www.springer.com/41230
https://doi.org/10.1007/s41230-023-3035-0

Progress in preparation of AlN-reinforced magnesium matrix composites: A review

Lu Chen, Shu-lin Lü, Di-jia Zhao, Wei Guo, Jian-yu Li, and *Shu-sen Wu

State Key Lab of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

Abstract: As a ceramic material, AlN has very good thermophysical and mechanical properties. In addition, AlN is an effective refining agent for Mg alloys because it has a lattice constant similar to that of Mg. Therefore, AlN is an ideal reinforcement for magnesium matrix composites (MMCs), and is attracting increasing attention. This review addresses the development of preparation technologies for AlN-reinforced Mg matrix composites. The mainstream preparation techniques include stir casting, melt infiltration, powder metallurgy, and in-situ methods. In addition, the advantages and disadvantages of these techniques are analyzed in depth, and it is pointed out that the next direction for the preparation of high-performance AlN-reinforced MMCs is less aluminization and multiple technologies integration.

Keywords: AlN; MMCs; preparation; thermophysical property; mechanical property

CLC numbers: TG146.22 **Document code:** A **Article ID:** 1672-6421(2024)01-001-10

1 Introduction

Magnesium matrix composites (MMCs) are the lightest metal matrix composites available with the advantages of low density, high specific strength and high specific stiffness [1]. Classified according to the morphology of the reinforcement phase, MMCs can be divided into particle-reinforced MMCs and fibre-reinforced MMCs, and the former being the most widely studied and applied. Particle-reinforced metal matrix composites offer isotropic mechanical properties, which make them advantageous as they do not require reinforcement orientation during the forming process. This feature makes particle-reinforced MMCs well-suited for traditional casting processes. The commonly used particle reinforcements in MMCs are SiC [2–5], Al_2O_3 [6–8], TiC [9,10], TiB_2 [11–13], and B_4C [14,15]. The basic physical parameters of the commonly used reinforcements in MMCs are given in Table 1. In recent years, the thermophysical properties of MMCs have attracted much attention, but these conventional particle reinforcements generally exhibit poor thermophysical properties. More critically, most of the particle reinforcements are incorporated into the magnesium matrix by ex-situ methods, which means that ideal interfacial bonding between the reinforcements and Mg matrix is difficult to achieve, resulting in MMCs with lower thermophysical properties.

AlN is a novel particle reinforcement with a hexagonal crystal structure and a lattice constant similar to Mg, which means it can act as a heterogeneous nucleation substrate for Mg and provide fine grain strengthening [16,17]. Furthermore, AlN is an ideal material for improving the thermophysical properties of magnesium alloys, as it has excellent thermophysical properties, with a thermal conductivity of 320 $W\cdot m^{-1}\cdot K^{-1}$ and a coefficient of thermal expansion of only 4.5×10^{-6} K^{-1}. Therefore, a promising MMC can be obtained by utilizing AlN as reinforcement, not only to achieve good mechanical properties, but also to obtain excellent thermophysical properties. Furthermore, AlN can be generated in-situ in the melt with only Al and nitride as raw materials, without the necessity of complex molten salt reactions, which is well suited to Al-containing magnesium alloys such as AZ91. Currently, the preparation and mechanical properties of AlN-reinforced magnesium matrix composites (AlN-MMCs) are the main focus of research. In this paper, the preparation techniques of AlN-MMCs were reviewed and summarized, the advantages and shortcomings of these techniques were discussed, and some new ideas or outlook for the preparation of AlN-reinforced MMCs were proposed.

***Shu-sen Wu**

Male, Ph. D, Professor. His research interests mainly focus on Al alloys, Mg alloys and their composites.

E-mail: ssw636@hust.edu.cn

Received: 2023-04-18; Accepted: 2023-06-11

Table 1: Physical parameters of commonly used reinforcements in MMCs [16,17]

Materials	Density ($g \cdot cm^{-3}$)	*E* (GPa)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	CTE ($\times 10^{-6} K^{-1}$)
AlN	3.3	310	320	4.5
SiC	3.2	430	270	4.6
TiB_2	4.5	575	64	7.6–8.6
TiC	4.9	437	17–21	7.5–7.7
Al_2O_3	4.0	220	24–39	5.4

2 Ex-situ methods for preparation of AlN-MMCs

2.1 Stir casting

The most commonly used technique for preparing particle-reinforced metal matrix composites is the stir casting process [18–20]. Due to the poor wettability of AlN with the molten magnesium, the wettability angle is greater than 120° at 700 °C [21]. Therefore, shear force is required to assist AlN to enter the molten magnesium melt. Imai et al. [22] proposed the use of the vortex technique to prepare AlN/Mg-5Al (wt.%) composites, which later became known as the stir casting technique. With this technique, Imai obtained homogeneously distributed AlN (average particle size=0.72 μm) composites with an AlN volume fraction of 15%. After extrusion and hot rolling, the grain size of the AlN/Mg-5Al (wt.%) composites was just under 2 μm, which is one-tenth of the grain size of the Mg-5Al (wt.%) alloy. Imai et al. [22] found that AlN/Mg-5Al (wt.%) composites exhibited superplasticity at high temperature and high strain rate, with an elongation of 200% at 673–698 K.

Mechanical stirring alone cannot achieve uniform distribution of nano-AlN. Therefore, ultrasonic techniques are often incorporated into the preparation process for achieving homogeneous dispersion of AlN. Cao et al. [23] prepared 1.0wt.% nano-AlN/AZ91D composites using ultrasonic techniques, and the process of preparation is schematically shown in Fig. 1(a). The room temperature and high temperature tensile properties of the composites are shown in Figs. 1(b, c), where the nano-AlN significantly improves the room temperature and high temperature strength of the matrix while maintaining the plasticity of the AZ91D matrix. Katsarou et al. [24] prepared 1.0wt.% nano-AlN/Elektron21 composites via an ultrasonic assisted stir casting technique. Compared to the Elektron21 matrix, the grain size of the composites was refined to 74.1 μm. Possibly due to the presence of Al impurities in the raw AlN, the properties of the composites in room temperature tensile and compression tests were not significantly different from those of the matrix. However, the minimum creep rate of the composites was reduced significantly. This is attributed to the fact that the addition of nano AlN increases the creep resistance of the composites.

In addition to applying ultrasonic to promote the wetting and dispersing behavior of AlN during stir casting, the simultaneous addition of AlN particles and Al to the magnesium melt also facilitates this process [25]. Giannopoulou et al. [26] added nano-AlN particles containing 25% Al nanoparticles into pure Mg and ZW0303 alloys by stir casting. In contrast to the results obtained by Katsarou et al. [24], both the AlN/Mg and AlN/ZW0303 composites exhibited a significant improvement in mechanical strength compared to the matrix. When 1.5wt.% of AlN was added, the yield strength of Mg was increased from 101 MPa to 159 MPa. The addition of AlN nanoparticles enhanced the elongation of Mg, but significantly reduced the elongation of ZW0303. This difference was attributed to the reaction of the Al element in the AlN particles with the Y element in the ZW0303, but the composites still exhibited superior overall mechanical properties. Moheimani et al. [27] chose to prepare a master alloy of Al with AlN and then added the master alloy to the Mg melt to promote the dispersion of AlN. They focused on the thermophysical properties of the composites, where nano AlN significantly improved the thermal conductivity of the composites. With the addition of only 2% nano AlN, the thermal conductivity of the EV31 alloy increased from 114.8 $W \cdot m^{-1} \cdot K^{-1}$ to 149.52 $W \cdot m^{-1} \cdot K^{-1}$. Similarly, Li et al. [28] obtained 0.8AlN/Mg-8Al composites by diluting a prefabricated Al-12.5AlN master alloy into the melt. The macroscopic morphology and microstructure of the Al-12.5AlN master alloy are shown in Figs. 2(a) and (b), where the fine AlN particles are homogeneously and dispersively distributed in the Al matrix. As shown in Fig. 2(c), the AlN in

