Synthesis and Thermal Stability of Nanocrystalline Mg-6Al-1Zn-1 Si Alloy Prepared Via Mechanical Alloying

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ABSTRACT

Thermal stability and the kinetics of the grain growth of nano-crystalline Mg-6Al-1Zn-1Si alloy prepared via mechanical alloying (MA) were investigated. It started with elemental powders, using analytical techniques including differential scanning calorimetry (DSC), X-ray diffraction (XRD), and scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS). The results showed that the MA-processed alloy was composed of an Mg-based supersaturated solid solution with small amounts of Al and $MgAl_2O_4$. Grain growth and Mg_2Si precipitation occurred upon annealing of the MA-processed Mg-based alloy. Nevertheless, grain growth in the MA-processed alloy was limited and the α-Mg grains with sizes in the range of 70 nm were still present after exposure to 450 °C. The alloy grain growth behavior can be described by the parabolic kinetic equation of grain growth. Higher strength values obtained after hot consolidation can be due to the refined microstructure and the formation of the Mg_2Si intermetallic phase.

1. Introduction

Magnesium alloys have been regarded as promising materials because of their low density and specific high strength and stiffness [1-3]. However, Mg alloys have been used limitedly in high performance applications due to their low mechanical properties [4]. Refining the grain size to nanostructure as well as in-situ alloying have been used in order to improve mechanical properties [5, 6]. Mechanical alloying is an appealing solid state technique to synthesize powders with controlled microstructure. This technique can produce very fine grain size down to nano-scale with flexibility in alloying [4].

Thermal stability of nanocrystalline materials is of fundamental scientific interest and of technological importance as well [7]. Since grain growth of nanocrystalline materials occurs during service or secondary process to form bulk alloys, a great deal of studies have been carried out in this respect in recent years [7-9]. Investigations on the stability of the grain size have been reported in various nanocrystalline Mg alloys, for example, Mg-12.1Cu [4], Mg-5Al-10.3Ti [8] and Mg-25at%Si [2].

So far, different mechanisms for nanograin stability have been reported including remnant pore drag, grain boundary segregation, solute drag, second phase (Zener) drag, and chemical ordering, all leading to an inhibition of grain

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growth [7,10,11]. To improve heat resistance in the Mg based alloys, developing an alloy containing thermally stable intermetallic phases is one of the most effective methods which can suppress the grain boundary sliding and dislocation motion [2, 12]. The intermetallic compound Mg_2Si is a thermally stable phase with low density and high strength to mass ratio [2]. The production of Mg_2Si by conventional methods usually results in heterogeneous microstructure with undesirable coarse grains [5, 12]. Recently, solid-state synthesis of Mg_2Si by mechanical alloying of elemental powders has been reported [5, 13]. However, it is usually difficult to synthesize Mg_2Si by direct mechanical milling due to stable oxide films forming on the Mg particles [5].

The present study was carried out to investigate the thermal stability and the kinetics of grain growth of nanocrystalline Mg-6Al-1Zn-1Si alloy prepared via mechanical alloying. The effects of mechanical alloying and hot consolidation on the mechanical properties of the alloy was also outlined.

2. Experimental

Elemental powders of Mg (>97%, Merck), Al (>98%, Merck), Zn (>99.9%, Merck), and Si (>98%, Sigma-Aldrich) were used as initiating materials. The powder blends with nominal composition of Mg-6Al-1Zn-1Si (%wt) were mechanically alloyed in a Retsch PM100 planetary ball mill at room temperature for 50 h. Ball to powder weight ratio of 20:1 was selected and the rotation speed was adjusted to 250 rpm.In order to prevent large temperature increment during the process, the experiment was periodically stopped every 25 min for 5 min. The weighing, filling, and handling of the powder were performed in a glove box under argon atmosphere.

