

DSC analysis of dissolution reaction in an as-cast and HPT-processed Mg-Gd alloy

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Abstract

The dissolution reaction kinetics were determined by differential scanning calorimetry (DSC) analysis for Mg-0.6Gd (wt.%) in an as-cast condition and after processing by high-pressure torsion (HPT) at room temperature for 20 turns. For the as-cast condition, the dissolution temperature was in the range of 634–658 K with an activation energy of 135 ± 9 kJ/mol. After HPT, the range of dissolution temperature decreased to 601–633 K, with a lower activation energy of 118 ± 10 kJ/mol. In both conditions, the Avrami and growth exponents are around 1.5, which suggests that the dissolved precipitates exhibit polyhedron-like morphology and that the dissolution process is dominated by bulk dissolution with a constant rate controlled by diffusion.

Keywords: Activation energy; Dissolution; Magnesium.

1. Introduction

Magnesium (Mg) and its alloys are characterized by low density and high specific strength, making them very attractive in diverse commercial applications, including transportation and biomedical fields [1]. Nevertheless, the poor formability of conventional Mg-based alloys at low temperatures, caused by the limited number of active slip systems and the formation of a strong basal texture, seriously restricts their widespread applications [2]. Currently, the addition of a limited amount of rare-earth (RE) elements is an effective approach for tailoring the mechanical performance of Mg-based alloys [3]. Various reports are available that aim to elucidate the role of RE elements on the high performance of Mg-RE alloys [4-7]. Indeed, the enhancement of the mechanical properties of Mg-RE alloys under conventional thermomechanical processing is mainly attributed to texture weakening, retardation of recrystallization and precipitation strengthening [4-7]. The mechanisms responsible for high-performance Mg-RE alloys have been examined and are now well understood [4-7]. However, the deformation of most Mg-RE alloys occurs at elevated temperatures to prevent failure, thereby increasing processing costs. Recent research indicates that Mg-RE alloys can be successively severely deformed at room temperature (RT) without cracking by high-pressure torsion (HPT) [8, 9]. It was also found that the deformation behaviour of Mg-RE alloys under HPT was different from that known under conventional thermomechanical processing [5, 9]. Thus, dynamic recrystallization was enhanced in Mg-0.6Gd (wt.%) alloy in comparison with AZ31 alloy during HPT at RT due to the fragmentation of second particles [5, 9]. Moreover, the precipitation developed during annealing of HPT-processed Mg-0.6Gd alloy failed to stabilize fine grains [10]. Ultimately, the deformation behaviour and phase transformation mechanisms in Mg-RE alloys require further exploration under severe plastic deformation at RT. Accordingly, the present study aims to examine the effect of HPT on the dissolution reaction of the Mg-0.6Gd alloy.

2. Experimental procedure

An as-cast Mg-0.6Gd alloy was provided by the Institute of Physical Metallurgy and Materials Physics, Germany. The HPT was performed on discs with diameters of 10 mm and thicknesses of 0.85 mm at RT for 20 turns under a pressure of 6.0 GPa with a rotational speed of 1 rpm. The DSC analyses were achieved in a DSC 404 Netzsch calorimeter under an argon atmosphere, over a temperature range of 298–723 K and a heating rate range of 10–40 K/min.

2.1. Non-isothermal calculation approach

Since the time, t , changes linearly with temperature, T , during the DSC measurement, the classical Johnson-Mehl-Avrami (JMA) equation can be expressed under non-isothermal conditions as follows [11]:

$$x = 1 - \exp \left[- \left(\frac{k(T-T_0)}{V} \right)^n \right] \quad (1)$$

where x is the crystallized fraction at t , n is the Avrami exponent, T_0 is the starting temperature, V is the heating rate and k is the reaction rate constant which can be obtained by the equation [11]:

