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A basis for the synthesis of quasicrystals

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Abstract. It has been established that quasicrystals with icosahedral point group symmetry occur in a rapidly solidified Mg_{32} (Al, Zn)$_{49}$ alloy chosen on the basis of its equilibrium crystal structure. This alloy has a natural tendency to form icosahedral atomic clusters stabilised by size difference amongst constituent atoms. Results highlight the relationship between equilibrium crystal structure and the tendency to form quasicrystals.

Keywords. Quasicrystals; rapid solidification, ternary aluminium-zinc-magnesium alloy.

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Shechtman *et al* (1984) have reported the existence of a solid metallic phase with icosahedral point group symmetry in rapidly solidified Al alloys with 10–14 at.% Mn, Fe or Cr. The phase has no translational order but possesses long-range orientational order. The observation has spurred hectic theoretical and experimental activity. For brief reviews Maddox (1985) and Heiney (1985) may be consulted. Levine and Steinhardt (1984) termed such phases as quasicrystals. Hitherto, it has been postulated that the icosahedral point group symmetry either arises from long range quasicrystalline order or from multiple twinning and the experimental studies have been based on rapidly solidified Al-Mn alloys (Chattopadhyay *et al* 1985; Field and Fraser 1984–85; Parthasarathy *et al* 1985 and references therein). We report here the observation of a similar phase in a rapidly solidified ternary alloy, Mg_{32} (Al, Zn)$_{49}$.

Our choice of the alloy was dictated by a consideration of its crystal structure which is based on the body-centred cubic (b.c.c.) lattice with 162 atoms in unit cube (Bergman *et al* 1957). Large clusters of atoms which pack with 5·3·2 symmetry properties and which are stabilised by size and valency differences are found at the centre and vertices of the b.c.c. lattice. Each lattice point is occupied by an atom which is in turn surrounded by 12 atoms located at vertices of an icosahedron. Twenty atoms are then placed out from centres of the 20 faces of the icosahedron. These define the vertices of a pentagonal dodecahedron. Twelve more atoms are also located at the centres of the pentagonal faces of the dodecahedron. The 32 atoms in the third sphere of aggregation together define the vertices of a rhombic triacontahedron. Location of a further 60 atoms at the rate of two per face of the triacontahedron leads to the atomic grouping defining the vertices of a truncated icosahedron. The last 12 atoms of the cluster are situated at the mid-points of 12 of the 20 hexagonal faces of the truncated icosahedron. The cluster thus has 117 atoms in all. Of these, the outermost 72 atoms of the cluster lie on the faces of a cubooctahedron. In this alloy, the smaller Al and Zn atoms form the inner spheres and the larger Mg atoms form the outer spheres of the icosahedrons at the centre of each cluster. Thus, all the 98 atoms of Al and Zn in the unit cell have icosahedral coordination. In addition to these 98 icosahedra, the unit cell contains 40 Friauf polyhedra and 24 other irregular polyhedra with coordination numbers of 14 and 15 (Pearson 1972). Besides, some transfer of valence electrons from Zn to Al and Mg has also been considered possible and can be expected to stabilise the icosahedral packings.

The 72 atoms in the outermost shell of each cluster are shared by neighbouring complexes and facilitate aggregation in b.c.c. lattice positions. Evidently, the clusters which basically have a 5·3·2 symmetry thus subordinate their 5-fold symmetry to the 4- and 3-fold symmetries so that they can pack themselves into the b.c.c. lattice. If rapid solidification techniques are employed to prevent the crystalline aggregation of these clusters, the 5·3·2 symmetry will show up provided the clusters form either fully or partially. We argue that the inherent tendency to form icosahedral clusters and their relative stability owing to size and electronegativity differences amongst the constituent atoms make the Mg_{32} (Al, $Zn)_{49}$ phase an appropriate candidate for yielding quasicrystals on rapid solidification. Our results fully support these arguments.

The alloy was prepared from high purity (> 99·99 at.%) constituent elements by melting them in desired proportion in an evacuated and sealed quartz tube. Microstructural observations on the resultant alloy showed that the ingot has a single phase and is homogeneous. The alloys were then melt spun under an argon cover into about 1 cm long and 2 mm wide flakes. The resultant foils had several large electron transparent regions and were consequently examined, without further preparation, using a JEOL 200 CX electron microscope.

