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Synthesis of bulk nanostructured Mg-based alloy via spark plasma sintering through in situ crystallization of an amorphous precursor

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Abstract
We present the synthesis of a bulk nanostructured Mg-based alloy that has a grain size less than 300 nm. A nanostructured Mg-Zn-Cu-Nd alloy with an exceptionally high hardness can be obtained through simultaneous consolidation and in situ crystallization of the amorphous Mg₈₄Zn₇Cu₃Nd₆ alloy precursor using the spark plasma sintering process. We evaluate the relationship between the microstructure and preparation conditions on the grain size of nanostructured Mg-based alloys during the sintering process. The hardness of the bulk sample produced from the sintered amorphous Mg-Zn-Cu-Nd precursor at 260 °C is maximized via the nanocrystallization of intermetallic compounds using the sintering process. The populated crystallization and confined growth of phases contribute to the refinement of gains in nanostructured Mg-based alloys.

Introduction

Many studies have developed lightweight and high-strength alloys for zero-emission transportation or high-energy-efficiency systems [1, 2]. In particular, lightweight alloys are gradually substituting plastics in transportation-related industries to reduce the body weight of structures and decrease fuel consumption [1, 2].

Nanocrystalline alloys, which have a homogeneous microstructure, show ductility combined with a high strength. Preparation processes to obtain nanocrystalline grains have been introduced, such as the equal channel angular process (ECAP) [3, 4] or the consolidation of Mg-based nanocrystalline powder via the spark plasma sintering (SPS) process [5, 6], and they are not observed in conventional Mg-based alloys [7, 8]. However, whether nanocrystals and the volume fraction contribute to enhancing the physical properties (i.e., strength) of Mg-based alloys, it is still difficult to obtain the bulk shape through conventional methods [7, 9]. Although secondary precipitation processes are crucial to strengthening Mg-based alloys, the spark plasma sintering (SPS) process is rarely considered a consolidation method because it accompanies the oxidation or melting of particles [10].

The amorphous state is known as the most effective precursor for nanostructure synthesis [11]. A high level of solute supersaturation in a highly undercooled condition of amorphous alloys provides a high driving free energy to promote the high nucleation rate that is essential for nanostructures [11]. The preparation of nanocrystalline materials allows for the crystallization of amorphous solids under appropriate thermal processes [12, 13] and provides a successful way to synthesize nanocrystalline alloys with homogeneous microstructures. It is important to control the properties resulting from the microstructure of Mg-based alloys, which is intrinsically determined by the devitrification of the amorphous precursor.

Due to their unique weight to high strength ratio (compared with conventional crystalline Mg-based alloys), the development of Mg-based amorphous alloys has also been intensively studied [5–9,14–17]. In particular, Mg-based amorphous alloys have recently presented the possibility of being biodegradable materials for
orthopedic implants and stents due to their low Young’s modulus and high strength [18–20]. Xu et al reported enhancing the mechanical properties of Mg-Cu-Ni-Zn-Ag-Y amorphous alloys by introducing TiB₂ reinforcements [14]. Xu et al investigated the effect of adding rare earth elements (REEs) on the formation of intermetallic phases in conventional Mg-based alloys with coexisting orthorhombic intermetallics with crystalline phases [16]. Moreover, the effect of REEs on the formation and physical properties of Mg-based amorphous alloys has been extensively investigated. Kim et al reported that Ce could enhance the mechanical properties of Mg-based amorphous alloys [9]. Li et al reported that Nd is an effective element for achieving a significantly enhanced strength of Mg-based amorphous alloys [15]. Zhang et al presented that the microalloying of Gd can play an important role in influencing the ductility of Mg-amorphous alloys [5]. Ozaki et al showed that mechanical alloying has improved mechanical properties compared with Mg-based metallic glasses by introducing chemical inhomogeneity [6]. Inoue et al reported that the formation of nanocrystalline Mg phases in quenched Mg-Cu-Y alloys shows superior strengths to that of monolithic amorphous phases [7]. A microstructural analysis has established, such that many Al-based amorphous alloys contain REs and transition metals (TM s) as solutes [11]. The initial crystallization corresponds to the primary phase formation (i.e., Al), yielding a sample that contains a high density of nanocrystals within an amorphous matrix [11, 12].

