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MICROSTRUCTURE AND PHASE EVOLUTION IN Mg-Gd AND Mg-Gd-Nd ALLOYS WITH ADDITIONS OF Zn, Y AND Zr

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Abstract

Microstructure and phase evolution in Mg-Gd and Mg-Gd-Nd based alloys with additions of Zn, Zr and Y were analyzed in the as-cast, solution treated and aged conditions. Alloys has been investigated after solution treatment at 540°C for 24hr followed by isothermal aging at 175°C up to 32 days by using of Vickers hardness, optical microscopy, scanning electron microscopy equipped with EDS, X-ray diffraction and transmission electron microscopy. It was found that the as-cast alloys contained primary α-Mg matrix, eutectic-like structures, cuboid-like phases and Zr-rich clusters. The homogenized and quenched alloys contained primary α-Mg solid solution, smaller amount of divorced eutectic compounds, enlarged cuboid-like particles and Zr-rich clusters. The eutectic phase was Mg_5Gd prototype with the composition $Mg_5(Gd_xNd_{1-x}$, x≈0.2). The compositions of the cuboid shaped particles are characterized by enlarged amount of Gd and can be written as $Mg_2(Gd_xY_{1-x})$ with x≈0.85 in the Mg-5Gd based alloy, and $Gd_4(Y_xNd_{1-x})$ with x≈0.5 in the Mg-6Gd-3.7Nd based alloy. The cuboid shaped particles grew during aging and reached ~3μm average size. Precipitation of β′′ and β′ phases during aging was observed. Mg-6Gd-3.7Nd based alloy reached a maximum value of microhardness after 16 days of aging; in Mg-Gd based alloy, microhardness increased more slowly and reached a maximum value after 32 days of aging.

Introduction

Magnesium alloys containing heavy rare earth metals are very attractive candidates for the automotive industry including racing cars and aerospace applications [1-7], due to their high strength properties combined with low density. Due to a large solubility of RE elements in Mg matrix at high temperature and its rapid decrease with lowering temperature, the Mg–RE alloys show remarkable age-hardening response during isothermal aging at 175°C, and thus high strength is to be expected.

Microstructural characterization of the Mg–RE alloys performed by many researchers [1-10] has confirmed a four staged precipitation sequence: [α-Mg supersaturated solid solution (S.S.S.S.) → $\beta''(DO_{19})$ → $\beta'(bco)$ → $\beta_1(fcc)$ → $\beta(fcc)$] [2,3,9,10], where the later precipitate can coexist with the former. Among the four precipitated phases, the coherent β′′and β′ phases are considered to be the primary strengthening phases [2,4,8,10]. The yield strength or hardness usually reaches a maximum, as the materials form a microstructure with fine β' precipitates during aging [1-4]. Among RE elements, Gd and Nd are considered as most promising for achievement of best Mg-RE alloys properties.

In the present work two Mg-RE alloys were investigated: Mg-Gd and Mg-Gd-Nd based alloys with additions of Zn, Zr and Y. Their specific compositions were selected in order to achieve maximum age hardening response, improved castability, grain refinement and strength. They were investigated by a combination of optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectrometry (EDS) and X-ray diffraction (XRD). Microhardness measurements were performed to reveal the effect of precipitation on the mechanical properties of the alloy.

Experimental

High purity Mg (99.9 wt.%) was molten in a mild steel crucible under a protective atmosphere CO_2 and HFC-134a (CF_3CH_2F) , high purity Gd (99.9 wt.%), Nd (99.9 wt.%) "for Mg-Gd-Nd-based alloy", Zr (99.9 wt.%), Mg–40Y (wt.%) and Mg–16Zr master alloys were added at a melt temperature of 760°C, then casting into steel mould preheated to ~200°C. The chemical composition of the investigated alloys were Mg-6Gd-3.7Nd-0.3Zn-0.18Y-0.15Zr and Mg-4.7Gd-0.37Zn-0.14Y-0.09Zr (wt.%).

Specimens cut from the cast ingot were solution treated (ST) at 540°C for 24hr, quenched into hot water of about 70°C, and then aged at 175°C in an oil bath for various periods of time up to 128 days, followed by water quenching.

The microhardness of aged specimens was measured by a Vickers hardness tester under a load of 50gr and holding time of 15sec. 20-40 indentations were conducted on each specimen. The specimens were polished with diamond paste and etched for 20sec in Ethanol 0.95%wt and HNO_3 0.05%wt (Nital) solution.

