Strengthening in magnesium alloys by icosahedral phase

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Abstract
Strengthening effects of quasicrystalline icosahedral phase has been studied in two alloys Mg95Zn4.2Y0.8 and Mg92.5Zn6.5Y extruded at 250 and 400 °C. The quasicrystal particles are facetted and show definite orientation relationships with the matrix. Due to its high symmetry and quasiperiodicity, the icosahedral phase can form strong interfaces with the matrix in various orientations. The icosahedral phase particles have a strong pinning effect on the grain boundaries, which stabilizes grain size. The icosahedral particles are resistant to coarsening, and remain hard at higher temperatures, imparting good strength with ductility at 200 °C. Very few deformation structures such as high dislocation density and twins are observed after extrusion or tensile tests. Dislocations commonly observed are c-type. Due to the stability of microstructure, various post-extrusion treatments are possible. In the Mg92.5Zn6.5Y alloy upon annealing at 400 °C the icosahedral phase transforms to a hexagonal Mg25Zn58Y17 phase. The icosahedral phase then reprecipitates on its interface, forming a nano-composite. Effects of microstructural features on the deformation behavior are described.

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1. Introduction

Being the lightest structural materials, magnesium alloys are very tempting for widespread applications. However, the problems of their low strength and poor ductility are still to be overcome. Different approaches are being tried to raise the strength and ductility of magnesium alloys. One among them is the use of quasicrystalline phase which exists as a stable phase in ternary Mg–Zn–RE alloys, where RE= Y or rare earth elements [1–4].

The icosahedral phase has very high lattice symmetry, of the order of 120. Its structure is quasiperiodic, instead of periodic, which gives it unusual properties, such as its very high hardness and low thermal and electrical conductivity at room temperature [5]. Its quasiperiodic order will make it hard to be sheared by dislocations. It would, thus, make an effective composite with other metallic phases.

An icosahedral phase of composition Mg3Zn6Y occurs in Mg–Zn—Y system [3]. This phase can exist in equilibrium with the magnesium phase [4]. On solidification of dilute alloys, it forms eutectically in interdendritic spaces. Recently, this phase has been studied as the strengthening phase in Mg–Zn–Y alloys [6–11]. The interdendritic icosahedral phase has been sought to be dispersed as nanoparticles in the matrix by thermomechanical means such as hot rolling [6–9] and extrusion [10,11]. These alloys exhibit high ductility with good strength and a highly stable microstructure at elevated temperatures. They seem to form strong interfaces with the matrix, enhancing the strength. The quasicrystalline icosahedral phase particles are facetted, showing a definite orientation relationship (OR) with the matrix [12]. The icosahedral phase, stable up to about 440 °C, is resistant to coarsening. The icosahedral phase particles also pin grain boundaries, retarding grain growth, and the thermally stable microstructure making it possible to perform post-extrusion heat treatments.

The strengthening effects of the icosahedral phase dispersed in two alloys Mg95Zn4.2Y0.8 and Mg92.5Zn6.5Y by extrusions at 250 and 400 °C are examined in this study, where the microstructure after various heat treatments are studied by transmission electron microscopy and mechanical strength are evaluated by tensile tests.
2. Experimental techniques

Two alloys Mg_{95}Zn_{4.2}Y_{0.8} (Alloy 1) and Mg_{92.5}Zn_{6.5}Y (Alloy 2) were prepared in an electric resistance furnace and cast in metallic moulds. These ingots were machined into rods (39 mm diameter) and extruded at a ratio of 10:1 at two different temperatures of 250 and 400 °C. Post-extrusion heat treatments were given by isothermal annealing at 400 °C (for 1 h) (‘solutionizing’ treatment) followed by ageing at 200 °C for 10 h. Microstructure was studied by transmission electron microscopy (TEM) using microscopes JEOL 2000FX-II and JEOL 4000EX-II. Samples for TEM observations were made by slicing by a diamond saw, followed by mechanical thinning and finally ion milling. Often the microstructural observations were made on tensile tested samples. The tensile tests were performed at room temperature (RT), 200 and 300 °C on samples with gauge length of 22 mm at strain rate $10^{-3}$/s.

