Microstructure and Lattice Parameters of AlN Particle-Reinforced Magnesium Matrix Composites Fabricated by Powder Metallurgy

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Abstract Magnesium matrix composites reinforced with AlN particles were fabricated by the powder metallurgy technique. The evolution of lattice constants and solid solubility levels of Al in α -Mg and the microstructure of Mg–Al/AlN composites were investigated in the present study. The results showed that the solid solubility of Al in α -Mg reached a relatively high level by the P/M process with a long time of milling. X-ray diffraction showed that the peaks of Mg phase clearly shifted to higher angles. The lattice constants and cell volume decreased significantly compared with those of standard Mg due to a significant amount of Al incorporated into α -Mg in the form of substitutional solid solution. The degree of lattice deformation decreased at a low sintering temperature and increased at higher sintering temperatures due to the presence of AlN. Microstructural characterization of the composites revealed a necklace distribution of AlN particles in the Mg matrix. Heat treatment led to precipitation of $\text{Mg}_{17}\text{Al}_{12}$ from the supersaturated α -Mg solid solution. The precipitate exhibited granular and lath-shaped morphologies in Mg matrix and flocculent precipitation around AlN particles.

KEY WORDS: Metal matrix composite; AlN particle; Microstructure; Lattice parameter; Powder metallurgy; Solid solubility

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1 Introduction

Metal matrix composites (MMCs) combine the high performance of the metal matrix and the superior strength and stiffness of the ceramic reinforcement and show great potential for applications in the automotive and aerospace industries due to their high specific modulus, strength, and thermal stability. Further, Mg is the lightest structural metal for commercial use today. Hence, the application of Mg for structural parts has prompted intensive research arising from the weight saving issue [1]. However, widespread application of Mg alloys suffers basically from three factors, viz., low strength, poor ductility, and lack of sufficient corrosion resistance. In order to overcome these limitations, various alloying elements and different forms of reinforcements have been used to produce magnesium alloys and magnesium matrix composites with enhanced properties. Among these, particle-reinforced magnesium matrix composites are of great interest since they exhibit

isotropic properties, are easier to manufacture, and often less expensive in comparison with the continuous fiber-reinforced MMCs [2].

Recently, magnesium matrix composites with SiC [3–5] or B₄C [6] reinforcement particles have been extensively studied. It was noted that the mechanical properties of the composites are significantly improved over those of the matrix alloy, but there is very little research on magnesium MMCs reinforced with AlN particles. AlN has the HCP structure with the lattice parameters of $a = 0.312$ nm and $c = 0.4988$ nm. Since these parameters are very close to those of the HCP Mg matrix with $a = 0.3209$ nm and $c = 0.5211$ nm, AlN can act as a very effective grain refiner for Mg–Al alloys [7]. Further, AlN exhibits a low density (3.26 g/cm³), high elastic modulus (308–315 GPa [8]), and strength (flexural strength of 426 MPa [9]). On the other hand, it has a low coefficient of thermal expansion (4.5×10^{-6} K⁻¹ in the temperature range of 293–673 K) and a very good thermal conductivity (110–170 W m⁻¹ K⁻¹) [10]. Therefore, AlN reinforcement can enhance the modulus, strength, hardness, and wear resistance of the metal matrix, as SiC and B₄C do, but can also be used as a functional material, particularly in electronic packaging industry [11]. Among the feasible techniques for the synthesis MMCs, powder metallurgy (P/M) technique provides a number of advantages [12, 13]. AlN particle-reinforced Mg matrix composites have exhibited excellent mechanical properties, lower coefficient of thermal expansion, and higher-dimensional stability [11, 14, 15].