In this study, we search for and combine binary systems (Mg-TMs and Mg-REEs) with congruent melting and deep eutectics to apply the nanocrystallization phase transformation concept in Mg-based amorphous alloys. As a result, a quaternary system, including transition metals (Zn, Cu) and rare earth elements (Nd, or Y), was selected with nanoscale intermetallics formed by in situ crystallization. The current results present a simple method to synthesize a bulk nanocrystalline Mg-based alloy with a high hardness through crystallization of an amorphous precursor and investigates the effect of in situ crystallization on the microstructures of the Mg-based
alloy, depending on the spark plasma sintering conditions. The phase transformation of crystalline phases with mechanical properties resulting from the simultaneous sintering and devitrification of the amorphous phase are also evaluated.

Figure 2. (a) DSC traces obtained during continuous heating at a heating rate of 40°C min⁻¹. (b) XRD patterns of bulk SPS Mg₈₄Zn₇Cu₃Nd₆ samples subjected to different sintering temperatures at 50°C, 260°C and 340°C, as well as those of the as-cast bulk ingot for comparison.
Materials and methods

Alloys with a nominal composition of Mg₈₄Zn₇Cu₃Nd₆ (at%) or Mg₅₇.₄₃Zn₁₂.₈₇Cu₃.₃₆Nd₂₄.₃₄ (wt%) were cast via induction melting under an Ar atmosphere (< 99.99% purity). The precasted ingots inductively remelted in an SiO₂ tube to prepare amorphous precursor ribbons, followed by melt spinning using Ar with 35 kPa gas pressure and a surface velocity of 40 m/s. The amorphous precursor ribbons had a thickness and width of approximately 20 μm and 3 mm, respectively. Mg-Zn-Cu-Nd amorphous particles were produced by the pulverization of amorphous ribbons with a size of under 50 μm. The particles were then consolidated into bulk samples using a 5-mm diameter and a 3-mm height tungsten carbide die using spark plasma sintering (SPS) with a heating rate of 40 °C/min (temperature accuracy: ± 0.5 °C; pressure: 500 MPa). There is a combined effect between thermal energy, pressure and electric energy that leads to localized melting within a short time during the SPS process. [5, 6, 21]. The thermal stability of the samples was studied in isochronal mode via differential scanning calorimetry (DSC) [TA Instruments DSC-Q100]. A structural analysis was characterized via x-ray diffraction (XRD) [Rigaku D/Max 2500PC with monochromatic Cu-Kα radiation]. The microstructure was analyzed using field emission scanning electron microscopy (FE-SEM, Quanta 200 FEG) with wave-dispersive x-ray spectroscopy (WDX), energy-dispersive x-ray spectroscopy (EDX) and electron backscattered diffraction (EBSD). The mechanical properties of the SPS samples were evaluated by both uniaxial compression and microhardness tests at room temperature. Compression tests were then conducted at room temperature at a strain rate of 3 × 10⁻⁴ s⁻¹ (Hounsfield TX0056-H25KT). Microhardness tests were then performed using a micro-Vickers hardness tester (Mitutoyo HM210A) under a 0.05 kgf load with a 10-second dwell time.

Results and discussion

Figure 1(a) shows the DSC results obtained from the melt-spun Mg₈₄Zn₇Cu₃Nd₆ (at%) amorphous ribbons during continuous heating. The DSC trace of the amorphous Mg-Zn-Cu-Nd ribbon exhibited an exothermic peak, corresponding to the glass transition at 137 °C. The three exothermic events, corresponding to crystallization peaks, correspond to sequential crystallization of the amorphous Mg-Zn-Cu-Nd ribbon. The amorphous materials occurred at the onset temperatures of Tx₁ = 152 ± 1 °C, Tx₂ = 221 ± 1 °C and Tx₃ = 295 ± 1 °C, respectively. The complete crystallization temperatures (Tc) of the three exothermic events were Tc₁ = 186 ± 1 °C, Tc₂ = 258 ± 1 °C and Tc₃ = 335 ± 1 °C with enthalpies DH₁ = −37.00 ± 0.1 J g⁻¹, DH₂ = −6.36 ± 0.4 J g⁻¹ and DH₃ = −7.39 ± 0.41 J g⁻¹, respectively.

