Magnesium Technology 2012
Edited by: Suveen N. Mathaudhu, Wim H. Sillekens, Neale R. Neelameggham, and Norbert Hort
TMS (The Minerals, Metals & Materials Society), 2012

Phase dissolution of γ-$Mg_{17}Al_{12}$ during homogenization of as-cast AZ80 Magnesium alloy and its effect on room temperature mechanical properties

Rahul R. Kulkarni[1], Nityanand Prabhu[1], Peter D. Hodgson[2], Bhagwati P. Kashyap[1]
[1]Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai, 400076, India
[2]Institute of Technology Research and Innovation, Deakin University, Waurn Ponds, Victoria 3217, Australia

Keywords: As-cast AZ80 Magnesium alloy, Homogenization treatment, Microstructure evolution, Mechanical properties

Abstract

As-cast AZ80 Mg alloy contains α-Mg, partially divorce eutectic of α and γ ($Mg_{17}Al_{12}$), fully divorce eutectic of α and γ, and lamellar eutectic of α and γ phases. During homogenization, second phase (γ-$Mg_{17}Al_{12}$) gets dissolved can change the mechanical properties. Therefore, the aim of the present work is to bring out the kinetics of dissolution of γ phase and evaluate its effect on mechanical properties. Microstructure evolution during homogenization was investigated as a function of time for 0.5 to 100 h and at the temperatures of 400° and 439°C. In as-cast state, this material was found to contain 70% α-Mg and 30% eutectic phase. With increasing homogenization time, dissolution of lamellar eutectic occurs first which is followed by dissolution of fully divorce eutectic and partially divorce eutectic. The dissolution kinetics of γ phase was analyzed based on the decrease in its volume fraction as a function of time. The time exponent for dissolution was found to be 0.38 and the activation energy for the dissolution of γ phase was found to be 84.1 kJ/mol. This dissolution of γ phase leads to decrease in hardness and tensile strength with increase in homogenization time.

1. Introduction

Magnesium alloys are attractive material for the automotive, medical and electronic industries due their light weight, high specific strength, high stiffness and high damping capability. In addition, magnesium and its alloys are suitable candidates for temporary medical implants due to their biodegradable property [1]. Among all the magnesium alloys, Mg-Al-Zn alloys are the most widely used wrought alloys at present due to their low cost [2]. Earlier studies on as-cast Mg-Al-Zn alloy show the presence of cellular product of α-Mg and γ-$Mg_{17}Al_{12}$ with partially and fully divorce eutectic of the same [3]. The cellular structure is characterized by lamellar morphology; the partially divorce eutectic is characterized by 'island' of α-Mg within γ-$Mg_{17}Al_{12}$ and the fully divorce eutectic is characterized by the single γ-$Mg_{17}Al_{12}$ phase/grain surrounded by α-Mg. These morphologies develop as a result of differential cooling rate during casting. The γ-$Mg_{17}Al_{12}$ is an intermetallic compound whereas the α-Mg is a solid solution of Al in Mg, with the former being harder phase than the latter [7]. The study of homogenization heat treatment of as-cast AZ91 alloy shows the dissolution of the second phase i.e. $Mg_{17}Al_{12}$ [4], which influences the mechanical properties of this alloy.

In the present work, microstructure evolution during homogenization of as-cast AZ80 Mg alloy is studied with an attempt to bring out the kinetics and mechanism of dissolution of γ phase. The progress in homogenization is evaluated in terms of change in mechanical properties of this alloy at room temperature.

2. Experimental details

2.1 Material:

The material used for study is as-cast AZ80 Mg alloy with chemical composition given in table I.

