EFFECT OF HEAT TREATMENT ON PHASE TRANSFORMATIONS IN Mg-Y-(Nd)-Zn ALLOYS

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Abstract
Phase transformations during isochronal annealing were investigated in squeeze cast Mg2Y1Zn and Mg2Y1Nd1Zn alloys. Electrical resistivity measurements at 77 K and room temperature, differential scanning calorimetry and microhardness measurements were performed. Transmission electron microscopy and optical microscopy revealed intermetallic phases at grain boundaries and in their vicinity and a relatively high density of stacking faults in grain interiors of both alloys. Resistivity annealing curves show matrix enrichment by solutes in both alloys during isochronal annealing up to 440 °C. Only a weak precipitation proceeds during isochronal annealing of both alloys. Mechanical properties tested by microhardness measurements do not deteriorate due to the isochronal annealing. If a repeated isochronal annealing of both alloys previously isochronally annealed up to 440 °C is performed, an early precipitation stage appears in both alloys at 80 °C – 200 °C. Thermal stability of microhardness remains very good also in the repeated heat treatment. Heat flow connected to the phase transformations up to 440 °C is only moderate, but a partial liquefaction was observed near to 500 °C in calorimetrical curves. The melting temperature shifts to lower temperatures in repeated isochronal annealing only in the Mg2Y1Zn alloy.

Keywords
Mg–Y–Zn alloys, phase transformations, electrical resistivity, microhardness, heat flow

1. INTRODUCTION
Mg alloys with rare earth (inclusive Y) are constantly in a research focus due to a possibility of their aging and a very good thermal stability of mechanical properties. Economical reasons aim to suppress concentrations of rare earth to a minimum combining the rare earth additions with other elements and maintaining so proper properties caused by tailored microstructures. Recently Mg-Y-Zn alloys have attracted attention due to their unusual microstructures including quasicrystalline secondary phases (e.g. [1]). Phases denoted as X-phase (Mg10Zn1Y1 composition, hcp structure), W-phase (Mg3Zn3Y2 composition, fcc structure) or I-phase (Mg3Zn6Y1 composition, icosahedral phase) can be found in the Mg-Y-Zn phase diagram rigorously depending on the concrete concentrations of Y and Zn and on their ratio [2]. The Mg-Y alloys with low Zn content contain either in the as cast state or after a heat treatment secondary phase particles or regions of ordered structures that exhibit a variety of long period stacking. High resolution electron microscopy enables very recently to study ordering, stacking, composition or arrangement of the alloying elements in these ordered structures. The 18R and 14H long period ordered structures frequently constitute in Mg-Zn alloys as Mg-Y-Zn [2], Mg-Gd(Y)-Zn [3, 4], Mg-Dy-Zn, Mg-Ho-Zn and Mg-Er-Zn alloys [5]. A very detailed study was needed to establish differences in composition and structure of the 18R (Mg10Y1Zn11, ordered base centred monoclinic lattice) found in the as cast state and of the 14H ((Mg12Y1Zn11, ordered hexagonal structure) developed during heat treatment in Mg-Y-Zn alloys [6].

It was proven that a small addition of Zn to Mg-Y alloys decreases the stacking fault energy in the Mg-matrix considerably and split dislocations or many planar faults formed on (0001) matrix plane were observed [7]. Segregation of Y and Zn at higher temperatures stabilizes and extends the separation of these extended dislocations; the faulted parts become their own microstructure and are observed as basal plates [8]. It leads to an enhanced creep resistance of these alloys up to high temperatures [9, 10].
The aim of this work was to investigate phase transformations during isochronal annealing in squeeze cast Mg2Y1Zn and Mg2Y1Nd1Zn alloys. Electrical resistivity measurements at 77 K and room temperature, differential scanning calorimetry and microhardness measurements were performed. Transmission electron microscopy and optical microscopy was used in microstructure investigation.

2. EXPERIMENTAL PROCEDURE

Two alloys were squeeze cast under a protective gas atmosphere of Ar + 1%SF₆. Their nominal composition is listed in Table 1. The isochronal annealing response of relative electrical resistivity changes was determined in the range 20 °C – 440 °C in both as cast materials. Isochronal annealing was carried out in steps of 20°C/20 min followed by quenching. This treatment was performed in a stirred oil bath up to 240 °C and the specimen was quenched into liquid nitrogen after each annealing step. Specimens wrapped in a steel foil were heat treated in a furnace at higher temperatures and each heating was followed by water quenching. The H-shaped specimens machined to dimensions of 1x8x75 mm³ were used for resistivity measurements at 77 K after each heating step. The value of the length represents the gauge length for the resistivity measurements. Relative electrical resistivity changes \( \Delta \rho / \rho_0 \) were obtained within an accuracy of \( 10^{-4} \). The resistivity was measured by means of the dc four-point method with a dummy specimen in series. The influence of parasitic thermoelectromotive force was suppressed by current reversal. Selected states of material were controlled by measurements at two temperatures (77 K and 293 K). The ratio \( RRR = \rho(293 \text{K}) / \rho(77 \text{K}) \) does not depend on the specimen form-factor and increases with increasing effective material purity.