Thermal stability of the milled powder was determined using a differential scanning calorimeter (DSC, NETZSCH STA 409 PC/PG) under argon atmosphere from room temperature to 600 °C at three different heating rates of 5, 10 and 20 °C/min. Based on the DSC results, the MA-processed alloy powder was isothermally annealed under argon atmosphere at 350, 400, 450, and 500°C for 1 h. To investigate the kinetics of grain growth, isothermal annealing data at 350 °C for 30, 60, and 180 minutes were used to calculate the grain growth rate. To obtain activation energy, the DSC results from different scanning rates were analyzed using Kissinger equation [14]:

$$\ln(\beta/T^2) = -(E/RT)+C \quad [1]$$

where β is the heating rate in the DSC scanning, T is the peak temperature of exotherm, E is the activation energy, R the gas constant, and C is a constant.The phase constituents of the as-milled powder before and after annealing were analyzed by X-ray diffraction (XRD, X'Pert Pro MPD, PANalytical) with Cu-K_α radiation. The grain size of the obtained powder was estimated from the broadening of the XRD peaks using the Williamson–Hall method [15]. Microstructure of the samples was characterized using scanning electron microscopy (SEM, KYKY EM-3200) equipped with energy dispersive spectroscopy (EDS).

To evaluate the mechanical strength, hot pressing was performed in a steel die (internal diameter:10 mm) at 350, 400, and 450 °C under the applied pressure of 300 MPa for 60 min under a high purity argon atmosphere. The heating rate was 10 °C/min. After consolidation, mechanical strength of the compacts was examined by compression test (ASTM E9) and Vickers hardness method (ASTM E92). A servo-control machine (Gotech, AI-7000L, China) at the strain rate of 1.66×10^{-3} s^{-1} was utilized for the compression test. The testing temperature was 25 °C. The Vickers hardness of the compacts was determined using a hardness tester (InstronWolpert, Germany) at the indentation load of 30 kg.

3. Result and discussion

3. 1. Characteristics of the powder

The XRD patterns of the powder mixture before and after milling for 50 h are presented in Fig. 1. As can be seen, after 50h of milling, all diffraction peaks are broadened and decreased evidently due to their mechanically-induced lattice strain and crystallite size reduction [16]. The absence of the Zn and Si peaks in the XRD pattern is due to their low

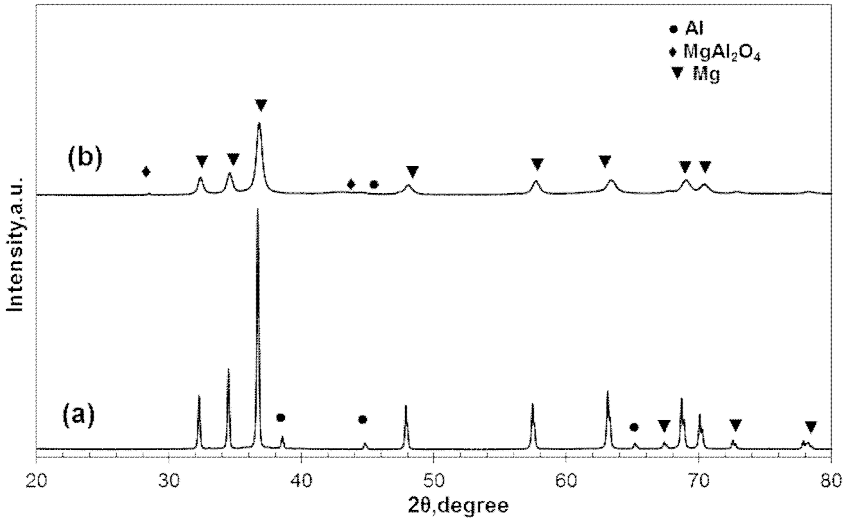

Fig. 1. XRD patterns of the powder mixtures for unmilled (a) and milled for 50 h (b)

