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Thermal stability and corrosion behaviour of Mg–Y–Nd and Mg–Tb–Nd alloys

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Abstract

The development of the microstructure in Mg–Y–Nd–Zr (commercial WE43) and Mg–Tb–Nd alloys and their thermal stability were investigated using electrical resistivity measurements and transmission electron microscopy. The mechanical properties were correlated with the microstructures developed. The creep resistance of both alloys is similar at elevated temperatures (473 K) but the minimum creep rate of WE43 at 623 K is lower than that of the Mg–Tb–Nd alloy as a result of the thermally more stable microstructure. The corrosion behaviour is one of the critical properties in the application of Mg alloys and can be generally improved by the addition of RE elements. It was shown that the corrosion characteristics of the two alloys studied differ substantially. Although the corrosion resistance of WE43 is not as good as some Mn containing Mg–RE alloys, it is much better than that of the Mg–Tb–Nd alloy with a similar total concentration of rare earth elements.

Keywords: Magnesium alloys; Rare earth; Microstructure; Corrosion; Mechanical properties; Creep

1. Introduction

High performance magnesium alloys are designed for applications under static and dynamic loading at temperatures above 470 K. The high creep resistance and strength required can only be attained by strong obstacles to both basal and non-basal slip which are stable at these temperatures. Hitherto, these conditions were best fulfilled by age-hardenable complex alloys containing rare earths (RE), including Y, in a particular combination. Not only the volume fraction but also the arrangement, the orientation relationship and aspect ratio of the precipitates affect the mechanical and creep properties [1,2]. Three basic types of sequential precipitation are known in Mg–RE supersaturated solutions, namely

- Mg–Y type [3]—(Y, Tb, Dy, Ho, Er, Tm, Lu):

  $\alpha'(\mathrm{hcp}) \rightarrow \beta''(\mathrm{DO_{19}}) \rightarrow \beta'(\mathrm{cbco}) \rightarrow \beta(\mathrm{Mg_{24}Y_5, bcc})$;

- Mg–Nd type [3,4]—(Ce, Nd):

  $\alpha'(\mathrm{hcp}) \rightarrow \beta''(\mathrm{DO_{19}}) \rightarrow \beta'(\mathrm{DO_3}) \rightarrow \beta(\mathrm{Mg_{12}Ndbct})$;

- Mg–Gd type [3–5]:

  $\alpha'(\mathrm{hcp}) \rightarrow \beta''(\mathrm{DO_{19}}) \rightarrow \beta'(\mathrm{cbco}) \rightarrow \beta(\mathrm{Mg_5Gd, fcc})$.

The β″ transient phase has a hexagonal DO_{19} structure ($a = 2a_{Mg}$, $c = c_{Mg}$) and is coherent in the hexagonal close packed (hcp) α′-Mg matrix in both decomposition sequences. The β′ (cbco—C base centred orthorhombic, $a = 2a_{Mg}$, $b \cong 8d(1\bar{1}00)_{Mg}$, $c = c_{Mg}$) is a transient phase semi-coherent with the α′-Mg matrix in the Mg–Gd type sequence. The β′ transient phase following the DO_{19} phase in the Mg–Nd type sequence has an fcc structure (DO_3, $a = 0.74$ nm, $d(220) \cong d(0002)_{Mg}$). These sequences may be modified in a particular Mg–RE binary alloy and also in more complex Mg–RE base alloys [6,7]. In particular, if Y and Nd are combined in WE alloys (Mg–Y–Nd–Zr), the precipitation sequence follows a slightly modified sequence of the Mg–Gd type with one intermediate transient fcc phase β_1

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($a = 0.74$ nm, $d(2\,2\,0) \cong d(0\,0\,0\,2)_{Mg}$) known from the Mg–Nd type precipitation sequence [3,8–11]:

$$\alpha'(\text{hcp}) \rightarrow \beta''(\text{DO}_{19}) \rightarrow \beta'(\text{cbco}) \rightarrow \beta_1(\text{fcc}) \rightarrow \beta(\text{Mg}_5\text{Gd, fcc})$$

Modification of the precipitation sequence and phase morphology depends not only on alloy composition but also on product technology and thermomechanical treatment [7,12].

The RE elements generally improve the corrosion behaviour of magnesium by enriching the corrosion product film developed, rendering it more corrosion resistant [13–15]. In order to estimate the differences in a possible application, the corrosion behaviour of the two alloys was studied in three selected aqueous solutions with different pH values using the electrochemical polarisation technique and the hydrogen evolution test.

