J Mater Sci (2009) 44:4155–4161
DOI 10.1007/s10853-009-3616-3

Behavior of magnesium and silicon in the formation of MgO/AlN composite

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Received: 26 January 2009 / Accepted: 18 May 2009 / Published online: 2 June 2009

Abstract MgO/AlN composites have been fabricated by directed metal nitridation of Al–Si alloy in flowing N_2 at 1473 K. A mixture of magnesia particles and chemically pure magnesium powder was placed on the surface of Al–Si alloy block as reinforcement materials. Mg powder initiates the infiltration and nitridation of Al alloy melt by eliminating protective Al_2O_3 film at the reaction frontier. New Mg vapor from the interface reaction between Al and MgO particles, keeps as continuous deoxidization agent as the added Mg powder. The spinel layer thickness due to the reaction of Al melt with MgO particles is controlled by Mg content. Si not only reduces the surface tension and viscosity of Al alloy melt, but also leads to increase in N_2 content.

Introduction

MgO/AlN composites, due to superior resistance against basic slag of MgO [1] and excellent thermal conductivity of AlN [2], are promising materials for application in the iron and steel industry. In the traditional process of refractory preparation, fine powders are usually mechanically mixed with coarse particles. However, this method is not suitable for fine AlN powder because of its hydration and hard sintering [3]. Lanxide Company reported that MgO/AlN composites have been produced by directed metal penetration and nitridation process. These composites have lower apparent porosity and higher strength compared to addition of Al powder into MgO composite [4]. Many researchers focused on this directed metal nitridation process because it assembles the fabrication of raw material and its sintering into one step by avoiding the pre-synthesis of AlN fine powder. This method also has the ability to tailor the composite properties by the selection of processing parameters [5–17].

It has been found that the volatile elements such as Mg, Li or Zn initiate the infiltration by breaking down the inert alumina layer on the top of Al- (Mg or Si or Zn) alloy melt and form a gaseous oxygen getter in terms of kinetic and thermodynamic viewpoints [5–11]. Metallic or ceramic matrix of AlN composites was determined by the oxygen partial pressure, which can be adjusted by H_2 in N_2 atmosphere [12, 13]. Additionally, Si is usually used in the directed metal nitridation process to modify the properties of the alloys [10]. LeHuy and Dallaire [14] reported that Si accelerated the nitridation of Al when Al–Mg–Si alloy was used. However, Scholz and Greil [8] found that nitridation ratio of Al decreased with the increase of Si. Rao and Jayaram [15] investigated the infiltration behavior of Al–8% Mg and Al–6% Mg–6.5% Si–0.3% Fe into Al_2O_3 preforms at 1173 K. They found that the former infiltration terminated after 2 mm but the latter could completely infiltrate full 6 mm height of 53 μm particulate preform. Even Al came out on top of the preform. Besides, the geometries of preform materials affected the properties and microstructure of obtained composites. For example, Sholz et al. [16] reported that the fracture strength and toughness of fiber-reinforced composite material was enhanced with the increase of spinel layer thickness between Al alloy and Al_2O_3 fibers, which was produced by directed metal

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nitridation. Daniel et al. [17] found that formation of moisture sensitive Al_4C_3 in SiC reinforced composites caused deterioration of mechanical properties, and Zhang et al. [18] found that the interface reaction between Al and magnesia and local gaseous Mg affected the microstructure of composites when Al infiltrated downward into MgO particles.

So far, no systematic work has been carried out on the influence of Mg and Si on the microstructure and growth mechanism of AlN/MgO composite fabricated by directed metal nitridation process. In this study, the influence of added Mg content on the final microstructure of composite was investigated by infiltrating Al–Si alloy upward to MgO particles preform. The behavior of Mg and Si during the formation of AlN/MgO composite was discussed, too.

Experimental procedure

Al–8.09 wt% Si alloy block (15 mm in diameter and 15 mm in height) was placed in a small graphite crucible with corundum powder as barrier material around the block. A preform served as reinforcement material that was loosely packed on the block (Fig. 1). The preform consisted of 0.5–1 mm fused magnesia particles (>98 wt% MgO) and chemically pure Mg powder (>99 wt%, 0.075–0.15 mm). Mg powder content varied proportional to the weight of the alloy block. The reactor tube was evacuated (<100 Pa) and then flushed with high purity N_2 gas (99.999%) three times at room temperature to reduce the oxygen partial pressure. High purity N_2 was fed into the tube with a rate of 20 mL/min to keep the atmosphere in tube nearly stationary during the experiment. In order to avoid the contamination of the tube during flushing with oxygen from atmosphere, the outcoming gas was channeled into water to create a higher pressure level inside the reaction chamber. The furnace was heated with a rate of 10 K/min. When the temperature reached the set temperature of 1473 K, the whole assembly was quickly shifted to the hot zone and then was held for 10 h. The furnace underwent free cooling to room temperature with N_2 flowing down to 933 K.