$$k = k_0 \exp \left(- \frac{E_a}{RT} \right) \quad (2)$$

where k_0 is the frequency factor, E_a is the activation energy and R is the universal gas constant. The dissolution of phase is considered as the inverse of phase nucleation and growth so that, in the present case, the undissolved fraction is equivalent to x . The x value is estimated based on the DSC measurement as follows [12]:

$$x = \frac{A_T}{A} \quad (3)$$

where A_T is the area under the corresponding peak between the onset temperature and a specific temperature T and A is the total area under the endothermic peak. The value of E_a is obtained by the Kissinger method [13]:

$$\ln \left(\frac{V}{T_p^2} \right) = C - \frac{E_a}{RT_p} \quad (4)$$

where T_p is the maximum temperature value of the dissolution peak and C is a constant. The n exponent is determined from T_p [14]:

$$n = \frac{2.5T_p^2 R}{\Delta T_p E_a} \quad (5)$$

where ΔT_p is the full width at half maximum of the dissolution peak. A modified Kissinger equation was proposed to estimate the grain growth exponent, m , as follows [15]:

$$\ln \left(\frac{V^n}{T_p^2} \right) = C_1 - \frac{mE_a}{RT_p} \quad (6)$$

where C_1 is a constant.

Table 1 summarizes the values of n and m for various nucleation and growth mechanisms [11]. The crystal growth morphology can be determined by calculating the ratio of times for two fixed degrees of x . The ratio of transformation times for 75 and 25% is often used in a manner that corresponds to [11]:

three-dimensional (3D) growth (polyhedron): $1.48 \leq \frac{t_{0.75}}{t_{0.25}} \leq 1.69$.

two-dimensional (2D) growth (plates): $1.69 \leq \frac{t_{0.75}}{t_{0.25}} \leq 2.20$.

one-dimensional (1D) growth (needles): $2.20 \leq \frac{t_{0.75}}{t_{0.25}} \leq 4.82$.

Table 1. Values of n and m for various nucleation and growth mechanisms [11].

	3 D growth		2 D growth		1 D growth	
	n	m	n	m	n	m
Bulk nucleation with varying numbers of nuclei						
Growth controlled by interface reaction	4	3	3	2	2	1
Growth controlled by diffusion	2.5	1.5	2	1	1.5	0.5
Bulk nucleation with constant number of nuclei						
Growth controlled by interface reaction	3	3	2	2	1	1
Growth controlled by diffusion	1.5	1.5	1	1	0.5	0.5

3. Results and discussion

Figs. 1a and 1b show the DSC curves measured at 10 and 40K/min, respectively. The DSC curves of both samples measured at 10 K/min display one endothermic peak (see arrows), indicating the dissolution reaction. Based on the equilibrium phase diagram of the Mg-Gd system, the dissolution phase is the Mg₅Gd phase [16]. The DSC curves obtained at 20, 30 K/min (not shown) present a similar evolution for both samples. Fig. 1b shows that the endothermic peak of the as-cast sample disappeared at 40 K/min, indicating that the time was insufficient for the dissolution to occur at this temperature. The difference in the DSC curve level between the samples may be due to the formation of grain boundary complexions like grain boundary wetting [17, 18]. Figs. 1c and 1d depict the dissolution peak after baseline subtraction against temperature for both samples. The T_p values are summarized in Table 2.

