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Grain growth kinetics of bulk AZ31 magnesium alloy by hot pressing

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ABSTRACT

Bulk AZ31 magnesium alloy was prepared by hot pressing followed by isothermal and isochronal annealing treatments. A study on the kinetics of grain growth was carried out. X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) were employed as analyzing tools for the structural evolution and thermal stability at elevated temperatures. The grain sizes were determined by the broadening of X-ray lines and TEM. The results showed that for annealing at temperature range of 300–400 °C, the grain growth kinetics can be well interpreted by the kinetic equation, $D^n - D_0^n = kt$, where $k = k_0 e^{(-E_g/RT)}$. The grain growth exponent n and activation energy E_g were calculated based on the experiment data. The activation energy for grain growth E_g was found to be 110 kJ/mol, which was higher by 18 kJ/mol than that for pure magnesium.

1. Introduction

Magnesium and magnesium alloys have been widely used in the electronics, aerospace and automotive industries due to their inherently low densities. Even though magnesium and magnesium alloys have high strength-to-weight ratio, they exhibit low ductility and low strength [1–5]. In this regard, many new methods have been developed to overcome these weaknesses and achieve desired properties [6–8].

It is reported that grain refining is an effective way to improve both mechanical strength and ductility of metallic materials [9]. In most cases, the relationship between the yield stress σ_y and the grain size d can be expressed by the Hall–Petch expression $\sigma_y = \sigma_0 + k_y d^{-1/2}$, where σ_0 and k_y are material constants. For magnesium and magnesium alloys, grain refining is very tempting for their high k_y value [1,9–12].

Mechanical alloying (MA) is a relatively new technique to prepare materials which are different to produce by traditional methods due to the high melting temperature of materials. It has attracted wide practical interest for it is a simple but powerful way to produce massive amounts of materials with nanocrystalline grains. Recently, it has been also reported that the hot pressing is workable in the fabrication process for a fully dense body. During this process, hot pressing is used to remove porosity, consolidate powder materials and weld together [13].

Since nanocrystalline structure is usually in the non-equilibrium state and apt to grow during heating. It is critical to understand grain growth behavior to control the grain-size-dependent properties for engineering applications. Some scholars have done investigations on the thermal stability of grain size in various materials, such as pure metals, oxides and composites and so on [14–17]. In this paper, isothermal and isochronal annealing experiments were carried out for bulk AZ31 magnesium alloy prepared by hot pressing, to clarify the thermal stability and kinetics of grain growth.

2. Experimental procedures

The industrial AZ31 magnesium alloy powders were used as the starting material and processed via mechanically assisted hydriding–dehydriding treatment. The nominal composition of AZ31 magnesium alloy powder is given in Table 1. The hydriding process was performed with the use of a planetary type QM-DY4 ball-mill supplied by Nanjing NanDa Instrument Plant. The ball to powder mass ratio was 60:1, the mill shaft rotation was 300 rpm and the hydrogen pressure for the hydriding was 1 ± 0.03 MPa. The dehydriding treatment was performed in an vacuum furnace equipment assembled at the HIT Powder Metallurgy Laboratory, under a vacuum better than 1×10^{-2} Pa. Microstructural observation by TEM was undertaken using an Philips-CM12 electron microscope operating at 30 kV and morphology was observed by a Hitachi S-570 SEM at 200 kV. For TEM, 3 mm samples were ultrasonically cut from bulk material, grinded and thinned in a Gatan Ar ion mill in liquid nitrogen cooled stage.

The SEM morphology of the nanocrystalline AZ31 magnesium alloy powders was shown in Fig. 1. To study the kinetic of grain growth of bulk AZ31 magnesium alloy, the powders were hot vacuum pressing into bulk disk with diameter of 5 mm and height of 3 mm under 120 MPa pressure at 300 °C.