Figure 1(b) shows the XRD patterns obtained for the heat treatment of Mg₈₄Zn₇Cu₃Nd₆ amorphous ribbons at different temperatures. The XRD pattern for the as-spun Mg-based amorphous ribbon showed a broad diffraction maximum, which is a typical characteristic of an amorphous structure. To evaluate the crystallization behavior upon heat treatment, the Mg-Zn-Cu-Nd amorphous ribbon was heated to each crystallization temperature at a constant rate of 40 °C min⁻¹ in DSC. As the sample was heated to the first exothermic peak finish temperature (Tc₁ = 186 °C), the XRD pattern showed sharp diffraction patterns from the α-Mg and MgZn₂ phases with a weak diffuse background, which was considered to be from the residual amorphous phase. When the sample was heated up to the second exothermic peak’s finished temperature (Tc₂ = 258 °C), the XRD pattern showed diffraction patterns of intermetallic Mg₅₂₋₆₆.₅Nd₇₋₇Zn₂₅.₈₋₄₀.₁ (τ₁ phase with an orthorhombic structure) with the previously observed α-Mg and MgZn₂ phases [16]. As the sample was further heated up to the third crystallization completed temperature (Tc₃ = 335 °C), the XRD pattern showed the diffraction peaks of intermetallic Mg₄Nd₅ and Nd(Mg,Zn)₃ (Pearson symbol cF16, space group Fm 3 m) with the previously observed phases [16].

To generate bulk specimens and investigate the mechanical properties, pulverized amorphous Mg₈₄Zn₇Cu₃Nd₆ (at%) ribbons were consolidated by the SPS method. Figure 2(a) shows the thermal analysis results during continuous heating of the sintered bulk samples at different temperatures. The DSC trace of the SPS Mg₈₄Zn₇Cu₃Nd₆ (at%) sample at 50 °C exhibited crystallization onset temperatures of Tₓ₁ = 155 ± 1 °C, Tₓ₂ = 221 ± 1 °C and Tₓ₃ = 295 ± 1 °C, as well as an integrated heat of crystallization values of DH₁ = −40.05 ± 0.11 J g⁻¹, DH₂ = −10.38 ± 0.11 J g⁻¹ and DH₃ = −6.42 ± 0.2 J g⁻¹, respectively. Compared with the DSC trace of the as melt-spun amorphous Mg-Zn-Cu-Nd ribbon, the first crystallization temperature of the SPS sample at 50 °C shifted to a slightly higher temperature. This may be explained by a local compositional fluctuation of the Mg-based amorphous alloy during sintering. The material is bonded by a viscous melt flow through the electric current at the particle surface during SPS [22]. However, the enthalpy of crystallization in the SPS sample at 50 °C was quite close to those obtained from monolithic as melt-spun amorphous Mg₈₄Zn₇Cu₃Nd₆ (at%) ribbon. In contrast, the SPS sample at 260 °C only showed that the weak third exothermic reaction (inset graph marked as a dashed box) corresponded to 7% of the remaining amorphous phase after the sintering process (AH₃ = −3.97 J g⁻¹). Moreover, no peak from the exothermic
reaction was observed in the DSC result for the sample sintered at 340 °C, due to complete devitrification of the amorphous phase during the sintering process.