3. Results and discussion

Due to higher alloying content, Alloy 2 has a higher amount of icosahedral phase. The stoichiometric icosahedral phase has Zn:Y ratio 6:1. In Alloy 1 effectively 0.7% Y goes into making the icosahedral phase. Alloy with 0.7% Y is reported to contain about 9 vol% icosahedral phase [8]. Alloy 2 is estimated to contain 1.4 times more icosahedral phase.

3.1. Microstructure of as-extruded alloys

Extrusion of the alloys resulted in finer grain sizes—3–5 μm in case of extrusion at 400 °C and 10–15 μm in case of extrusion at 250 °C. No deformation structures such as extensive twinning or dislocations were observed even in case of extrusion at the lower temperature of 250 °C. X-ray diffractions along and transverse to the extrusion directions showed a strong texturing after extrusion at 400 °C such that basal planes were aligned along the extrusion direction. Such texturing occurred on extrusion at 250 °C but not so strongly. Fig. 1(a) and (b) show the grain structure of Alloy 2 after extrusion at 250 and 400 °C. The dark contrast phase is the icosahedral phase which was distributed as submicron sized particles on the grain boundaries and nano-sized particles in the matrix.

3.2. Interfaces of the icosahedral phase with the matrix

These particles were well facetted on fivefold and twofold planes in the case of extrusion at 400 °C. They always showed a definite orientation relationship with the matrix, the predominant one shown in Fig. 2 and described in detail by Singh et al. [12], in which an icosahedral twofold axis occurs along the Mg hexagonal axis. Two other icosahedral twofold axes perpendicular to this occur along [100] and [120]. The faceting occurred mainly on the basal plane of the matrix phase, which matches with a twofold plane of the icosahedral plane, and prismatic planes which match with twofold and fivefold planes of the icosahedral phase. An example of this faceting is shown in Fig. 2(b). The icosahedral phase in the matrix on extrusion at 250 °C often had irregular shape.

Grain boundary icosahedral phase also show definite orientation relationships with matrix grains, as for example shown by a composite diffraction patterns from one particle in Fig. 1(c). Though the orientation relationship shown in Fig. 2 is the most common one, at least four other orientation relationships also exist, shown by Singh et al. [13]. The high symmetry of the icosahedral phase ensures a high possibility that as a grain boundary phase it would form an orientation relationship with either of the grains.
across the grain boundary. An example is shown in Fig. 3, where the icosahedral phase at the grain boundary is in a fivefold zone axis orientation and composite diffraction patterns from each of the two grains is shown. It shows orientation relationship of Fig. 2 with the grain A, and a more complex orientation relationship with grain B. Faceting occurs in both the grains. Definite orientation relationships mean matching and strong interfaces.

Another property of the quasicrystalline icosahedral phase ensures formation of matching and strong interfaces with the matrix. The icosahedral phase facets on fivefold and twofold planes. Occurrence of strong reflections in reciprocal space show that the dominant interatomic distances on these planes are about 2.45 and 2.34 Å, respectively. These interplanar spacings match those of the crystalline phase at the interface. The quasiperiodicity, however, generates other spacings on a particular plane, which makes possible matching with a number of other crystalline planes.

### 3.3. Effect of heat treatment

#### 3.3.1. Precipitation

Rod-like precipitates of precursor phase $\beta_1'$ parallel to the hexagonal axis occurred in the matrix. In Alloy 1 extruded at 400°C, equilibrium phase $\text{MgZn}$ also occurred nucleated on dislocations. For finer precipitation heat treatment was performed on the extruded alloys. An isothermal treatment was performed at 400°C, below the eutectic temperature, for 1 h in order to dissolve fine precipitates in the matrix. This treatment is referred to as ‘solutionizing’ here. Subsequently, an isothermal anneal was given at 200°C for 10 h for growth of precipitates.

Fine $\beta_1'$ rods renucleated on solutionizing. In addition, a phase termed $\tau_1$, a defected structure related to monoclinic $\text{Mg}_9\text{Zn}_7$ phase, and to a phase reported as $\tau$ in a $\text{Zn}$–$\text{Mg}$–$\text{RE}$ alloy [14] nucleated in the matrix. In Alloy 1, fine precipitates of this phase transformed to the icosahedral phase on further annealing at 200°C. This phase often nucleated at icosahedral-magnesium interface in both the alloys. This phase appears to be distinct from the ternary $\tau_1\text{Mg}_{85}\text{Zn}_{6}\text{Y}_{9}$ phase reported in the $\text{Mg}$–$\text{Zn}$–$\text{Y}$ alloy system [15,16]. The $\tau_1\text{Mg}_{85}\text{Zn}_{6}\text{Y}_{9}$ phase is reported to have a long period structure along the hexagonal axis of the matrix. In the case of the $\tau_1$ phase observed here there are diffused diffraction streaks perpendicular to the hexagonal axis.