Even though the microstructure and crystal structure of materials play an important role in the development of advanced alloys and are the basis for further research, solid solution formation, known to cause solute strengthening, has also been important [16]. In recent years, there have been several investigations on the microstructure and solid solution formation in magnesium alloys. Gao *et al.* [17] investigated the effect of addition of rare-earth elements (Gd and Y) on the mechanical properties of Mg solid solutions. Zhou *et al.* [18] investigated the major mechanical and electronic properties of Mg solid solutions containing Li, Al, or Cd using first-principle calculations. Counts *et al.* [19] predicted the structure and properties of the bcc Mg–Li alloys. Zhang *et al.* [20] investigated the microstructure of PM AZ91 alloy after extrusion and found that a composite structure is developed with uniformly dispersed β particles located at the α -Mg grain boundaries, and that the extrusion temperature had a profound effect on the final microstructure.

In this work, Mg–Al matrix composites reinforced with AlN particles have been synthesized through P/M method at different sintering temperatures. The lattice parameters and microstructure analysis of Mg–Al/AlN composites are

investigated. The correlation between the position of diffraction peaks and crystal structure, and the effects of AlN and sintering temperature on the crystal structure of Mg–Al/AlN composites are discussed and analyzed. In addition, the effect of AlN particles on the morphology of Mg₁₇Al₁₂ precipitates after heat treatment is also discussed.

2 Experimental

Commercial powders of Mg (>99% purity, 75 μ m, Kemio Chemical Reagents Co., Ltd, China), Al (>99% purity, 10 μ m, Titled Metal Materials Co., Ltd, China), and AlN (>99% purity, 1–3 μ m, Eno High-Tech Material Development Co., Ltd, China) were selected as the raw materials in this study. Powder mixtures with the designed composition of 81.9 wt% Mg, 8.1 wt% Al, and 10 wt% AlN were mixed to synthesize the composite (the mass ratio of Mg to Al is about 91:9 as the composition of AZ91). Another alloy composition of 91 wt% Mg and 9 wt% Al was also prepared to compare the effects of AlN on the Mg–Al alloy. Thirty-five grams of the powder mixture together with agate balls, to maintain a ball-to-powder weight ratio of 8:1, was loaded into 500-mL nylon vial. Milling was conducted under argon atmosphere. About 2 wt% of stearic acid (99% purity, Tianjin Fuchen Chemical Reagents Factory, China) was used as a process control agent to minimize agglomeration of powder particles to each other and to the walls of the container and the grinding balls. A GLM roller mill (Xiangtan city instruments Co., Ltd, China) was used for mechanical milling at 70–100 r min⁻¹ for over 24 h.

The milled powders were cold-compacted into strips with the dimensions of 50 mm (length) $\times$ 5 mm (width) $\times$ 6 mm (height) under a pressure of 200 MPa. The green compacts were sintered at 550, 585, and 620 °C for 1 h under a protective argon atmosphere. Each experimental set included both the Mg–Al alloy and the Mg–Al/AlN composite, with the Mg–Al alloy working as a baseline for purposes of comparison.

The phase analysis of the milled powders and sintered specimens was conducted by X-ray diffraction (XRD, X'Pert PRO) with CuK α radiation. An internal calibration for peaks was conducted beforehand by recording the diffraction patterns of a pure silicon standard sample. The microstructure of the powders and the sintered specimens was observed using an optical microscope (OM, Leica DMI5000M) and a scanning electron microscope (SEM, VEGAI XMUINCA) equipped with energy-dispersive X-ray spectrometry (EDS) system. The lattice constants were determined by using the diffractometer method [21–23]. After recording the diffraction patterns, the Bragg equation

and formula for interplanar distances for hexagonal crystals were used:

$$\lambda = 2d \sin \theta, \quad (1)$$

$$\frac{1}{d^2} = \frac{4}{3} \times \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}, \quad (2)$$

where d is the interplanar spacing, θ and λ are the Bragg angle and the wavelength of the incident X-ray, respectively, a and c are lattice constants, and h , k , and l are the Miller indices of the plane from which diffraction is occurring. A standard weighted least-squares analysis and cell refinement procedures were employed by the Jade software to determine the lattice parameters of Mg.