Figure 2(b) compares the XRD patterns of the Mg84Zn7Cu3Nd6 (at%) conventional gravity-casted ingot and the SPS samples at varying sintering temperatures between 50 °C and 340 °C. The XRD pattern of the sample sintered at 50 °C showed broad diffused diffraction maxima of the amorphous phase; this phenomenon suggests that the amorphous phase is retained without a significant growth of crystallines at a low sintering temperature. As the sintering temperature increased to 260 °C, additional diffraction peaks corresponding to primary α-Mg, Mg41Nd5 and Mg(52.2–66.5)Nd(7.7)Zn(25.8–40.1) intermetallic compounds formed via crystallization of the residual amorphous material were visible. When the sintering temperature was increased to 340 °C, corresponding to the third exothermic reaction complete temperature, the XRD pattern showed clear sharp diffraction peaks from MgCu2, N and Mg41Nd5 (lattice parameters a = 741.3 pm, b = 720 pm, and c = 680 pm) and the intermetallic Mg(52.2–66.5)Nd(7.7)Zn(25.8–40.1) (orthorhombic τ1: lattice parameters a = 970/980/984 pm, b = 1120/1150/1135 pm, and c = 950/960/963 pm) τ1 phases [16]. The XRD pattern of the SPS sample showed a dominant peak from the Mg-Nd-Zn ternary intermetallic phase, compared to those of the heat-treated sample, showing a dominant peak from α-Mg. The XRD patterns of the SPS samples showed similar results to those of heat-treated ribbon samples, without a change in devitrification by the synthesis method. However, the XRD pattern of the conventionally gravity-casted Mg84Zn7Cu3Nd6 (at%) ingot showed a completely different result from those of SPS- or heat-treated ribbon samples by the formation of α-Mg and MgZn3 intermetallics as major phases due to the slow cooling rates, which were closely related to the solute distribution [23].

Figures 3(a) and (b) show SEM micrographs obtained from the SPS bulk samples at 260 °C and 340 °C, respectively. As shown in figure 3(a), the microstructures of the SPS sample at 260 °C exhibited a rather featureless contrast without any pores between the particle boundaries. White contrast regions corresponding to the intermetallic compounds were observed in the enlarged view of the consolidated surface, as shown in figure 3(c). When the sintering temperature increased to 340 °C, the size and volume fraction of the intermetallics increased [shown in figure 3(b)]. Figure 3(d) shows an enlarged view of the consolidated surface of the SPS sample at 340 °C; the overall microstructure exhibited a featureless gray contrast without pores. However, several spherical-shaped intermetallics are clearly visible in the SEM image [shown in figure 3(b)] of the 340 °C SPS sample. Figure 3(e) shows an enlarged SEM image of the intermetallic phase that is readily visible due to the black dendritic-shaped contrast regions inside the white contrast region resulting from crystallization of the τ1 phase.
The elemental composition of the intermetallics was determined by area-scan WDX intensity profiles that were extracted from each element spectrum of the intermetallic region (250 × 250 µm²) in the SPS samples corresponding to figures 3(c)–(e). The quantitative chemical composition analysis results are summarized in table 1. The average composition in the matrix region of the 260 °C SPS sample (No. 2) was similar to that of the matrix region of the 340 °C SPS sample (No. 3); thus, the overall compositional homogeneity of the as-sintered matrix samples was confirmed. However, the average composition in the intermetallic that precipitated in the 340 °C SPS sample (No. 3) showed slight differences in the composition of the matrix due to the higher contents of Nd and Zn elemental compositions. The composition of the intermetallic phase corresponded to the τ₁ phase,

| Sample           | Sintering Temp. (°C) | Mg (at.%) | Nd (at.%) | Cu (at.%) | Zn (at.%) | O (at.%) |
|------------------|----------------------|-----------|------------|-----------|-----------|----------|
| No. 2 matrix     | 260                  | 78.88 ± 0.5 | 6.37 ± 0.4 | 3.69 ± 0.5 | 8.06 ± 0.3 | 3.00     |
| No. 3 matrix     | 340                  | 78.81 ± 0.5 | 6.44 ± 0.4 | 3.62 ± 0.5 | 7.89 ± 0.3 | 3.24     |
| No. 3 intermetallics | 340              | 72.06 ± 0.5 | 7.58 ± 0.4 | 4.16 ± 0.5 | 9.42 ± 0.3 | 6.78     |
matching the XRD results in figure 2(b). The increased concentrations of Nd and Zn are supposedly from solute enrichment via the initial crystallization of primary α-Mg [15].