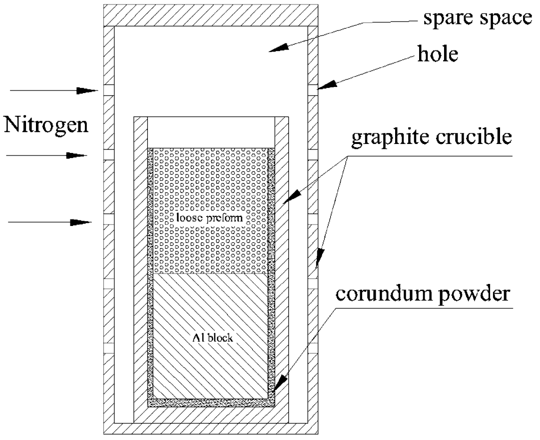

Fig. 1 Experimental set-up for MgO/AlN composite fabricated by directed metal nitridation of Al–Si alloy

The weight of the whole sample assembly before and after nitridation was measured in order to calculate the weight gain from the nitridation. The weight gain α was calculated according to the reaction (1).

$$2\mathrm{Al(l)} + \mathrm{N_2(g)} = 2\mathrm{AlN(s)} \qquad (1)$$

$$\alpha = (M_{\mathrm{Al}}/M_{\mathrm{N}}) \times \left(m_{\mathrm{af}} - m_{\mathrm{bf}} + m_{\mathrm{Mg}}\right) \times 100\%/m_{\mathrm{Al}}$$

where M_{Al} and M_{N} respectively denote the molar masses of elements Al and N. Therefore, the value of $M_{\mathrm{Al}}/M_{\mathrm{N}}$ is considered as the coefficient of Al nitridation. m_{af} and m_{bf} respectively denote the weights of the assembly after and before the experiment. m_{Mg} denotes the weight of Mg powder mixed in the preform. At high temperature, magnesium played as a vapor and was assumed evaporating from the crucible because of its high vapor pressure. It might deposit on the surface of the furnace tube in the form of either MgO or Mg_3N_2 depending on the oxygen content in the flowing N_2. Therefore, the weight influence of magnesium from oxidation or nitridation on the weight gain of the whole sample was neglected. The loss of Al due to its own evaporation was also neglected. As a result, the weight gain reflects the extent of Al melt nitridation.

After experiments, the as-received samples were sectioned longitudinally and polished for microstructure observation using optical microscopy (OM, Axoskop 40Apol, Zeiss, Germany) and scanning electron microscopy (SEM, XL30TMP, Philips, Holland) equipped with energy dispersive spectroscopy (EDS, PHOENIX, EDAX, USA). Also, as-received samples were investigated by X-ray diffraction (XRD, XPERT PRO, Philips, Holland) to identify the phase composition.

Results

Infiltration and nitridation

Molten alloy spontaneously infiltrated into the MgO preform due to the presence of Mg powder, where MgO particles were bonded tightly. On the other hand, the non-infiltrated MgO particles remained loose and were easily removed. Therefore, the height of as-received samples indicates the extent of Al infiltration into preform (Fig. 2). No infiltration happened when the preform consisted only of MgO particles. Once Mg powder was added to the powder mixture for the preform, the infiltration happened.

