

## ***In situ* reaction mechanism of MgAlON in Al–Al<sub>2</sub>O<sub>3</sub>–MgO composites at 1700°C under flowing N<sub>2</sub>**

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**Abstract:** The Al–Al<sub>2</sub>O<sub>3</sub>–MgO composites with added aluminum contents of approximately 0wt%, 5wt%, and 10wt%, named as M<sub>1</sub>, M<sub>2</sub>, and M<sub>3</sub>, respectively, were prepared at 1700°C for 5 h under a flowing N<sub>2</sub> atmosphere using the reaction sintering method. After sintering, the Al–Al<sub>2</sub>O<sub>3</sub>–MgO composites were characterized and analyzed by X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The results show that specimen M<sub>1</sub> was composed of MgO and MgAl<sub>2</sub>O<sub>4</sub>. Compared with specimen M<sub>1</sub>, specimens M<sub>2</sub> and M<sub>3</sub> possessed MgAlON, and its production increased with increasing aluminum addition. Under an N<sub>2</sub> atmosphere, MgO, Al<sub>2</sub>O<sub>3</sub>, and Al in the matrix of specimens M<sub>2</sub> and M<sub>3</sub> reacted to form MgAlON and AlN-polytypoids, which combined the particles and the matrix together and imparted the Al–Al<sub>2</sub>O<sub>3</sub>–MgO composites with a dense structure. The mechanism of MgAlON synthesis is described as follows. Under an N<sub>2</sub> atmosphere, the partial pressure of oxygen is quite low; thus, when the Al–Al<sub>2</sub>O<sub>3</sub>–MgO composites were soaked at 580°C for an extended period, aluminum metal was transformed into AlN. With increasing temperature, Al<sub>2</sub>O<sub>3</sub> diffused into AlN crystal lattices and formed AlN-polytypoids; however, MgO reacted with Al<sub>2</sub>O<sub>3</sub> to form MgAl<sub>2</sub>O<sub>4</sub>. When the temperature was greater than (1640 ± 10)°C, AlN diffused into Al<sub>2</sub>O<sub>3</sub> and formed spinel-structured AlON. *In situ* MgAlON was acquired through a solid-solution reaction between AlON and MgAl<sub>2</sub>O<sub>4</sub> at high temperatures because of their similar spinel structures.

**Keywords:** composites; metal aluminum; nitrogen atmosphere; magnesium aluminum oxynitride; reaction mechanism

### **1. Introduction**

Magnesia-based refractories with good resistance to alkali slag and high-ferric slag possesses poor resistance to thermal shock and slag penetration, which restrains their development and broad application [1–3]. The most effective method to solve this problem is to composite the oxide with non-oxides. The resulting composites typically have high hot strength, good thermal shock resistance, and excellent corrosion resistance to metallurgical slag [4–7]. In the 1970s, the Japanese introduced graphite into magnesia and prepared magnesia–carbon refractories, which prolonged the service life of refractories for electric furnaces and converters to ten times the service life of the original oxide refractories [8]. However, carbon easily solves into molten steel, resulting in the steel's carburization [9]. In addition, the use of phenolic resin or an organic binder leads to a series of environmental problems. Thus, researchers began to investi-

gate non-oxide–oxide systems without carbon.

In 1959, Yamguchi and Yanagida [10] reported the possibility of a spinel-type phase in the Al<sub>2</sub>O<sub>3</sub>–AlN system. Over the next several years, other researchers confirmed that a spinel-type phase named aluminum oxynitride (AlON) indeed exists in this system [11–14]. As a new ceramic material, AlON offers researchers additional options in oxide–non-oxide systems [15–17]. It has great potential as a carbon-free, environmentally friendly refractory. AlON has two crystal structures [15,18]: wurtzite-structured AlN-polytypoids and spinel-structured AlON. However, AlON is only stable at (1640 ± 10)°C or higher temperatures and under a certain oxygen partial pressure and nitrogen partial pressure [19]. Because many of the foreseen applications of AlON correspond to this temperature region, this instability poses serious drawbacks on the actual applicability of the AlON non-oxide system. Therefore, extensive efforts have been devoted to making AlON stable at lower temperatures,

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leading to the discovery that the addition of MgO or MgAl<sub>2</sub>O<sub>4</sub> could lower the stable temperature to 1640°C; the newly formed solid-solution is named magnesium aluminum oxynitride spinel (MgAlON) [20].