3 Results

3.1 Phase Component

Figure 1 shows the XRD patterns of the milled Mg–Al powders and Mg–Al/AlN powders. From the XRD results, it can be seen that the structure of the Mg–Al powders and Mg–Al/AlN powders did not show any change after milling. No new phase was observed, and the positions of the diffraction peaks of the milled Mg phase match very closely with those of the standard diffraction peaks of Mg, indicating that milling has mainly played the role of mixing the constituent elements and that there was no oxidation and/or chemical reaction of the powders as well.

Figure 2 shows the XRD patterns of the Mg–Al alloy and the Mg–Al/AlN composite sintered at different temperatures. For the Mg–Al/AlN composite, there was no difference in the phase constitution at different sintering

Fig. 1 XRD patterns of Mg–Al powder mixture **a** and Mg–Al/AlN powder mixture after milling **b**

Fig. 2 XRD patterns of Mg–Al alloys and Mg–Al/AlN composites sintered at different temperatures

temperatures, and all the Al peaks disappeared in all specimens. In the meanwhile, the intermetallic compound $\text{Mg}_{17}\text{Al}_{12}$ was formed. MgO peaks could also be observed clearly apart from the two predominant phases of Mg and AlN, which suggests that partial oxidation of Mg had occurred during sintering. The source of oxygen is possibly from the oxygen contained in the green preforms or that entrapped on the surfaces of the AlN particles. Moreover, the reaction between stearic acid and metal powder was usually considered as another source of MgO; however, it can be ignored in this study due to the low content of stearic acid in the mixture powders. Mg–Al alloys, however, have the same phases as in the above case except for the absence of AlN compared with Mg–Al/AlN composites. This clearly suggests that the addition of AlN did not cause the formation of any new phase. On the other hand, the intensities of the diffraction peaks of $\text{Mg}_{17}\text{Al}_{12}$ phase are different between Mg–Al alloys and Mg–Al/AlN composites due to the different volume fractions of the constituent phases, arising from the addition of AlN. Additionally, the vertical lines in Fig. 2 represents the standard diffraction peak positions of Mg (PDF No. 89-5003). It is clear from this figure that the Mg diffraction peaks for both the sintered Mg–Al alloys and Mg–Al/AlN composites have shifted to higher angles, but the magnitude of shifting was different at different temperatures.

The amount of shifting of Mg peaks in the Mg–Al alloy and the Mg–Al/AlN composite at different sintering temperatures is shown in Fig. 3. This figure shows that the presence of AlN reduced the magnitude of shift of peak positions. Further, with increasing temperature of sintering, the magnitude of shifting decreased, and at the highest temperature of sintering (620 °C), the shift was more for the composite. The lattice parameters of Mg–Al/AlN

Fig. 3 Shifting of Mg peaks in Mg–Al alloys and Mg–Al/AlN composites at different sintering temperatures

composites and unreinforced matrix alloy sintered at different temperatures are listed in Table 1. It is noted that the lattice constants and cell volumes of all the samples decreased compared with that of standard Mg. The calculated lattice parameters varied between 0.31836 and 0.31907 nm for “*a*” and between 0.51750 and 0.51831 nm for “*c*” and the cell volumes varied from 0.04542 to 0.04568 nm³. But, the *c/a* ratio varied between 1.6238 and 1.6256, which is higher than 1.6236 for standard Mg. Therefore, it can be concluded that the shrinkage of the *a*-axis is greater than the *c*-axis for the whole unit cell.

Figure 4 plots the Mg cell volume for both the Mg–Al alloys and Mg–Al/AlN composites at different temperatures of sintering. For Mg–Al alloys, the maximum shrinkage of 2.24% of the Mg cell was observed at a sintering temperature of 550 °C, and the shrinkage decreased gradually at higher sintering temperatures. However, the shrinkage of Mg cell volume for the Mg–Al/AlN composites exhibited a trend that decreased first and then increased as the sintering temperature increased; the maximum level was 1.89% at a sintering temperature of 550 °C.