Isothermal and isochronal annealing treatments were carried out under argon atmosphere at temperatures between 300 °C and 400 °C with different annealing times from 30 min to 600 min, respectively. All the annealing treatments were done in an electric resistance furnace. The heating rate was controlled at 10 °C/min. The average grain sizes were estimated by the broadening of X-ray diffraction peaks.

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Table 1
Chemical composition of nanocrystalline AZ31 magnesium alloy powder.

Element	Al	Zn	Mn	Mg
Mass%	2.95	1.05	<0.02	Others

The grain size measurement and structural characterization were estimated using XRD using Cu Kα radiation operating at 50 kV and 50 mA with a scanning speed of 0.02°/s. The grain size *D* is given by the following equation:

$$B = 1.05\frac{\lambda}{d\ \cos\theta} \quad (1)$$

where *B* is the line broadening width, θ_B, Bragg diffraction angle, λ, the wave length of X-ray.

3. Results and discussion

3.1. Kinetics of grain growth

In order to study grain growth kinetics, hot pressing bulk AZ31 magnesium alloy disks are annealed at different temperatures and for different durations. Fig. 2 shows the XRD spectra of the bulk AZ31 magnesium alloy disks after isothermal annealing at 300 °C for several selected durations. It can be seen that an increase in intensity and peak narrowing of XRD peaks. It has occurred as a result of increase in grain size. The phases of MgO and $Al_{12}Mg_{17}$ can also be detected in the XRD pattern. The line broadening data are then processed according to Eq. (1). The grain size of bulk AZ31 magnesium alloy estimated as a function of annealing time is given in Fig. 3, which shows the plots of grain size (*D*) versus annealing time (*t*) at different temperatures.

From Fig. 3, it can be seen that the grain size of bulk AZ31 magnesium alloy disks increases gradually with increasing the annealing time as most metallic materials. As the annealing time is increased to 600 min, the ultimate grain sizes increase to 65 nm, 75 nm, 95 nm, 125 nm and 165 nm with increasing annealing temperatures from 300 °C to 400 °C, respectively. The grain growth rate is determined by both the annealing temperature and the annealing time. In general, the grain growth of bulk AZ31 magnesium alloy is very sensitive to the annealing temperature. Fig. 4 shows TEM images of bulk AZ31 magnesium alloy annealing for 600 min at 400 °C. In Fig. 4, Mg is identified to be the dominant phase with

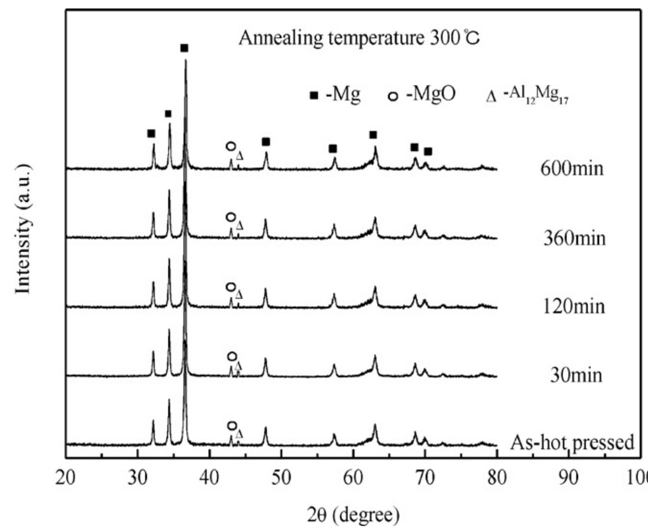

Fig. 2. XRD spectra of the bulk AZ31 magnesium alloy disks after isothermal annealing at 300 °C.