#### 3.3.2. Stabilization of grain size

Grains grew to final sizes of 15–20 µm in the alloys upon annealing at 400°C in all alloys. Thus the grain growth was substantial in the case of alloys extruded at 400°C, but not significant in the case of alloys extruded at 250°C. The final grain size is limited by the icosahedral phase particles, which retard the movement of grain boundaries. Even nano precipitates of icosahedral phase had strong pinning effect on the grain boundaries, as seen in Fig. 4.

The icosahedral phase particles became rounded on heating to 400°C, indicating that it becomes soft at this temperature. The particles, however, retained their orientation relationship with the matrix. No coarsening of the icosahedral phase occurred. However, a tendency for the grain boundary icosahedral phase to coalesce was observed, which indicates increased grain boundary diffusion at 400°C.

#### 3.3.3. Formation of nano-composite structures

The $\tau_1$ phase nucleating at the icosahedral-magnesium interface formed a nano-composite. This happened more notably in case of Alloy 1. A more prominent nano-composite formed in Alloy 2. On annealing of Alloy 2 at 400°C the quasicrystal phase at the grain boundaries transformed to a hexagonal $\text{H–Mg}_{25}\text{Zn}_{38}\text{Y}_{17}$ phase with lattice parameters $a = 9.1$ and $c = 9.5$ Å. This H phase is the same as a pre-eutectic phase in a eutectic involving icosahedral phase [17]. The quasicrystal then re-precipitates on its interface with magnesium, forming a nano-composite, through an apparent reaction

$$\alpha - \text{Mg} + \text{H} \to \text{I}$$

(1)
where ‘I’ represents the icosahedral phase. Fig. 5(a) shows microstructure of Alloy 2 (extruded at 400 °C) after annealing at 400 °C. The dark phase at grain boundaries is no longer icosahedral phase but the H phase. The rough shape is due to the icosahedral phase at the interface. Fig. 5(b) shows an interface between the two phases. The interface is planar with a ledged structure. The H phase shows the following orientation
relationship with the matrix

\[ \frac{[001]}{Mg} \parallel \frac{[100]}{Mg} \]

\[ \frac{(010)}{Mg} \parallel \frac{(010)}{Mg} \]

(2)

The H phase orientation relationship with the icosahedral phase is such that an icosahedral twofold axis occurs along the hexagonal axis and another twofold along [100], while a fivefold axis occurs nearly along [110] hexagonal axis. However, this relationship was not found to occur in all the cases examined.

3.4. Mechanical strength of the alloys in as-extruded and heat treated conditions

Fig. 6 shows tensile strength at RT of Alloy 1 and Alloy 2 extruded at 250 °C. In the as-extruded condition the yield strengths at RT are near 200 MPa, UTS about 300 MPa with elongations 15–20%. Strengths of the Alloy 2 are higher by 15–20 MPa as compared to those for the Alloy 1. Upon annealing at 400 °C, there is a drop in strength, particularly the yield strength which falls by 15% in the case of Alloy 1 and 9% for Alloy 2. Subsequent annealing at 200 °C raises the YS significantly, to above the levels of as-extruded alloys, especially in the case of Alloy 2 where it becomes 240 MPa. The strength of Alloy 2 is consistently higher than for the Alloy 1, which is attributed to a larger volume fraction of icosahedral phase in Alloy 2.

On annealing at 400 °C (solutionizing), the drop in YS of the Alloy 1 is quite drastic, in which there is smaller amount of quasicrystal particles, and other precipitates get dissolved. On further annealing at 200 °C quasicrystal precipitates appear, with a simultaneous increase in the YS. The lengthened \( \beta' \) rods, which grow to several hundred nanometers in length, also contribute to strength.