It is known that the devitrification process can introduce compositional changes by solute redistribution during crystallization [1, 15]. In the amorphous region, the solute concentration increases as the solute is extracted from the crystalline phase by crystallization of primary α-Mg. In contrast, the solute concentration decreases with an increasing volume fraction of precipitates resulting from the crystallization of intermetallic phases. This concentration redistribution phenomenon is known as the confined phase mixture model, which is occasionally observed in the progressive crystallization of fine-scale precipitates into the amorphous region [15].

Figure 4(a) shows the backscattered SEM image of the SPS Mg₈₄Zn₇Cu₃Nd₆ alloy at 260 °C, displaying the intermetallics within the matrix phase. EDX examinations were performed for the analysis of the elemental distribution in this intermetallic phase area scan. Figures 4(b)–(f) display the EDX mapping on a 250 × 250 μm² area showing the concentrations of O as well as Cu, Mg, Nd and Zn. The EDX analysis revealed that the black regions in figure 4(a) were mostly comprised of Mg [figure 4(d)], and the content of Nd in the white region was relatively high [figure 4(e)]. Additionally, lean concentrations of Cu and Zn were confirmed in this phase [figures 4(c) and (f), respectively]. An EDX analyses also confirmed an enrichment of O in the Nd-rich region [figure 4(b)]. REEs form oxides by directly reacting in the melt due to a high affinity for oxygen from very low Gibbs free energies of formation [24]. These oxides can act as nuclei of the primary phase during crystallization [25].

Figures 5(b)–(d) show the EBSD analysis results and the surface morphology of the SPS samples. The grain size distribution of the bulk samples consolidated at different SPS temperatures from 50 °C to 340 °C is compared with that of the as-spun amorphous ribbon in figure 5(a). The EBSD map, shown in figure 5(a), exhibited no discrete grains in the as-melt-spun ribbon, even under a high magnification due to the intrinsic nature of the amorphous phase. The grains of the SPS bulk samples consistently distributed a high number of small grains (~300 nm), with few independent large grains (~1 μm) at sintering temperatures from 50 °C to 340 °C, as shown in figures 5(b)–(d). The overall size of the grains in the crystallized Mg-based alloys was maintained at less than a micrometer (<300 nm). The EBSD investigation revealed that the sintering temperature is not a critical parameter on the grain size or growth of the SPS bulk samples. Figures 5(e)–(h) show SEM images of the surface taken from the cross section of samples. As shown in figures 5(f)–(h), some particle interfaces were observed in the polished surface of the SPS samples (marked as yellow arrows), originating from the initial surfaces of melt-spun ribbons compared with the smooth surface without any grains or boundaries [figure 5(e)].

The mechanical properties of amorphous precursor Mg-based alloys sintered at different temperatures were investigated via micro-Vickers hardness tests and compression tests. As shown in figure 6, the average measured hardness values for the as-melt-spun and SPS samples at different sintering temperatures were 243 kg mm⁻² (as-melt-spun), 192 kg mm⁻² (50 °C), 285 kg mm⁻² (260 °C) and 270 kg mm⁻² (340 °C). These values were comparable to those of Mg-Cu-Y amorphous ribbon aging at 0.7Tg over 100 h, as reported by Castellero et al.
[26], and were higher than those of commercial Mg-based alloys, low-density, high-entropy alloys, as well as the Mg-based metallic glasses [2]. The inset SEM images in figure 6 show indentation marks of the SPS samples at 50 °C and 260 °C. The representative indent from a sintering temperature at 50 °C was surrounded by circular shear bands that are typically observed in the indentation of bulk amorphous alloys and represented deformation in an elastic, perfectly plastic mode [27–29]. However, the indent image from the sintering temperature at 260 °C could not detect the surrounding shear band, and the size of the indent was relatively small due to the increased volume fraction of crystallines. The hardness improvement obtained by elevating the sintering temperature from 50 °C to 260 °C reflects the increasing devitrification of the intermetallic phases.