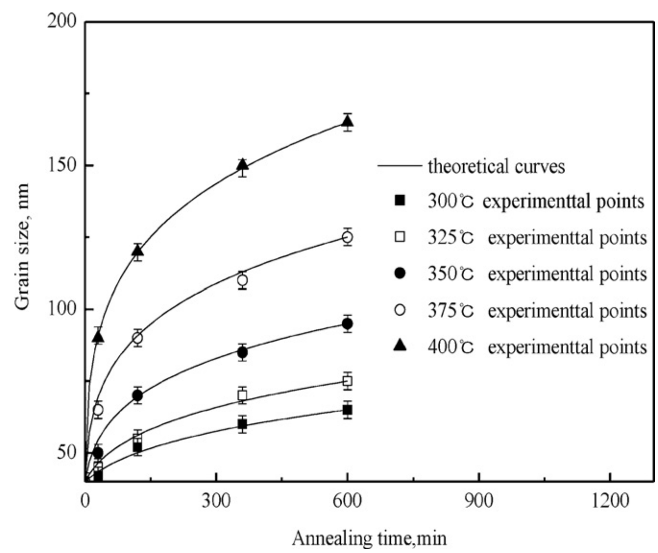

Fig. 3. Grain size against annealing time at different temperatures.

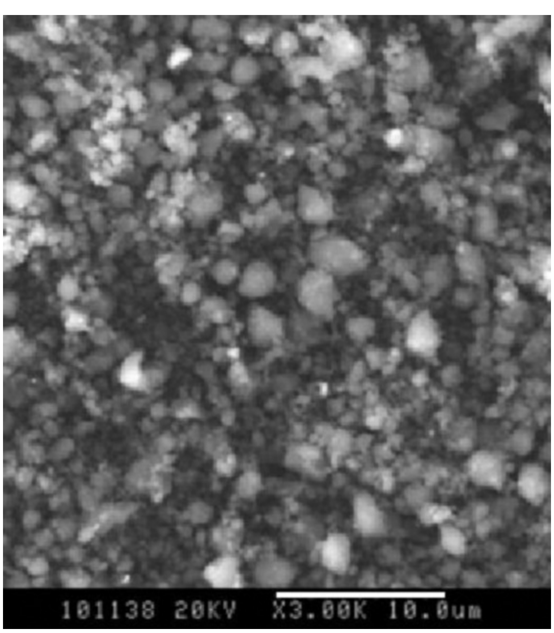

Fig. 1. SEM pattern of the nanocrystalline AZ31 magnesium alloy powders.

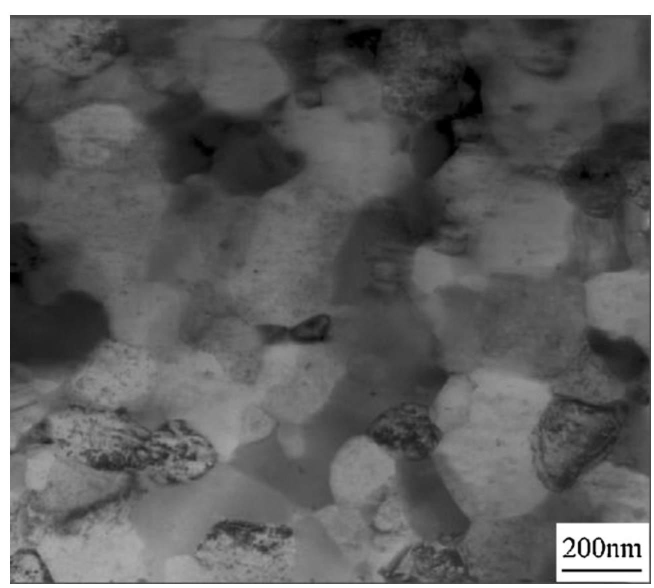

Fig. 4. TEM images of bulk AZ31 magnesium alloy annealing for 600 min at 400 °C.