The stability of mechanical properties was measured by Vickers microhardness HV0.5 at room temperature in Wilson Wolpert 401 MVD microhardness tester. Ten indentations were evaluated and the average together with its standard deviation was determined. The same isochronal heating procedure as in the resistivity study was used for obtaining microhardness annealing curves.

The microstructure investigation of the as cast state was realized using transmission electron microscopy (TEM) and electron diffraction (JEOL JEM 2000FX electron microscope). An analysis of phases precipitated out was also supported by energy dispersive X-ray microanalysis (EDS) by BRUKER microanalyzer. The optical microscopy in Olympus microscope BX 51 was used in structure studies.

Calorimetrical measurements were performed in the NETZSCH DSC 200 F3 Maia calorimeter at the constant heating rate of 10 K/min under a flowing N₂ gas atmosphere. After heating up to 520 °C, specimens were cooled without regulation in the calorimeter and repeatedly heated with the same constant heating rate.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Y [wt.%]</th>
<th>Nd [wt.%]</th>
<th>Zn [wt.%]</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>WZ21</td>
<td>2</td>
<td>-</td>
<td>1</td>
<td>balance</td>
</tr>
<tr>
<td>WEZ211</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>balance</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1 As cast alloys

The as cast structure of both alloys investigated is shown in Figs. 1 and 2. Grains are almost equiaxed in both alloys with the grain size (50 ± 8) µm and (70 ± 11) µm in the WZ21 alloy and in the WEZ211 alloy, respectively. A layer of a secondary phase or phases along grain boundaries is observed in both materials. Its volume fraction determined by usual stereological methods is little larger in the WZ21 alloy (~ 0.25) than in the WEZ211 alloy (~ 0.18).
Microstructure investigation has revealed a complicated phase composition in the grain boundary layer of the WZ21 alloy. It consists of ribbons of a Mg-(Zn,Y) phase having a long-period ordered structure and of very thin plates between, both embedded parallel to α-matrix basal planes – see Fig. 3. The aspect ratio of the thin plates is very high. The long period stacking structure phase is known as the X-phase in MgYZn alloys [2, 11].

Various periodicity types of the ordered structure were reported in these alloys (e.g. [10, 12, 13]) depending on the Zn/Y ratio, but the exact type of periodicity could not be determined here. Thin basal plates were already observed in other Mg-Zn alloys (e.g. Refs. [9, 14]) and contrary to the long period stacking structure phases they can be found also in alloys without Zn additions (e.g. [15]). The characteristic feature of grain interiors is a high density of stacking faults (Fig. 4) rarely observed in Mg alloys due to high stacking fault energy of Mg [8].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>HV0.5</th>
<th>RRR</th>
<th>180 °C</th>
<th>280 °C</th>
<th>340 °C</th>
<th>440 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>WZ21</td>
<td>53 ± 1</td>
<td>2.382</td>
<td>48.9 ± 0.4</td>
<td>48 ± 1</td>
<td>51 ± 1</td>
<td>52 ± 1</td>
</tr>
<tr>
<td>WEZ211</td>
<td>51 ± 1</td>
<td>2.164</td>
<td>49 ± 1</td>
<td>55 ± 1</td>
<td>54 ± 1</td>
<td>49 ± 1</td>
</tr>
<tr>
<td>WZ21 - repeated annealing</td>
<td>49 ± 1</td>
<td>2.193</td>
<td>52 ± 1</td>
<td>54 ± 1</td>
<td>51 ± 1</td>
<td>47 ± 1</td>
</tr>
<tr>
<td>WEZ211 - repeated annealing</td>
<td>49 ± 1</td>
<td>1.976</td>
<td>55 ± 1</td>
<td>54 ± 1</td>
<td>50 ± 2</td>
<td>48 ± 2</td>
</tr>
</tbody>
</table>
Grain boundaries are decorated by grain boundary eutectic in the WEZ alloy – Fig. 5. The structure of the eutectic phase is of Mg$_3$Nd type (fcc structure) with lattice parameter approximately equal to 0.74 nm. No ordered long period phase or basal plates were revealed by TEM in grain boundary layers of the WEZ211 alloy, but their existence cannot be excluded in a limited extend. Number density of stacking faults observed in grain interiors – Fig. 6 seems to be unaffected by Nd addition as no significant difference was found compared to the WZ21 alloy. Dislocation splitting with similar features was observed in the Mg-4Y-3Nd-1Zn-1Mn alloy, too and causes an outstanding creep resistance of this alloy [9].

The described as cast microstructure produces an intermediate alloy strengthening as demonstrated by microhardness values – Tab. 2. The values of both alloys are very similar, the secondary grain boundary phases as well as the split dislocations are most probably the cause for the measured values.