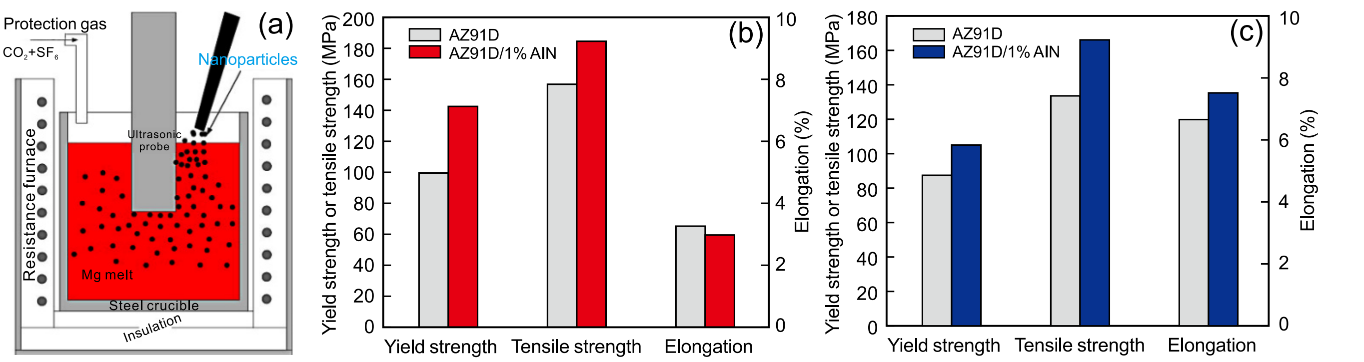

Fig. 1: Schematic diagram of the preparation process (a) and mechanical properties of 1.0wt.% nano-AlN/AZ91D composites at room temperature (b) and 200 °C (c) [23]

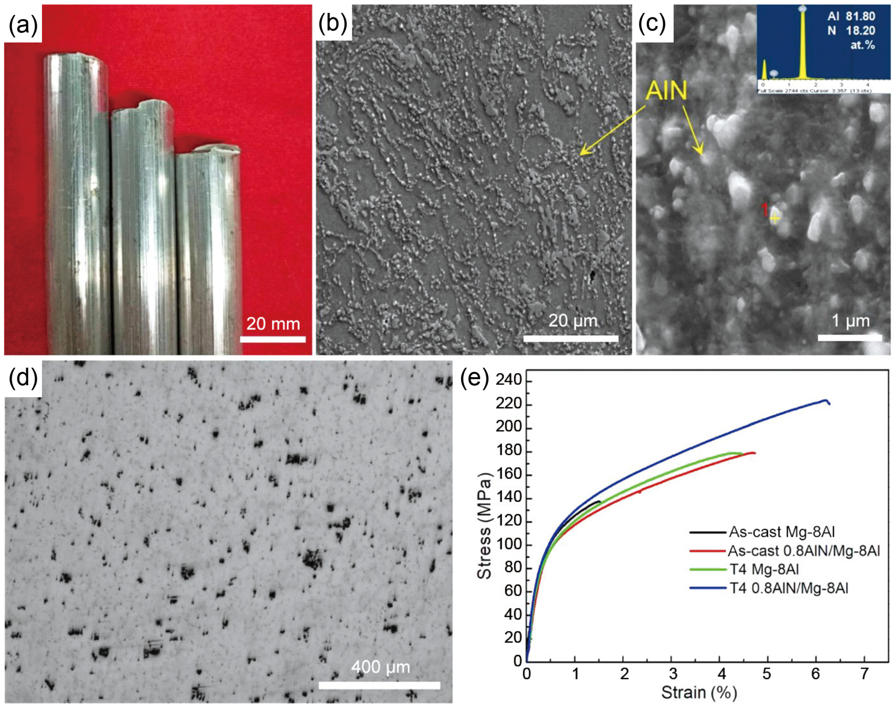

Fig. 2: (a) Al-12.5AlN master alloy, (b) microstructure of Al-12.5AlN, (c) morphology of nano AlN, (d) microstructure of 0.8AlN/Mg-8Al composites, (e) stress-strain curves of Mg-8Al and 0.8AlN/Mg-8Al composites at room temperature [28]

the Al-12.5AlN master alloy is submicron and its average particle size is less than 200 nm. Since AlN is added to the magnesium melt as an Al-12.5AlN master alloy, the stirring time of the whole process lasts only 2 min to obtain the 0.8AlN/Mg-8Al composite, as shown in Fig. 2(d). The strength and elongation of the 0.8AlN/Mg-8Al composites were increased by 31% and 213%, respectively compared to the matrix alloy, as shown in Fig. 2(e).

2.2 Melt infiltration method

Good AlN-MMCs can be fabricated using the stir casting technique with the aid of assistive techniques. Unfortunately, it is difficult to obtain composites with a high AlN content by this method. In contrast to the stirring casting process, the melt infiltration approach involves firstly preparing AlN preforms and then infiltrating molten magnesium into the cavities of the AlN preforms to produce composites with a high AlN content. The diagram of the infiltration process is shown in Fig. 3, and the infiltration can be either from the bottom up or in the direction of gravity. León et al. [29] fabricated AlN/Mg composites via pressureless infiltration, with the AlN volume fraction reaching 48%. The Young's modulus of the composites was found to be between 90–110 GPa, while the tensile strength reached a maximum value of 390 MPa. These values are significantly higher than those obtained via stir casting method for composite preparation. Bedolla [30] and Falcon-Franco et al. [31] extended this pressureless infiltration approach to the preparation of AlN/AZ91 composites, achieving an elastic modulus three times as that of the matrix alloy, approximately 133 GPa. Arreola-Fernández et al. [32] utilized a pressureless infiltration process to develop 50vol.% AlN/AZ91E composite and studied its dry abrasion capabilities. The resulting average wear coefficient (0.53–0.65) was found to be twice that of AZ91E, while its wear rate was only 10% of that observed in AZ91E. After analyzing the microstructure, Arreola-Fernández et al. [32] discovered substantial discrepancies between the wear mechanisms of the composite and the matrix. Abrasive wear was identified as the primary failure mechanism for AZ91E, whereas oxidation was found to be the main cause of wear loss for AlN/AZ91E composite. Melt infiltration is a well-established technique in the field of MMCs. Advanced preparation techniques such as pressure infiltration [33], negative pressure infiltration [34], and liquid-solid extrusion following vacuum pressure infiltration technique (LSEVI) [35] have been developed. However, only a few studies on pressureless infiltration have been reported for AlN-MMCs. Due to poor

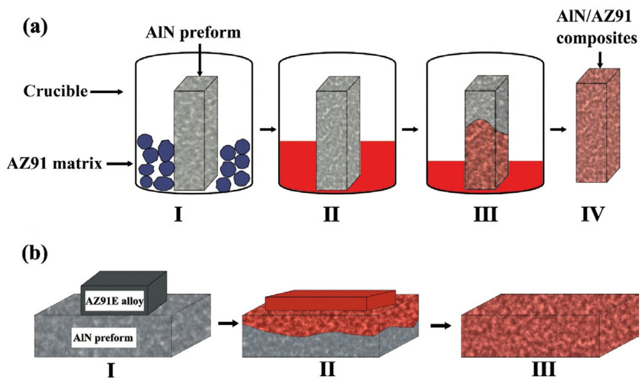

Fig. 3: Schematic diagram of the preparation process of AlN/AZ91 composite by pressureless infiltration: (a) anti-gravity directional infiltration [30]; (b) gravitational directional infiltration [31]

wettability between AlN and magnesium melt, it is evident that pressureless infiltration has its limitations. Therefore, more advanced melt infiltration techniques need to be applied in order to overcome this issue.

