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Mechanical properties of naturally aged Mg–Zn–Cu–Mn alloy

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Abstract

The Mg–Zn-based alloys exhibit a remarkable response to ageing at reduced temperatures including ambient temperature. A favorable combination of a very high ductility, appreciably high yield strength and hardness almost equal to that in the T6 condition, can be achieved in the naturally aged cast Mg–Zn–Cu–Mn alloy. The strengthening is produced by a dense dispersion of fine coherent and semi-coherent precipitates and the deformation most likely involves basal and prismatic slip to a greater degree than twinning, which is more pronounced in the T6 condition. When ageing is conducted at an intermediate temperature, further significant hardening beyond that in the T4 and T6 conditions is achieved due to the formation of a high number density of four different types of precipitates.

Keywords: Magnesium alloys; Natural ageing; Mechanical properties; TEM; SEM

1. Introduction

Magnesium alloys as the lightest structural metal material are among the most attractive candidates for the automotive and aerospace applications. However, the mechanical properties of most magnesium alloys are inadequate for many applications. Limited deformability (ductility) at room temperature, along with the pronounced plastic anisotropy, represents the main reasons why alloys suitable for the wrought products are notably underrepresented and undeveloped. The mechanical properties of many suitable magnesium alloys can be increased by age hardening, however the number density of the precipitates formed by this process is very low, typically orders of magnitude lower than in the age hardenable aluminium alloys. Such widely spaced and often coarse precipitates are then easily bypassed by mobile dislocations thus the strengthening effect is rather limited. In the case of aluminium alloys, ageing alone has been one of the most effective modes of increasing the mechanical properties. Critical dispersion of the strengthening precipitates has most commonly been produced and enhanced by additional alloying and by appropriate ageing regimes. It has also been established that the nucleation of precipitates and their dispersion, as well as the kinetics of precipitate nucleation and growth, are all highly dependant on the distribution and concentration of vacancies [1–3].

Precipitation hardening in magnesium alloys on the other hand, is still rather poorly explored and insufficiently developed area. The effect of the precipitation on the deformation behavior is even less clear. Also, no significant hardness increase during the ambient temperature ageing was reported in the prior work on Mg–Zn alloys [4,5], leading to an assumption that the interactions between the alloying elements and vacancies in magnesium alloys might be weak. This would account for the often slow kinetics of the precipitation and low number density of the precipitates formed. Age hardening at reduced temperature, such as at ambient temperature (natural ageing), commonly observed in most age hardenable aluminium alloys, generally indicates an appreciable concentration of vacancies in the solid solution after quenching and their strong interaction with the alloying elements, typically by clustering. In some aluminium alloys, e.g., in Al–Cu–Li–Ag–Mg–Zr alloys, the mechanical properties achieved after natural ageing for several years can even reach that of the artificially aged material due to the formation of a dense dispersion of fine Guinier Preston (GP) zones [6].

Recent report shows however that natural ageing of a considerable magnitude occurs also in magnesium alloys [7]. It was found that for the Mg–Zn-based alloys hardness in the naturally aged condition generally almost equals that in the artificially aged T6 condition. The comparison between the tensile properties of the naturally and artificially aged alloy is presented in

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this paper. The time to maximum hardness varies between several months (e.g. for a binary Mg–Zn alloy and ZK60) to a few weeks (e.g. in Mg–Zn–Cu or Mg–Zn–Ti alloys), which depends strongly on the type of the additional alloying elements present in the alloy. Some alloying elements were found to accelerate the natural ageing, e.g. Cu or Ti, which is typically accompanied with the improved artificial ageing response. Unlike Cu, Ti is not detrimental to the corrosion resistance of magnesium alloys and it was found that it also has a very pronounced grain refining effect [7].

The Mg–Zn alloys are known for their marked response to artificial ageing compared to other magnesium alloys. Most commercially interesting alloys are grain-refined by the addition of Zr (ZK series). Alloying with rare earth (RE) elements generally increases the mechanical properties at elevated temperatures [8] and also the alloy cost, while alloying with Cu (ZC series) [9–11], Ag [12], Au [13] and Ca [14] can significantly increase the number density of the precipitates in the T6 condition. The decomposition of the supersaturated solid solution (SSSS) in the Mg–Zn-based alloys occurs through the formation of a number of intermediate phases, many of which have not yet been fully characterized. These alloys have been commonly subjected to the T6 heat treatment and their ageing sequence above 150 °C has been reported to be as follows [4,5,12,15–18]: SSSS → pre-β' → β'_1 (rods and blocky precipitates ⊥ $\{0001\}_{Mg}$; possibly Mg_4Zn_7) → β'_2 (mainly coarse and sparse discs || $\{0001\}_{Mg}$ and some laths ⊥ $\{0001\}_{Mg}$; $MgZn_2$) → β equilibrium phase (MgZn or Mg_2Zn_3).

