Formation of Quasicrystalline Particles in an Isothermally Aged Al-10 Mg-0.5 Ag (mass%) Alloy

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The trace additions of Ag to binary Al-Mg alloys promote precipitation of a phase in the under-aged condition. The structures of the phase in an Al-10 Mg-0.5 Ag (mass%) alloy have been characterised using transmission electron microscopy and electron microdiffraction. An icosahedral quasicrystalline phase, which is identified by the electron microdiffraction patterns, has been found in the Al-10 Mg-0.5 Ag (mass%) alloy after solution treatment, water quenched and then aged during the time between 20 and 40 min. at 240°C. The orientation relationship between the quasicrystalline phase and the α-Al matrix is as follows; i5 // ⟨011⟩α and i3 // ⟨111⟩α. A uniform distribution of finer-scale (typically 20 nm), faceted precipitate particles was observed within the core of the grains, but the precipitates became coarser (60–80 nm) approaching the grain boundary precipitate-free zone.

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1. Introduction

Since the first remarkable discovery of the icosahedral quasicrystalline phase in the rapidly solidified Al-14 at% Mn alloy was made by Shechtman et al.,1 intensive investigations have been carried out to explore the alloy systems with compositions for the formation of icosahedral phases and to identify structures and their relationships with the crystalline phases.2 Icosahedral quasicrystalline phases have been found in several alloy systems, especially Al-transition metals based alloys, which are generally produced by rapid quenching3 and/or mechanical alloying4 techniques. Great progress on understanding of the structure of icosahedral quasicrystalline phases was made by recognising5,6 that there are two major classes of icosahedral quasicrystals, such as Al-Mn-Si7 and Mg-Al-Zn8 types. These types are described in terms of quasi-periodic arrangements of the Mackay icosahedral clusters in Al-Mn and Al-Mn-Si alloys and Pauling triacontahedral clusters in Mg-Al-Zn and Al-Cu-Li alloys.

A stable ternary compound in the Al-Cu-Li alloy, formerly designed as T2 (Al4CuLi3) by Hardy and Silcock,9 has been found to exhibit an icosahedral quasicrystal structure when the alloy was produced by either conventional casting with low solidification rates (formed as dendrites) or subjected to isothermal ageing treatments of supersaturated solid solution (formed as precipitates).10 However, the intrinsic strengthening effect of T2 phase is very low on an Al-2.1 Li-2.1 Cu-1 Mg (mass%) alloy heated at 250°C.11 Formation of an icosahedral quasicrystalline phase in an Al-9 Li-1 Cu-0.05 Zr (at%) alloy by solid-state reaction was reported that particles at grain boundaries were being nucleation and growth which exhibit five-fold symmetry.12

The crystal structure of the stoichiometry phase Mg232(Al,Zn)40 was shown to have a cubic crystal structure based on a body centred cubic lattice with 162 atoms,8 which are a classic example of a close-packed structure dominated by icosahedral coordination shells.13 It has been suggested that equilibrium phases having a high proportion of icosahedral coordinated atoms can be rapidly solidified from the melt into the icosahedral quasicrystalline phases.14 Based on the value of the quasilattice constant and existence of Mg32(Al,Zn)49 type Frank-Kasper phase in the Al-Mg-Zn system, it has been suggested that the structure of icosahedral phase belonged to the Mg-Al-Zn class of atomic decoration of the quasicrystal lattice.5 Trace additions of Ag are known to stimulate the precipitation behaviour in all Al alloys containing Mg, with an acceleration in the kinetics of the age-hardening response and an increase in the maximum hardness achievable.15 Polmear and Sargent first found that the age-hardening response in the Al-Mg alloys was remarkably improved by small concentrations of Ag, and the precipitates were very finely distributed in the matrix.16 Wheeler et al. proposed that peak hardness in the ternary Al-Mg-Ag alloy can be associated with fine scale precipitates of a T phase, Mg32(Al,Ag)49 (space group Im3, body-centred cubic structure, a = 1.416 nm),17 rather than precipitation of the β phase, Al3Mg2 (space group Fd3m, face-centred cubic structure, a = 2.824 nm).18,19 However, all characterisation work has to date involved mainly indirect experimental methods, such as X-ray diffraction techniques. It thus remains that precipitate microstructures and precipitate phases during isothermal ageing are not thoroughly and convincingly understood.