The aim of this work was to substitute yttrium in the WE43 alloy by terbium, in order to study the microstructure development in both alloys after the same heat treatment and to correlate the developed microstructures to mechanical properties and to study the corrosion behaviour.

2. Experimental procedure

The alloys studied, with the composition listed in Table 1, were produced by squeeze casting under a protective gas atmosphere (Ar + 1% SF_6). After a solution heat treatment (800 K/8 h for WE43 and 800 K/4 h for Mg–Tb–Nd) the mean grain size increased to more than 400 μm in the Mg–Tb–Nd alloy but remained at about 40 μm in the WE43 alloy, most probably due to the grain refining effect of Zr. No other heat treatment influenced the grain size. The cast alloys have very little porosity (see the measured and calculated densities in Table 1). The isochronal annealing response of the relative electrical resistivity changes was measured over the range 293–800 K. Annealing was carried out in steps of 30 K/30 min and was followed by quenching. Heat treatments were performed in a stirred oil bath up to 513 K or in a furnace with an argon protective atmosphere at higher temperatures. Relative electrical resistivity changes $\Delta\rho/\rho_0$ were obtained with an accuracy of 10^{-4}. The resistivity was measured using the dc four-point method with a dummy specimen in series. The influence of parasitic thermo-electromotive forces were suppressed by current reversal. The thermal stability of the mechanical properties during heat treatment was measured by Vickers hardness HV3 at room temperature. The tensile tests were undertaken at temperatures from room temperature to 673 K at a constant strain rate $\approx 10^{-4}\ s^{-1}$. The specimens were mounted in the preheated deformation machine furnace 15 min before the test started. This time was proved to be sufficient for specimen heating up to the deformation temperature (up to 673 K). The minimum creep rates were determined (mostly by creep dip tests) at 473–623 K.

Transmission electron microscopy (TEM) and electron diffraction were carried out to determine the microstructure of the alloy after specified treatments. An analysis of the phases precipitated was also supported by energy-dispersive X ray microanalysis. Studies of the microstructure were undertaken on a JEOL JEM 2000FX and a Philips 200CM electron microscope equipped with a LINK AN 1000 and an EDAX microanalyser, respectively. The specimens for TEM were prepared by the same isochronal annealing procedure as those for electrical resistivity and hardness measurements.

Electrochemical potentiodynamic polarization tests were carried out using a PC-controlled laboratory potentioscan (model Wenking PGS 95). Two corrosive solutions were used: (1) a neutral 300 ppm NaCl solution; (2) an alkaline 100 ppm NaCl solution adapted to pH 12 by adding NaOH. Polarisation plots were obtained by scanning the potential at a rate of 20 mV/min, beginning at −500 mV below the open circuit potential. Monitoring started 15 min after free immersion.

The hydrogen evolution measurements consisted in placing the Mg specimen onto a glass seat in a beaker glass containing ∼1200 ml of a 3% NaCl borax-buffered solution with a pH 9.3. A burette with a funnel end was placed over the specimen to collect all the hydrogen generated on the specimen surface. The hydrogen volume, which is equal to the displaced test solution, was gradually recorded.

3. Experimental results and discussion

Fig. 1 shows isochronal annealing curves of electrical resistivity measured at 77 K together with the relative changes in hardness HV3 measured at room temperature for both alloys. The electrical resistivity decreases in two temperature ranges (the first one ends at 513 K in WE43 and at 483 K in Mg–Tb–Nd, the second one at 633 K in WE43 and at 603 K in Mg–Tb–Nd). The first stage is connected with a slight hardness increase in both alloys starting with HV3 = 66 ± 2 in WE43 alloy and 56 ± 1 in Mg–Tb–Nd alloy. In the second stage hardness changes are insignificant in the WE43 alloy, while a distinct increase in hardness, followed by a decrease, at the end of the stage were observed in the Mg–Tb–Nd alloy. An increase in the electrical resistivity above 633 K and 603 K is associated with a decrease in hardness.

Microstructural studies revealed the formation of tiny plates of the transient DO_{19} phase in the WE43 alloy annealed up to

Table 1
Composition of alloys studied, their measured and calculated density

Alloy	Y (wt.%)	Nd (wt.%)	Tb (wt.%)	Gd (wt.%)	Zr (wt.%)	Density ($kg\,m^{-3}$)	
						Measured	Calculated
WE43	2.95	2.48	–	0.15	0.30	1819 ± 1	1813
Mg4Tb2Nd	–	2.53	3.96		–	1829 ± 2	1825