Optimization of solution treatment of ZK60 magnesium alloy using differential scanning calorimetry and electron microscopy

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Abstract

A method for optimization of solution treatment of ZK60 magnesium alloy was proposed based on differential scanning calorimetry (DSC) and electron microscopy. It was shown that the calorimetric measurements could very sensitively identify the type and amount of secondary phases present in cast materials and help to find out the optimal processing temperature and time. The temperature of 360 °C was identified as the optimal temperature for the solution treatment of ZK60 alloy. The microstructure after optimized processing was documented by light and electron microscopy. The $MgZn_2$, Mg_4Zn_7 and $ZrZn_2$ secondary phases were identified by electron diffraction and EDS microanalysis. The mechanical properties, namely ductility at elevated temperatures, were determined in deformation tests and compared to processing at conditions reported in literature.

Key words: magnesium, ZK60, electron microscopy, TEM, DSC, phase, ductility

1. Introduction

Magnesium alloys, because of their potential applications as lightweight materials, have attracted a great research interest [1–5]. The technology of using cast magnesium alloys for the preparation of mechanical and structural parts has advanced considerably. However, the application of cast metal parts is limited, thus also the wrought metal parts should be replaced by magnesium alloys for full realization of the weight reducing possibilities. This possibility is severely limited due to the lack in plastic processing and forming technologies.

The reason for the limited forming behaviour is mainly the crystalline structure of magnesium, which is hexagonal-closed-packed (HCP), a structure that leads to scantiness of slip systems, for the detailed description see e.g. [6]. As a result, magnesium and its alloys show poor plastic deformation potential at room temperature and the forming processes in magnesium materials are possible only under strictly controlled conditions, such as deformation rate, process temperature, loads, lubricants, etc. Nevertheless, crucial is namely the microstructure of the material for forming, as grain size, isotropy and phase composition.

In ZK series alloys (magnesium alloyed with zinc and zirconium), the addition of Zr leads to an increase of the strength of the material [7]. Presence of Zr leads to formation of stable $ZrZn_2$ particles, which decrease mobility of grain boundaries and stabilize fine-grained structure even at high temperatures [8]. As regards the micromechanics of plastic deformation, unlikely to most commonly used AZ series alloys which exhibit a balanced slip of $\langle a \rangle$ and $\langle c + a \rangle$ dislocations, the ZK series alloys prefer a non-basal $\langle c + a \rangle$ slip [9]. Twinning plays generally an important role in the deformation of magnesium-based alloys, see e.g. [10]. If ZK series alloys are prepared by severe plastic deformation (SPD), the grain structure can be refined to submicrometer range [11]. Figueiredo and Langdon [12, 13] have reported that magnesium ZK60 alloys exhibit excellent superplastic properties after SPD.

Thermal treatment of ZK60 alloys has been investigated in the past [14–17] resulting in a rather broad interval of recommended processing parameters, namely the temperature of solution treatment up to 430 °C and annealing times up to 10 hours. The aim of this work is to suggest a method for optimization of

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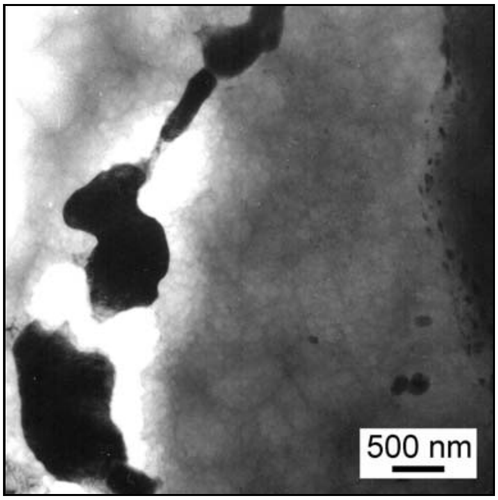

Fig. 1. Particles on grain boundary, mostly of $MgZn_2$ phase.