Table I Chemical Composition of AZ80 Mg alloy

Element	Al	Zn	Mn	Si	Mg
wt%	7.7	0.4	0.15	0.2	Balance

2.2 Microstructure study:

The metallographic specimen of size 10 mm x 10 mm x 2 mm was cold mounted and mechanically polished with the diamond paste of 0.25 μm at the final stage. After polishing, the sample was cleaned with ethanol using ultrasonic cleaning. Etching was done with 10 ml HF and 90 ml water (which makes α-Mg as white and γ-$Mg_{17}Al_{12}$ as dark) and the same was examined under optical microscope at 1000X and in Hitachi S-3400N scanning electron microscope (SEM). To confirm the phases, energy dispersive spectrometry (EDS) attached with SEM was carried out.

2.3 X-ray diffraction study:

X-ray diffraction study was carried out on the sample of size 2 x 2 x 1 mm^3. Cu-K_α source was used in X'pert model Philips made XRD machine over the scanning range of 2θ equal to 5 to 90°.

2.4 Homogenization heat treatment:

Phase diagram of Mg-Al (see Figure 5 later) shows eutectic transformation at 437°C with aluminum composition around 33% in Mg. To know the transformation temperature range, differential scanning calorimetry (DSC) was used. To avoid the partial melting of segregated solute, homogenization heat treatment was carried out at 400° and 439°C over the time period of 0.5 hr to 100 hr. Samples were heated to these temperatures for particular time period and then quenched in water. Each sample was then polished and etched for metallography, and the phase analysis was done using Olympus-image analyzer at 100X. The volume fraction of γ-$Mg_{17}Al_{12}$ phase was measured over 10 fields within the sample. The fraction transformed was calculated using the statistical analysis for error bar estimated at 95% confidence level.

2.5 Mechanical Testing:

Tensile specimens of Φ 4.5 mm x 16mm gauge length were prepared. These were homogenized at 400° and 439°C for 3 hr. Tensile test was carried out at the constant initial strain rate of 10^{-4} s^{-1} at room temperature using an Instron Universal testing machine with 5 kN capacity.

Macro-hardness was measured in HRt scale with 15 kg load and dwell time of 15 sec at five different places in each of the homogenized samples. An average of five readings for each sample was taken for analysis. The Vickers's micro-hardness was measured in the individual phases to know the relatively harder and softer phases. During this hardness measurement, the load was kept at 100 gm for 15 sec. Total 10 readings were taken in each phase. The mean microhardness (VHN) values are presented with error bar better than 4% at the confidence level of 95%.

3. Results and Discussion

3.1 Microstructure study:

As cast microstructure consists of mainly three parts α-Mg (both primary and eutectic), γ-eutectic particles and lamellar γ-precipitates (cooling rate of casting being sufficiently low, discontinuous precipitation can occur) which are shown in Figure 1 and Figure 2

When an alloy is solidified, it follows the primary solidification metallurgy. α-Mg will grow dendritically by rejecting the Al and Zn into the inter-dentritical liquid. When this region accumulates the Al, which is having eutectic composition, γ-$Mg_{17}Al_{12}$ will grow with further under-cooling of the alloy. This is known as divorce eutectic solidification [5]. This eutectic growth morphology has been studied by Nave et.al [3]. According to them, the morphologies were developed because of the differential cooling rate during solidification.

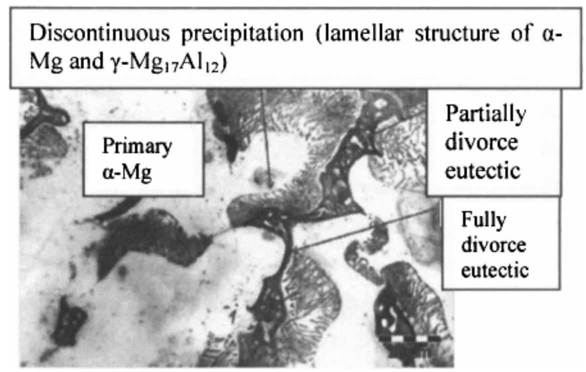
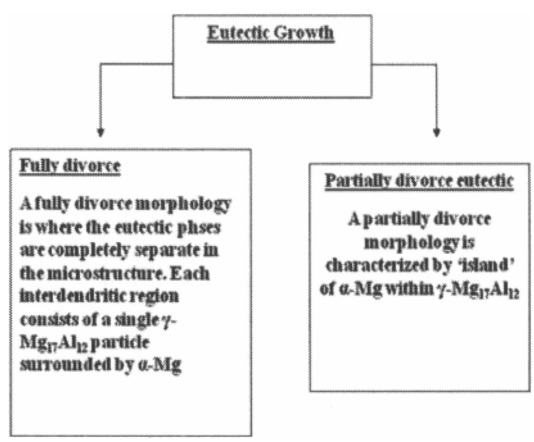