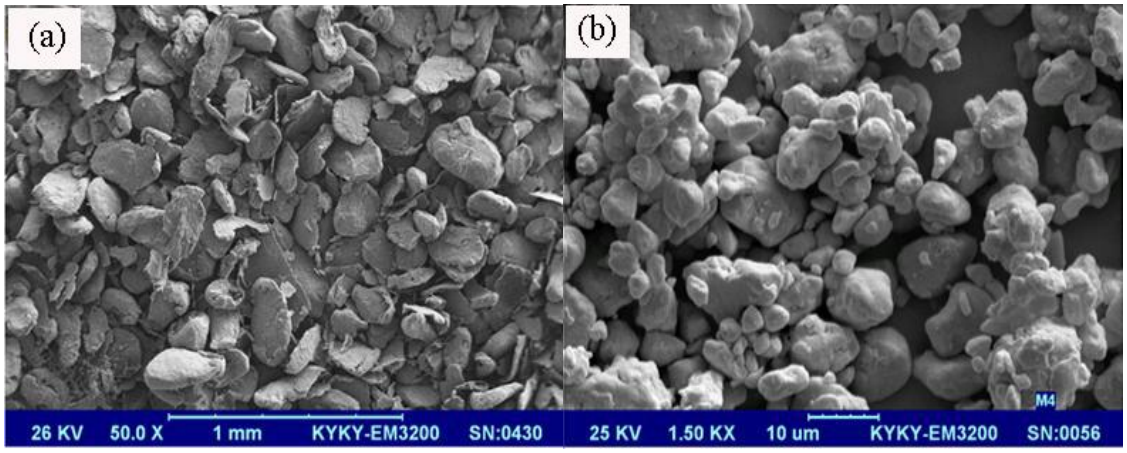

Fig. 2. SEM micrographs of the powder mixtures for unmilled (a) and milled for 50 h (b)

concentrations. The peak shifting of the Mg reflections to higher 2θ values is also observed. This suggests the formation of the Mg-based solid solution during milling. Since the atomic size of the Al element is smaller than that of the Mg element, the dissolution of this element is expected to reduce the lattice parameter of Mg. The appearance of the peaks of $MgAl_2O_4$ determines the oxidation of magnesium during the process. Very weak Al peaks are observed in the MA-processed sample, which suggest the incomplete solubility of Al in Mg matrix. Fig. 2 shows the size and morphology of the powder particle of the unmilled and milled powders for 50 h. Based on Fig. 2, after 50 h of milling, the particles are fragmented and become considerably small in size and granular in shape.

3. 2. Structural evolution at elevated temperatures

For a thorough understanding of thermal behavior, DSC analyses of the as-milled powder was carried out at three different heating rates, namely 5, 10, and 20 °C/min (Fig. 3). It can be seen that the onset and peak temperature shift to higher temperatures with the increase of the heating rates. In all DSC curves, two exothermic peaks are observed from room temperature to 500 °C. A broad exothermic peak (P_1) occurs between 400-460 °C. This exothermic peak, observed in many MA-processed powder systems, may have originated from grain growth, strain relaxation and decomposition of metastable solid solution into component elements [17, 18]. Moreover, there is an exothermic peak (P_2) at ~480°C.