In the case of Alloy 2, which has significantly higher icosahedral phase content, the change in strength upon heat-treatment is not as much as in the case of Alloy 1. Upon annealing at 400 °C (solutionizing), a mixture of icosahedral phase particles and tiny precipitates form in the matrix. Upon further anneal at 200 °C, mainly the icosahedral phase particles remain in the matrix. A simultaneous increase in the YS by 20–50 MPa shows the effectiveness of the icosahedral phase in strengthening.

The RT strength is highest in case of extrusion at 400 °C due to the finer grain size. The higher temperature strength were, however, not good. After heat treatment the strength levels became similar to the same alloys extruded at 250 °C.

Fig. 7 shows the effect of heat treatment on tensile strength at 200 °C. In both the alloys the strength is raised on annealing at 400 °C, but subsequent annealing at 200 °C indicates an overaged condition. In Alloy 2, the YS at 200 °C in the as-extruded condition is about 150 MPa while UTS is over 180 MPa. On annealing at 400 °C, there is over 13% increase in the YS and over 33% increase in the UTS. On the subsequent annealing at 200 °C, there is a marginal improvement in the YS, but a drop in the UTS.

3.5. Deformation structures

No deformation structures were observed even in the samples extruded at 250 °C. No high densities of dislocations or twins were found. Thus the recrystallization occurs rapidly. No high densities of dislocations and twins were found after tensile tests either. Fig. 8 shows dislocations in a grain of a sample of Alloy 2 extruded at 400 °C, solutionized and annealed, tensile tested at RT. In the image with two-beam condition with \{100\} reflection no dislocations are observed. In this image precipitates can be observed clearly. There are small rod-like \( \beta' \) precipitates perpendicular to the basal plane, as well as dark rounded icosahedral phase precipitates, to some of which are attached \( \tau_1 \) precipitates. The \{002\} two-beam image shows complex contrast due to strain. A corresponding weak-beam image is shown, in which wavy lines are identified to be c-type dislocations. It is rather unusual that c-type dislocations are activated in these alloys rather than a-type.

High density of dislocations is observed in some samples, particularly those deformed at higher temperature, such as shown in Fig. 3. In this sample tensile tested at 200 °C, wavy patterns of regions of higher dislocation density are observed. In the composite diffraction pattern with a grain boundary

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Fig. 6. Strength at RT of (a) Alloy 1 and (b) Alloy 2 extruded at 250 °C in as-extruded, solutionized (annealed at 400 °C 1 h) and solutionized + annealed (200 °C 10 h) conditions.
icosahedral phase, the diffraction spots from the matrix appear as arcs, while the spots from the icosahedral phase are discrete. This indicates that the matrix in the vicinity of the icosahedral phase in highly deformed, while the icosahedral phase itself remains rigid. In the samples deformed at 300 °C there was evidence of deformation of the icosahedral phase itself. Thus, the loss of strength at 300 °C can be attributed to the loss of rigidity of the icosahedral phase.

4. Conclusions

The role of icosahedral phase in strengthening has been studied in two alloys Mg_{95}Zn_{4.2}Y_{0.8} (Alloy 1) and Mg_{92.5}Zn_{6.5}Y (Alloy 2) extruded at two different temperatures of 250 and 400 °C. The following conclusions are arrived at:

(1) Icosahedral phase is dispersed in the extruded alloys as 500 nm to micron size particles on the grain boundaries and 50–100 nm particles in the matrix. These particles are faceted with a definite orientation relationship with the matrix in the case of extrusion at 400 °C, and are irregularly shaped in the case of extrusion at 250 °C.

(2) Due to a high symmetry of the icosahedral phase, it is likely to form definite orientation relationships and matching interfaces with matrix grains in different orientations.

(3) The icosahedral phase particles retain their strength even at higher temperatures of 200 °C.

(4) Strong pinning effect of the icosahedral phase on grain boundaries stabilizes the grain size in alloys.

(5) Annealing of Alloy 2 at 400 °C transforms the grain boundary icosahedral phase to a hexagonal H phase, and icosahedral phase precipitates on its surface, forming a nanocomposite.
(6) Alloy 2 showed constantly better strength due to its higher quasicrystal content. Upon annealing (400 °C) and ageing at 200 °C, it showed a remarkable improvement in RT yield strength to 240 MPa, UTS 300 MPa and elongation almost 20%.

(7) Heat treatment improved the YS of Alloy 2 at 200 °C to over 170 MPa, with a UTS 240 MPa and elongation nearly 30%.

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