Figure 1. Optical micrograph showing the as-cast structure of AZ80 Mg alloy

The chart below shows that the eutectic growth in as-cast structure consists of two parts (i) fully divorce eutectic, (ii) partially divorce eutectic.



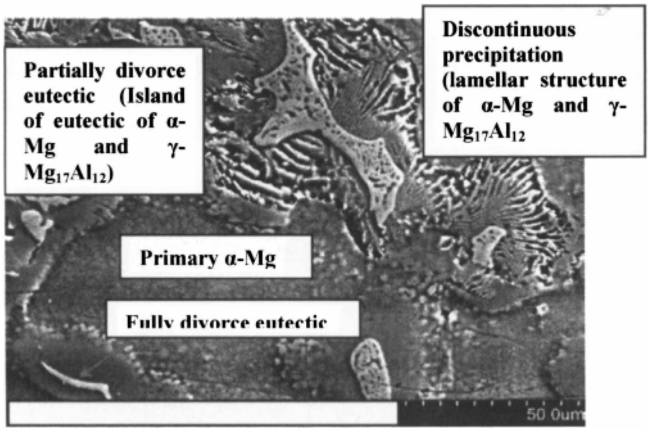


Figure 2. SEM micrograph showing the as-cast structure of AZ80 Mg alloy

EDS analysis (figure 3) confirms the phases α-Mg and $Mg_{17}Al_{12}$ in the form of divorce eutectic with different morphologies. Atomic % of elements in each of these phases are given in table 2. Actual ratio of Mg:Al = 60.39: 37.57 = 1.61 nearly matches with standard ratio of Mg:Al = 17:12 = 1.42, which confirms the intermetallic compound to be $Mg_{17}Al_{12}$.

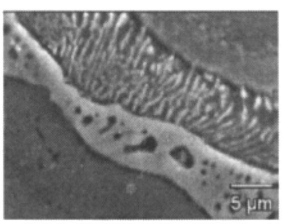


Figure 3. SEM-EDS point analysis with composition stated in table II

Table II Elements in atomic % (SEM-EDS)

	Mg-K	Al-K	Si-K	Mn-K
pt1	60.39	37.57	0.03	0.08
pt3	81.79	11.57	0.11	0.00

3.2 X-ray diffraction study:

Peaks in the figure 4 shows that $Mg_{17}Al_{12}$ is present in proportion less than that of Mg.

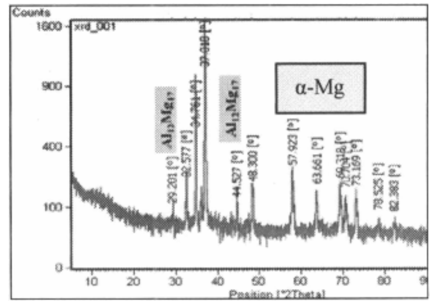


Figure 4. XRD pattern for as-cast AZ80 Mg alloy

3.3 Effect of Homogenization heat treatment:

The as-cast material is inhomogeneous in terms of phase size, phase morphology and their distributions. Also, from the phase diagram (Figure 5), it is observed that above the solvus line, the eutectic (a mixture of α-Mg and β-$Mg_{17}Al_{12}$) converts into the single phase α-Mg having maximum solubility of Al in Mg. So, precipitation behavior was studied at the temperatures below the transformation temperature and at the transformation temperature.