The microstructures of the transparent regions varied as a function of their thickness. The most transparent regions had an average grain size of 2 μm while the grains were 2–3 times larger in the relatively thicker regions. These are essentially nodular in nature (figure 1a) and appear to be having several sectors defined by lines drawn from a central point within each nodule (figure 1b). These sectors are well delineated when they are in diffraction contrast. Diffraction patterns from these grains were recorded with particular emphasis being placed on the determination of point group symmetry. It was observed that the 5·3·2 symmetry characteristic of the clusters was exhibited by these sectors in each case. Figure 2 shows the selected area diffraction patterns obtained from one of the grains. To start with, the plane of the foil was normal to a 2-fold axis. The diffraction patterns showing 3-fold and 5-fold rotational symmetry were obtained on tilting the foil through 20·9° and 58·3° respectively from the initial condition. The symmetry elements thus confirmed the presence of quasicrystals with icosahedral point group symmetry. In the bright field condition, regions with 5-fold symmetry axis being parallel to the electron beam exhibited the maximum diffraction contrast. When the same were oriented with the 3-fold and 2-fold axes parallel to the beam, the contrast progressively decreased. In dark field and when viewed along the 2-fold axes, the regions show fine particulate appearance.

The number and nature of the 2-fold symmetry patterns help establish the type of polyhedra and their aggregation. In our case, the diffraction pattern showing 2-fold symmetry varied considerably. We could record patterns similar to those reported by earlier investigators and attributed to vertex and edge-modelled icosahedra. Patterns exhibiting 2-fold symmetry but different from figure 2c are reproduced in figure 3.

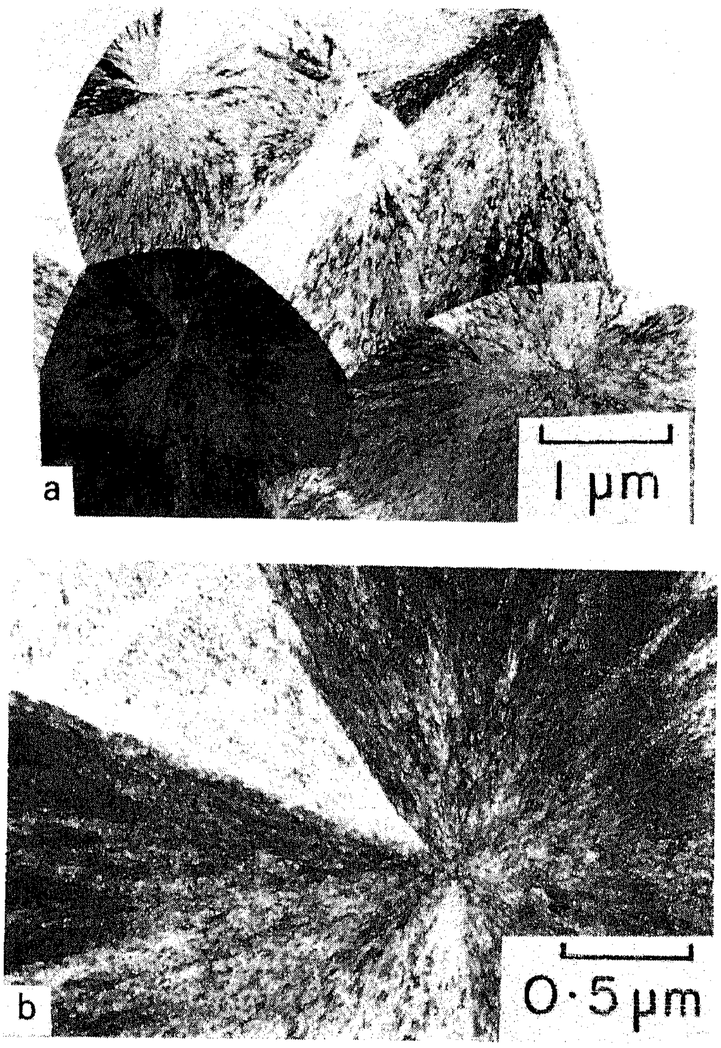

Figure 1. Microstructure of rapidly solidified $Mg_{32}(Al, Zn)_{49}$ alloy showing (**a**) grains with nodular appearance and (**b**) a magnified grain showing different sectors in diffraction contrast.