The purpose of this paper is to report results of a microstructures examination of the quasicrystalline precipitates phase formed by isothermal ageing process but without employment of rapid solidification in the process. Identification of the quasicrystalline precipitates was carried out using the transmission electron microscopy with the electron diffraction techniques.

2. Experimental Procedures

An alloy of the nominal composition Al-10 Mg-0.5 Ag...
(mass%) was prepared from Al (99.96%), Mg (99.9%) and Ag (99.9%) by induction heating under an air atmosphere and casting into a mild steel mould. The Mg was added just prior to pouring in the mould in order to prevent any loss of oxidation. After these ingots were homogenised for 52 h at 300°C, surfaces of the ingots was scalped each side. These ingots then were hot rolled to approximately 0.3 mm for TEM specimens.

Solution treatment for ageing was carried out in a salt bath at 500°C for 1 h, water quenched and then ageing in an oil bath for 20, 30 and 40 min at 240°C.

The specimens for TEM observations were punched mechanically from the strips of 0.3 mm in thickness after appropriate heat treatments, then dry grounding to a thickness of 0.1–0.15 mm. These thin foils were prepared by twin-jet electropolishing in a solution of 33 vol% nitric acid and 67 vol% ethanol at temperature range between 0°C and –10°C, using a Tenupol-3 jet polisher operating at 0.2 A and 12 V.

Microstructures were observed by a Philip CM20 transmission electron microscope (TEM) at 200 kV. Microbeam electron diffraction patterns were recorded by conventional TEM mode using a 30 μm condenser lens aperture and an electron probe 40–100 nm.

3. Experimental Results

The bright field (BF) images of the precipitate particles in the Al-10 Mg-0.5 Ag (mass%) alloy aged 0.5 h at 240°C, together with the corresponding SAED patterns, are shown in Fig. 1. The electron beam is the approximately parallel to the (110)\textsubscript{\textit{c}} orientation. The regions close to the grain boundary (Fig. 1(a)) contained evidence of a precipitate-free zone (PFZ) and the coarse-scale, faceted precipitate particles adjacent to that zone. The precipitate became coarser (60–80 nm) approaching the grain boundary precipitate-free zone. The coarser distribution adjacent to the PFZ presumably reflects a lower nucleation rate in these regions, perhaps arising from a combination of a depleted solute and a reduced vacancy concentration. A uniform distribution of much finer-scale (typically 20 nm), faceted precipitate particles was observed within the core of the grains, (Fig. 1(b)), suggesting that such precipitate particles are homogeneously nucleated from the supersaturated solid solution of the aluminium matrix during isothermal ageing treatment. The refined scale of these precipitate particles implies a higher nucleation rate. In order to first assess whether the crystal structure of these precipitate particles of different scale within these different regions were the same, or not, selected area electron diffraction (SAED) patterns were taken from representative regions (a) adjacent to grain boundary and (b) at core of grain in the Al-10 Mg-0.5 Ag alloy aged 0.5 h at 240°C. The electron beam is the approximately parallel to a (110)\textsubscript{\textit{c}} direction.

![Fig. 1 Transmission electron micrographs showing the morphologies of faceted precipitate particles with different distributions recorded from regions (a) adjacent to grain boundary and (b) at core of grain in the Al-10 Mg-0.5 Ag alloy aged 0.5 h at 240°C. The electron beam is the approximately parallel to a (110)\textsubscript{\textit{c}} direction.](image)

![Fig. 2 BF images recorded in different two-beam diffraction conditions. The operating vectors \( \mathbf{g} \) are (a) [1\( \text{I} \)]\textsubscript{\textit{c}} and (b) [2\( \text{I} \)]\textsubscript{\textit{c}}, with the electron beam parallel to [0\( \text{I} \)]\textsubscript{\textit{c}}.](image)

... images were taken under different two-beam diffraction conditions, and these are shown in Fig. 2. The operating vectors \( \mathbf{g} \) were (a) [1\( \text{I} \)]\textsubscript{\textit{c}} and (b) [2\( \text{I} \)]\textsubscript{\textit{c}} in the [0\( \text{I} \)]\textsubscript{\textit{c}} zone axis pattern. Precipitate particles with both diamond-shaped profiles and rectangular projected images were observed. It is noteworthy that these particles were generally associated with a little strain field (coherent elastic strains), which is clearly indicated (arrows) in Figs. 2(a) and (b). The strain fields associated with those precipitate particles formed during isothermal ageing processes may provide an increase of the hardness in the ternary Al-10 Mg-0.5 Ag (mass%) alloy. A similar type of morphology and distribution of the precipitate particles were observed in the sample aged 20 and 40 min at 240°C.
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A series of microbeam electron diffraction patterns (Fig. 3(a)–(f)) recorded from a single large scale (~50 nm) diamond-shaped particle in the Al-10 Mg-0.5 Ag alloy aged 0.5 h at 240°C.