The DSC curve was obtained at the heating rate of 10°C/min (Figure 6). The endothermic peak in the DSC curve shows transformation from two phases α and γ to single phase α-Mg at 439°C

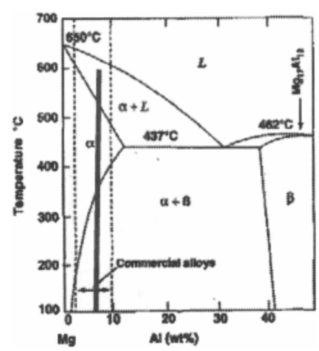


Figure 5. Magnesium rich side of Mg-Al phase diagram with the Al content in AZ80 marked by bold solid line

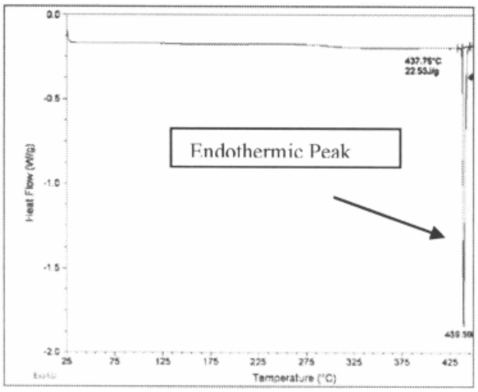


Figure 6. DSC curve shows the endothermic peak at 439°C

Figure 7 shows different microstructures of homogenized samples in terms of fraction transformed plotted as a function of time at 400°C. It can be seen from the microstructures that as the time period increases the more and more precipitates get dissolved; after 100 hr it is almost fully dissolved. The data points are found to fit into the sigmoidal curve with $R^2 = 0.93$. The same analysis was done at 439°C over the homogenization periods of 0.5, 1, 3, 24, 72, and 100 hr. These data points also fit well into similar sigmoidal curve (Figure 8). It can be seen that dissolution time required is less at 439°C as compared to that at 400°C which is due to the fact that diffusion for dissolution becomes faster at higher temperature.

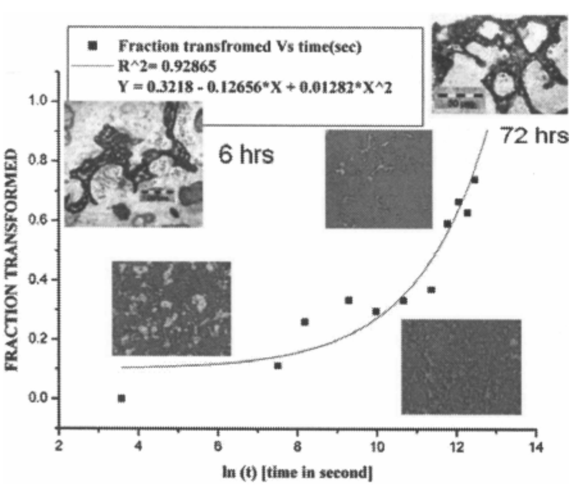


Figure 7 Change in microstructure of homogenized samples plotted in terms of fraction transformed as a function of time at 400°C

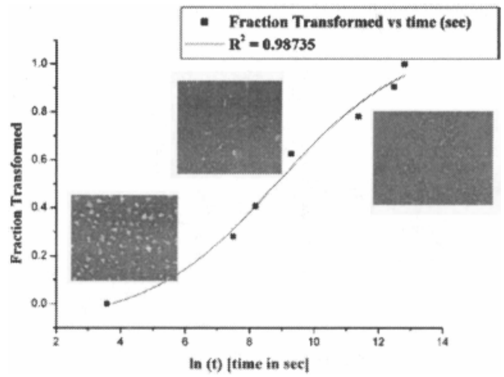


Figure 8 Change in microstructure of homogenized samples plotted in terms of fraction transformed as a function of time at 439°C

Further, it is observed that with increasing homogenization time, dissolution of lamellar eutectic occurs first, which is followed by dissolution of fully divorce eutectic and partially divorce eutectic (figure 7). The dissolution process is associated with diffusion. The concentration gradient is not uniform in partially divorce eutectic which may be a possible reason that the partially divorce eutectic takes more time for dissolution.