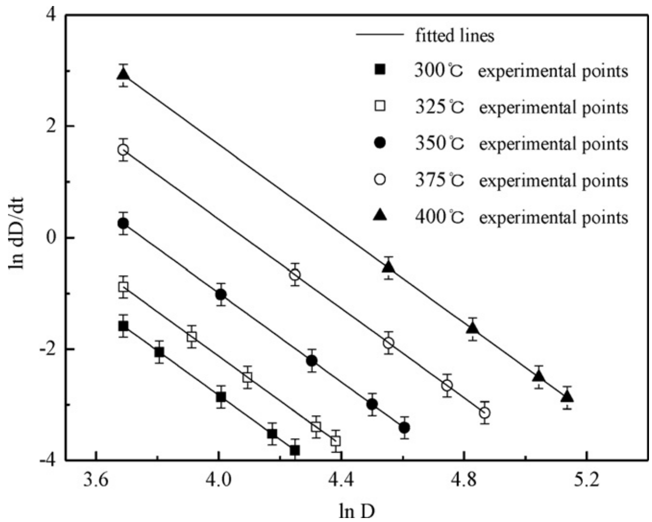

Fig. 5. Plot of ln(dD/dt) versus ln(D).

the average grain size of 180 nm, which is in agreement with the XRD results. Besides, the scattered spots apart from Mg phase in the diffraction patterns could be MgO and $Al_{12}Mg_{17}$ phase.

Parabolic kinetic equation of grain growth for isothermal annealing is suitable for engineering materials, it is also reported that nano-materials still obeyed this kinetic equation of grain growth [17–19]:

$$D^n - D_0^n = kt \quad (2)$$

where D_0 and D are the average grain sizes at different times, respectively, and where n is the grain growth exponent value and k is the grain growth constant which can be expressed by Arrhenius equation $k = k_0 \exp(-E_g/RT)$.

The grain growth rate (dD/dt) is taken from the tangent on the respective curves in Fig. 3 and the logarithm of grain growth rate (dD/dt) can then be plotted versus the logarithm of grain size D, as is shown in Fig. 5. Fig. 5 depicts the plot of ln(dD/dt) versus ln D for bulk AZ31 magnesium alloy. From Fig. 5, value of grain growth exponent, n can be calculated from the slope of the ln dD/dt versus ln D for the samples annealed at 300 °C, 325 °C, 350 °C, 375 °C and 400 °C, respectively. The similar linear relationships are observed and the slope is calculated to be −4 for the annealed samples.

From Eq. (2), the grain growth rate, dD/dt, can be derived as:

$$\ln\left(\frac{dD}{dt}\right) = \ln\left(\frac{k}{n}\right) - (n-1)\ln(D) \quad (3)$$

The grain growth exponent n values can be calculated to be 5 at this investigated condition. It the linear relationship is clearly seen, so that grain growth equation can be described:

$$D^5 - D_0^5 = kt \quad (4)$$

We can figure out the relationship between the value of $D^5 - D_0^5$ and annealing time (t), as shown in Fig. 6. The slopes of plot in Fig. 6 shows the various values of k and n at various temperatures for bulk AZ31 magnesium alloy, and they are presented in Table 2.

Table 2
The values of k and n at different temperatures.

Annealing temperature (°C)	k (μm^4/min)	n
300	2.6×10^6	5
325	5.3×10^6	5
350	1.6×10^7	5
375	6.1×10^7	5
400	2.4×10^8	5

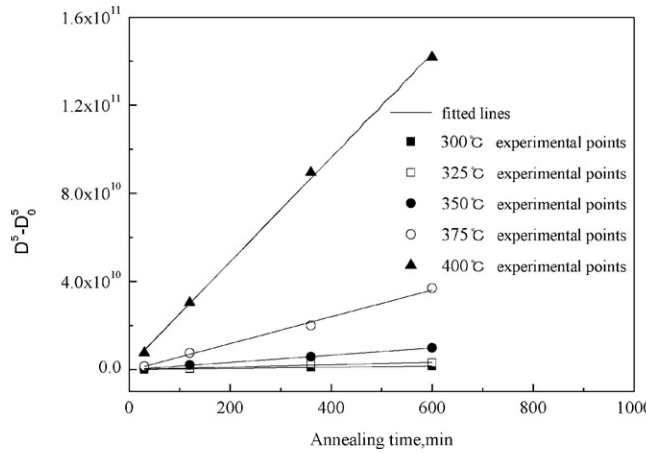

Fig. 6. Plot of ($D^5 - D_0^5$) against annealing time.