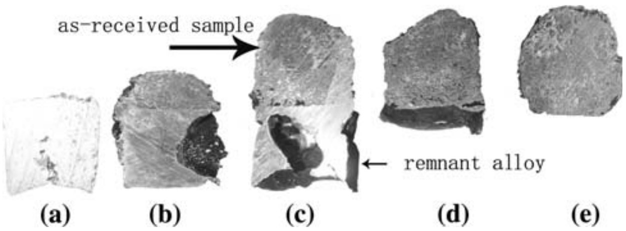

Fig. 2 Cross-section appearances of the as-received samples along the growth direction with 0 wt% **a**, 3 wt% **b**, 5 wt% **c**, 7 wt% **d**, and 10 wt% **e** Mg

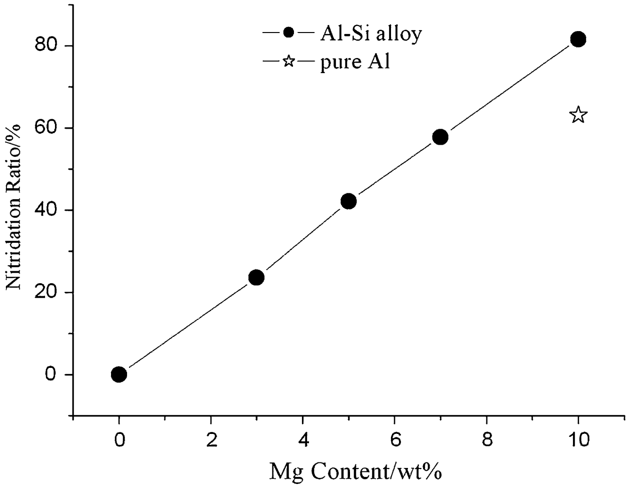

Fig. 3 Influence of the Mg content on the weight gain of the as-received samples

For example, when 3 wt% Mg powder was added, the infiltration height reached half of the original preform height and a hole in the remnant alloy was left after Al was transported into the preform. The preform added with 5 wt% Mg was completely infiltrated by Al alloy. By comparison, the entire alloy infiltrated into the preform as Mg content was higher than 5 wt%.

It is also clear that nitridation of Al alloy only occurred in the presence of Mg powder mixed with the MgO particles (Fig. 3) and increased linearly with the increase of Mg content. Remarkably, although the weight gain was about 81% when the content of Mg powder was 10 wt%, Al melt had fully infiltrated into the perform (Fig. 2).

Phase composition and microstructure

The longitudinally polished sections of as-received samples were examined by XRD (Fig. 4), where hexagonal AlN, periclase, $MgAl_2O_4$, Si, and Mg_2Si were found in all the samples. When 3 wt% Mg was added into the preform, metallic aluminum was the main phase and $MgAl_2O_4$, the second phase in the composite. With the increase of Mg content, the amount of AlN increased rapidly. To the contrary, the amount of Al decreased slowly. The amount of $MgAl_2O_4$ decreased to lower value when Mg content was 5 and 7 wt%. When Mg content was 10 wt%, AlN predominated in the sample and followed by $MgAl_2O_4$. The amount of phases containing Si kept constant in all the samples.

The phase distribution in the sample was observed with optical microscopy (Fig. 5). When Mg content was 3 wt%, both white metallic phase and gray ceramic phase could be found among MgO particles, where the white metallic phase predominated. Also, macro-pores occurred in the ceramic-rich matrix indicating incomplete infiltration. As 5 wt% Mg was used, white metallic phase appeared to be dispersed in the matrix and the gray ceramic phase occupied most part of the matrix with less pores. With the further