To study the kinetics of dissolution, Johnson-Mehl-Avrami- Kolmogorov (JMAK) equation for phase transformation [6] as given below was used-

$$X(t) = 1 - \exp\{-((k(T)t)^n\}$$

Here, $k(T)$ represents temperature dependent isothermal rate constant and n represents the time exponent. To calculate these parameters, log log (1/1-X) vs. log t was plotted from the data at 400°C and 439°C. From the plots presented in Figure 11, the value of k (T) is found to be 4.6 x 10^{-6} s^{-1} and 5.68 x 10^{-7} s^{-1}, respectively. The value of n is determined to be 0.37 and 0.39. These values of n lie between 0 and 1, which is the indication that the rate of transformation decreases with increasing time.

$k(T)$ is taken to follow Arrhenius type relationship

$$k(T) = k_0 \exp(\frac{-Q_{eff}}{RT})$$

where Q_{eff} is the effective activation energy for transformation.

The value of Q_{eff} is obtained to be 84.1 kJ/mol from vs. 1/T in figure 12. This value of Q_{eff} is closer to the activation energy grain boundary diffusion in Mg (92 kJ/mole) [8]

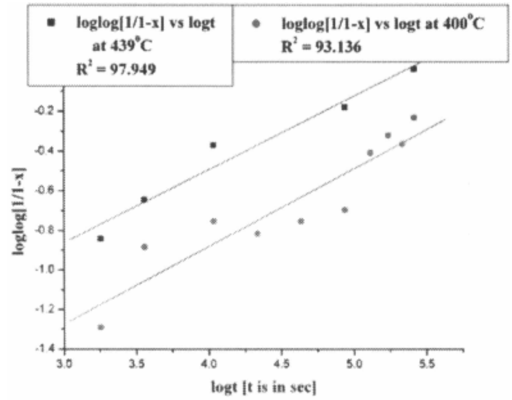


Figure 11 plot of loglog (1/1-x) vs. log t at 400 and 439°C

3.4 Variation in Hardness and Tensile Properties:

Micro-hardness test of the phases shows that the γ-$Mg_{17}Al_{12}$ (VHN = 89.77+/-3.59) is harder than α-Mg (VHN = 67+/-3.72). There is a lot of variation in macro-hardness over the homogenization period at both the temperatures of 400 and 439°C (Figure 12), which can be attributed to the variation in the distribution of second phase.

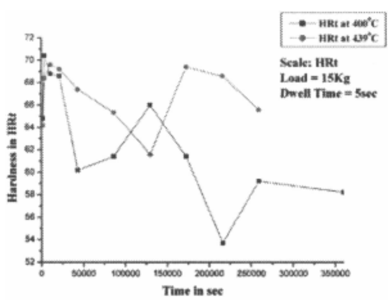


Figure 42 Variation in hardness as a function of dissolution time at 400 and 439°C

Tensile tests of samples subjected to isochronal annealing of 3 hr at 400 and 439°C show that the yield and ultimate tensile strengths are higher at 400°C than that at 439°C. This is possibly due to the decrease in the phase proportion of second phase as the temperature is increased. The proportion of second phaseγ-$Mg_{17}Al_{12}$ at 400°C (24%) is greater than at 439°C (13%). However, the tensile ductility is found to be less in case of the specimen which is homogenized at 439°C for 3 hrs (14%) than that at 400°C for 3 hrs (7%). This may be due to the distribution of γ-$Mg_{17}Al_{12}$ second phase which is more uniform for the specimen homogenized at 400°C than that of 439°C.