2.3 Powder metallurgy

Even with ultrasonic assistance, it is a challenging task to completely disperse AlN particles in Mg melt due to the poor wettability between AlN and liquid magnesium. Consequently, some researchers have used powder metallurgy to prepare AlN-MMCs, which has the advantage of dispersing the particles using solid-solid mixing without considering the wettability between the reinforcing phase and the matrix. Sankaranarayanan et al. [36] mechanically mixed magnesium powder with AlN powder and subsequently cold pressed the mixed powder into shape and then microwave sintered to obtain AlN/Mg composites. With an increase in AlN content, the grain size and CTE of the composites were significantly reduced compared to pure Mg, as shown in Table 2. The composites' strength and plasticity were significantly enhanced, demonstrating the viability of AlN-MMCs manufactured using powder metallurgy technology. Chen et al. [37] produced composites with a moderate AlN content by incorporating ball milling to reduce particle agglomeration during mechanical mixing. He used a step-by-step ball milling method, and the schematic diagram of this method is given in Fig. 4(a). Firstly, AlN was ball milled with bulk Mg to coat the Mg on the AlN surface, which was demonstrated in Figs. 4(b). Immediately, the matrix alloy powder was also ball-milled and broken to the same size, and then all the raw materials were further mixed and dispersed. Chen pointed out that the conventional ball milling method leads to the distribution of AlN particles along the grain boundaries, which is prone to brittle fracture at the grain boundaries. Figures 4(c–f) compare the microstructure of the composites prepared by the stepwise ball milling method and the conventional technique, and clearly shows that a more homogeneous composites can be obtained by Chen's method. A further study from Chen et al. [38] shows that this improved

Table 2: Grain size, CTE and mechanical properties of AlN/Mg composites [36]

Materials	Grain size (μm)	CTE ($\times10^{-6}$ K^{-1})	YS (MPa)	UTS (MPa)	Elongation (%)	Microhardness (HV)
Pure Mg	28.2±7.7	28.5±1.1	96±6	137±9	6.0±3.0	41±3
0.2AlN/Mg	23.8±7.9	27.3±0.6	102±6	159±8	11.0±2.2	49±3
0.4AlN/Mg	19.6±6.2	26.9±0.4	120±1	164±3	8.4±0.9	55±3
0.8AlN/Mg	19.4±5.3	25.4±1.3	129±5	176±3	6.3±0.4	53±8

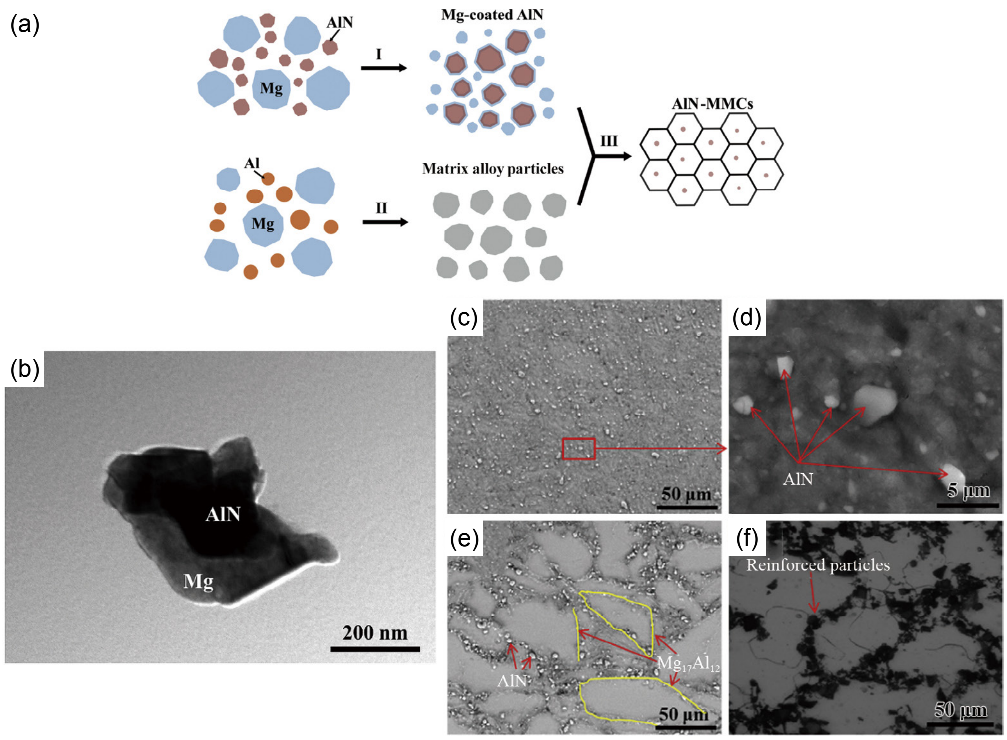

Fig. 4: Preparation of AlN-MMCs with effectively dispersed AlN particles proposed by Chen: (a) schematic illustration; (b) TEM image of Mg-coated AlN; (c) SEM image of AlN/Mg-Al composites; (d) enlarged image of the red selection in (c); (e) chain-like distribution of AlN shaped by conventional ball milling method; (f) chain-like distribution of SiC shaped by stirring casting [37]

ball milling process, compared to the conventional process, has the potential to reduce the thermal expansion of the materials as well as to improve the thermal conductivity of the materials, which is important for expanding the applications of AlN-reinforced MMCs.

3 In-situ method for preparation of AlN-MMCs

The major advantage of AlN over other reinforcements is that it can be generated in-situ in the magnesium melt. Although TiC and TiB_2 can also be produced in-situ by molten salt reactions, the raw materials are too expensive and the by-products are difficult to remove [39, 40]. The in-situ formation of AlN in Al melts is relatively well developed and the reaction mechanism can be similarly applied to the in-situ preparation of AlN-MMCs. In terms of elemental composition, the in-situ production of AlN requires the introduction of an aluminum source and a nitrogen source into the melt. The nitrogen sources introduced are relatively varied, not only nitrogen gases like N_2 [41,42] and NH_3 [43], but also solid nitrogen sources like Mg_3N_2 [44], BN [45] and Si_3N_4 [46].