4. Discussion

It is now well known that selected area electron diffraction (SAED) patterns recorded from isocohedral quasicrystalline phases display two-fold, three-fold and five-fold rotational symmetry with the golden ratio, which is a non-uniform scaling factor equal to the characteristic number of icosahedral quasiperiodicity $\tau = (1 + \sqrt{5})/2 = 2 \cos(\pi/5) = 1.618$. The microbeam electron diffraction patterns presented in Figs. 3(d), (c) and (b) clearly demonstrated two-fold, three-fold and five-fold rotational symmetry with the golden ratio, respectively. It has been described that a quasicrystalline phase can be characterised by a quasilattice constant $a_\text{Q}$ which corresponds to the edge length of the rhombohedra (either prolate or oblate) that must be packed quasi-periodically to form three-dimensional Penrose tiling. Since the three-dimensional Penrose tiling structure can be generated by projections from a six-dimensional simple-cubic lattice, the cubic lattice constant $a_c$ and the value of $a_\text{Q}$ are related, and this relationship may be expressed in the form $a_c = (4 + 8/\sqrt{5})^{1/2}a_R$. From the presently observed microdiffraction patterns, the quasilattice constant $a_\text{Q}$ of icosahedral phase may be estimated from an expression of the form $a_\text{Q} = \tau^2 d_{\text{SAED}}/2$, where $\tau$ is the golden mean, and $d_{\text{SAED}}$ represents the spacing of planes perpendicular to the five-fold axis giving rise to the most intense diffracted beams. Careful measurements for the $d_{\text{SAED}}$ value in the present 5-fold electron microdiffraction patterns gave a value of $a_\text{Q} = 0.505 \pm 0.01$ nm. The lattice parameter $a_c$ of the corresponding crystalline cubic approximant may be derived from an equation of the form $a_c = (4 + 8/\sqrt{5})^{1/2}a_R$, and is thus

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Comparison of experimental and theoretical tilt angles between major zone axes in matrix and icosahedral precipitate phase.</th>
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<tbody>
<tr>
<td>$\alpha$-matrix</td>
<td>$[011]_{\alpha}$</td>
</tr>
<tr>
<td>$\alpha$-Al</td>
<td>5-fold</td>
</tr>
<tr>
<td>$i$-matrix (present research)</td>
<td>63°</td>
</tr>
<tr>
<td>$i$-matrix (Shechtman et al. 1984)</td>
<td>63.43°</td>
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Figures 3(a)–(f) show a series of microbeam electron diffraction (MBED) patterns recorded from a series of relatively large scale, diamond-shaped particles in the Al-10 Mg-0.5 Ag (mass%) alloy aged 0.5 h at 240°C. A regular array of diffraction spots from the precipitate particle is observed in a $(110)_i$ direction (Fig. 3(a)). Most notably, the precipitate pattern in Fig. 3(b), recorded near to a second $(110)_i$ orientation, exhibits five-fold rotational symmetry. The misorientation between the precipitate five-fold axis and the matrix $(110)_i$ axis was experimentally obtained during a large angle tilting experiments, and was approximately 2–4 degrees tilted away from the $(110)_i$ matrix zone axis towards the matrix $(002)_i$ direction. Figure 3(c) exhibits the three-fold rotational symmetry in the precipitate pattern in the $(111)_i$ orientation. The angle of tilt required to move from the axis of five-fold symmetry to that of three-fold symmetry was approximately 37 degrees. Two-fold rotational symmetry is detectable in the precipitate diffraction pattern in the $(112)_i$ orientation, when the specimen is tilted approximately 21 degrees from the $(111)_i$ to the $(112)_i$ zone axis, as shown in Fig. 3(d). Figure 3(e) shows a regular array of diffraction spots from the precipitate particle which is observed in the $(001)_i$ orientation when the sample is tilted from the $(112)_i$ axis of (d) to the nearest $(001)_i$ matrix orientations, while Fig. 3(f) shows a second variant of the five-fold rotational symmetry which is observed in an $(011)_i$ orientation that is 60 degrees from that shown in Fig. 3(b).
calculated to have a value of 1.390 ± 0.028 nm. This is in good agreement with the lattice parameter of the crystalline T phase (a = 1.416 nm).8)