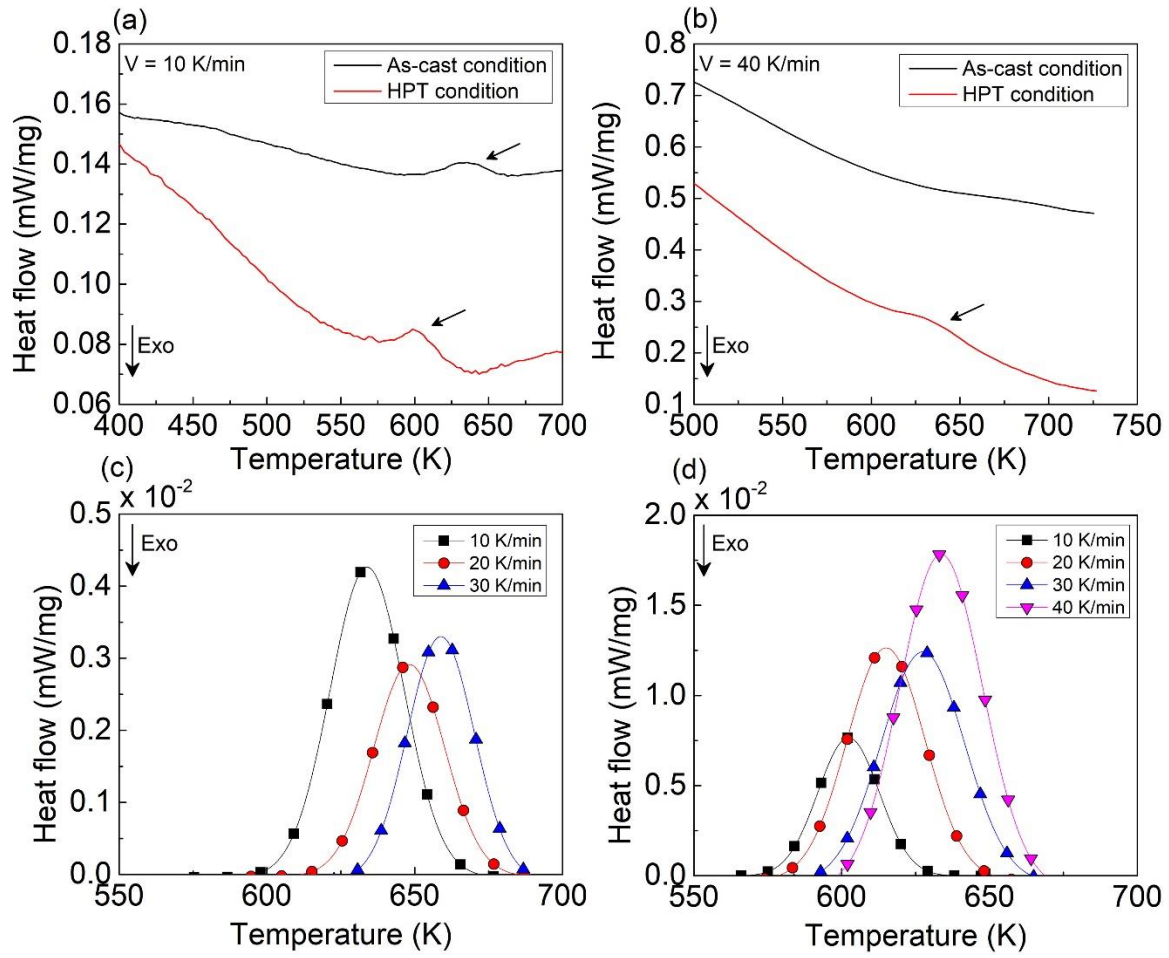


Fig. 1: DSC curves of as-cast and HPT-processed samples measured at (a) 10 and (b) 40K/min. Dissolution peaks against the temperature for the (c) as-cast and (d) HPT-processed samples.

The dissolution reaction, as confirmed by the higher T_p values with increasing heating rates, is a thermally-activated and kinetically controlled process. The T_p range decreased from 634–658 for the as-cast samples to 601–633 K after HPT.

Table 2. Values of T_p , $t_{0.75}/t_{0.25}$ ratio and n with heating rates for the samples.

Heating rate (K/min)	As-cast condition			HPT condition		
	T_p (K)	$t_{0.75}/t_{0.25}$	n	T_p (K)	$t_{0.75}/t_{0.25}$	n
10	634	1.50	1.80	601	1.48	1.80
20	648	1.57	1.70	615	1.50	1.66
30	658	1.63	1.60	628	1.57	1.65
40	—	—	—	633	1.59	1.61

As displayed in Fig. 2a, the activation energies were calculated from the slope of the $\ln(V/T_p^2)$ against $1000/RT_p$ plots. For the as-cast condition, the E_a value was equal to 135 ± 9 kJ/mol, which corresponds to the activation energy for lattice self-diffusion in Mg (~ 135 kJ/mol) [19].