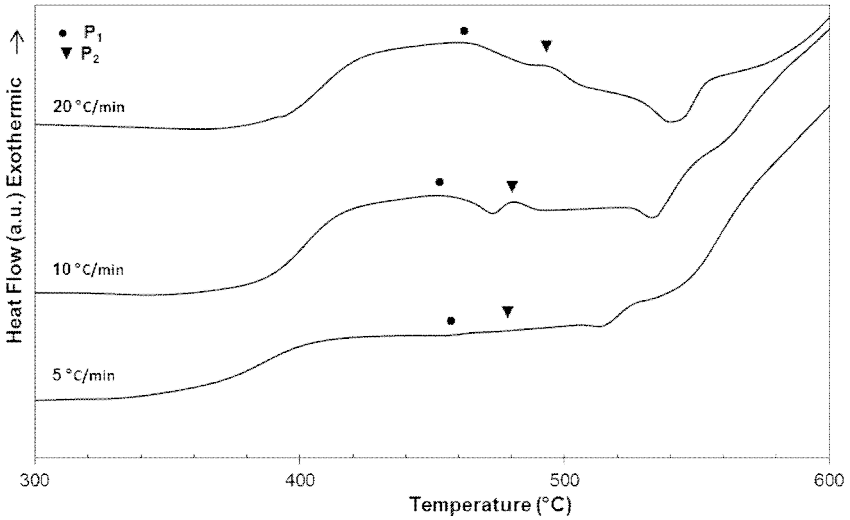

Fig. 3. DSC curves of the 50 h milled powders at different heating rates

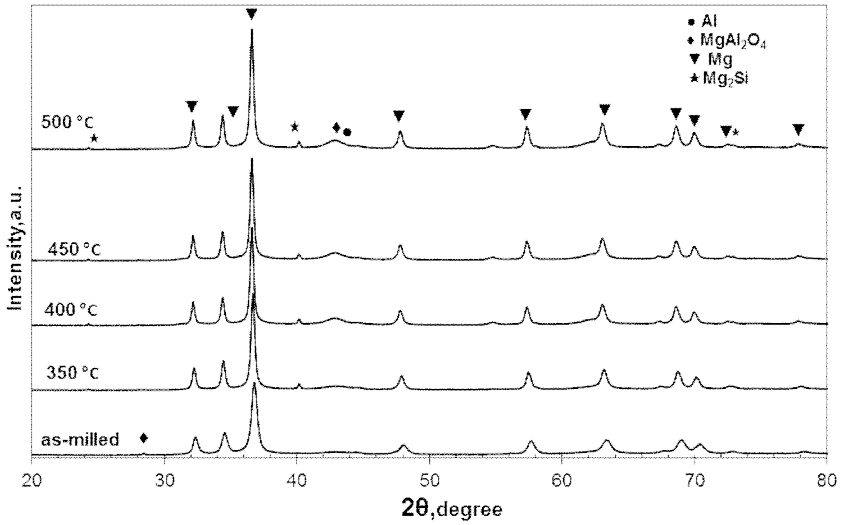

Fig. 4. XRD patterns of the MA-processed powders as a function of the annealing temperature

To understand the reactions observed in the DSC curves, isothermal annealing was performed. Fig. 4 shows the XRD patterns after annealing at 350, 400, 450, and 500 °C for 1 h. For comparison, the corresponding pattern of the as-milled powder is also shown. As can be seen, after annealing, new diffraction peaks corresponding to the Mg_2Si intermetallic phase are observed. Also, no new phase formation was noticed with increasing the annealing temperature up to 500 °C.

Fig. 5 shows the XRD patterns after isothermal annealing at 350°C for different durations. It can be notified that diffraction peaks of Mg_2Si are evident in system after 30 min. Additionally, the characteristic $MgAl_2O_4$ peaks are also observed, with their intensities increasing at longer annealing duration. In the equilibrium state the intermetallic phase of Mg_2Si is formed by adding Si to Mg [19, 20]. The results of the present investigation demonstrate that the Mg_2Si intermetallic compound is not formed in the as-milled system, which is in agreement with previous reports [5, 21]. In fact, direct synthesis of Mg_2Si by mechanical milling is usually difficult, as stated by Wang et al. [5] for the formation of nanocrystalline Mg_2Si through solid-state reaction. Based on the DSC and XRD results (Figs. 3 and 4), it can be deduced

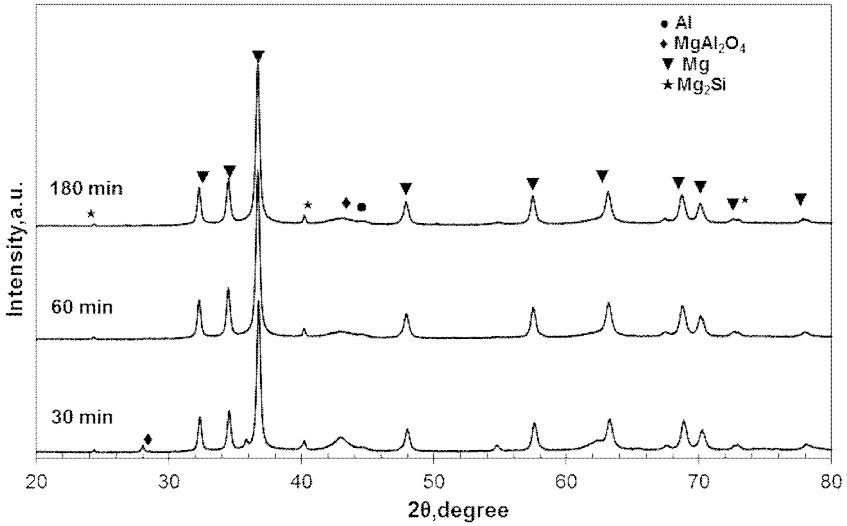

Fig. 5. XRD patterns of the MA-processed powders as a function of the annealing durationat 350°C