Fig. 4 Shrinkage levels of Mg cell for both the Mg–Al alloys and Mg–Al/AlN composites at different sintering temperatures

3.2 Microstructure

Figure 5 shows the micrographs of the starting powder (Mg, Al and AlN) and the milled powder mixture of Mg–Al/AlN (powder mixture and surface of magnesium). It is

Table 1 Lattice parameters of Mg in the Mg–Al alloys and the Mg–Al/AlN composites sintered at different temperatures, where A and C represent Mg–Al alloy and Mg–Al/AlN composite, respectively

Lattice parameter	Standard Mg	A-550 °C	A-585 °C	A-620 °C	C-550 °C	C-585 °C	C-620 °C
<i>a</i> (nm)	0.32088	0.31836	0.31881	0.31894	0.31873	0.31907	0.31889
<i>c</i> (nm)	0.52099	0.51750	0.51815	0.51831	0.51812	0.51810	0.51806
Cell volume (nm ³)	0.04646	0.04542	0.04561	0.04566	0.04558	0.04568	0.04562
<i>c/a</i>	1.6236	1.6255	1.6253	1.6251	1.6256	1.6238	1.6246

Fig. 5 SEM micrographs of initial starting powders (Mg, Al and AlN) before milling and the powder mixtures of Mg–Al/AlN after milling (powder mixture and surface of magnesium)

seen that the powders are uniformly mixed, and the particle size of the as-milled Mg is significantly smaller than the as-received Mg. In addition, it should be noted that many small particles of AlN and Al are dispersed on the surface of Mg.

The microstructure and EDS analyses of Mg–Al/AlN composites are presented in Fig. 6, where the gray regions of the grain interior are Mg matrix which contains some amount of Al dissolved in it, i.e., the Mg(Al) solid solution. The Mg(Al) solid solution has the same hexagonal close-packed crystal structure as that of Mg; however, the Mg matrix contained up to 4.94 at.% Al which is far more than the room temperature equilibrium solid solubility limit of Al in Mg (about 2 at.%). Since the grain boundary regions contain mainly Mg and Al, as shown in the area 2 in Fig. 6, combined with the XRD analysis (Fig. 2), it can be concluded that the main phase in this region is Mg₁₇Al₁₂. In addition, a small amount of oxygen is detected in this region, indicating that the grain boundary is more prone to be the source of oxygen and Mg is oxidized partially. Moreover, the polygonal particles are AlN reinforcements in Mg–Al/AlN composites, which can be seen from the area 3 in Fig. 6, and they have a necklace-type distribution.

Fig. 6 Microstructure and EDS analysis of Mg–Al/AlN composites fabricated by P/M process

The optical micrographs of Mg–Al/AlN composites with different magnifications are shown in Fig. 7, where Fig. 7a represents the overall microstructure and Fig. 7b

Fig. 7 Optical micrographs of Mg–Al/AlN composites with different magnifications: **a** overall microstructure; **b** distribution of AlN

Fig. 8 Concentration variation of Mg and Al elements across this region in the Mg–Al/AlN composites (numbers 1 and 2 represent the center of the grain boundary and AlN, respectively)

represents the distribution of AlN particles. The composite is made up of white α -Mg matrix, black β -Mg₁₇Al₁₂ phase, and gray AlN particles, in which the β -Mg₁₇Al₁₂ phase is located mainly along grain boundaries. It can be seen that most of the AlN particles exist along grain boundaries, and only a small amount exists in the grain interior.

Figure 8 shows the concentration variation of Mg and Al in the grain boundary region with AlN particles, where the horizontal dashed line represents the line along which measurements were taken. The numbers 1 and 2 represent the center of the grain boundary and AlN, respectively. It may be seen that the concentration of Al is maximum both at the center of the grain boundary width and the AlN particle and decreases gradually as we move away from these regions on either side. This indicates that Al is distributed in an inhomogeneous manner in the magnesium matrix and may be due to the non-equilibrium processes during preparation of the samples.