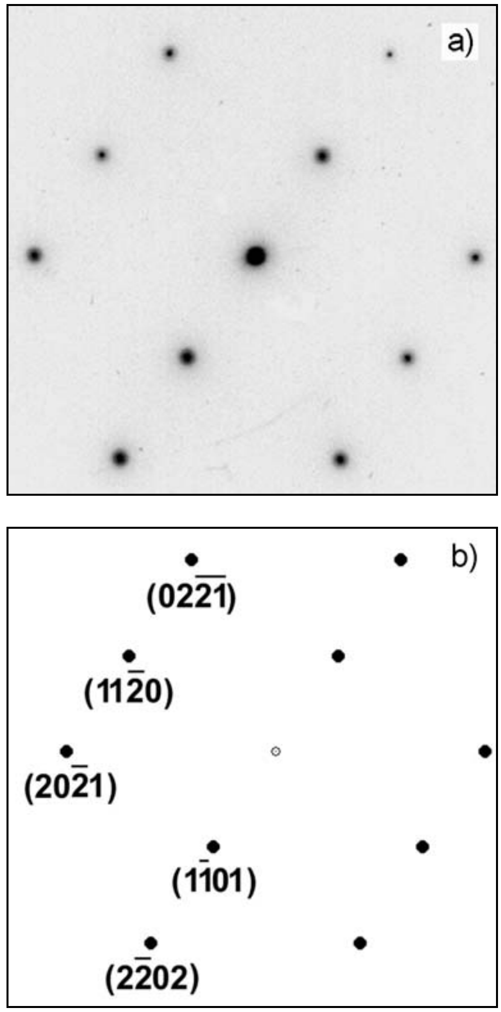

Fig. 2. Diffraction pattern from a particle containing Zn: a) compared with a simulated pattern, b) indexed unambiguously as [1 −1 0 −2] pole patterns of $MgZn_2$ hexagonal phase.

solution thermal treatment of magnesium ZK60 alloy based on experimental results obtained using differential scanning calorimetry (DSC) and electron microscopy.

2. Experimental procedure

Thermal analysis was performed using high temperature differential scanning calorimeter NETSCH DSC 404C flushed with argon at 40 ml min^{-1}. For the observation of microstructure the scanning electron microscope JEOL 50XA with a Bruker QUANTAX 200 energy dispersion microanalysis system (EDS) and transmission electron microscope JEOL 200FX with energy dispersion analyzer (EDAX) Link AN 10000 were used. Tensile tests were performed using a screw-driven Instron 5882 machine.

From the ingots of direct chill (DC) cast magnesium ZK60 alloy, the samples were cut for the DSC measurements, light and electron microscopy and tensile tests. The samples for tensile tests were flat samples, 1 mm thick and 6 mm wide with gauge lengths of 40 mm. Tensile tests were performed at the initial strain rates of 0.01 s^{-1} and 0.05 s^{-1} at 300 ℃ and 350 ℃. These conditions are typical for forming of the material at high temperatures (forging).

3. Experimental results

The investigations of the microstructure of the as-cast material by transmission electron microscopy (TEM) showed particles of secondary phases, predominantly at the grain boundaries. The majority of these particles were identified as $MgZn_2$ particles, whereas the diffraction pattern from another (less common) Zn containing particles can be, most probably, interpreted on the base of monoclinic structure Mg_4Zn_7. Figure 1 shows particles at grain boundary, mostly of $MgZn_2$ phase. A diffraction pattern from a particle containing Zn indexed unambiguously as [1 −1 0 −2] pole pattern of $MgZn_2$ hexagonal phase is shown in Fig. 2. The diffraction pattern has been taken from one of the small particles that decorate the grain boundary on the right.

The results of DSC measurements in the as-cast condition are shown in Fig. 3. From DSC, the temperature of 360 ℃ was identified as the optimal temperature for solution treatment. After annealing for 2 hours at 360 ℃ in an argon atmosphere, the peak between 340 ℃ and 350 ℃ was not observed any more in DSC spectrum leading us to conclusion that the phase transformation was finished during annealing.

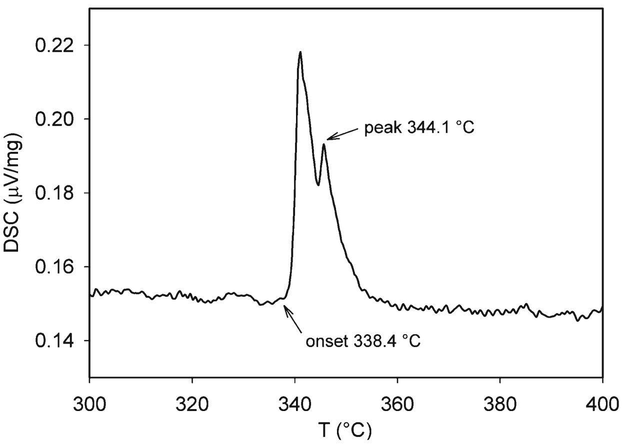

Fig. 3. DSC signal from ZK60 alloy in as-cast state.