It is to be recognised that crystals with an apparent five-fold axis of symmetry may also occur as a result of multiple twinning, and not as a result of true icosahedral symmetry.20) The faces of a regular icosahedron may be generated by the \{111\}_a planes of an appropriate assembly of twenty twin-related crystals, which have a tetrahedral form defined by facets parallel to \{111\}_a. If a cubic crystal is given a slight rhombohedral distortion (α = 92.88 degrees), then the angle between the \{111\}_a planes is equal to 72 degrees and an assembly of \{111\}_a tetrahedra may be assembled in twin-related orientations to construct an icosahedron. Therefore, it has been proposed that icosahedral and decacwinal quasi-crystals are the result of icostatwin and decatwin assemblies formed from cubic crystals.21) Apparent five-fold symmetry, resulting from multiple twinning, has been observed, for example, in heavily microtwinned particles of the T\textsubscript{T} phase formed in an Al-2.5 Li-1.2 Cu-0.7 Mg-0.1 Zr (mass%) alloy22) as a result of grain boundary precipitate particles formed by over-aged at 325°C after solution treated and water quenched. In the present research, an attempt was made to determine whether these precipitate particles were truly of icosahedral structure or multiply-twinned crystals using high resolution transmission electron microscopy (HRTM).

Although the attempt was largely unsuccessful due to difficulties associated with producing suitably clean and thin specimens of appropriate orientations, very limited experimental observations suggested no evidence of defect microstructures within the particles.

The combinations of those considerations above mentioned and evidence from MBE patterns presented in Fig. 3 would suggested that the sharpness and sphericity of the electron diffraction spots in all three zone-axis diffraction patterns, combined with the observation that all main diffraction spots are perfectly aligned and angles between major row of reflections are as required for the icosahedral symmetry of zone axis, are an indication that the alloy is not a collection of multiple-twinned nanoscale crystallites.23) It is interesting to note that the newly found quasicrystalline metastable precipitate particles appear to be the primary strength phase in the Al-10 Mg-0.5Ag (mass%) alloy aged at 240°C.24–26) This result is a quite important to design the quasicrystalline metastable phase has been firstly observed in the Al-10 Mg-0.5 Ag (mass%) alloy aged 20, 30 and 40 min at 240°C. The uniformly dispersed icosahedral quasicrystalline particles are formed from the supersaturated solid solution (the α-Al phase) by solid-state reaction. The orientation relationship between the icosahedral quasicrystalline phase and the matrix phases has been identified as i5 // \{011\}_α, i3 // \{111\}_α, and i2 and i5 is almost the parallel to \{112\}_α and \{110\}_α with the misorientation of ~3 degrees respectively. This newly found icosahedral phase appeared to be the same orientation relationship reported previously by Shechtman et al.25) This icosahedral quasicrystalline phase belong to the Al-Zn-Mg group confirmed by the quasilattice constant \(a_\text{q} = 0.505 ± 0.01\) nm. The six-dimensional simple-cubic lattice, the cubic lattice constant \(a_\text{c}\) has a value of 1.390 ± 0.028 nm. This is in good agreement with the lattice parameter of the crystalline T phase (a = 1.416 nm).8)

5. Conclusions

The icosahedral quasicrystalline metastable phase has been firstly observed in the Al-10 Mg-0.5 Ag (mass%) alloy aged 20, 30 and 40 min at 240°C. The uniformly dispersed icosahedral quasicrystalline particles are formed from the supersaturated solid solution (the α-Al phase) by solid-state reaction. The orientation relationship between the icosahedral quasicrystalline phase and the matrix phases has been identified as i5 // \{011\}_α, i3 // \{111\}_α, and i2 and i5 is almost the parallel to \{112\}_α and \{110\}_α with the misorientation of ~3 degrees respectively. This newly found icosahedral phase appeared to be the same orientation relationship reported previously by Shechtman et al.25) This icosahedral quasicrystalline phase belong to the Al-Zn-Mg group confirmed by the quasilattice constant \(a_\text{q} = 0.505 ± 0.01\) nm. The six-dimensional simple-cubic lattice, the cubic lattice constant \(a_\text{c}\) has a value of 1.390 ± 0.028 nm. This is in good agreement with the lattice parameter of the crystalline T phase (a = 1.416 nm).8)

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REFERENCES