Koczak et al. [47] reported that the in-situ formation of carbides and nitrides can be achieved by introducing gas into the active melt. The technique not only produces fine and diffuse reinforcements, but also provides extremely stable thermodynamic and kinetic reaction processes. Ye et al. [48] demonstrated that AlN particles can be produced in-situ in the melt by introducing N_2 into the Mg-Al melt via a liquid nitriding reaction and this reaction can be divided into two stages:

$$N_2 + 3[Mg] = Mg_3N_2 \quad (1)$$

$$2[Al]_{Mg} + Mg_3N_2 = 2AlN + 3[Mg] \quad (2)$$

Unfortunately, the AlN particles produced by Ye using the liquid nitriding technique were large and only found in the top of the melt. Yang et al. [49] improved this process and generated in-situ AlN nanoparticles in the melt based on Ye's study. Yang made two major improvements, firstly by changing the nozzle from a single large nozzle to 18 small nozzles, and secondly by applying a stirring treatment as shown in Fig. 5(a) to the melt to promote AlN dispersion when nitrogen gas was bubbled in. The mechanical properties of the in-situ AlN/Mg-9Al composites produced by this technique were greatly improved, with an improvement in tensile strength from 150 MPa to 226 MPa and an elongation increase from 4.18% to 21%. Figures 5(b–d) show the microscopic morphology of AlN prepared using the bubbling method, with the size of AlN between nanometer and submicron. AlN is not only fine but also has a very clean interface with Mg, as shown in Fig. 5(e), meaning there is a strong interfacial bond between Mg and AlN. In addition to the strong interfacial bonding between in-situ AlN and the Mg matrix, the presence of in-situ AlN also contributes to a reduction in grain size of Mg-9Al from 90–100 μm to 30–40 μm. This reduction in grain size is another factor leading to improved properties.

The advantage of liquid nitriding is that the reaction is fast and no impurities remain in the melt. However, it is probable that gas will remain in the melt and form pores, which can have a fatal impact on the properties of the composite material. Solid-state sources of nitrogen have been extensively investigated due to their ability to avoid gas pore formation. One of the simplest solid-state sources of nitrogen used is Mg_3N_2. In fact, the second stage of the reaction process proposed by Ye is the generation of AlN using solid Mg_3N_2, and the extent and rate of this reaction determine the size and purity of AlN. Fan et al. [50] has carried out a detailed study of the thermodynamics and kinetics of this reaction and has given the rule for the effect of the addition of alloying elements on this reaction. The Gibbs free energy of Eq. (2) decreases

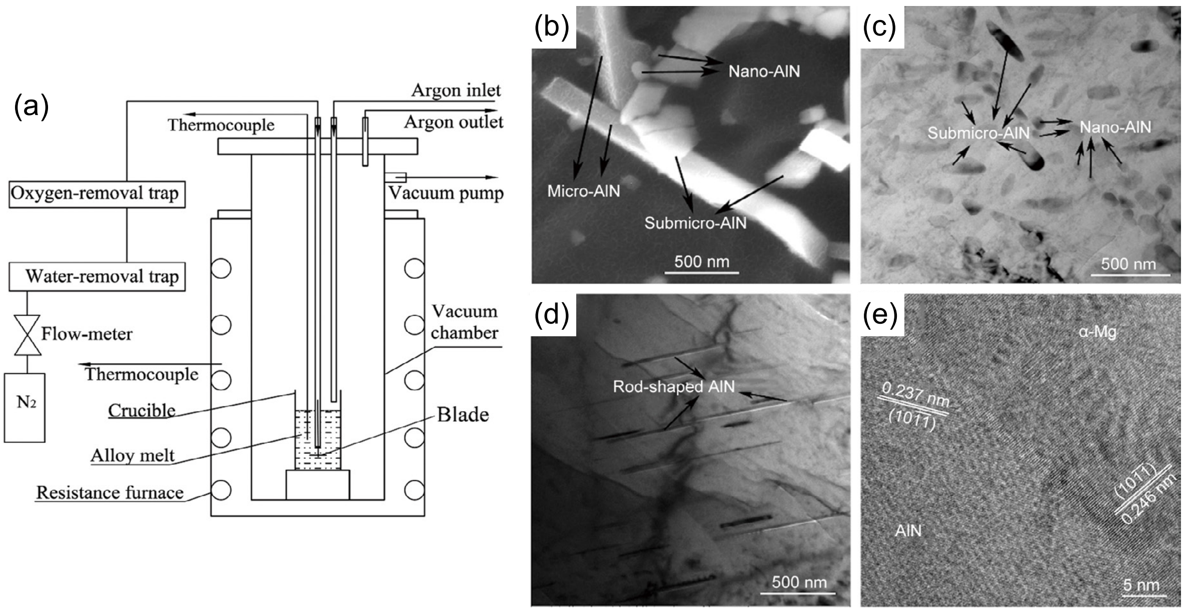

Fig. 5: In-situ preparation of AlN-MMCs by melt bubbling method: (a) schematic diagram of the device; (b–e) TEM image of in-situ AlN/Mg-9Al composites [49]

significantly with an increase in Al content, indicating that the increase in Al content promotes the progress of the reaction. For the third alloying element, Mn, Nd and La increase the reaction free energy, while Cu, Zn and Si decrease the reaction free energy, as shown in Fig. 6(a). From the kinetic point of view, Nd, Ce, Ni, La, Si and Zn all promote the diffusion of Al elements in the melt and facilitate the formation of AlN. However, an excessive amount of Cu can hinder the diffusion of Al and limit its reaction, as can be seen in Fig. 6(b). The element Mn is not involved in Fig. 6(b), but it can be seen from the data in Table 3 that even a small amount of Mn can greatly enhance the diffusion coefficient of Al, much more than other alloying elements. Collectively, most of the alloying elements can play a role in promoting Eq. (2), with Mn playing the most significant role among them.

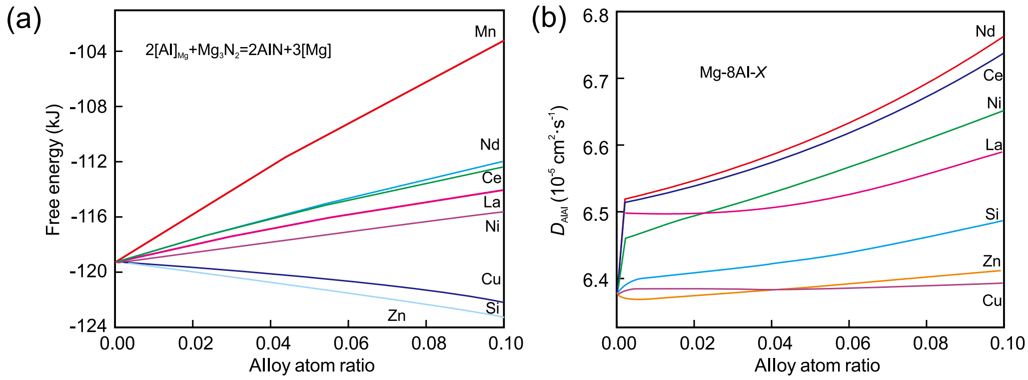

Fig. 6: Effect of alloying elements on reaction Eq. (2): (a) Gibbs free energy varied with different alloying elements at 973 K; (b) mutual diffusion coefficient of Al at 973 K with different alloying elements [50]

Table 3: Effect of alloying elements on mutual diffusion coefficient of Al in Mg melts (T=973 K)

Concentration (at.%)	Mutual diffusion coefficient of Al (10^{-5} $cm^2 \cdot s^{-1}$)							
	Si	Ce	Cu	Nd	Ni	La	Zn	Mn
0.2	6.4005	6.5162	6.3871	6.5196	6.4605	6.4991	6.3665	6.8045
2.0	6.4077	6.5360	6.3838	6.5440	6.4962	6.4972	6.3733	7.6780
4.0	6.4209	6.5709	6.3829	6.5837	6.5289	6.5061	6.3819	–
6.0	6.4391	6.6165	6.3843	6.6328	6.5660	6.5253	6.3914	–
8.0	6.4613	6.6729	6.3877	6.6933	6.6072	6.5536	6.4017	–
10.0	6.4867	6.7387	6.3925	6.7635	6.6529	6.5897	6.4130	–