A comprehensive characterization utilized OM, SEM, TEM, EDS and XRD was carried out in order to elucidate the as-cast, homogenized and aged micro-structure of the alloys. Metallographic specimens were polished and etched in an Acetic Glycohol etching solution (100ml ethanol, 20ml water, 6gr picric acid and 5ml acetic acid). Thin foils for TEM characterization were prepared by ion beam thinning, and were examined at the acceleration voltage of 200 kV. The compositions of the matrix and of secondary phases in the TEM specimens were analyzed by EDS instrument attached to the SEM, operating at 10kV.

The constituent phases of the alloy in different conditions were identified by XRD with Cu Kα radiation. Details for the XRD: (start/end angle: 15-100°, step size: 0.01°, speed duration time: 0.45).

Results

As-cast microstructure

Fig.1 shows the as-cast alloys (a) for Mg-Gd-Nd alloy and (b) for Mg-Gd alloy. Consist mainly of the α-Mg phase as a matrix, eutectic-like structures, cuboid-like phases and Zr-rich clusters.

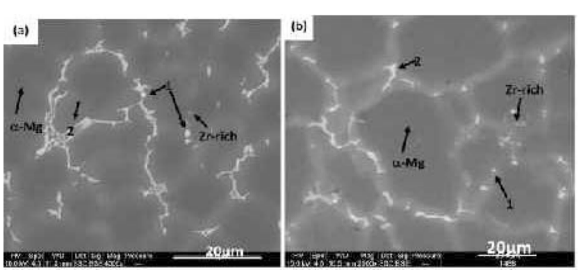

Fig. 1. Microstructure of the as-cast sample (a) for Mg-Gd-Nd alloy and (b) for Mg-Gd alloy: SEM image shows the cuboid-like phase (1) and eutectic-like structure (2).

The cuboid-like particles are frequently observed in the association with Zr-rich clusters and eutectic-like structures in the grain boundary as shown in Fig. 1.

The compositions of the phases were analyzed by EDS SEM using TEM samples shown in Tables. 1. Taking into account the small size of cuboids, EDS analysis results were inevitably influenced by the region around them, making the results just semi-quantitative to a certain extent.

Table 1. Compositions of different phases in Mg-Gd and Mg-Gd-Nd based alloys, measured by EDS SEM.

As- cast	Mg at%	Gd at%	Nd at%	Y at%	Zr at%	Phase
Mg-5Gd	99.01	0.52	-	0.14	0.15	α-Mg
	82.43	17	-	0.53	0.0	Eutectic
	77.96	19.63	-	1.79	0.0	Cuboid
	89.27	4.7	-	2.37	3.69	Zr rich
Mg-6Gd-3.7Nd	99.06	0.42	0.21	0.14	0.16	α-Mg
	84.82	7.43	7.73	0.0	0.0	Eutectic
	51.03	15.3	1.38	32.28	0.0	Cuboid
	94.03	1.51	0.76	0.0	3.7	Zr rich

ST microstructure

The purpose of homogenization for precipitate hardened Mg-RE alloys is to dissolve soluble as cast phases into α-Mg matrix and obtain supersaturated solid solution by quenching. The microstructure of the alloy was investigated in the ST and aged (175°C) conditions. It was observed that the homogenized alloy contained primary α-Mg solid solution, eutectic structures, cuboid shaped phases and Zr-rich clusters (Fig. 2).

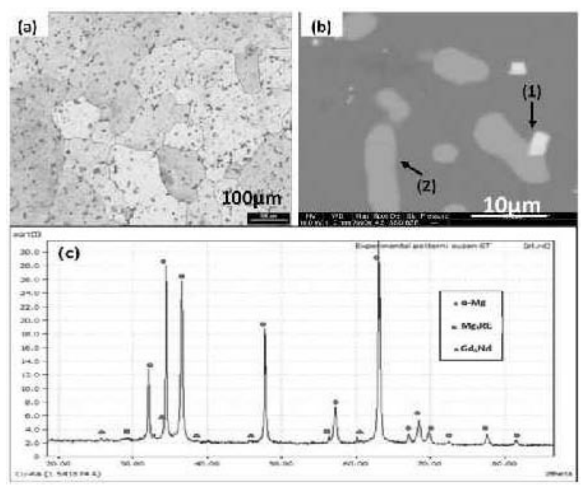

Fig. 2. Microstructure of the ST Mg-6Gd-3.7Nd based alloy: (a) Optical image showing the grain size and (b) SEM image showing the cuboid shaped phase (1) and eutectic structure (2). (c) X-ray diffraction.

As can be seen from X-ray diffraction patterns, the ST alloys contained primary α-Mg solid solution, eutectic phase Mg_5RE and cuboid shaped phases: Gd_4Nd for Mg-Gd-Nd based alloy (Fig. 2c) and Mg_2Gd for Mg-Gd based alloy (Fig. 3).