Regarding the HPT condition, E_a decreases to 118 ± 10 kJ/mol which is close to the activation energy for boundary self-diffusion in Mg (~ 92 kJ/mol) [19].

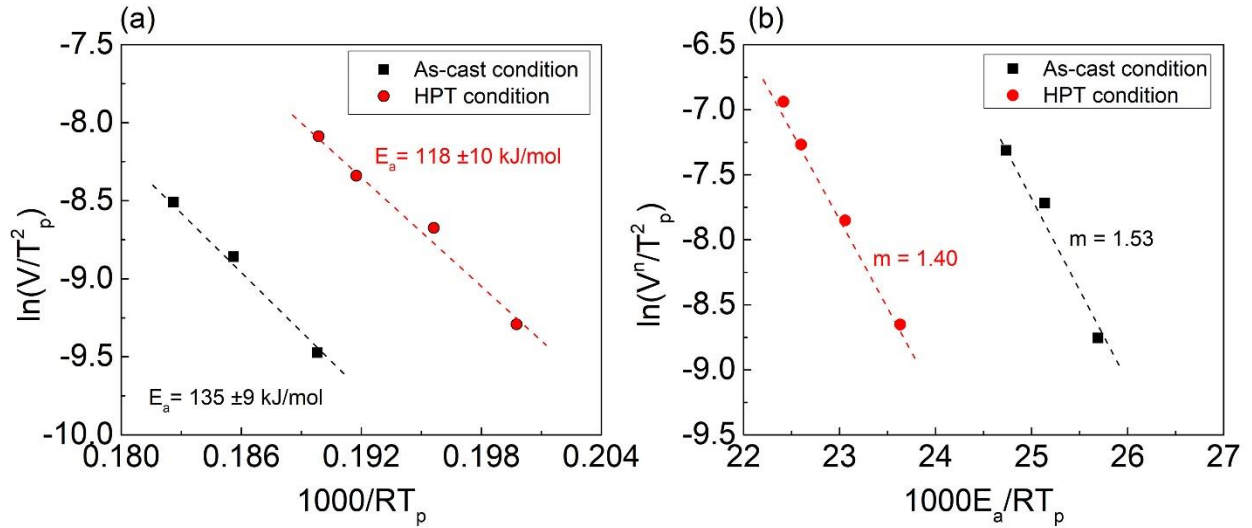


Fig. 2: (a) $\ln(V/T_p^2)$ against $1000/RT_p$ and (b) $\ln(V^n/T_p^2)$ against $1000E_a/RT_p$ for both samples.

The dissolution reaction is accelerated due to the grain refinement and numerous defects such as dislocations and vacancies induced by HPT which increase the mobility of solute atoms and therefore enhance diffusion [9]. In addition, HPT caused the fragmentation of the Mg_5Gd phase already existing in the as-cast sample which facilitated its dissolution [8, 9].

The $t_{0.75}/t_{0.25}$ ratios as a function of heating rates are shown in Table 2. The average $t_{0.75}/t_{0.25}$ ratios are 1.56 and 1.68 for the as-cast and HPT conditions, respectively, which means that the precipitate phase exhibits a 3D shape with polyhedron-like morphology. It is apparent that the shape of the precipitate phase is independent on the heating rate and sample condition.

The average n values calculated from the values listed in Table 2 are 1.70 and 1.68 for the as-cast and HPT conditions, respectively. To access the m exponent, Fig. 2b displays $\ln(V^n/T_p^2)$ against $1000E_a/RT_p$ and the m values are 1.40 and 1.53 for the as-cast and HPT conditions, respectively. Based on Table 1, the n and m values under as-cast and HPT conditions are both close to 1.5 which indicates that the dissolution of precipitates with a polyhedron-like morphology is principally dominated by bulk dissolution with a constant rate controlled by diffusion. Consequently, the HPT does not affect the dissolution mechanism.