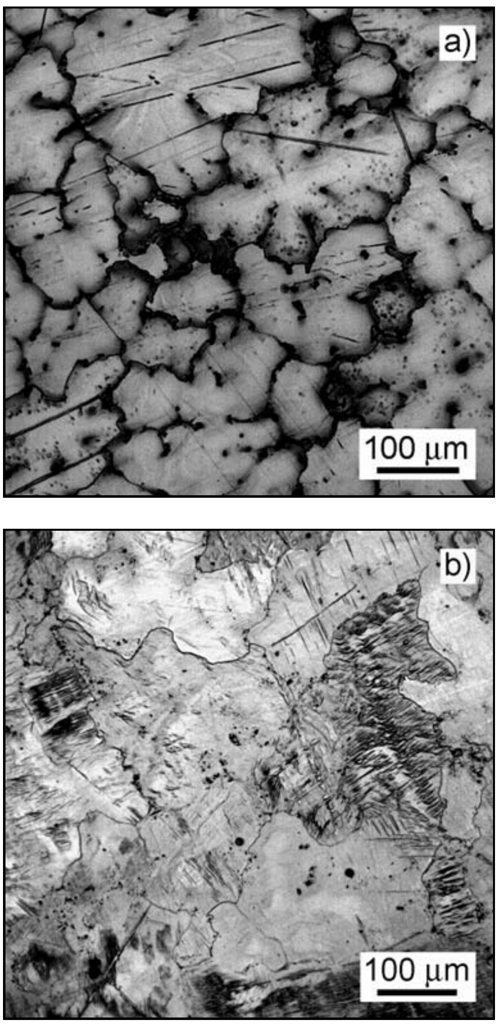

Fig. 4. The effect of annealing: a) as-received state, b) annealed 2 hours at 360 °C.

In Fig. 4 the light micrographs of the alloy in the as-received state and after annealing 2 hours at 360 ℃ are

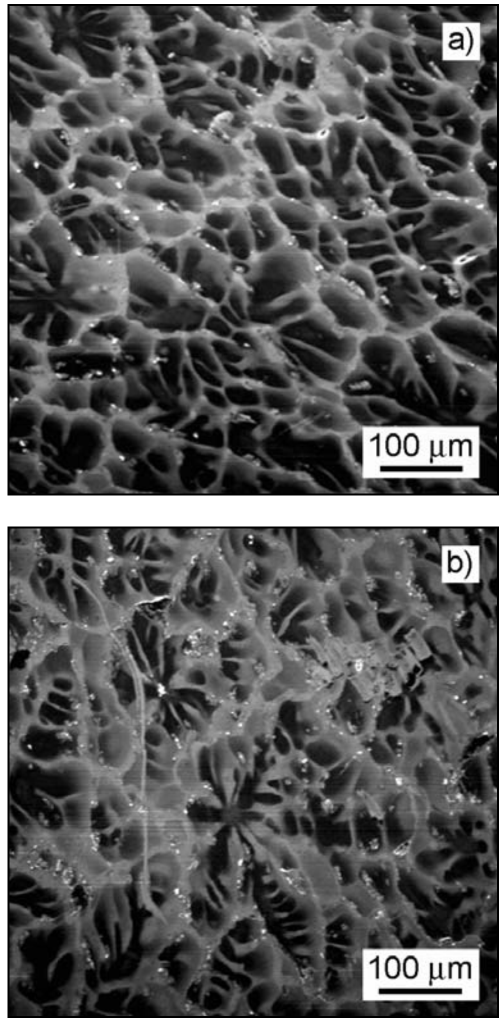

Fig. 5. SEM micrographs of samples annealed: a) 10 hours at 390 ℃, b) 2 hours at 360 ℃.

shown. Secondary phases in grain boundaries were not observed any more after annealing, which confirms the conclusions made on the base of DSC measurements.