The β -Mg₁₇Al₁₂ phase has two different morphologies, as shown in Fig. 9. One is continuous black network microstructure along the grain boundaries, which is

the eutectic β -Mg₁₇Al₁₂ phase and the whole black and white area is the (α -Mg + β -Mg₁₇Al₁₂) eutectic. The other is discontinuous white particles (marked with red arrows) mainly along the grain boundaries, which is divorced eutectic morphology of β -Mg₁₇Al₁₂ phase. Compared with Mg–Al alloys, some of the divorced eutectic for Mg–Al/AlN composites is located in the grain interior because of the interaction between AlN and the magnesium matrix.

The morphologies of Mg₁₇Al₁₂ precipitates after heat treatment are shown in Fig. 10. There are two main morphologies of Mg₁₇Al₁₂ precipitation for Mg–Al/AlN composites. One is the mixture of granular and lath-shaped morphologies (Fig. 10b), which is more homogeneously distributed in the Mg matrix for Mg–Al/AlN composite relative to precipitation near the grain boundaries in the unreinforced matrix alloy (Fig. 10a). Moreover, the amount of the precipitate is significantly greater, and its size is smaller due to the addition of AlN reinforcement. This indicates that the presence of AlN particles can promote nucleation of Mg₁₇Al₁₂ precipitation and retard its

Fig. 9 Micrographs of $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase in Mg–Al alloys **a** and Mg–Al/AlN composites **b**

Fig. 10 Morphologies of $\text{Mg}_{17}\text{Al}_{12}$ precipitation after annealing at 200 °C for 10 h of Mg–Al alloys **a**, matrix of Mg–Al/AlN composites **b** and around AlN particles **c**, and EDS results of the marked areas (the samples were gold-sputtered before observation)

growth. The other morphology is flocculent precipitates around AlN particles (Fig. 10c).

4 Discussion

4.1 Shifting of Mg Diffraction Peaks and Lattice Parameter

From the comparison of Figs. 1 and 2, it may be noted that while no alloying occurred in the milled powders, the formation of $\text{Mg}_{17}\text{Al}_{12}$ and shifting of the Mg diffraction peaks took place during sintering. Therefore, it is possible to conclude that these effects in the sintered sample were a result of the exposure of these samples to a high temperature during sintering. It is well known that the constituent powder particles get fragmented to smaller and smaller sizes during milling, and that intimate mixing occurs. Additionally, during milling since the powder particles experience severe plastic deformation, a variety of crystal defects such as dislocations, vacancies, grain boundaries, and others are introduced. However, it is only after exposure to higher temperatures, such as during sintering, that significant diffusion occurs. This is further enhanced by the presence of defects, which act as short-circuit diffusion

paths [12, 13]. It may be noted that the shifting of Mg diffraction peaks is due to the solid solubility of Al in Mg, which is related to the interdiffusion between atoms mainly controlled by temperature [24].

According to the theory of X-ray diffraction [21, 23], the shifting of diffraction peaks is related to either the solid solution formation or presence of elastic strains in the material. It is important to note that even though both the “*a*” and “*c*” parameters decreased (Table 1), the magnitude of decrease is different for these two parameters and consequently, the “*c/a*” ratio in the solid solution is higher than in the pure metal. This may result in some differences in the deformation behavior of the solid solution alloys and the pure metal. Ganeshan *et al.* [25] calculated the lattice parameters of Mg–Al alloys (2.77 at.% Al) using first principles and obtained the results of $a = 0.3183$ nm, $c = 0.5177$ nm, $c/a = 1.627$ and a cell volume of 0.04541 nm³, which are close to the experimentally obtained results in this study. The above authors also concluded that elements that cause a decrease in the lattice constants increase the bulk modulus, thus making it possible to estimate the influence of cell shrinkage on the bulk modulus.

The changes in the lattice parameters of the solid solution are closely related to the dissolution of foreign solute atoms with a different atomic radius compared with that of

the solvent atom, leading to either lattice dilation or contraction [18, 25]. In the present study, the lattice parameters of Mg are smaller than the standard Mg for the Mg–Al/AlN composite. Therefore, it may be concluded that the main reason for the decrease in the lattice parameters is due to dissolution of Al atoms in the Mg lattice. However, the magnitude of decrease was influenced slightly by the presence of AlN phase in the composite.