Table 1. Grain Sizes of α-Mg and Mg_2Si as a function of annealing temperature

Grain size (nm)	as-milled	Annealing temperature (°C)		
		350	400	450
α-Mg	45	52	63	70
Mg_2Si	-	51	77	85

that the exothermic peak P_1 is attributed to the Mg_2Si phase. Moreover, the exothermic peak P_2 can be related to the completion of the Mg_2Si formation by the reaction of residual Mg and Si at higher temperature, as no new phase formation was observed in the XRD patterns. It has been reported that the reaction between Mg and Si and the formation of Mg_2Si take place at very high temperatures due to oxide films covering the particles [5]. However, it is known that processes such as mechanical alloying change the formation temperature of Mg_2Si. Sun et al. [2] have reported the temperature of 545°C for the synthesis of in-situ Mg_2Si compound from Mg and Si elemental powders. Wang et al. [5] have reported that after 60 h of milling, the formation temperature of Mg_2Si decreases from ~460 °C to ~180°C in the Mg-37%Si system. As the powder mixtures are processed by high-energy milling, the following events would happen: (i) Grain refinement and defect generation; (ii) Cracking of the oxide films;(iii) In-situ alloying of the elements. When the oxide films are cracked as a result of milling, the fresh surfaces would lead to direct contact of Mg with Si;consequently, Mg would begin to react to Si at lower temperature for the milled powder.

3. 3. Kinetics of grain growth

For the study of grain growth, the grain sizes of α-Mg and Mg_2Si affected by temperature for a one-hour annealing have been estimated using the Williamson-Hall method, as shown in Table 1. As can be seen, the grain sizes of both Mg and Mg_2Si increase from 52 to 70 and 51 to 85nm with annealing temperature, respectively.

Fig. 6 shows the grain sizes of α-Mg as a reaction to annealing time at 350°C. It should be noted that the grain size of α-Mg changes relatively largely below 60 minutes, but starts to decrease gradually above 60 minutes, and finally reaches 66 nm after 180 minutes.

The parabolic kinetic equation of grain growth can be used in some nanocrystalline materials for isothermal annealing using the following equation [22]

$$D^n - D_0^n = ct \quad [2]$$

where n is the grain growth exponent and c is a constant. The logarithm of grain growth rates taken from the tangents on the respective curves from Fig 6 is plotted against the