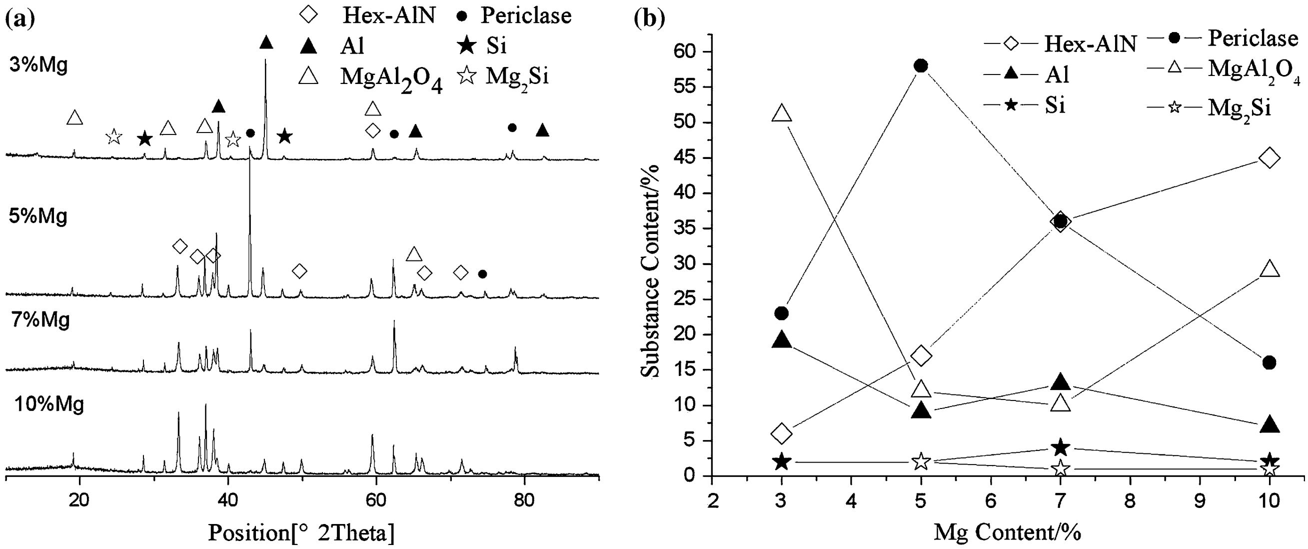

Fig. 4 XRD patterns **a** and semiquantitative analysis **b** on the cross sections of the as-received samples with various Mg content

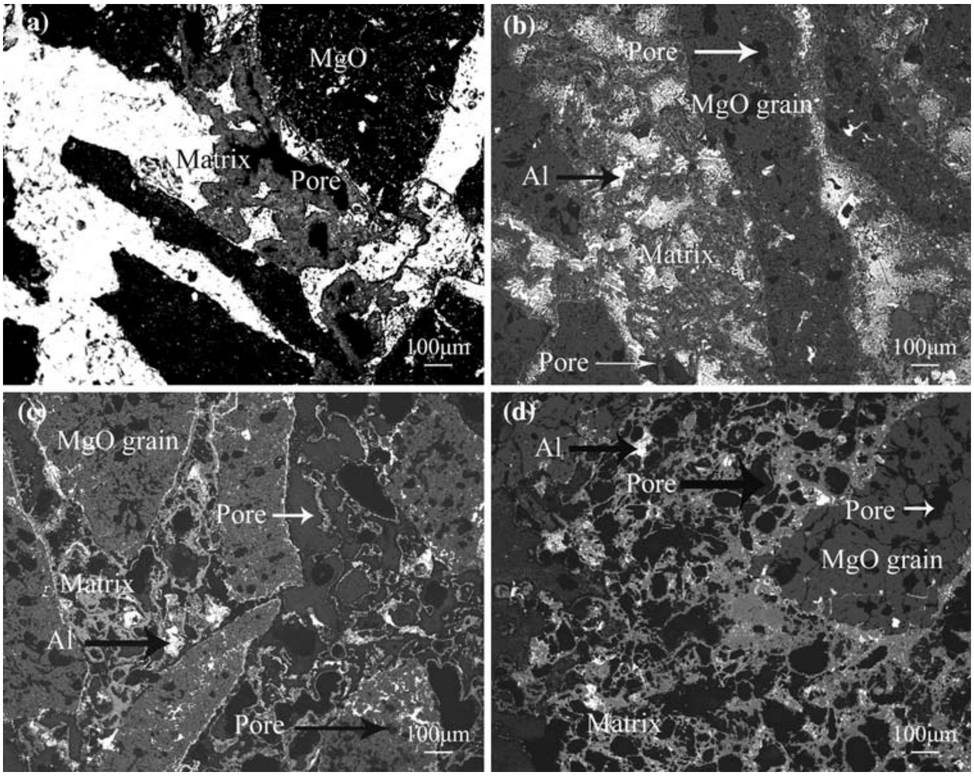

Fig. 5 Optical microstructure of the as-received samples doped with 3 wt% **a**, 5 wt% **b**, 7 wt% **c**, and 10 wt% **d** Mg

increase of Mg content in the MgO preform, the matrix mainly consisted of ceramic phase. Apparently, high density of macro and micro pores appeared in the matrix.

SEM/EDS examination showed that Si grains not only occurred isolated within the matrix, but also presented with AlN phases together (Fig. 6). In order to clarify the influence of Mg content on the reaction between Al and MgO particles, EDS line scans have been performed across MgO particles (Fig. 7). When Mg content was only 3 wt%, elementary Mg and Al appeared synchronously in one particle. An exception was that the pores in one MgO particle were filled with Al. It indicates almost the whole one MgO particle has reacted with Al. However, when Mg content was 5 and 7 wt%, only less part of one MgO particle was reacted. With the increase of Mg content to 10 wt%, the thickness of the reaction layer relative to the particle size increases. The above line scanning map results are consistent with the observation of XRD. They confirm that the $MgAl_2O_4$ was mainly obtained from the interface reaction between Al and MgO particles.