Depending on the position of the solute atoms in the solvent lattice, the solid solution can be either substitutional or interstitial. A clear illustration of the type of solid solution in Mg–Al/AlN composites is needed for a better understanding of its crystal structure. Mg has a hexagonal close-packed (hcp) crystal structure, and therefore, the atomic radius R can be calculated from the relationship: $a = 2R$, where a is the lattice parameter. This relationship, however, is valid only when the axial ratio is ideal, i.e., $c/a = 1.633$, where c is the lattice parameter along the Z -axis of the lattice. But the values of c/a in this present study are not ideal, and therefore, the following relationship can be used [24]:

$$\left(\frac{a^2}{3} + \frac{c^2}{4}\right)^{\frac{1}{2}} = 2R. \quad (3)$$

The radii of the tetrahedral and octahedral voids (r_t and r_o) in the hcp lattice are related to the atomic radius according to the relationship [24]:

$$r_t = 0.225R, \quad (4)$$

$$r_o = 0.414R. \quad (5)$$

The atomic radius of Mg is 0.15983 nm, and thus, the radii of the tetrahedral and octahedral interstitial sites are 0.03596 and 0.06617 nm, respectively. However, the atomic radius of Al is 0.14340 nm, which is much larger than that of the tetrahedral and octahedral interstices of Mg. Assuming that Al atoms are dissolved in the α -Mg lattice in interstitial positions to form a solid solution, then the α -Mg lattice will expand and the lattice constants will be larger because the radius of the Al atom is larger than that of either tetrahedral or octahedral interstices in Mg. But the experimental results in this study clearly show that the lattice has contracted and the lattice constants are smaller, suggesting that the dissolution of Al in α -Mg is not consistent with the formation of an interstitial solid solution. On the other hand, if the Al atoms dissolved substitutionally in the α -Mg lattice, the position of Mg atom is substituted by Al atom with a smaller size and this will cause a decrease in the lattice constants of Mg, which is consistent with the present experimental results. In addition, Zhou *et al.* [18] investigated the effects of different solute atoms on the Mg-based alloys by employing the first-principle calculations and showed that the decrease in the

lattice constants and cell volumes of Mg is mainly due to the smaller size of the solute atoms. For the decrease in the lattice constants and cell volumes of Mg in this study, it may be due to the non-equilibrium processes during milling and sintering. The distribution of Al is inhomogeneous in the magnesium matrix (Fig. 8), and the α -Mg will be closer to its equilibrium state nearer the center of Mg grain. Because there is not enough time for Al atoms to segregate from the supersaturated α -Mg, Al atoms get incorporated into α -Mg to form substitutional solid solution and the cell volumes decrease.

4.2 Effect of Temperature on the Mg–Al/AlN Crystal Structure

Table 1 shows that both the lattice constants a and c of Mg solid solution are different at different sintering temperatures in both the monolithic and composite systems. Therefore, it is better to discuss the lattice deformation using the cell volume rather than using either the a or c parameter. The shift of Mg peaks (Fig. 3) is consistent with the shrinkage level of Mg cell volume (Fig. 4). It is also obvious that the larger the shrinkage of the Mg cell, the greater is the shift of Mg peaks to higher angles. Compared with unreinforced matrix alloy, the lattice deformation of Mg–Al/AlN composites is more complex with increasing sintering temperature. This may be due to the thermal mismatch between AlN and Mg–Al alloys at different temperatures.

The temperature dependence of diffusion coefficient is commonly expressed by the Arrhenius equation [24]:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (6)$$

where D is the diffusion coefficient, D_0 is the pre-exponential factor, Q is the activation energy, R is the universal gas constant, and T is the absolute temperature. It can be seen that the diffusion coefficient increases exponentially with the temperature. At a low sintering temperature, the diffusivity of Al is lower, and so the presence of AlN can slightly reduce the diffusion of Al atoms into the α -Mg lattice, resulting in a situation where the solubility of Al in α -Mg is less, and consequently reducing the lattice deformation of Mg–Al/AlN composites compared with unreinforced matrix alloy at 550 °C (Fig. 4).