This optimized thermal treatment at 360 ℃ was compared with a thermal treatment for 10 hours at 390 ℃, i.e. an intermediate temperature and maximum time as used in literature [14–17]. The SEM images of the microstructure presented in Fig. 5 showed no significant differences between these two annealing treatments; only a small amount of particles of secondary phases were found, predominantly in the grain boundaries.

The ductility of a material is crucial for forming; therefore the optimized thermal processing was verified by tensile tests at temperatures 300 ℃ and 350 ℃, used usually for forging of magnesium alloys. The results of the tests at 300 ℃ are presented in Fig. 6. The elongations to failure of the samples after optimized thermal treatment 2 hours at 360 ℃ are comparable or better than those after annealing for 10 hours at

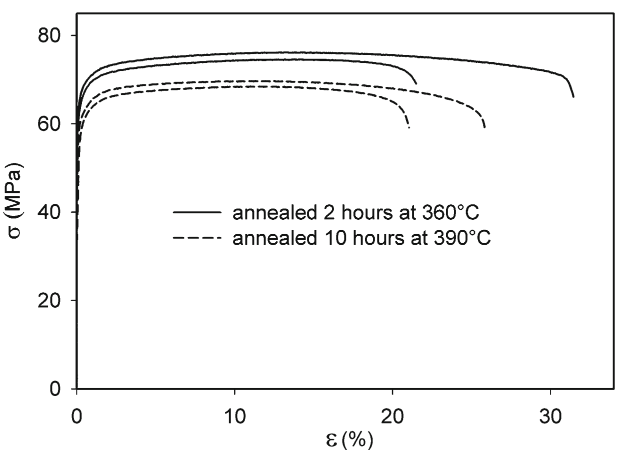

Fig. 6. Comparison of flow curves at 300 ℃ and strain rate of 0.05 s^{-1}.

390 ℃. Similar results have been received also at deformation temperature 350 ℃ (not shown).

4. Discussion

Composition of the particles of secondary phases, i.e. hexagonal $MgZn_2$ and monoclinic Mg_4Zn_7 phases as has been determined from TEM diffraction is in accordance with the study of Gao and Nie concerning the binary Mg-8.%Zn alloy [18] where both $MgZn_2$ and Mg_4Zn_7 phases were identified after ageing at 200 ℃. Besides these two phases, the addition of Zr leads to the formation of $ZrZn_2$ precipitates which decrease the mobility of grain boundaries and lead thus to the stabilization of fine-grained structure [8, 19] and positively affects both plasticity during forming and strength at the operating temperature of the eventual final part. In the present study, this finding [8, 19] has been confirmed by the microanalysis (EDS) of the particles at the grain boundaries that identified particles of stoichiometric composition corresponding to $ZrZn_2$. We have not observed any precipitates containing all three alloying elements (Mg, Zn, Zr) what is in accordance with [8] where the $Mg_7(Zn, Zr)_3$ precipitates have been observed in ZK60 alloy only after the processing that included also a pre-straining, not in the case of solely thermal treatment.

If we compare the optimized conditions of solution treatment found in the present study to the literature data [14–17], the most similar are the conditions proposed by Chen et al. [17], i.e. annealing at 375 ℃ for 3 hours. Unfortunately the criteria for selecting this temperature are not stated in the study [17] although the subsequent optimization of the ageing treatment (i.e. precipitation hardening as a part of the T6 process) is described in very deep detail. Moreover, in another study of these authors [16], significantly different conditions have been used: 430 ℃ for 6 hours, which leads us to the conclusion that the temperature of solution treatment has been selected rather arbitrarily in the region above the dissolving temperature of secondary phases. Nevertheless, setting the temperature and time of the thermal treatment to higher values than it is necessary for the complete dissolving of secondary phases leads to the growth of grain size and thus to the deterioration of the properties of the material.

5. Conclusions

The following conclusions can thus be drawn based on the results of this study:

1. From DSC measurements, the temperature of 360 ℃ and time of 2 hours were found as optimal conditions for solution treatment of ZK60 alloy. The tensile tests verified that the mechanical properties (particularly the ductility at the temperature of forming) after the solution treatment at conditions proposed in the present study are comparable or better than after the treatment reported in literature.

2. The majority of secondary phases present in the structure before the solution treatment were identified as $MgZn_2$ and Mg_4Zn_7 by TEM.

3. Stable particles that remained at the grain boundaries after solution treatment were identified as $ZrZn_2$ phase by the means of EDS microanalysis.

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