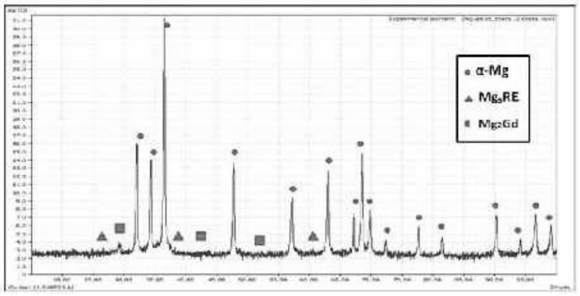

Fig. 3. X-ray diffraction pattern of the ST Mg-5Gd based alloy.

The eutectic structures were the products of a 'quasibinary eutectic reaction' L→α-Mg+β-Mg_5RE. The eutectic phase in the Mg-5Gd based alloy was characterized to be Mg_5Gd. The microstructure of the homogenized Mg-6Gd-3.7Nd based alloy contained two-phase skeleton-like eutectic structures (Fig. 4) with the Mg_5Gd-prototype phase of the composition $Mg_5(Gd_xNd_{1-x}$, x≈0.2).

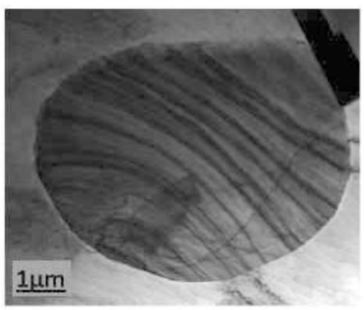

Fig. 4. Microstructure of the ST Mg-6Gd-3.7Nd based alloy: TEM observations of eutectic-like structure.

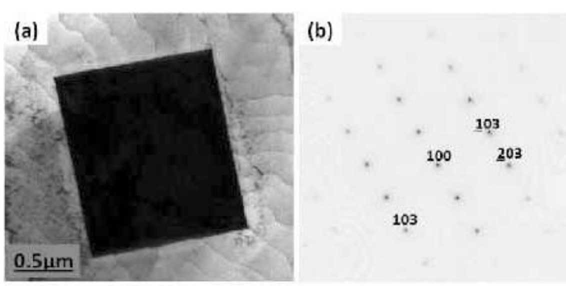

Fig. 5. Microstructure of the ST Mg-6Gd-3.7Nd based alloy: (a) TEM images of cuboid shaped phase and (b) SAED pattern with Z.A$[\bar{1}2\bar{1}0]$.

The compositions of the cuboid shaped particles after homogenization are characterized by higher amount of Gd and can be presented as $Mg_2(Gd_xY_{1-x})$ with x≈0.85 in the Mg-5Gd based alloy, and $Gd_4(Y_xNd_{1-x})$ with x≈0.5 in the Mg-6Gd-3.7Nd based alloy.

The cuboid shape phase was characterized to have Gd_4Nd type HCP crystal structure with $a \approx 0.365\text{nm}$, $c \approx 0.5798\text{nm}$.

<u>Microstructure of aged samples</u>

Microstructure of the aged samples consists of the eutectic structure, cuboid shaped particles and small precipitates uniformly distributed in the matrix. The cuboid shaped particles grow during aging up to ~3 μm in size; SEM+EDS analysis revealed that their composition did not change.

Crystal structure and composition of precipitates within the α-Mg matrix were investigated by TEM (Figs. 6-7); there were diffuse spots between the α-Mg matrix spots in the selected area electron diffraction (SAED) patterns, which were brighter than the matrix spots. TEM images and corresponding SAED patterns of precipitates in a specimen aged for 16 days (peak-aged specimen) are shown in Fig.6. It was observed that the microstructure contains a high number density of fine plate shape β″ precipitates and a little number of globular particles β′ uniformly distributed within the α-Mg matrix.

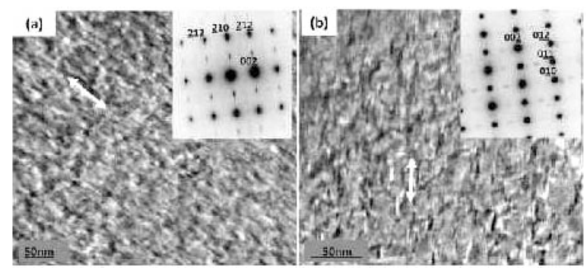

Fig. 6. TEM images and corresponding SAED patterns of Mg-Gd-Nd alloy aged for 16days at 175C: Z.A $[01\bar{1}0]_\alpha$ in (a) and Z.A $[2\bar{1}\bar{1}0]_\alpha$ in (b).