According to the analysis of Fan et al. [50], the presence of Si in the Mg melt promotes the formation of AlN, while it also produces hard Mg_2Si within the Mg matrix, further enhancing the mechanical properties of the composites. Zhang et al. [51] proposed that the following reactions may also occur in the molten Mg:

$$Si_3N_4 + 4[Al]_{Mg} = 4AlN + 3[Si]_{Mg} \quad (3)$$

Si_3N_4 initially reacts with the Al element in the Mg melt to form AlN, resulting in the release of Si. Then, the Si element combines with Mg to form Mg_2Si particles, and finally the (AlN+Mg_2Si)/Mg composite can be obtained. After the reaction, the size of AlN remains basically the same as that of Si_3N_4, because AlN is produced by replacing the Si element in Si_3N_4 with Al element. However, Si_3N_4 as a nitrogen source introduces excessive Si elements and results in coarse primary Mg_2Si. In order to control the morphology of Mg_2Si, Zhang et al. [51] incorporated a small amount of Ti into the magnesium melt to minimize the size of Mg_2Si for achieving proper performance of the (AlN+Mg_2Si)/Mg composite. Gao et al. [52] prepared in-situ AlN/Mg-8Al composites by using BN as solid nitrogen. Mg powder, Al powder and BN powder were firstly mixed proportionally and then cold-pressed to obtain preformed blocks. Finally, the AlN/Mg-8Al composites were fabricated by holding the preformed blocks at 550 °C for 1 h in a vacuum shaft furnace. During this process, the following reactions took place:

$$[Al] + BN = AlN + [B] \quad (4)$$

$$Mg + 2[B] = MgB_2 \quad (5)$$

Different from Zhang's experiments, Si_3N_4 is required to react with Al in the Mg melt at 800 °C, whereas the reaction between BN and Al occurs in the solid state. Fine in-situ formed AlN particles, distributed in chains on the Mg matrix, can be observed in Fig. 7(a). The solid powder is premixed, which not only minimizes the elemental diffusion path, but also homogeneously distributes the reacted AlN in the matrix.

Mechanical properties test results show that the hardness of the in-situ AlN/Mg-8Al composite is 54% higher than the matrix, and the compressive strength reaches 295 MPa, while the matrix only reaches 181 MPa. The fracture morphology observation in Figs. 7(c) and (d) reveals the presence of AlN chains on the shear surface. Gao et al. [52] suggests that this distribution of chain-like AlN surrounds the Mg matrix and that the particle chains may be subjected to higher stresses or pile up more dislocations during loading [53, 54].

The AlN-MMCs prepared by several in-situ techniques mentioned above are summarized in Table 4. The sizes of AlN prepared by in situ techniques is usually at the submicron level, with very few reaching several nanometer levels. Accordingly, the fine AlN allows these AlN-MMCs to possess excellent mechanical properties, and the as-cast elongation can even reach 42%. However, as shown in Table 4, even for the same material prepared by the same in-situ method, there are great differences between the mechanical properties. This discrepancy may arise from variations in the extent of in-situ reaction, highlighting the need for further research to regulate and optimize the in-situ reaction of AlN-MMCs.

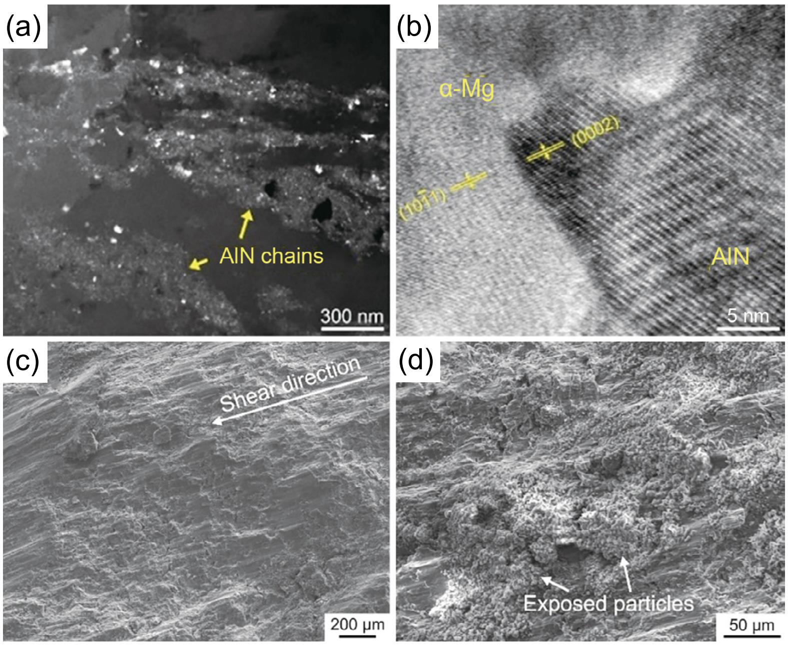

Fig. 7: TEM images and fracture morphology of in-situ AlN/Mg-8Al composites: (a) dark field image; (b) HRTEM image; (c) low magnification of shear fracture; (d) high magnification of shear fracture [52]

Table 4: Mechanical properties and AlN's size of AlN-MMCs prepared by in-situ methods

Materials (state)	Synthesis technology	Size of AlN	UTS (MPa)	Elongation (%)	Other performances	Ref.
AlN/ZA91	Liquid nitriding method	23.7–231.2 nm	240±10	20±3	–	[55]
AlN/AZ91 (rolled)	Liquid nitriding method	23.7–231.2 nm	351±6	10.5±0.6	–	[55]
AlN/Mg-9Al	Liquid nitriding method	<1 μm	220±10	42±5	–	[49]
(AlN+Mg_2Si)/Mg	Liquid-solid (Si_3N_4) reaction	0.5 μm	–	–	–	[56]
AlN/Mg-8Al	Solid-solid (BN) reaction	13±1.5 nm	–	–	UCS*=295±5 MPa Hardness (HBW)=89.5±2.3	[52]

*UCS for ultimate compressive strength

4 Discussion

AlN-reinforced MMCs are currently under investigation, with more diverse preparation techniques being explored than for other composites, particularly in-situ preparation techniques. The advantages and disadvantages of different preparation techniques for AlN-MMCs are summarized and compared in Table 5, and their limitations are mainly discussed below. Using stir-casting method, even with the assistance of ultrasonic techniques, achieving a completely homogeneous distribution of nano-AlN can be difficult. Not only AlN enrichment in the grain boundary region can be observed, but also obvious AlN clusters can be seen. Furthermore, in order

Table 5: Comparison of different synthesis technology for AlN-MMCs

Synthesis technology		Advantages	Shortcomings	
Ex-situ technology	Stir casting	Applicable to a wide range of substrate materials, suitable for AlN-MMCs above submicron size	Unable to obtain uniformly distributed nano-AlN-MMCs and low AlN content in the composite	The base alloy is limited to Mg-Al alloys
	Melt infiltration	The prepared composites possess high AlN content, strength and hardness	Limited sample size and poor plasticity	
	Powder metallurgy	Overcomes the poor wettability of AlN/Mg	High risk factor of ball milling process	
In-situ technology	Liquid nitriding method	In-situ generation of nanoscale AlN particles	AlN is not uniformly distributed in the direction of gravity	
	Liquid-solid (Si_3N_4) reaction	Achieveing hybrid enhancement (in-situ+Mg_2Si)	The size and content of Mg_2Si is difficult to control	
	Solid-solid (BN) reaction	Low reaction temperature and fine size of AlN	High porosity of sample	

to incorporate AlN into the Mg melt, it is generally necessary to introduce extra Al elements into the matrix, thus changing the alloy composition, which may affect the properties of the composite in turn.