3.2 Heat treated alloys

Isochronal annealing curves of relative resistivity changes (Fig. 7) in both as cast alloys show a matrix enrichment with solutes during isochronal annealing up to 440 °C. The resistivity increase in the WZ21 alloy is preceded by an insignificant early precipitation process in the temperature range 120 °C – 180 °C. The dissolution of phases existing in the as cast state of both alloys is modified only by a precipitation process situated between annealing temperatures 280 °C and 340 °C. The resistivity response of both alloys to this matrix purification is only moderate and does not exceed ~ 3 % of the initial value. Dissolution of precipitates existing in both as cast alloys as well as those developed during the isochronal annealing up to 340 °C exhibit some complex features in the range 340 °C – 440 °C. The RRR and microhardness values of the specimens annealed up to the selected temperatures are listed in Tab. 2. The RRR values agree very well with the resistivity response to the annealing. Phase transformations proceeding during the isochronal annealing up to 440 °C do not deteriorate mechanical properties; microhardness exhibits very stable values in the course of annealing, as can be seen in Tab. 2. Heat flow response to the annealing with the constant rate of 10 K/min is very poor up to ~ 460 °C. A significant endothermic reaction shown in thermograms in Fig. 8a appears in both heated as cast alloys above this temperature and is typical for a partial liquefaction of secondary phase in both investigated alloys. Optical microscopy of WZ21 and WEZ211 alloys annealed isochronally up to 480 °C, which is presented in Figs. 9 and 10, show no grain growth. The layers along grain boundaries sharpen and their volume fraction decreases.

Fig. 7: Relative resistivity changes due to isochronal annealing in as cast WZ21 and WEZ211 alloys and in those repeatedly heat treated.

Fig. 8: a) Thermograms of WZ21 and WEZ211 cast alloys at constant heating rate 10 K/min, b) shift of secondary phase melting temperature with repeated heating is shown for both alloys.
3.3 Repeatedly heat treated alloys

If a repeated isochronal annealing of both alloys previously isochronally heat treated up to 440 °C is performed, the early precipitation stage starts already at 80 °C in both alloys, the resistivity decreases by annealing up to 200 °C and its absolute value is close to that of the previously annealed state – Fig. 7. The resistivity increase in the range 200 °C – 280 °C is very similar to that in the first annealing procedure and the main precipitation process at 300 °C – 340 °C having a less complicated character is more pronounced. Resistivity values after annealing at 440 °C exceed those resulted from the first annealing procedure. The development of the RRR values agrees very well with results of the resistivity annealing curves – see Tab. 2. Despite phase transformations dissimilarities in the first and in the repeated heat treatment, no significant microhardness changes were found – Tab. 2. It is probable that either some form of short-range order or submicroscopic precipitates develop in the temperature range up to 200 °C. Enrichment of solid solution during the first annealing at high temperatures and quenching enhances this process during the second heat treatment in the WZ21 alloy and enables it in the WEZ211 alloy. Similar features of resistivity annealing curves were found in a Mg-2.8 wt%Nd-1.3 wt%Zn alloy [16] without any evidence of phase transformations by TEM; activation energy of this precipitation process was close to the activation energy for the movement of vacancies in magnesium and kinetics exponent equaled 0.5.

Melting temperature of the liquefying phase in the WZ21 alloy shifts considerably to lower temperatures during the repeated heat treatment in the calorimeter (see Fig. 8b), but remains already constant, if this heat treatment is repeated again. It seems that the liquefyng is not exactly the eutectic but more likely a peritectic reaction as supposed for the X-phase in [11]. No shifting in melting temperature of the liquefying phase in the repeated heat treatments was found in the WEZ211 alloy. This allows supposing, that the phase behaves as eutectic, which is also supported by the microstructure form of the grain boundary phase in this alloy – Fig. 5.

4. CONCLUSIONS

Squeeze cast Mg2Y1Zn and Mg2Y1Nd1Zn alloys (nominal composition in wt.%) are characterized by a homogeneous grain structure with relatively thick grain boundary layers. Regions of ribbons of a Mg-(Zn,Y) phase having a long-period ordered structure and regions of very thin basal plates were found in the Mg2Y1Zn grain boundary layers. Grain boundaries are decorated by grain boundary eutectics in the Mg2Y1Nd1Zn cast alloy. Unusually high density of stacking faults was observed in grain interiors of both alloys. Relatively low electrical resistivity changes due to phase transformations resulting from isochronal annealing up to 440 °C were revealed, dissolution of phases present in the as cast state proceeds above 340 °C in both alloys. If the repeated isochronal annealing is performed, an early precipitation stage at 80 °C – 200 °C appears in both alloys. Thermal stability of microhardness is very good up to annealing temperature 440 °C and is not influenced by heating repetition. A partial liquefaction was observed in 10K/ min linear heating procedure near 480 °C. The melting temperature of liquefying phase in the Mg2Y1Zn alloy...
decreases in the repeated heating run showing a peritectic reaction. No melting temperature shift was found in the Mg2Y1Nd1Zn alloy.

ACKNOWLEDGEMENT

The work of TK and MV is a part of activities of the Charles University Research Center "Physics of Condensed Matter and Functional Materials". This work was also supported by the Czech Science Foundation (project 106/09/0407).

REFERENCES