Combination of reflections from the two precipitates, β″and β′, appears in the corresponding SAED pattern (Fig. 6). The β″ precipitates with DO_{19} structure $(a \sim 2a_{\alpha-Mg} = 0.64\text{nm}, c \sim c_{\alpha-Mg} = 0.52\text{nm})$ correspond to diffuse spots at 1/2 distance of $\{01\bar{1}0\}_\alpha$ or $\{2\bar{1}\bar{1}0\}_\alpha$ reflections, with the following orientation relationships (OR): $[0001]_{\beta''}//[0001]_\alpha$, $\{01\bar{1}0\}_{\beta''}//\{01\bar{1}0\}_\alpha$; and the β′ phase with Base Centered Orthorhombic (BCO) structure ($a \sim 2a_{\alpha-Mg} = 0.64\text{nm}$, $b \sim 2.2\text{nm}$, $c \sim c_{\alpha-Mg} = 0.52\text{nm}$) gives rise to the additional spots at 1/4 $\{01\bar{1}0\}_\alpha$, 1/2 $\{01\bar{1}0\}_\alpha$ and 3/4 $\{01\bar{1}0\}_\alpha$, with the following OR: $[001]_{\beta'}//[0001]_\alpha$, $\{100\}_{\beta'}//\{2\bar{1}\bar{1}0\}_\alpha$.

The microstructure of Mg-Gd-Nd alloy aged for 64 days and Mg-Gd alloy aged for 78 days contain a little number of small precipitates β' with plate-shaped β_1 precipitates (Fig. 7). The β_1 precipitates with FCC structure ($a \approx 0.74$nm), with the following OR: $[110]_{\beta_1}//[0001]_{\alpha}$, $\{\bar{1}12\}_{\beta'}//\{1\bar{1}00\}_{\alpha}$.

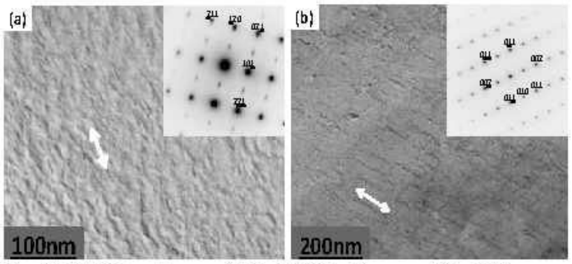

Fig. 7. SAED patterns of Mg-Gd-Nd alloy aged for 64days with Z.A $[10\bar{1}2]_{\alpha}$ (a) and of Mg-Gd alloy aged for 78days with Z.A $[2\bar{1}\bar{1}0]_{\alpha}$ (b) .

Microhardness

The microhardness evolution during isothermal aging at 175°C up to 64days for Mg-Gd-Nd-based alloy and 78 days for Mg-Gd-based alloy are shown in Fig. 8. Microhardness of the Mg-Gd-Nd based alloy reached a maximum value of ~ 100 HV after 16 days of aging. In the Mg-Gd based alloy, microhardness increased more slowly and reached a maximum value of ~ 70 HV after 32 days of aging. Further aging led to decrease in the microhardness.

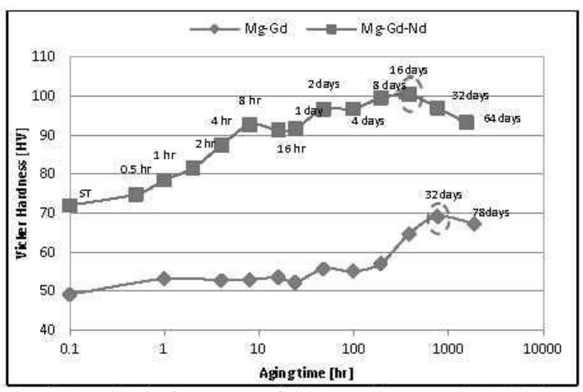

Fig. 8. Age hardening curve of the two alloys aged at 175°C

Discussion

The as-cast microstructures of the Mg-Gd and Mg-Gd-Nd based alloys with additions of Zn, Zr and Y consisted of primary α-Mg solid solution, skeleton-like eutectic structure, small Y-rich cuboid-like particles and Zr-rich clusters. The eutectic structures were the products of a 'quasibinary eutectic reaction' L→α-Mg+β-Mg_5RE. The eutectic phase was characterized to have Mg_5Gd type FCC crystal structure with $a \approx 2.2$nm and a composition of $Mg_5(Gd_xNd_{1-x}$, x≈0.2).