Conclusions

The effect of HPT on the dissolution reaction kinetics of Mg-0.6Gd alloy was investigated using DSC analysis. The main conclusions are:

- After HPT, the dissolution peak and activation energy decreased from 634–658 to 601–633 K and 135 ± 9 to 118 ± 10 kJ/mol, respectively.
- The dissolution mechanism was unaffected by HPT. The dissolution process (n and $m \approx 1.5$) is primarily dominated by bulk dissolution with a constant rate which is controlled by diffusion.

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References

- [1] S.V.S. Prasad, S.B. Prasad, K. Verma, R.K. Mishra, V. Kumar, S. Singh, J. Magnes. Alloy 10 (2022) 1-61.
- [2] B.L. Mordike, T. Ebert, Mater. Sci. Eng. A 302 (2001) 37-45.
- [3] I.-H. Jung, M. Sanjari, J. Kim, S. Yue, Scripta Mater. 102 (2015) 1-6.
- [4] S. Sandlöbes, S. Zaeferrer, I. Schestakow, S. Yi, R. Gonzalez-Martinez, Acta Mater. 59 (2011) 429-439.
- [5] N. Stanford, M.D. Callaghan, B. de Jong, Mater. Sci. Eng. A 565 (2013) 459-468.
- [6] T. Xiao, B. Sun, J. Zhang, Z. Li, S. Liu, R. Wu, Mater. Lett. 368 (2024) 136691.
- [7] M. Saad Patel, A. Rahaman, R. Jose Immanuel, Mater. Lett. 370 (2024) 136808.
- [8] O. Ould Mohamed, H. Azzeddine, Y. Huang, T. Baudin, P. Bazarnik, F. Brisset, M. Kawasaki, T.G. Langdon, Adv. Eng. Mater. 25 (2023) 2201794.
- [9] O. Ould Mohamed, P. Bazarnik, Y. Huang, H. Azzeddine, T. Baudin, F. Brisset, T.G. Langdon, J. Mater. Eng. Perform. 33 (2024) 2860-2874.
- [10] O. Ould Mohamed, P. Bazarnik, Y. Huang, H. Azzeddine, T. Baudin, F. Brisset, M. Kawasaki, T.G. Langdon, Mater. Today Commun. 38 (2024) 108305.
- [11] M. Romero, J. Martín-Márquez, J.M. Rincón, J. Eur. Ceram. Soc. 26 (2006) 1647-1652.
- [12] M.I. Barrena, J.M. Gómez de Salazar, L. Pascual, A. Soria, J. Therm. Anal. Calorim. 113 (2013) 713-720.
- [13] H.E. Kissinger, Anal. Chem. 29 (1957) 1702-1706.
- [14] J.A. Augis, J.E. Bennett, J. Therm. Anal. 13 (1978) 283-292.
- [15] K. Matusita, S. Sakka, J. Non-Cryst. Solids 38-39 (1980) 741-746.
- [16] L.L. Rokhlin, Magnesium Alloys Containing Rare Earth Metals: Structure and Properties CRC Press, London, 2003.
- [17] B. Straumal, R. Valiev, O. Kogtenkova, P. Zieba, T. Czeppe, E. Bielanska, M. Faryna, Acta Mater. 56 (2008) 6123-6131.
- [18] B. Straumal, K. Tsoy, A. Druzhinin, V. Orlov, N. Khrapova, G. Davdian, G. Gerstein, A. Straumal, Metals 13 (2023) 1407.
- [19] H.J. Frost, M.F. Ashby, Deformation-Mechanism Maps: The Plasticity and Creep of Metals and Ceramics, Pergamon Press, Oxford, 1982.