Although the in-situ process overcomes the problem of poor wettability between AlN and Mg, improvements are still required. Firstly, the extent of the in-situ reaction is difficult to control, especially in the case of the nitrogen gas-liquid reaction method. The nitrogen does not constantly remain in the Mg melt, but constantly evaporates. This means that a continuous flooding of the melt with nitrogen is required to ensure that the reaction from Al to AlN is complete. This process is time consuming, expensive and tends to result in high melt gas contents, even leading to Mg_3N_2 generation. Wettability between solid nitrogen source and Mg melt must be considered when using a solid nitrogen source such as BN. If the wettability between the two is poor, the area of contact between the raw material powder and the Mg melt will be shallow, and the rate of reaction will be low. In addition, some solid nitrogen sources react from the powder surface to the interior. The closer to the powder, the less reaction takes place, so the reaction time must be prolonged accordingly to ensure that the reaction is complete. Gao et al. [57] avoided this problem by using a solid reaction, but the resulting composites with low density and tiny pores were observed in AlN/Mg-8Al. The second point is that the in-situ nitrogen source introduces new alloying elements such as Si and B into the matrix. In the case of Si_3N_4, for every 1wt.% of AlN produced, 0.95wt.% of Mg_2Si is generated. Excess Mg_2Si is detrimental to the mechanical properties of MMCs, and thus the amount of AlN is limited to control the Si content.

Upon analyzing the compositions of composites studied above, it is evident that Al element plays a critical role in preparing AlN-reinforced MMCs. In the ex-situ preparation process, Al element plays the role of promoting the wetting of AlN and Mg melt. In the in-situ preparation process, Al is an essential raw material for the reaction. However, in some applications, the amount of Al in Mg alloys and composites is controlled as much as possible. For thermally conductive Mg alloys, the Al element can significantly reduce the thermal conductivity of the alloy. For instance, conventional AZ91 magnesium alloy, which is a common matrix alloy for the development of AlN-reinforced MMCs, has a thermal conductivity of only 45 $W \cdot m^{-1} \cdot K^{-1}$ [58]. Therefore, the application of AlN-reinforced MMCs is limited because the excellent thermophysical properties of AlN are not fully exploited due to the presence of Al elements. In the ex-situ method, it is important to consider how to prepare AlN/Mg composites in conditions with low or zero Al. In the case of in-situ preparation process, precise control over the extent of reaction is necessary to ensure complete formation of AlN while minimizing its detrimental effect on thermal conductivity of matrix.

We have carried out a study on AlN-MMCs in the hope of contributing to the development of AlN-MMCs. The study focuses on the thermophysical properties of AlN-MMCs, including its thermal conductivity and coefficient of thermal expansion. As mentioned earlier, the presence of Al element in Mg leads to decreased thermal conductivity; therefore, Al element was not introduced during the entire preparation process. In order to solve the problem of poor wettability between AlN and Mg, the semi-solid stirring technique was introduced in the preparation of the composite. With the assistance of the semi-solid technique, AlN/Mg-Zn-Cu composites were successfully prepared to achieve the lower aluminization. Furthermore, the co-reinforcement of Mg_2Si and AlN was also achieved to reduce the thermal expansion coefficient of the composite to 16×10^{-6} K^{-1}, which is significant for the application of AlN-MMCs in the field of packaging materials. Therefore, AlN-MMCs still have more room for development, and new preparation techniques and application fields need to be paid attention.

AlN-MMCs are still at the laboratory development stage and have not yet been in industrial use, mainly because the preparation technology for AlN-MMCs is difficult to support large-scale production. Regarding structural materials, SiC-MMCs have been more extensively researched and industrially produced compared to AlN-MMCs, which have received little attention. It is only in recent years that

AlN has been the focus of attention as the third generation thermal substrate material and has been applied to Cu-based and Al-based composites [59-62], while AlN-MMCs are still in their infancy. To distinguish themselves from other MMCs, AlN-MMCs must fully exploit the excellent electrical and thermophysical properties of AlN. This presents new challenges in their preparation technology.

5 Outlook

Generally, to fully exploit the advantages of AlN, especially the thermophysical properties of AlN, the current AlN/Mg preparation technology is not satisfactory. In order to obtain AlN/Mg composites with more desirable properties, the preparation technology of AlN/Mg can be improved from the following aspects:

(1) Pre-dispersion and surface treatment of nano-AlN raw material can facilitate its dispersion in the melt, leading to a reduction in the Al content of the composite system.

(2) An in-depth investigation into the thermodynamics and kinetics of in-situ AlN generation is necessary to develop a more efficient and abundant reaction system. The reaction by-products should enhance the mechanical properties of the composites as much as possible or be easily separated from the melt to obtain a higher AlN content.

(3) By combining ex-situ and in-situ methods, ultrasound can be applied to provide localized high temperature and pressure, promoting rapid solute diffusion. This approach effectively reduces both the required temperature and time for the melt reaction.