Discussions

The results of the present study demonstrate that Mg plays an important role not only on nitridation and infiltration of

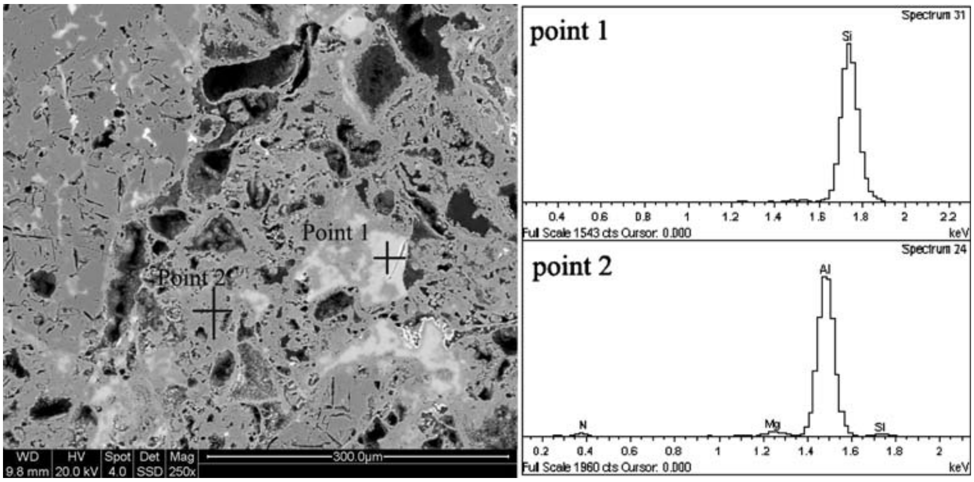

Fig. 6 Presence of Si in the matrix of the as-received sample

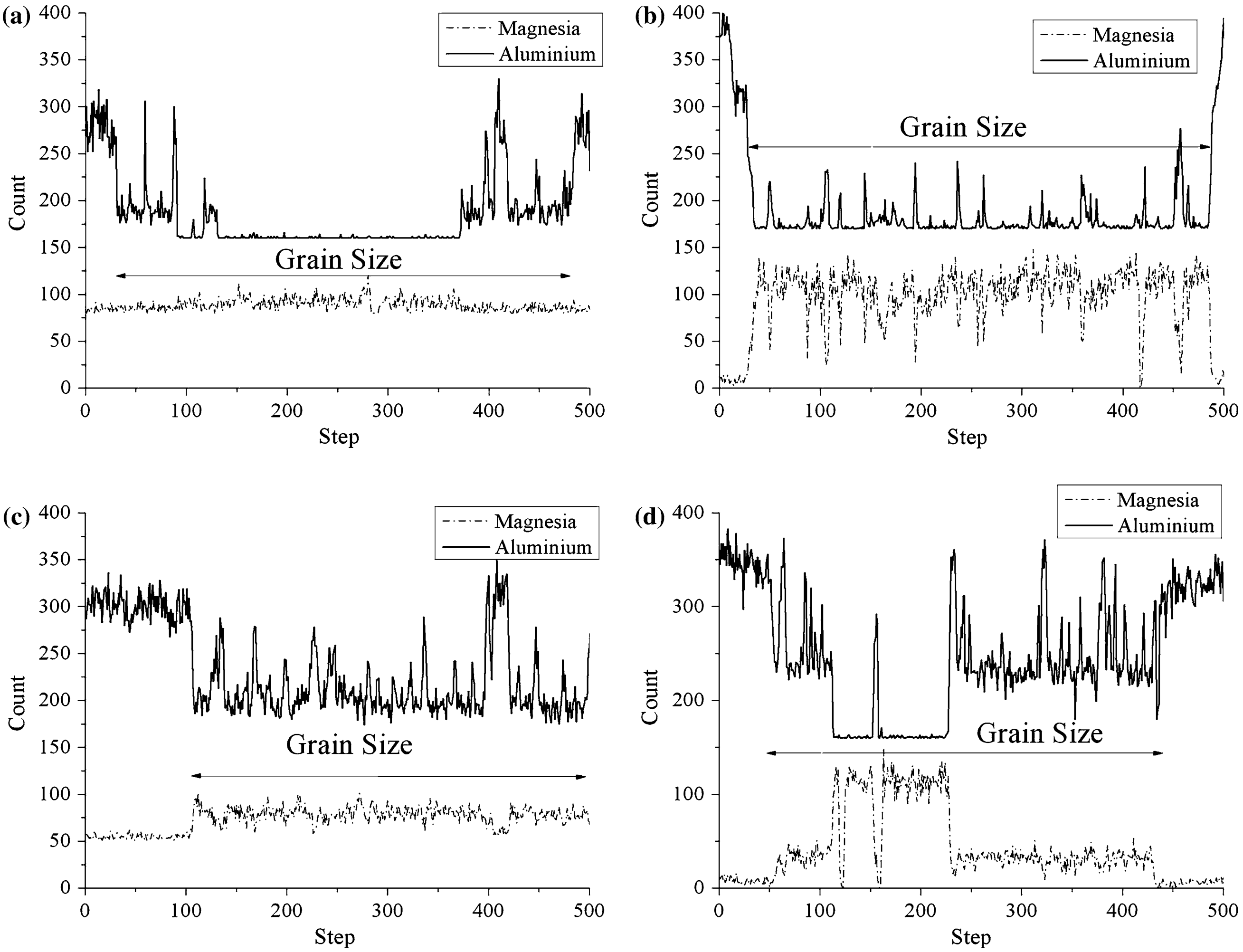

Fig. 7 Line scanning map of typical MgO particles in the as-received samples doped with 3 wt% **a**, 5 wt% **b**, 7 wt% **c**, and 10 wt% **d** Mg

Al alloy melt, but also on phase composition and microstructure. As described by Rao et al. [15], Mg is first directly eliminating the protective Al_2O_3 film on the surface of melt and then forms a porous magnesium aluminum spinel layer according to reaction 2. Furthermore, a small amount of oxygen in nitrogen containing atmosphere oxidized Mg into MgO. Thereafter, new formed MgO fell on the surface of alloy melt followed by further reaction with protective Al_2O_3 film to form $MgAl_2O_4$, according