MgAlON has been reported to exist at both room temperatures and high temperatures [21] and to possess excellent slag resistance and thermal shock resistance. MgAlON composites have therefore become the subject of intensive research interest. Yang *et al.* [22] studied MgAlON-bonded magnesia and spinel composites. Pichlbauer *et al.* [20] synthesized MgAlON-bonded magnesia refractories at 1800°C using MgO as the aggregate and AlN–MgO–Al<sub>2</sub>O<sub>3</sub> mixing powder as the matrix. The common synthesis methods mainly adopt AlN as the starting material [23–24], which requires harsh processing conditions, restricting the industrial application of MgAlON-bonded magnesia refractories. The issue of how to prepare MgAlON at lower temperatures has become a key point. Therefore, in this work, metal aluminum powder was introduced into the Al<sub>2</sub>O<sub>3</sub>–MgO system and MgAlON-bonded magnesia refractories were obtained at 1700°C. The composites after calcination were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) to investigate the formation mechanism of MgAlON.

## 2. Experimental section

Metal aluminum powder, tabular alumina,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> micropowder, fused magnesite micropowder, and sintered magnesia powder were used as the raw materials, and ther-

mosetting phenolic resin was used as the binder. The ratio of aggregate to matrix was 65:35, and the formulations of M<sub>1</sub>, M<sub>2</sub>, and M<sub>3</sub> are specified in Table 1. The batched materials were mixed in a mixer for 30 min and shaped under 300 MPa by a hydraulic machine into specimens of 40 mm × 40 mm × 125 mm. After drying at 300°C for 24 h, three specimens (M<sub>1</sub>, M<sub>2</sub>, and M<sub>3</sub>) were placed in a crucible and heat treated. The heat treatment was conducted at 580°C for 8 h and then 1700°C for 5 h in a graphite tube furnace under flowing nitrogen. The matrix composition based on the AlN–Al<sub>2</sub>O<sub>3</sub>–MgO ternary phase diagram plotted by Willem *et al.* [17] is shown in Table 2, and the chemical composition of the raw materials is shown in Table 3.

**Table 1. Formulations of specimens** wt%

Raw material	Grain size	Specimen		
		M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>
Fused magnesite particles	5–3 mm	5	5	5
	3–1 mm	35	35	35
	1–0 mm	25	25	35
Tabular alumina	1–0 mm	6	6	6
$\alpha$ -Al <sub>2</sub> O <sub>3</sub> micropowder	≤5 $\mu$ m	6	6	6
Metal aluminum powder	≤325 mesh	0	5	10
Sintered high-purity magnesia	≤200 mesh	23	18	13

**Table 2. Matrix composition analysis of specimens M<sub>1</sub>, M<sub>2</sub>, and M<sub>3</sub>** mol%

Specimen	Al <sub>2</sub> O <sub>3</sub>	AlN	MgO
M <sub>1</sub>	0.12	0	0.88
M <sub>2</sub>	0.11	0.17	0.72
M <sub>3</sub>	0.10	0.33	0.57

**Table 3. Particle size and chemical composition of raw materials**

Raw material	Particle size	Chemical composition / wt%							
		MgO	Al <sub>2</sub> O <sub>3</sub>	Al	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O
Fused magnesite	≤48 $\mu$ m	97.5	—	—	0.63	0.76	—	—	—
$\alpha$ -Al <sub>2</sub> O <sub>3</sub> micropowder	≤5 $\mu$ m	—	99.40	—	0.19	—	0.02	0.04	0.08
Tabular alumina	1–0 mm	—	99.50	—	0.05	—	—	0.02	0.06
Metal aluminum powder	325 mesh	—	—	99.3	—	—	—	—	—
Sintered high-purity magnesia	200 mesh	97.8	—	—	0.50	1.34	—	—	—

XRD, SEM, and EDS were used to analyze and characterize the composites after calcination. XRD analyses were conducted using an X-ray diffractometer (PANalytical, X'pert powder; working voltage: 40 kV; current: 40 mA) employing Cu K $\alpha$  radiation; the sample were scanned in the 2 $\theta$  range from 10° to 90° in steps of 0.013° with a scanning time of 2 min. SEM analysis was performed using a scanning electron microscope (FEI, X-3500N).