Besides the icosahedron, there are several other polyhedra belonging to the 5·3·2 symmetry family. Some of these are the dodecahedron (a dual of icosahedron), icosidodecahedron, rhombic triacontahedron, etc. Of these, the last named is of particular significance. It is composed of 10 acute and 10 obtuse rhombohedra and is the three-dimensional analogue of the decagon in the two-dimensional Penrose lattice (Mackay 1982). It may be recalled that it is also an intermediate state in the clustering of atoms in Mg_{32} (Al, $Zn)_{49}$ phase. Work is in progress to establish the stereographic projections of the symmetry elements of a large number of sectors in the nodular grains to explore the possibility of some of these polyhedra being present. Such analysis may also be expected to throw light on the extent of clustering during rapid solidification.

A distinguishing feature of the microstructure in rapidly solidified Mg_{32} (Al, $Zn)_{49}$ alloy is that the electron transmitting regions of the foil are entirely composed of grains exhibiting 5·3·2 symmetry (figure 1a). This is in contrast to the case of rapidly solidified Al-Mn alloys in which the precipitates with this symmetry are embedded in an aluminium matrix. As a consequence, our foils are extremely brittle.

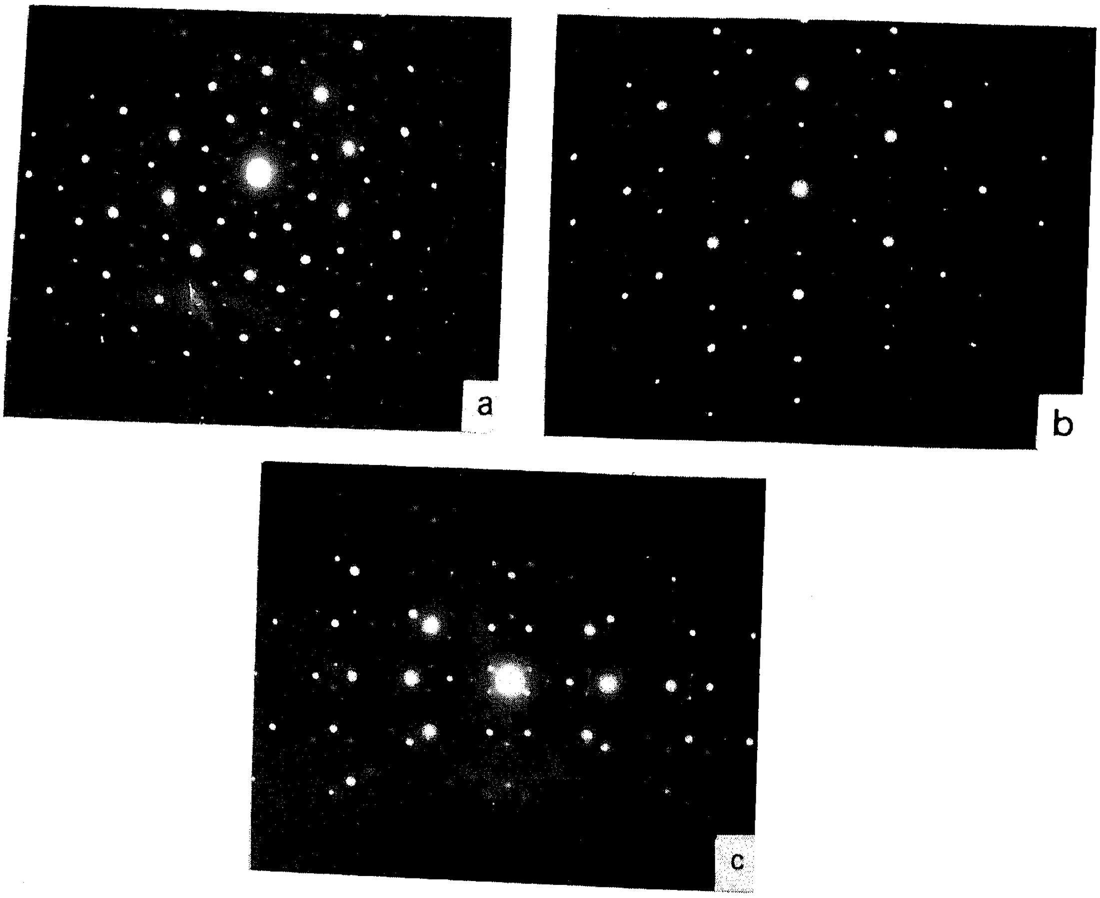

Figure 2. Selected area diffraction pattern from a typical grain of rapidly solidified $Mg_{32}(Al, Zn)_{49}$ alloy. (**a**)–(**c**) show diffraction patterns characterising (**a**) 5-fold (**b**) 3-fold and (**c**) 2-fold rotational symmetry.

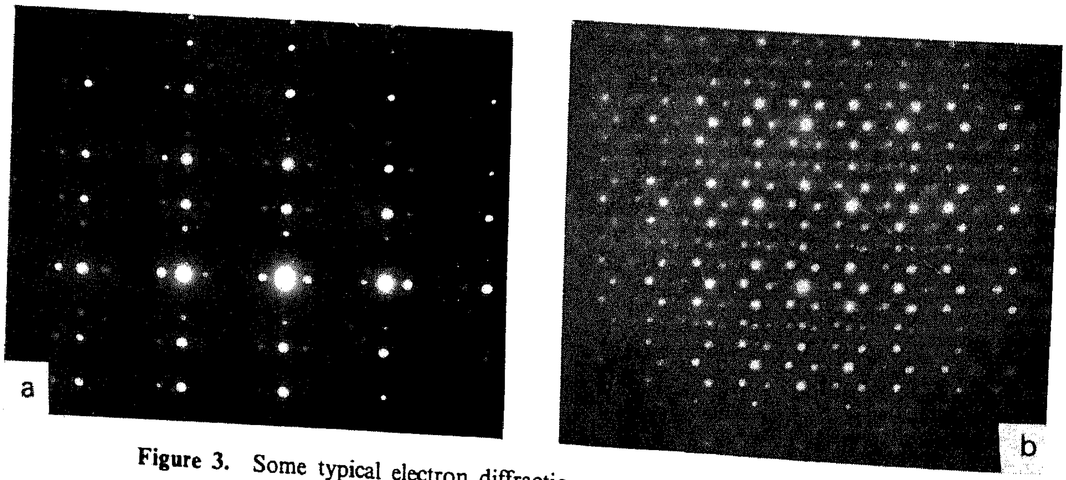

Figure 3. Some typical electron diffraction patterns corresponding to 2-fold rotational symmetry in a rapidly solidified Mg_{32} (Al, Zn)$_{49}$ alloy.

Occasionally, the foils studied showed an interesting microstructure wherein small, well-defined and distinct features were found at the centres of the nodular grains (figure 4). Diffraction analysis has shown that these are perfectly crystalline. Diffraction