to reactions 3 and 4 [19]. In our experiments, a thick $MgAl_2O_4$ layer was found between parent alloy and MgO particles in Fig. 8. It reveals that Mg, whatever it presents in the form of alloy or elementary powder, can play as remover of Al_2O_3 film

$$3Mg(g) + 4Al_2O_3(s) = 3MgAl_2O_4(s) + 2Al(l) \quad (2)$$

$$2Mg(g) + O_2(g) = 2MgO(s) \quad (3)$$

$$MgO(s) + Al_2O_3(s) = MgAl_2O_4(s) \quad (4)$$

During the directed metal nitridation process, high oxygen content is considered to inhibit the nitridation and infiltration of Al alloy seriously. Swaminathan et al. [12] reported that oxygen at lowest values did not interfere with either infiltration or nitridation reaction. However, at intermediate values, nitridation was suppressed yet infiltration continued. Once oxygen content exceeded the

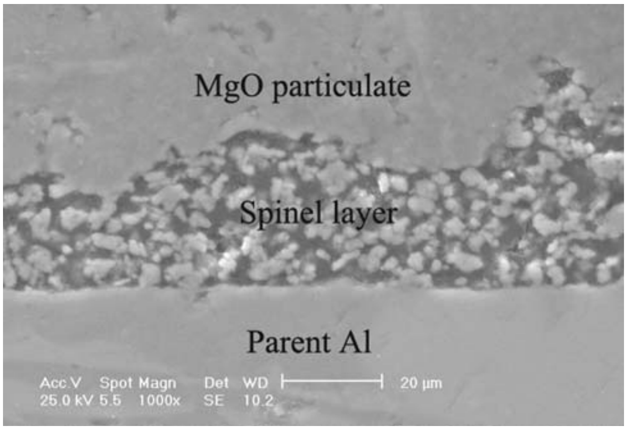

Fig. 8 $MgAl_2O_4$ layer between the preform and parent alloy in the as-received sample