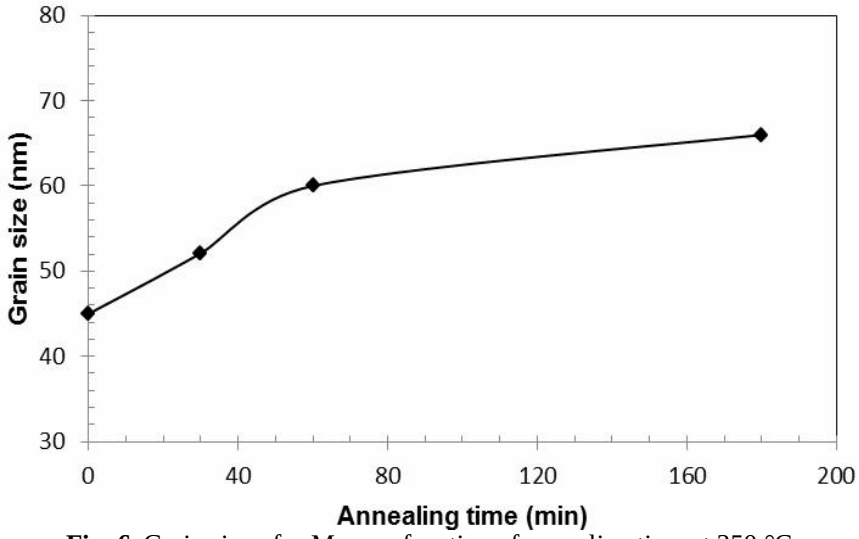

Fig. 6. Grain size of α-Mg as a function of annealing time at 350 °C

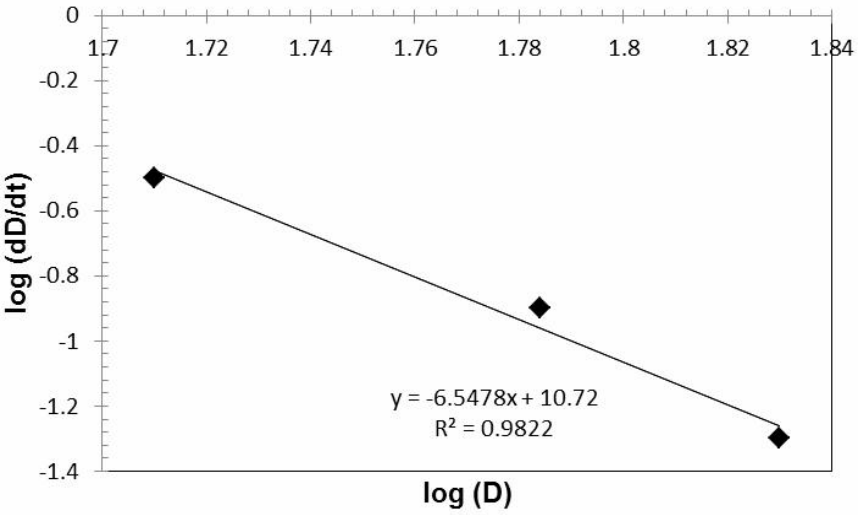

Fig. 7. Plot of log (d*D*/d*t*) versus log (D) at 350 °C

logarithm of D (Fig. 7). Linear relationships are obtained with the slope of -6.3. The rate of grain growth can be calculated by:

$\log (dD/dt) = (1-n) \log D + \log (c/n)$ [3]

The grain growth exponent n at 350 °C can be estimated to be 7.3. Fig. 8 shows the log ($D^{7.3}$-$D_0^{7.3}$) versus the log (t) plot for the Mg-6Al-1Zn-1Si system. As can be seen, linear relationships are observed and the grain growth can be depicted as $D^n - D_0^n = ct$.

To obtain activation energy, DSC results from different scanning rates were analyzed by Kissinger equation. By the linear fit of the experimental data to formula (1), the activation energies corresponding to the P_1 and P_2will be 376.4 and 317.3 kJ/mol, respectively. Sun et al. [2] have reported 376 kJ/mol activation energy for the solid state synthesis of Mg_2Si at 445°C in the Mg-25at.%Si alloy. The value of 190±5 kJ/mol at 540°C has been reported by Wang et al. [5] for the synthesis of Mg_2Si from blended Mg and Si powders according to the stoichiometric composition of Mg_2Si. In fact, higher value of grain growth exponent, *n*, and the large increase in activation energy for the Mg-6Al-1Zn-1Si system can be due to the presence of the Mg_2Si intermetallic phase. Here, it could be said that at high temperature, grain growth takes place, which would lead to the release of grain boundary energies and

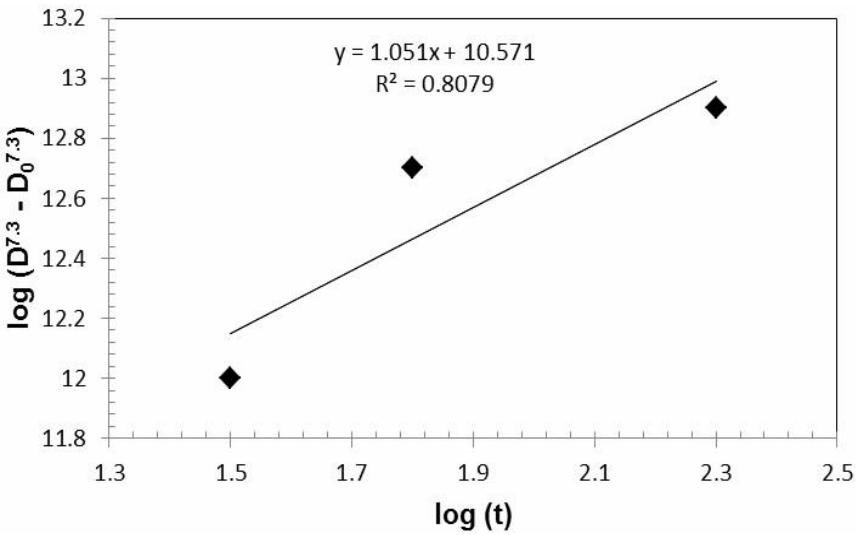

Fig. 8. Plot of log (D^n-D_0^n) versus log (t)