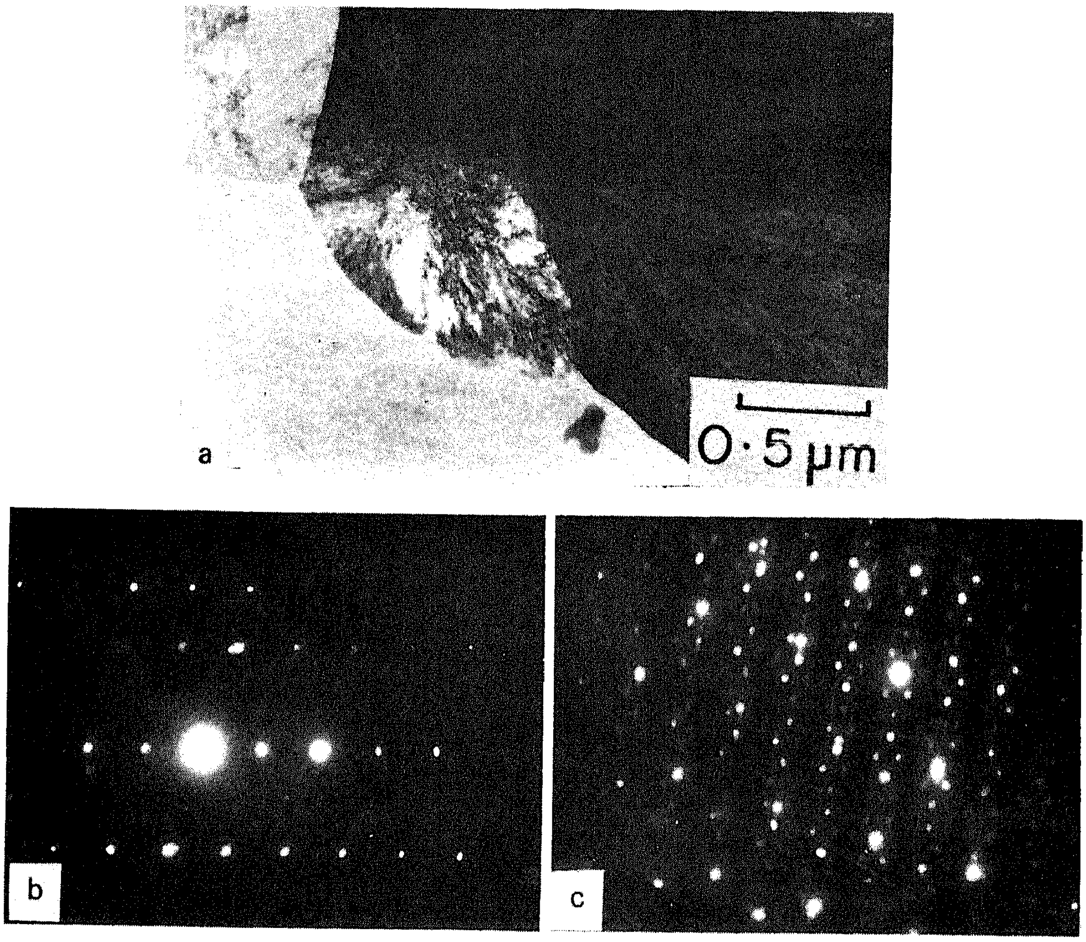

Figure 4. Quasicrystalline regions coexisting with perfect crystals in rapidly solidified $Mg_{32}(Al, Zn)_{49}$ alloy. (**b**) shows the diffraction patterns from the perfect crystal while (**c**) taken from the interface region has both crystalline and quasicrystalline diffraction patterns superimposed on each other.

patterns obtained from the surrounding regions are characteristic of quasicrystals. Such a microstructure could have arisen either during the formation of the tape or on its subsequent ageing. Experiments are in progress to ascertain their origin.

Field and Fraser (1984–85) have shown that the observed 5·3·2 symmetry can be attributed to the presence of an icoshedron generated by the (111) planes of 20 twin related rhombohedrally distorted cubic crystals. As discussed by these authors, such icosahedra do occur in vapour deposited films but consist only of 20 crystallites. Existence of long range 5·3·2 symmetry demands a highly correlated twinning process. It is likely that periodic twinning over extremely closely spaced intervals, as opposed to multiple twinning, will provide the necessary correlations. Preliminary structure imaging studies have shown the presence of such periodic twinning and this aspect is currently under investigation.

The present study points out the possibility of tailoring alloy compositions for generating and studying quasicrystals on the basis of the equilibrium crystal structure. Several other ternary alloys are isostructural with $Mg_{32}(Al, Zn)_{49}$. Besides a large family of intermetallic compounds dominated by icosahedral packing exist (Pearson

1972). All these may yield quasicrystals on rapid solidification and lead to a better understanding of these novel phases. Such a possibility is being explored and 5·3·2 symmetry polyhedra have already been established in the rapidly solidified isotypic alloy $Mg_4(Cu, Al)_6$ (Sastry *et al* 1985). Help extended by the National Electron Microscope Facility funded by the Department of Science and Technology, Government of India is gratefully acknowledged. We thank Professors S. Ranganathan and E. S. Raja Gopal and Dr. K. Chattopadhyay for making available preprints of their work.

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