The diffusivity of Al increases gradually with increasing sintering temperature, and it would surpass the effect of hindering produced by AlN when the temperature reaches a certain level. When the sintering temperature rises to 585 °C, the effect of hindering reduces and the gap between Mg–Al alloys and Mg–Al/AlN composites decreases. In addition, due to the increased diffusivity, the distribution of Al atoms in Mg is more uniform at higher temperatures. However, due to the lattice strain arising

from the thermal mismatch between AlN and Mg matrix at a higher sintering temperature, the lattice distortion of Mg–Al/AlN composites is slightly increased compared with the unreinforced matrix alloy at 620 °C (Fig. 4).

The relationship between lattice constants and solubility of Al in Mg in the Mg–Al system can be expressed per the following empirical formula [26]:

$$a = 2.807 + 4.0234 \times 10^{-3} \times (100 - x), \quad (7)$$

$$c = 4.672 + 5.3864 \times 10^{-3} \times (100 - x), \quad (8)$$

where x represents the mole solubility of Al in Mg. The lattice constants of Mg–Al alloys and Mg–Al/AlN composites are listed in Table 1. The corresponding solubility was calculated using the above empirical formulae, and the results are listed in Table 2. Although the calculated values are slightly higher than those of the experimental results, the results obtained from the current calculations can help us in estimating the influence of temperature. It may be noted that the room temperature solubility of Al in Mg decreases with increasing sintering temperature in the Mg–Al alloys, but decreases first and then increases for the Mg–Al/AlN composite. The variation of solubility with increasing temperature is very well consistent with the shifting of Mg peaks. Besides, it should be noted that the more the segregation of Al atoms which are the source of Mg₁₇Al₁₂, the less the solid solubility of Al in α -Mg.

4.3 Microstructural Characterization

For the Mg–Al/AlN composite, most of the AlN particles are present along grain boundaries. This kind of particle distribution is called “necklace-type” [4]. This is very normal for metal matrix composites, especially for composites obtained by casting methods [3–5, 27]. The authors reported that the necklace distribution was caused by the “push” effect of liquid/solid interface during solidification, and most particles were pushed ahead of the solidification front while primary magnesium grains grew, so these particles clustered in the intergranular regions during the impingement with other growing grains. However, there are two main reasons for this result in the present work. First, the specimens were fabricated using powder metallurgy technique, and most of the AlN particles are on the surface of Mg powders after milling of the powder mixtures (Fig. 5). This observation suggests that the AlN content on the surfaces and between Mg powder particles is

far higher than in the interior of the Mg powders. Secondly, the great difference in the sizes of the raw Mg and AlN powders results in the AlN particles to agglomerate in the gaps of the coarse Mg particles. It has been reported in the literature [28] that the reinforcement distribution will depend on the relative sizes of the matrix and reinforcing particles in powder processed material. And if the matrix powder is large relative to the reinforcement, the reinforcing particles will agglomerate in the interstices of the coarse particles. Jiang *et al.* [6] have fabricated B₄C particle-reinforced magnesium matrix composites by powder metallurgy methods, and they also concluded that the size difference between the matrix and reinforcement particles is the main reason for the formation of the necklace microstructures.