(4) Efforts should be made to enhance the existing in-situ preparation techniques for AlN-MMCs, focusing on improving the stability and controllability of in-situ reactions. This is crucial for enhancing the performance of AlN-MMCs and promoting their wider applications.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Nos. 52175321, and 51771080).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Nie K B, Wang X J, Deng K K, et al. Magnesium matrix composite reinforced by nanoparticles – A review. J. Magnes. Alloys, 2021, 9(1): 57–77. DOI:10.1016/j.jma.2020.08.018.
[2] Wang X J, Wang N Z, Wang L Y, et al. Processing, microstructure and mechanical properties of micro-SiC particles reinforced magnesium matrix composites fabricated by stir casting assisted by ultrasonic treatment processing. Mater. Des., 2014, 57: 638–645. DOI:10.1016/j.matdes.2014.01.022.
[3] Poddar P, Srivastava V C, De P K, et al. Processing and mechanical properties of SiC reinforced cast magnesium matrix composites by stir casting process. Mater. Sci. Eng. A, 2007, 460–461: 357–364. DOI:10.1016/j.msea.2007.01.052.
[4] Deng K K, Wu K, Wu Y W, et al. Effect of submicron size SiC particulates on microstructure and mechanical properties of AZ91 magnesium matrix composites. J. Alloys Compd., 2010, 504(2): 542–547.
[5] Jiang A, You Z, Duan Z, et al. Effects of SiC_p on microstructures of semi-solid extruded AZ91D magnesium alloys in recrystallization process. China Foundry, 2021, 18(6): 565–573. DOI:10.1007/s41230-021-1005-y.
[6] Rahmany-Gorji R, Alizadeh A, Jafari H. Microstructure and mechanical properties of stir cast $ZX51/Al_2O_{3p}$ magnesium matrix composites. Mater. Sci. Eng. A, 2016, 674: 413–418. DOI:10.1016/J.MSEA.2016.07.057.
[7] Sameer Kumar D, Suman K N S, Tara Sasanka C, et al. Microstructure, mechanical response and fractography of $AZ91E/Al_2O_{3(p)}$ nano composite fabricated by semi solid stir casting method. J. Magnes. Alloys, 2017, 5(1): 48–55. DOI:10.1016/J.JMA.2016.11.006.
[8] Cao W, Zhang C, Fan T, et al. In situ synthesis and damping capacities of TiC reinforced magnesium matrix composites. Mater. Sci. Eng. A, 2008, 496(1–2): 242–246. DOI:10.1016/j.msea.2008.06.032.
[9] Chen L Q, Dong Q, Zhao M J, et al. Synthesis of TiC/Mg composites with interpenetrating networks by in situ reactive infiltration process. Mater. Sci. Eng. A, 2005, 408(1–2): 125–130.
[10] Jiang Q C, Li X L, Wang H Y. Fabrication of TiC particulate reinforced magnesium matrix composites. Scr. Mater., 2003, 48(6): 713–717. DOI:10.1016/S1359-6462(02)00551-1.
[11] Meenashisundaram G K, Seetharaman S, Gupta M. Enhancing overall tensile and compressive response of pure Mg using nano-TiB_2 particulates. Mater. Charact., 2014, 94: 178–188. DOI:10.1016/j.matchar.2014.05.021.
[12] Wang Y, Wang H Y, Xiu K, et al. Fabrication of TiB_2 particulate reinforced magnesium matrix composites by two-step processing method. Mater. Lett., 2006, 60(12): 1533–1537. DOI:10.1016/j.matlet.2005.11.065.
[13] Stalin B, Ravichandran M, Mohanavel V, et al. Investigations on microstructure and mechanical properties of Mg-5wt.% Cu-TiB_2 composites produced via powder metallurgy route. J. Min. Metall. Sect. B Metall., 2020, 56(1): 99–108. DOI:10.2298/jmmb190315047S.
[14] Aydin F, Sun Y, Ahlatci H, et al. Investigation of microstructure, mechanical and wear behaviour of B_4C particulate reinforced magnesium matrix composites by powder metallurgy. Trans. Indian Inst. Met., 2017, 71(4): 873–882. DOI:10.1007/S12666-017-1219-2.
[15] Meher A, Mahapatra M M, Samal P, et al. Synthesis, microstructure and mechanical properties of magnesium matrix composites fabricated by stir casting. Mater. Today Proc., 2019, 18: 4034–4041. DOI:10.1016/j.matpr.2019.07.346.
[16] Fu H M, Zhang M X, Qiu D, et al. Grain refinement by AlN particles in Mg-Al based alloys. J. Alloys Compd., 2009, 478(1–2): 809–812. DOI:10.1016/j.jallcom.2008.12.029.
[17] Huang S J, Chen Z W. Grain refinement of AlN_p/AZ91D magnesium metal-matrix composites. Met. Mater., 2011, 49(4): 259–264. DOI:10.4149/KM_2011_4_259.
[18] Deng K, Shi J, Wang C, et al. Microstructure and strengthening mechanism of bimodal size particle reinforced magnesium matrix composite. Compos. Part Appl. Sci. Manuf., 2012, 43(8): 1280–1284.
[19] Zhu J, Jiang W, Li G, et al. Microstructure and mechanical properties of SiC_{np}/Al6082 aluminum matrix composites prepared by squeeze casting combined with stir casting. J. Mater. Process. Technol., 2020, 283: 116699. DOI:10.1016/j.jmatprotec.2020.116699.
[20] Wu S, Yuan D, Lü S, et al. Nano-SiC_p particles distribution and mechanical properties of Al-matrix composites prepared by stir casting and ultrasonic treatment. China Foundry, 2018, 15(3): 203–209. DOI:10.1007/s41230-018-8009-2.
[21] Shi W, Kobashi M, Choh T. Wettability of molten magnesium on carbon and AlN. Journal Jpn. Inst. Met., 2000, 64(5): 335–338. DOI:10.2320/jinstmet1952.64.5_335.
[22] Imai T, Lim S W, Jiang D, et al. Superplasticity of a AlN/Mg-5wt%Al alloy composite made by a vortex method. Scr. Mater., 1997, 36(5): 611–615. DOI:10.1016/S1359-6462(96)00429-0.
[23] Cao G, Choi H, Oportus J, et al. Study on tensile properties and microstructure of cast AZ91D/AlN nanocomposites. Mater. Sci. Eng. A, 2008, 494(1–2): 127–131. DOI:10.1016/J.MSEA.2008.04.070.
[24] Katsarou L, Mounib M, Lefebvre W, et al. Microstructure, mechanical properties and creep of magnesium alloy Elektron21 reinforced with AlN nanoparticles by ultrasound-assisted stirring. Mater. Sci. Eng. A, 2016, 659: 84–92. DOI:10.1016/j.msea.2016.02.042.

[25] Yang H, Huang Y, Song B, et al. Enhancing the creep resistance of AlN/Al nanoparticles reinforced Mg-2.85Nd-0.92Gd-0.41Zr-0.29Zn alloy by a high shear dispersion technique. Mater. Sci. Eng. A, 2019, 755: 18–27. DOI:10.1016/j.msea.2019.03.131.

[26] Giannopoulou D, Dieringa H, Bohlen J. Influence of AlN nanoparticle addition on microstructure and mechanical properties of extruded pure magnesium and an aluminum-free Mg-Zn-Y alloy. Metals, 2019, 9(6): 667. DOI:10.3390/met9060667.

[27] Moheimani S K, Dadkhah M, Mosallanejad M H, et al. Fabrication and characterization of the modified EV31-based metal matrix nanocomposites. Metals, 2021, 11(1): 125. DOI:10.3390/met11010125.

[28] Li Z, Gao T, Xu Q, et al. Microstructure and mechanical properties of an AlN/Mg-Al composite synthesized by Al-AlN master alloy. Int. J. Met., 2019, 13(2): 384–391. DOI:10.1007/S40962-018-0261-0/figures/9.

[29] León C A, Arroyo Y, Bedolla E, et al. Properties of AlN-Based magnesium-matrix composites produced by pressureless infiltration. Mater. Sci. Forum, 2006, 509: 105–110. DOI:10.4028/www.scientific.net/msf.509.105.

[30] Bedolla E, Lemus-Ruiz J, Contreras A. Synthesis and characterization of Mg-AZ91/AlN composites. Mater. Des., 2012, 38: 91–98. DOI:10.1016/j.matdes.2012.02.001.

[31] Falcon-Franco L, Rosales I, García-Villarreal S, et al. Synthesis of magnesium metallic matrix composites and the evaluation of aluminum nitride addition effect. J. Alloys Compd., 2016, 663: 407–412. DOI:10.1016/j.jallcom.2015.12.078.

[32] Arreola-Fernández C, Lemus-Ruiz J, Jiménez-Alemán O, et al. Wear behavior of AZ91E/AlN metal matrix composites. Mater. Lett., 2022, 317(132080): 132080. DOI:10.1016/j.matlet.2022.132080.

[33] Chen S H, Jin P P, Schumacher G, et al. Microstructure and interface characterization of a cast $Mg_2B_2O_5$ whisker reinforced AZ91D magnesium alloy composite. Compos. Sci. Technol., 2010, 70(1): 123–129. DOI:10.1016/j.compscitech.2009.09.015.

[34] Braszczyńska-Malik K N, Kamieniak J. AZ91 magnesium matrix foam composites with fly ash cenospheres fabricated by negative pressure infiltration technique. Mater. Charact., 2017, 128: 209–216. DOI:10.1016/j.matchar.2017.04.005.