The constant k value of grain growth rate in Eq. (4) can be expressed:

$$k = k_0 \exp\left(\frac{-E_g}{RT}\right) \quad (5)$$

where k_0 is the pre-exponential term, R is the gas constant, E_g is the activation energy for grain growth, and T is the absolute temperature of annealing.

Adapting Eq. (5) in the logarithmic form:

$$\ln k = \ln k_0 - \left(\frac{E_g}{RT}\right) \quad (6)$$

The Arrhenius plots of ln(k) and $1/T$ shown in Fig. 7 enable us to calculate activation energy E_g for grain growth. In Fig. 6, the plot slope is estimated to be −13.23. Referring to Eq. (6), the activation energy can be deduced to be 110 kJ/mol.

3.2. Discussion

In this paper, the value of grain growth exponent n is 5 for the investigated bulk AZ31 magnesium alloy. The grain growth exponent n is the measure of resistance to grain boundary motion. In the ideal case, the grain growth exponent should be 2. The previous studies showed that the n value ranges from 2 to 8 for different magnesium alloys [12,17,20]. There are many factors affecting the grain

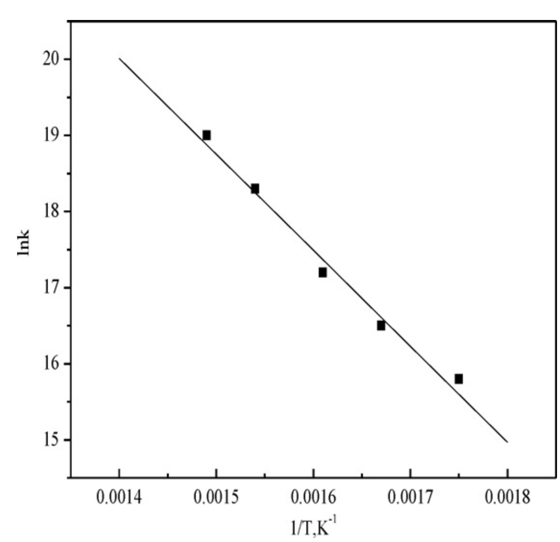

Fig. 7. Arrhenius plot of the rate constant, ln(k) versus $1/T$.

growth kinetics, not only associated to microstructural and compositional parameters but also porosity, impute and heterogeneities [12,20]. In this paper, the value of grain growth exponent n is 5, which may be that, hot pressing bulk AZ31 magnesium alloy has nanocrystalline structure with 40 nm grain size. Nanocrystalline magnesium alloy has much more boundaries which are convenient to move, so these grains can grow up quickly during annealing at elevated temperature.

As shown above, the activation energy E_g of the investigated hot pressing bulk AZ31 magnesium alloy was found to be 110 kJ/mol. Compared with the value 92 kJ/mol [12,17] as reported for as-cast pure Mg, it is about 18 kJ/mol higher. The large increase in activation energy compared to cast pure Mg may be due to the presence of MgO and $Al_{12}Mg_{17}$ intermetallic phase. The appearance of Al and Mg atoms in the AZ series of alloys modify the rate of grain growth and grain sliding in magnesium based alloys. So the effect of MgO, $Al_{12}Mg_{17}$ and alloying appear to hinder grain growth of Mg. Lambri et al. [21] has found an activation energy of 110 kJ/mol for the motion of grain boundaries in AZ91 alloy, despite the differences in the concentration of alloying elements. The above results show that hot pressing bulk AZ31 magnesium alloy exhibits grain size stability.