Table 3 Tension Test Data

Tensile properties	0.2% proof stress (MPa)	Ultimate Tensile strength (MPa)	Braking stress (MPa)	Elongation %
400°C (3hr)	109	179	178	14
439°C (3hr)	55	78	75	7

In the present study, the solutionizing of γ-$Mg_{17}Al_{12}$ phase was done for the period of 0.5 to 100 hrs only at 400° and 439°C. The dissolution behavior at both the temperatures are seen to be similar with n = 0.37 to 0.39. However, the understanding of the mechanism for dissolution requires the extension of this study to a range of temperatures, in which case a precise value of the activation energy could bring some insight, instead of that based on the limited data only at the above two temperatures.

4. Conclusions

1. As cast AZ80 alloy consists of α-Mg, partially and fully divorce eutectic of α and γ ($Mg_{17}Al_{12}$), and lamellar eutectic of α and γ phases.
2. Phase proportion of γ - $Mg_{17}Al_{12}$ decreases with increase in time at both the temperatures of 400 and 439°C. The decrease of γ phase is associated with diffusion process.
3. With increasing homogenization time, dissolution of lamellar eutectic occurs first which is followed by dissolution of fully divorce eutectic and partially divorce eutectic.
4. The kinetics of transformation follows sigmoidal curve, which is an indication of time dependent phenomenon. The values of time exponent n are found to be 0.37 and 0.39 for homogenization temperature 400 and 439°C respectively. These values lying between 0 and 1, which suggest the rate of transformation decreases with increase in time. The effective activation energy for transformation was obtained to be 84.1 kJ/mol.

5. Homogenization at 439°C shows lower yield strength of 55 MPa and ultimate tensile strength of 78 MPa as compared to the corresponding values of 109 and 179 MPa obtained at 400°C. The room temperature elongations to failure after the above treatment were 7% and 14% respectively.

5. References

1. Hamid Reza Bakhsheshi Rad, Mohd Hasbullah Idris , Mohammed Rafiq Abdul Kadir, Saeed Farahany, *"Microstructure analysis and corrosion behaviour of biodegradable Mg-Ca implant alloys"*, Mat. Design, (2011) 1-30.
2. H.T. Zhou, Q.B. Li, Z. K. Zhao, Z.C. Liu, S.F.Wen, Q.D.Wang, *"Hot workability characteristics of magnesium alloy AZ80—A study using processing map"*, Mater. Sci. Engg. A, 527 (2010) 2022–2026.
3. M. D. Nave, A. K. Dahle and D.H. StJohn, *"Eutectic growth morphology in Magnesium-Aluminium alloys"*, Magnesium Technology, the minerals, metals materials society, 2000, 233-242.
4. Tianping Zhu, Zhan W. Chen, and Wei Gao, *"Dissolution of Eutectic β-$Mg_{17}Al_{12}$ Phase in Magnesium AZ91 Cast Alloy at Temperatures Close to Eutectic Temperature"*, Journal of Mater. Engg and Performance, 19 (2010), 860-867.
5. Tianping Zhua, , Zhan W. Chenb, Wei Gaoa, *"Microstructure formation in partially melted zone* during gas tungsten arc welding of AZ91 Mg cast alloy", mater. Charact., 59 (2008) 1550 – 1558.
6. A. K. Jena, M. C. Chaturvedi, *"Phase transformation in Materials*", prentice Hall, new Jersey, 1992.
7. I.A. Yakubtsova, B.J. Diaka, , C.A. Sagera, B. Bhattacharyab, W.D.MacDonaldc,1, M. Niewczasb, *"Effects of heat treatment on microstructure and tensile deformation of Mg AZ80 alloy at room temperature"*, Mater. Sci. and Engg. A 496 (2008) 247–255
8. B.H. Lee1, K.S. Shin and C.S. Lee1, *"High Temperature Deformation Behavior of AZ31 Mg Alloy"*, Mater. Sci. Forum 475-479 (2005) pp. 2927-2930