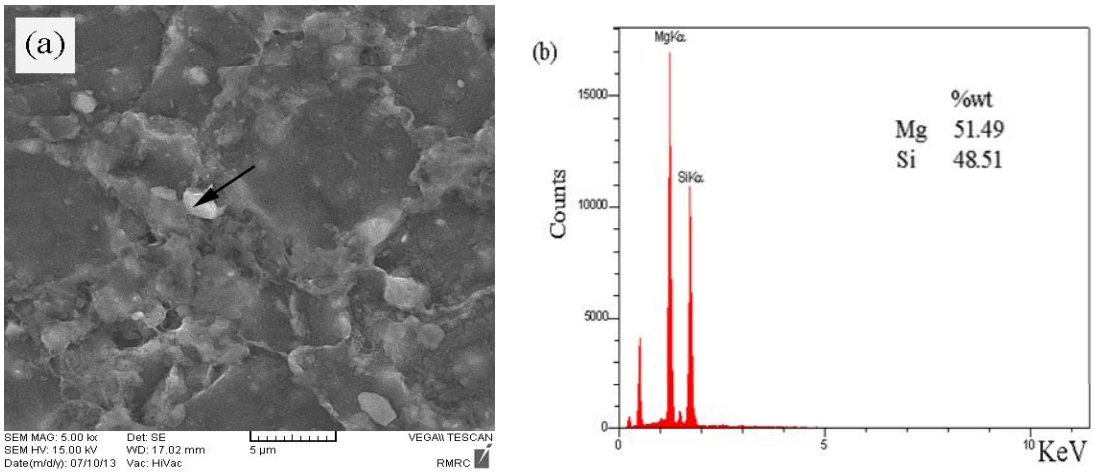

Fig. 9. (a) SEM micrograph of the Mg-6Al-1Zn-1Si powder annealed at 350°C for 1h and (b) EDX spectrum of the intermetallic phase

would contribute partly to the DSC peaks [4]. However, the effect of grain boundary energies on the DSC peaks has been withdrawn.

3. 4. Mechanical properties of consolidated samples

To evaluate the mechanical properties, hot pressing was performed at 350, 400 and 450 °C under the applied pressure of 300 MPa for 60 min.Two important observations whichwere made during the consolidation process were α-Mg grain coarsening and precipitation of the Mg_2Si intermetallic compound(see Fig. 9 as a typical case).

The mechanical strength of the consolidated samples at room temperatureis reported in Table 2. It is noticeable that the compressive strength of the milled compact is higher than that of the un-milled compact. It is reported that the dispersion of second-phase reduces the rate of grain growth because the driving pressure for the grain growth is compensated by the pinning force from the particles. Grain growth inhibition associated with dispersed second-phase particles have been reported in a wide variety of non-ferrous metals [23]. Here, a relatively higher strength value is obtained due to fine grain size and the formation of the Mg_2Si intermetallic phase. Anyway, the results indicate the higher hardness of the milled compacts compared with the un-milled compacts. The refined microstructure induced

Table 2. Hardness and compressive strength of the hot consolidated samples. The mechanical properties of the un-milled compact consolidated at 350 °C is reported for comparison

Process	Compressive Strength (MPa)	Hardness (HV_{30})
Un-milled +consolidated at 350°C	199	75
milled +consolidated at 350°C	297	120
milled +consolidated at 400°C	290	114
milled +consolidated at 450°C	278	106

by the mechanical alloying process and the formation of the Mg_2Si phase improved the hardness.

4. Conclusion

The thermal stability and kinetic of grain growth of the Mg6Al-1Zn-1Si alloy powders with ultra-fine grain microstructurehave been investigated. The effects of the annealing temperature on microstructures and the effects of grain size on mechanical properties were evaluated. The following conclusions can be drawn from this study:

1. Nanocrystalline Mg-6Al-1Zn-1Si alloy powders with the mean grain size of 45 nm have been developed after 50 h of ball milling. With proper control of the consolidation temperature, an ultrafine grain size and uniformgrained structure bulk Mg-6Al-1Zn-1Si alloy can be produced. After consolidation, Mg_2Si particles were observed in the microstructure.

2. The bulk alloys with fine grain size microstructure reveal extraordinary high strength; a compressive strength of 297 MPa and a hardness of 120 HV_{30} have been obtained. The high strength of the alloy may be associated with refined microstructure and the dislocation–particle interaction.

3. The grain growth behavior of the alloy can be described by the parabolic kinetic equation of grain growth.High value of the grain growth exponent, n, and the large increase in activation energy are observed due to the presence of the Mg_2Si intermetallic phase.

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