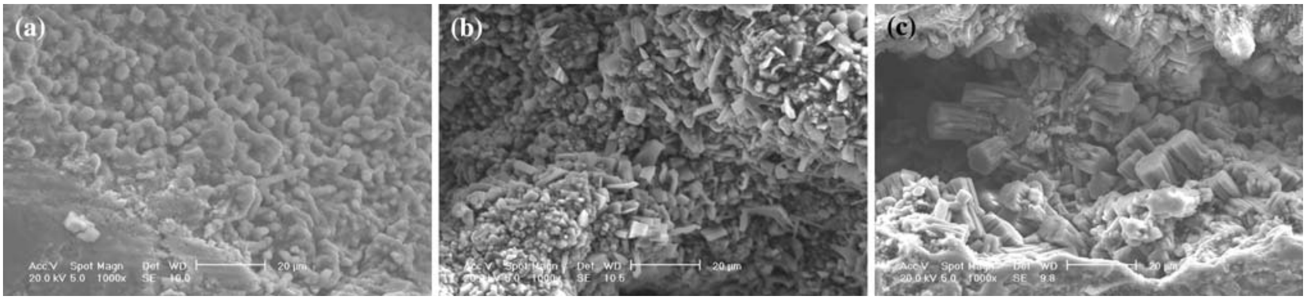

Fig. 9 AlN morphologies in the as-received samples in the presence of 5 wt% **a**, 7 wt% **b**, and 10 wt% **c** Mg

critical higher value, the melt was passivated without any infiltration. Therefore, N_2–H_2 atmosphere was always chosen for the experiment to prevent the contamination of oxygen [12, 13]. Mg kept playing a deoxidizing agent at the frontier of nitridation [20]. Especially, reaction between Al and MgO particulates releases gaseous Mg according to reaction 5. Due to the thermo-equilibrium state of Mg with O_2 at the nitridation frontier, gaseous Mg will diffuse outside till it reaches the abundant O_2 area and acts as a continuously de-oxidation agent. As long as Mg is present at the frontier of reaction, the oxygen partial pressure will be far below the equilibrium value of AlN and Al_2O_3 [10]. This also benefits the growth of AlN crystals, as shown in Fig. 9, where the grain size of AlN crystals increased significantly with the increase of Mg content.

$$2\mathrm{Al(l)} + 4\mathrm{MgO(s)} = \mathrm{MgAl_2O_4(s)} + 3\mathrm{Mg(g)} \qquad (5)$$

Mg powder addition also affects the interface reaction process between Al and MgO particles. Line scanning results showed that the thickness of the spinel layer depended on the Mg content (Fig. 7). The formation of spinel is promoted by processing temperature, and determined by mutual diffusion of Mg^{2+} and Al^{3+} [21]. Therefore, the reaction extent mostly depends on the contact time between Al and MgO particles if treating temperature is fixed. When Mg content was as low as 3 wt%, the infiltration was predominant and Al due to the prolonged contact time reacted with MgO particles strongly. However, when Mg content was 5 or 7 wt%, Al nitridation became intensive during its infiltration. Less Al could keep long time contact with MgO particles before it transformed into AlN. Further increasing Mg content in the preform caused a relative quick infiltration of Al. Since Al nitridation still was controlled by interface diffusion of N_2 into Al melt [22], the longer contact time of Al with MgO particles guaranteed the sufficient interface reaction process.

Several studies have reported the influence of Si on the surface tension and viscosity of alloy. For example, Hatch reported [23] that the surface energy of pure Al was 861 mN/m and adding 5 wt% Si could decrease the surface energy to 808 mN/m at 973 K. Si can also reduce the viscosity [24] of molten Al, e.g., the viscosity of pure Al is 9.1×10^{-4} Pa S in 1173 K, while Al–5 wt% Si is 8.5×10^{-4} Pa S. Therefore, Si enhances the wetting and the infiltration ability of molten alloy to preform.

Although Si was detected in all the as-received samples, the possible reactions involved in nitridation process still need to be considered carefully. Based on the binary phase diagram (Fig. 10), Al–8.09 wt% Si turned into melt at 1473 K and the saturation molar percentage of Si in Al–Si alloy is 0.65. Therefore, the concentration of Si in the alloy changed from a to b because directed metal nitridation of Al alloy is a process consuming Al. The activities of Al and Si before nitridation were 0.9220 and 0.0779, respectively according to Medima model [25]. Thermodynamic calculation with FACTSAGE5.5 shows that Si dissolved in the alloy can react with nitrogen into Si_3N_4 (reaction 6), and Al in the alloy also can reduce Si_3N_4 to Si in terms of reaction 7. Combining reactions 6 and 7 equal reaction 1 that is direct nitridation of Al by nitrogen. Figure 11 shows the Gibbs free energy of reactions 6, 7, and 1 as a function of Si concentration in the alloy melt. It indicates that the nitridation of Si is much easier with the increase of Si concentration, and the ability of Al reducing Si_3N_4 to AlN and Si decreases. Nevertheless, the Gibbs free energy of