The hardness was highest (figure 6) for the SPS sample obtained by sintering at a temperature just above the second crystallization temperature (Tc2). The maximum Hv value of ~295 kg mm−2 was ~20% higher than those of the as melt-spun amorphous alloys. It is known that the total solute concentration in the amorphous phase has a linear relation with the micro-Vickers hardness [30]. For the Mg-Zn-Cu-Nd alloys in the present work, the concentration of solutes in the phases at each sintering temperature was examined via WDX analyses (figure 4 and table 1). The WDX regional scan analysis results in table 1 suggest that the solute content of the matrix sintered at 260 °C was 21.12 at%, a value very close to 21.19 at%, which was the solute content in the matrix obtained from the 340 °C sintered sample. In the 260 °C sintered sample, the peak hardness was observed to arise from solute enrichment in the intermetallic phase (27.94 at%), resulting from the expulsion of solute elements via primary α-Mg crystallization, which observed a similar mechanism in Al-based amorphous alloys [12].

The average hardness values of the amorphous phase, primary crystalline, and vitrified matrix were 192 kg mm−2, 237 kg mm−2, and 276 kg mm−2, respectively. The hardness of the vitrified matrix increased to a maximum of 295 kg mm−2 in the 260 °C sintered sample through a mixture of intermetallic and residual amorphous via partial crystallization in Mg-based amorphous alloys. The cause may be related to the internal confinement effect among phases on the composite effect of refined microstructures [12, 13]. The maximum hardness in figure 5 is shown with novel nanoscale phase mixtures. A critical factor in synthesizing the bulk alloys with optimum microstructures is maintaining the phase mixture during SPS sintering. If the SPS bulk sintering temperature from 50 °C to 260 °C shows a similar mechanism in Al-based amorphous alloys [12].

The compressive strength of the sintered sample at 260 °C was 224 MPa with a 2.9% strain (S1). The strength and plastic strain of the sample sintered at 340 °C were reduced to 2.6% and 130 MPa, respectively. The absence of discernible plasticity for the sintered samples was comparable to the observations for typical Mg-based amorphous alloys and Mg-based nanocrystalline alloys [5, 14, 17]. However, the overall strength of the sintered samples is lower than the converted value from the hardness, which could be explained by the deformation mode being different between uniaxial compression and indentation. The material under the indenter is deformed under constraint conditions by the surrounding material [31]. Therefore, the maximum strength from uniaxial compression is different from the conversion of the hardness results of the sintered Mg-Zn-Cu-Nd alloys. Another possible explanation for the large difference between the strength converted from hardness and the actual strength obtained from the compressive test in the same Mg-based alloys is the incoherency of the initial particle boundaries resulting in weak bonding, acting as a possible crack source [32]. The typical consolidation method in amorphous materials is using atomistic contact between particles via surface extension during deformation at elevated temperatures. However, even when the consolidate is performed at a supercooled liquid temperature, if the particle contacts incoherently it becomes weakly bonded without an inner particle bonding by extension of the surface [32]. Therefore, if spherical shaped powders were used rather than irregularly shaped pulverizing particles as amorphous precursors for the consolidation process, then the mismatching between hardness and strength would be resolved for the lightweight application parts.

Conclusion

In this study we obtained nanostructured Mg-based alloys with a uniform grain size through appropriately-adjusted nanocrystallization of amorphous precursors. The hardness of the SPS Mg-Zn-Cu-Nd alloy at temperatures above 260 °C showed the highest value. The multiple crystallization steps play important roles in enriching the Nd solute in the intermetallics via polymorphic phase transformation. The hardness of in situ devitrified Mg-based alloys reached 295 kg mm−2 in a 260 °C sintered sample due to the multiple phase mixture effect. However, the present results showed a mismatch between the hardness and the compressive strength of the pre-existing oxide on the surface of the particles. Thus, this technique provides a high constraint hardness to develop nanocrystalline Mg-based alloys with superior weight-to-mechanical property ratios.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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