After ST the cuboid-like particles were characterized by higher amount of RE elements in comparison to the as-cast alloys. In the Mg-5Gd based alloy the cuboids had a composition of $Mg_2(Gd_xY_{1-x}$, x≈0.85), and the cubic crystal structure with $a \approx 0.855$nm (Fig.3).

In the Mg-Gd-Nd alloy the Gd and Nd atoms are transferred during ST from eutectic-like structure to cuboid-like particles to form the cuboid shaped phase with the stable composition $Gd_4(Nd_xY_{1-x}$, x≈0.5) (Fig. 2b). This phase has HCP crystal structure ($a \approx 0.365$nm, $c \approx 0.5798$nm). The cuboid shaped particles grow during aging and reach ~3μm average size.

Aging of solution treated and quenched alloys results in precipitation of β'' and β' phases, and their transformation to β_1 phase. Generally, the precipitation sequence in the investigated alloys during aging is identical to that reported for many Mg-RE alloy systems [2,3,8,9], i.e. the four staged precipitation sequence:$[\alpha - \mathrm{Mg\ S.S.S.S.} \rightarrow \beta''(D0_{19}) \rightarrow \beta'(\mathrm{bco}) \rightarrow \beta_1(\mathrm{fcc}) \rightarrow \beta(\mathrm{fcc})]$. The peak of microhardness (16 days of aging for Mg-Gd-Nd based alloy and 32 days for Mg-Gd based alloy) corresponds to a maximum density in the combination of $\beta''$and β' precipitates (Fig.6).

The difference in the peak aging time is explained by faster diffusion of Nd in comparison to Gd in Mg matrix. Ab initio calculations of diffusion of several RE impurities in Mg were performed recently by Huber et al. [11]. For Nd and Gd they obtained the diffusion activation energies of 1.05 and 1.17 eV, respectively. Assuming the equal pre-exponential factors, the ratio of diffusion coefficients of Nd and Gd at 175°C can be estimated as D_{Nd}/D_{Gd}=exp(0.12 eV/kT) ~ 20. In the coarsening regime (the over aging stage) the precipitate number density ,N_V , decreases with time, $N_V^{-1} \sim \alpha_{LSW} \cdot t \sim D_{RE} \cdot t$, where α_{LSW} is the coefficient of the LSW-coarsening theory. The microhardness roughly is inversely proportional to a distance between precipitates [13], and thus, is proportional to $N_V^{1/3}$. So, one can expect that the over aging stage in the Mg-Gd alloys would be substantially longer (to ~ $20^{1/3}$=2.7 times) than in the Mg-Nd alloys. The microhardness curves for Mg-Gd-Nd and Mg-Gd based alloys (Fig.8) confirm this evaluation.

The plate shape coherent β'' precipitates in $\alpha -$ Mg matrix have OR: $[0001]_{\beta''}//[0001]_{\alpha}$, $\{01\bar{1}0\}_{\beta''}/$

$/\{01\bar{1}0\}_{\alpha}$. The globular precipitates β' have OR: $[001]_{\beta'}//[0001]_{\alpha}$, $\{100\}_{\beta'}//\{2\bar{1}\bar{1}0\}_{\alpha}$. These results are similar to those reported by Zheng et al. [9] for Mg-11Gd-2Nd-0.5Zr.

The over aging resulted in disappearance of β'' and β' and formation of β_1 precipitates (Fig. 7). The plate shape β_1 precipitates have OR: $[110]_{\beta_1}//[0001]_{\alpha}$, $\{\bar{1}12\}_{\beta'}//\{1\bar{1}00\}_{\alpha}$. These processes are accompanied by decrease of microhardness (Fig.8).

Conclusion

The Mg-Gd-Nd and Mg-Gd based alloys with additions of Zn, Zr and Y were investigated in the as-cast, ST and aged conditions. Skeleton-like eutectic structure α-Mg+β-$Mg_5(Gd_xNd_{1-x}$, $x\approx0.2)$ and cuboid shaped particles were found in all conditions. Y-rich cuboid-like particles found in the as-cast alloy transformed to cuboid shaped phases during ST, $Gd_4(Nd_xY_{1-x}$, $x\approx0.5)$ in the Mg-Gd-Nd alloy and $Mg_2(Gd_xY_{1-x}$, $x\approx0.85)$ in the Mg-Gd alloy. They grow during aging. Precipitation of plate shape β'' and globular β' particles during aging resulted in microhardness increase. The further aging results in coarsening of $\beta''$and β' precipitates and their transformation to β_1 phase.

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