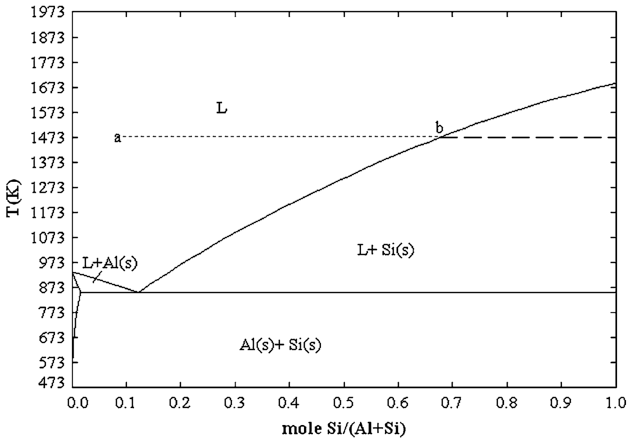

Fig. 10 Phase diagram of Al–Si alloy

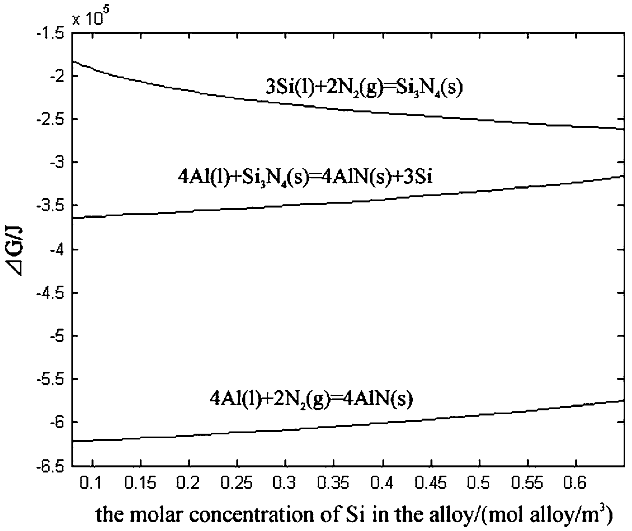

Fig. 11 Standard Gibbs free energy of the three reactions as a function of the mole concentration of Si in Al–Si alloy

reaction 7 is still lower than reaction 6. Indeed, Si finally acts as a catalyst during the nitridation of Al and precipitates with AlN as illuminated by reaction 8 [26]. This is the reason why the nitridation ratio of Al–Si alloy was higher than that of pure Al block, as shown in Fig. 3. If the nitridation rate was faster than the precipitation rate of Si, isolated Si will appear, as shown in Fig. 6.

$$3Si(l) + 2N_2(g) = Si_3N_4(s) \tag{6}$$

$$4Al(l) + Si_3N_4(s) = 4AlN(s) + 3Si(s) \tag{7}$$

$$\begin{aligned}[Al, Si] \overset{N_2}{\cdots\cdots} [Al] + AlN(s) \\ + Si_3N_4(s) \overset{N_2}{\cdots\cdots} AlN(s) + Si(s)\end{aligned} \tag{8}$$

Conclusion

Al–8.09 wt% Si alloy infiltration into the preform of MgO particles mixed with Mg powder was investigated to examine the behavior of Mg and Si and their influence on the phase compositions and microstructure of AlN/MgO composites. The main findings of the work are: (1) Mg powder initiates the infiltration and nitridation of Al by eliminating protective Al_2O_3 film on the Al melt surface at the beginning of experiment. (2) Both original additive Mg and new generated Mg from the interface reaction between Al and MgO particles accelerate the infiltration and nitridation of Al and affect the interface reaction between Al and MgO particles. (3) Si not only improves the surface tension and viscosity of melt, but also accelerates the nitridation by enhancing the diffusion ability of N_2 in the melt.

Acknowledgements The authors thank the financial support of the National Natural Science Fund of China, under Grant No.50572076 and Ministry of Education of China under Grant No.20040488001.

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