[35] Qi L, Li S, Zhang T, et al. An analysis of the factors affecting strengthening in carbon fiber reinforced magnesium composites. Compos. Struct., 2019, 209: 328–336. DOI:10.1016/j.compstruct.2018.10.109.

[36] Sankaranarayanan S, Habibi M K, Jayalakshmi S, et al. Nano-AlN particle reinforced Mg composites: Microstructural and mechanical properties. Mater. Sci. Technol., 2015, 31(9): 1122–1131. DOI:10.1179/1743284714Y.0000000686.

[37] Chen J, Bao C, Ma Y, et al. Distribution control of AlN particles in Mg-Al/AlN composites. J. Alloys Compd., 2017, 695: 162–170. DOI:10.1016/j.jallcom.2016.10.190.

[38] Chen J, Bao C G, Liu Z W, et al. Thermal properties of Mg-Al/AlN composites fabricated by powder metallurgy. Acta Metall. Sin. Engl. Lett., 2018, 31(6): 641–649. DOI:10.1007/S40195-017-0689-x/figures/9.

[39] Xiao P, Gao Y, Yang C, et al. Microstructure, mechanical properties and strengthening mechanisms of Mg matrix composites reinforced with in situ nanosized TiB_2 particles. Mater. Sci. Eng. A, 2018, 710: 251–259. DOI:10.1016/j.msea.2017.10.107.

[40] Zhang S L, Zhao Y T, Chen G, et al. Effects of in situ TiB_2 particle on microstructures and mechanical properties of AZ91 alloy. J. Alloys Compd., 2010, 494(1–2): 94–97. DOI:10.1016/j.jallcom.2009.10.103.

[41] Liu Y Q, Cong H T, Wang W, et al. AlN nanoparticle-reinforced nanocrystalline Al matrix composites: Fabrication and mechanical properties. Mater. Sci. Eng. A, 2009, 505(1–2): 151–156. DOI:10.1016/j.msea.2008.12.045.

[42] Zheng Q, Reddy R G. Mechanism of in situ formation of AlN in Al melt using nitrogen gas. J. Mater. Sci., 2004, 39(1): 141–149. DOI:10.1023/b:jmsc.0000007738.14116.fd.

[43] Cui C, Li Y, Wu R, et al. Particle-matrix interface microstructure of in situ TiC_p-AlN_p/Al composite. Compos. Sci. Technol., 2012, 72(12): 1423–1429. DOI:10.1016/j.compscitech.2012.05.016.

[44] Kobashi M, Okayama N, Choh T. Synthesis of AlN/Al alloy composites by in situ reaction between Mg_3N_2 and aluminum. Mater. Trans. JIM, 1997, 38(3): 260–265. DOI:10.2320/matertrans1989.38.260.

[45] Lee K B, Sim H S, Heo S W, et al. Tensile properties and microstructures of Al composite reinforced with BN particles. Compos. Part Appl. Sci. Manuf., 2002, 33(5): 709–715.

[46] Li C, Cui C, Wang X, et al. Enhanced grain refinement of in-situ AlN-TiN/Al composite inoculant on aluminum assisted by ultrasonic treatment. Mater. Lett., 2019, 255: 126592. DOI:10.1016/j.matlet.2019.126592.

[47] Koczak M J, Premkumar M K. Emerging technologies for the in-situ production of MMCs. JOM, 1993, 45(1): 44–48. DOI:10.1007/bf03223365/metrics.

[48] Ye H Z, Liu X Y, Luan B. In situ synthesis of AlN in Mg-Al alloys by liquid nitridation. J. Mater. Process. Technol., 2005, 166(1): 79–85. DOI:10.1016/j.jmatprotec.2004.06.033.

[49] Yang C, Zhang B, Zhao D, et al. In-situ synthesis of AlN/Mg-Al composites with high strength and high plasticity. J. Alloys Compd., 2017, 699: 627–632. DOI:10.1016/j.jallcom.2017.01.005.

[50] Fan T, Zhang C, Chen J, et al. Thermodynamics and kinetics to alloying addition on in-situ AlN/Mg composites synthesis via displacement reactions in liquid Mg melt. Metall. Mater. Trans. Phys. Metall. Mater. Sci., 2009, 40(11): 2743–2750. DOI:10.1007/S11661-009-9966-2.

[51] Zhang C, Fan T, Cao W, et al. Size control of in situ formed reinforcement in metal melts-theoretical treatment and application to in situ (AlN+Mg_2Si)/Mg composites. Compos. Sci. Technol., 2009, 69(15–16): 2688–2694. DOI:10.1016/j.compscitech.2009.08.011.

[52] Gao T, Li Z, Hu K, et al. Assessment of AlN/Mg-8Al composites reinforced with in situ and/or ex situ AlN particles. Materials, 2020, 14(1): 52. DOI:10.3390/ma14010052.

[53] Huang L J, Geng L, Peng H X. Microstructurally inhomogeneous composites: Is a homogeneous reinforcement distribution optimal?. Prog. Mater. Sci., 2015, 71: 93–168. DOI:10.1016/j.pmatsci.2015.01.002.

[54] Huang L J, Geng L, Wang B, et al. Effects of extrusion and heat treatment on the microstructure and tensile properties of in situ TiB_w/Ti6Al4V composite with a network architecture. Compos. Part Appl. Sci. Manuf., 2012, 43(3): 486–491. DOI:10.1016/j.compositesa.2011.11.014.

[55] Zhang B, Yang C, Sun Y, et al. The microstructure, mechanical properties and tensile deformation mechanism of rolled AlN/AZ91 composite sheets. Mater. Sci. Eng. A, 2019, 763: 138118. DOI:10.1016/J.MSEA.2019.138118.

[56] Zhang C, Fan T, Cao W, et al. (AlN+Mg_2Si)/Mg composites in situ synthesis and scale effect of particulate on damping capacity. Mater. Sci. Eng. A, 2009, 508(1–2): 190–194. DOI:10.1016/J.MSEA.2009.01.060.

[57] Zhang R, Liu G, Si N, et al. Effects of Si alloying and T6 treatment on mechanical properties and wear resistance of ZA27 alloys. China Foundry, 2016, 13(2): 93–100. DOI:10.1107/s41230-016-5090-2.

[58] Sumida M, Jung S, Okane T. Solidification microstructure, thermal properties and hardness of magnesium alloy 20 mass% Gd added AZ91D. Mater. Trans., 2009, 50(5): 1161–1168. DOI:10.2320/matertrans.F-M2009802.

[59] Chmielewski M, Weglewski W. Comparison of experimental and modelling results of thermal properties in Cu-AlN composite materials. Bull. Pol. Acad. Sci. Tech. Sci., 2013, 61(2): 507–514. DOI:10.2478/bpasts-2013-0050.

[60] Lv J, Huang Y, Fu R, et al. AlN/Cu composite ceramic substrate fabricated using a novel TiN/AgCuTi composite brazing alloy. J. Eur. Ceram. Soc., 2020, 40(15): 5332–5338. DOI:10.1016/j.jeurceramsoc.2020.07.060.

[61] Ashok Kumar B, Murugan N. Metallurgical and mechanical characterization of stir cast AA6061-T6-AlN_p composite. Mater. Des., 2012, 40: 52–58. DOI:10.1016/j.matdes.2012.03.038.

[62] Mohanavel V, Ravichandran M. Influence of AlN particles on microstructure, mechanical and tribological behaviour in AA6351 aluminum alloy. Mater. Res. Express, 2019, 6(10): 106557.