The optimal mechanical properties during artificial ageing are generally associated with the formation of the transition β'_1 phase, mainly in the form of rods. The initial stage of precipitation leading to the formation of β'_1 and the precipitation at lower temperatures have been extremely rarely investigated. Takahashi et al. [19] based on their X-ray diffraction (XRD) studies reported on the formation of two types of GP zones in an Mg–Zn alloy during ageing at intermediate temperatures. One type were denoted GP1 zones, formed during ageing below 60 °C as plates parallel to $\{11\bar{2}0\}_{Mg}$ planes, and the other type were the GP2 zones formed below 80 °C as oblate spheroids on $\{0001\}_{Mg}$ planes [19]. These precipitates have not been characterized or even clearly observed by the transmission electron microscopy (TEM). An additional type of GP zones has also been reported to form as discs parallel to basal planes [20]. The most recent studies on the naturally aged Mg–Zn-based alloys showed that the strengthening was produced mainly by thin planar precipitates on $\{11\bar{2}0\}_{Mg}$ planes (possibly the GP1 zones) and prismatic precipitates of an unknown phase perpendicular to the basal plane of magnesium [7], but also some very sparsely distributed planar precipitates on the basal planes (possibly the GP zones [20]) and solute co-clusters [21].

In this paper the tensile properties of the naturally and artificially aged Mg–Zn–Cu–Mn alloy are compared and correlated with the microstructures developed. Possible deformation modes at room temperature are also discussed as a function of the precipitates formed in the two tempers. An additional heat treatment at an intermediate temperature leading to a further increase in hardness and modified microstructure is also presented.

2. Experimental methods

An alloy having a composition Mg–6Zn–2Cu–0.1Mn (in wt%) was prepared from pure magnesium and Mg–Zn, Mg–Cu and Mg–Mn pre-alloys (prepared from pure components in the same manner) using an induction melting furnace under protective Ar atmosphere, and then cast as a ∼500 g ingot into a 45 mm (dia.) × 150 mm pre-heated permanent mould made of steel. The alloy was homogenized at 440 °C for 48 h and solution heat treated at 460 °C for 5 h prior to quenching in cold water and ageing. Ageing was performed at 160 °C (T6), 98 °C and 70 °C in an oil bath, and at ambient temperature (T4) in air. Age hardening response was monitored by Vickers microhardness measurements made using a load of 50 g and the values reported here were averaged from at least 12 measurements. The consistency of the measurements was confirmed using a load of 300 g. The tensile properties were tested at room temperature in accordance with Australian Standard AS 1391–2005 on five specimens from each temper. The initial strain rate was $8 \times 10^{-4}\,s^{-1}$. The cylindrical samples having a gauge length of 25 mm and a diameter of 5 mm were machined from the heat-treated alloy. Optical microscopy observations were performed on alloy specimens after etching the surface of the specimens using etchant 8 (acetic-picral) [22] in order to reveal grain boundaries. The grain size of the alloy was determined from five randomly selected fields for each alloy specimen in accordance with the planimetric method described in the ASTM standard E 112-96 (2004) and expressed as an average number of grains per square millimeter ($\overline{N_A}$). The value of $\overline{N_A}$ was determined to be 96, i.e. the grain size of the alloy was significantly larger than that of the alloys used in the previous study due to a different preparation [7]. Specimens for the TEM observations were prepared from aged material by electropolishing in a solution of 22.32 g $Mg(ClO_4)_2$ and 10.6 g LiCl in 1000 ml methanol and 200 ml 2-butoxy-ethanol at about −45 °C and 90 V. Conventional TEM observations were performed using Phillips CM200 microscope operated at 200 kV, while for the high resolution TEM (HRTEM) observations FEI Tecnai G2 F30 microscope operated at 300 kV was used. Scanning electron microscopy (SEM) of the polished specimens in the as homogenized condition and fractured tensile specimens in aged conditions was performed using a JEOL JSM 5400 scanning electron microscope equipped with JEOL JED 2140 energy dispersive X-ray (EDX) microanalyzer.

3. Results and discussion

3.1. Age hardening

Hardness curves of Mg–6Zn–2Cu–0.1Mn alloy for ageing at 160 °C (T6), 98 °C, 70 °C and at ambient temperature (T4) are compared in Fig. 1. Current observations are consistent with the recently reported study [7] and show that the hardness increment of 32 VHN was produced by the artificial ageing and that hardness in the naturally aged condition almost equals that in the artificially aged temper. It should be noted that the lower absolute values of hardness reported here are primarily due to a significantly larger grain size of the alloy used in the current