In the present case, the higher values of the grain growth exponents indicate that the grain growth is not only complex compared with conventional coarse-grained alloys but also requires higher activation energy.

4. Conclusions

Grain growth of bulk AZ31 magnesium alloy was investigated using the X-ray line-broadening. The grain size increases with increasing time and temperature during isothermal or isochronal annealing. The kinetics of grain growth can be well described by the kinetic equation: $D^5 - D_0^5 = kt$, when the annealing temperature is in the range of 300–400 °C. The activation energy E_g was found to be 110 kJ/mol, which is about 18 kJ/mol higher than that for the as-cast pure magnesium due to the effect of MgO, $Al_{12}Mg_{17}$ and alloying appearing to hinder grain growth of Mg.

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References

[1] S.H. Kang, Y.S. Lee, J.H. Lee, J. Mater. Process. Technol. 201 (2008) 436–440.
[2] W.N.A.W. Muhammad, Z. Sajuri, Y. Mutoh, Y. Miyashita, J. Alloys Compd. 509 (2011) 6021–6029.
[3] Y. Miyahara, Z. Horita, T.G. Langdon, Mater. Sci. Eng. A 420 (2006) 240–244.
[4] H. Sevik, S.A., S. Kurnaz, J. Alloys Compd. 508 (2010) 110–114.
[5] M.E. Alam, S. Han, Q.B. Nguyen, A.M. Salem, M. Gupta, J. Alloys Compd. 509 (2011) 8522–8529.
[6] K. Matsubara, Y. Miyahara, Z. Horita, T.G. Langdon, Acta Mater. 51 (2003) 3073–3084.
[7] S.M. Fatemi-Varzaneh, A. Zarei-Hanzaki, J.M. Cabrera, J. Alloys Compd. 509 (2011) 3806–3810.
[8] M. Paramsothy, J. Chan, R. Kwok, M. Gupta, J. Alloys Compd. 509 (2011) 7572–7578.
[9] K. Kubota, M. Mabuchi, K. Higashi, J. Mater. Sci. 34 (1999) 2255–2262.
[10] H. Zhao, Y. Song, M. Li, S. Guan, J. Alloys Compd. 508 (2010) 206–211.
[11] Y.H. Chew, C.C. Wong, F. Wulff, F.C. Lim, H.M. Goh, Thin Solid Films 516 (2008) 5376–5380.
[12] Q. Miao, L. Hu, X. Wang, E. Wang, J. Alloys Compd. 493 (2010) 87–90.
[13] D. Veljovic, B. Jokic, R. Petrovic, E. Palcevskis, A. Dindune, I. Mihailescu, D. Janackovic, Ceram. Int. 35 (2009) 1407–1413.
[14] L. Guoxian, L. Zhichao, W. Erde, J. Mater. Sci. 31 (1996) 901–904.
[15] D. Ye, D.C. Jia, Z.H. Yang, Z.L. Sun, P.F. Zhang, J. Alloys Compd. 506 (2010) 88–92.
[16] E. Contreras, R. Esquivel, V.L.M. Saucedo, A. Paniagua, H. Dorantes, Mater. Sci. Eng. A 527 (2010) 7775–7778.
[17] P. Cao, L. Lu, M.O. Lai, Mater. Res. Bull. 36 (2001) 981–988.
[18] O.N. Senkov, M.L. Övecoglu, N. Srisukhumbowornchai, F.H. Froes, Nanostruct. Mater. 10 (1998) 935–945.
[19] S. Kawanishi, K. Isonishi, K. Okazaki, Mater. Trans. JIM 34 (1993) 49–53.
[20] M.A. Thein, L. Lu, M.O. Lai, Compos. Sci. Technol. 66 (2006) 531–537.
[21] O. Lambri, W. Riehemann, Z. Trojanova, Scr. Mater. 45 (2001) 1365–1371.