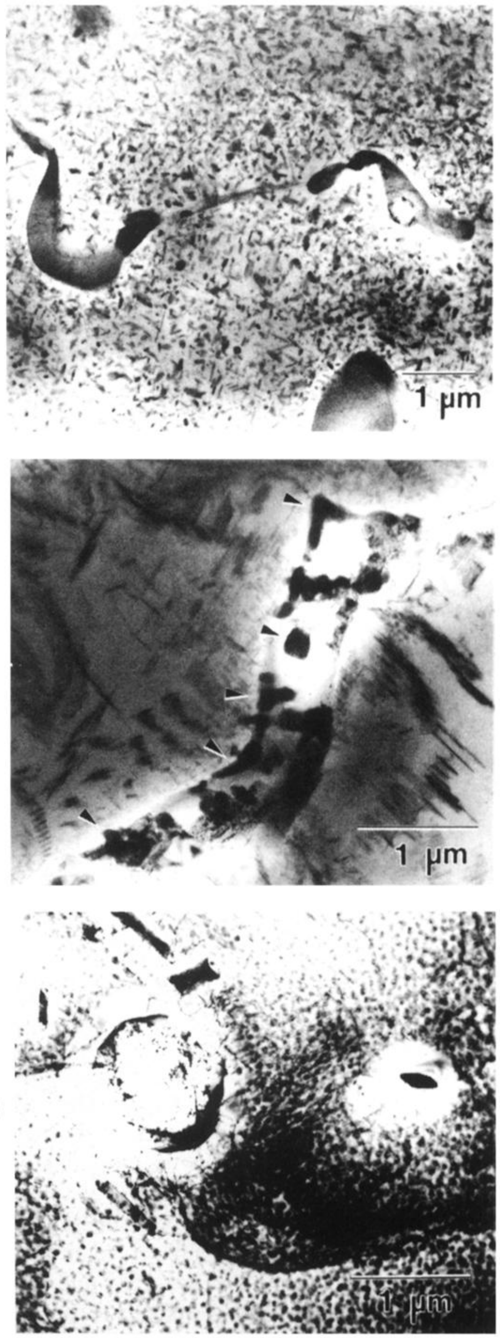

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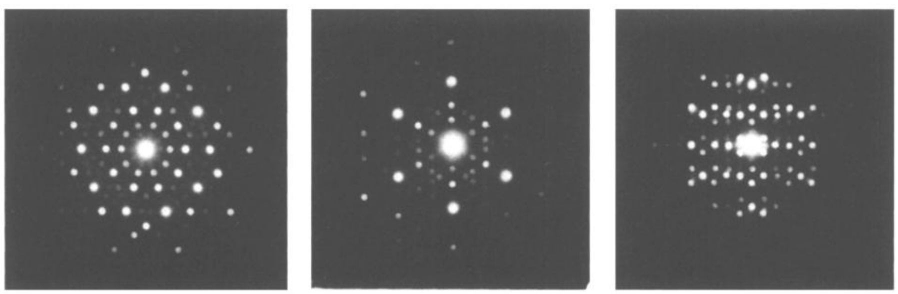

(a) (b) (c)

FIG. 2. Electron-diffraction patterns for (a) fivefold axis, (b) threefold axis, and (c) twofold axis of Al-Li-Zn icosahedral particle.