According to the Mg–Al equilibrium phase diagram [29], the eutectic phase will not be expected to appear when the Al content is around 9 wt% (the composition in this study). However, in practice, the equilibrium state is hardly achieved due to lack of sufficient time for equilibrium cooling at each temperature [29, 30]. Moreover, the process of powder metallurgy also promotes the occurrence of non-equilibrium state. On the one hand, the distribution of Al was not fully uniform in the Mg matrix and the Al content on the surface and grain boundaries was higher than in the interior of Mg after milling (Fig. 5). On the other hand, the Al solute in the α -Mg lacks sufficient time to uniformly diffuse (Fig. 8), resulting in the further raise of Al concentration in the grain boundaries. Therefore, the Al concentration in the grain boundaries will exceed the solubility limit of Al (12.7 wt%) in the Mg–Al equilibrium phase diagram, and the eutectic phases will be formed with the eutectic reaction ($L \rightarrow \alpha\text{-Mg} + \beta\text{-Mg}_{17}\text{Al}_{12}$) occurring at 437 °C. The eutectic products attached to the primary α -Mg matrix and parts of $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase exist in the form of divorced eutectic (Fig. 9). Besides, the Mg₁₇Al₁₂ is usually located near the AlN particles for Mg–Al/AlN composites (Fig. 9b). Li *et al.* [31] fabricated AZ91/SiC composites by powder metallurgy and found that the Mg₁₇Al₁₂ precipitates are always located near the SiC particles, and they believe that this is the result of high stress field near SiC due to thermal mismatch between Mg matrix and SiC particles during thermal process.

Completion of eutectic solidification does not necessarily mark the end of phase transformations; precipitation may occur in the supersaturated areas of the α -Mg when

Table 2 Calculated solubility limit of Al in Mg for Mg–Al alloys and Mg–Al/AlN composites sintered at different temperatures, where A and C represent Mg–Al alloy and Mg–Al/AlN composite, respectively (in at.%)

A-550 °C	A-585 °C	A-620 °C	C-550 °C	C-585 °C	C-620 °C
6.5099	5.3473	5.0351	5.4764	5.0675	5.3274

the cooling rate is sufficiently slow [29]. In this study, the cooling rate is too fast relative to equilibrium process, so the precipitation of $\text{Mg}_{17}\text{Al}_{12}$ from the supersaturated α -Mg solid solution is not obvious. However, two main morphologies of $\text{Mg}_{17}\text{Al}_{12}$ precipitates for Mg–Al/AlN composites after annealing were found (Fig. 10). The precipitates are different in morphology and size with the unreinforced matrix alloy. These are likely to form due to the thermal mismatch between the Mg matrix and AlN particles during the thermal process, which results in the high stress field near AlN and induces the formation of $\text{Mg}_{17}\text{Al}_{12}$ flocculent precipitation around AlN. Meanwhile, the nucleation of $\text{Mg}_{17}\text{Al}_{12}$ precipitation in Mg matrix is promoted by the effect, and there are more precipitates with smaller size in Mg–Al/AlN composites than in the unreinforced matrix alloy. Further, it should be noted that the flocculent precipitation has not been seen in other magnesium matrix composites. Wang *et al.* [32] investigated the effect of hot deformation on microstructure and mechanical properties; they found that the change in $\text{Mg}_{17}\text{Al}_{12}$ morphology from network to favorable fine granular shape has significantly improved the mechanical properties of magnesium alloy. Even though the effects of β phase morphology on the properties of Mg–Al alloys have been widely studied, no research has been reported for AlN particle-reinforced magnesium matrix composites fabricated by P/M methods. We plan to undertake this study to explain the relationship between the microstructure and properties of Mg–Al/AlN composites.

5 Conclusions

1. The diffraction peaks of Mg matrix phase clearly shifted to higher angles. The lattice constants and cell volume decreased significantly since a lot of Al atoms were incorporated into the Mg matrix lattice in the form of substitutional solid solution.
2. The solid solubility of Al in α -Mg reached 4.94 at.% by the P/M process with a long-time milling and a non-equilibrium process.
3. The presence of AlN reduced the degree of lattice deformation at a low sintering temperature, but enhanced it at a high sintering temperature.
4. The microstructural characterization of the composites revealed a necklace-type distribution of AlN particles in the magnesium matrix.
5. Annealing resulted in the formation of $\text{Mg}_{17}\text{Al}_{12}$ precipitates from the supersaturated α -Mg solid solution, with two different morphologies of granular and lath-shaped mixture in Mg matrix and flocculent precipitation around AlN particles.

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