## 3. Results and discussion

### 3.1. Phase composition

Fig. 1 shows the XRD patterns of specimens M<sub>1</sub>, M<sub>2</sub>, and M<sub>3</sub> after firing. As observed in Fig. 1, specimen M<sub>1</sub> is composed of MgO and spinel, whereas specimens M<sub>2</sub> and M<sub>3</sub> consist of MgO, AlN-polytypoids (Al<sub>8</sub>O<sub>3</sub>N<sub>6</sub> and Al<sub>10</sub>N<sub>8</sub>O), and a spinel phase. The aluminum metal was not detected.

The marked areas in Fig. 1 are enlarged in Fig. 2. These enlargements reveal that, compared with the characteristic peaks of the spinel phase in the XRD pattern of specimen M<sub>1</sub>, those in the XRD patterns of specimens M<sub>2</sub> and M<sub>3</sub> shift toward larger angles and their diffraction intensity increases with increasing aluminum addition. Therefore, the spinel phase in specimens M<sub>2</sub> and M<sub>3</sub> is deduced to be MgAlON for the following reasons. First, MgAlON can exist above 1400°C under flowing nitrogen with a low oxygen partial pressure [19]. Second, it has smaller crystal lattice parameters than MgAl<sub>2</sub>O<sub>4</sub> and its diffraction peaks shift toward those of MgAl<sub>2</sub>O<sub>4</sub>. We also observed that the content of MgAlON increases with increasing aluminum addition. Cannard *et al.* [24] noted that AlN can accommodate MgO at high temperatures. Thus, aluminum in specimens M<sub>2</sub> and M<sub>3</sub> are completely nitridized into AlN, which then further reacts with Al<sub>2</sub>O<sub>3</sub> and MgO to form MgAlON and AlN-polytypoids (containing some MgO) after being soaked at 580°C and fired at 1700°C.

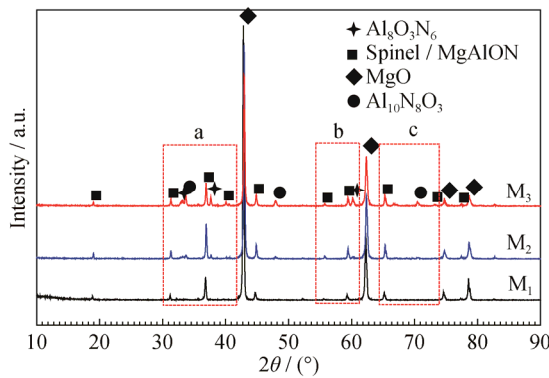


Fig. 1. XRD patterns of specimens M<sub>1</sub>, M<sub>2</sub>, and M<sub>3</sub>.

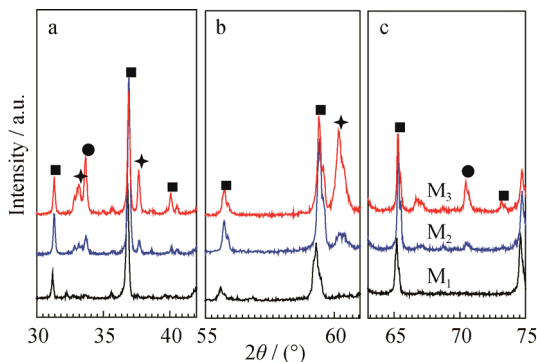


Fig. 2. XRD patterns of the marked areas (a, b, c) in Fig. 1.

### 3.2. Phase morphology and organization structure

Fig. 3 shows the SEM images of specimens M<sub>1</sub>, M<sub>2</sub>, and M<sub>3</sub>. These specimens were all well sintered after being fired at 1700°C for 5 h. The enlarged images in Figs. 3(d)

and 3(f) show that, compared to specimen M<sub>1</sub>, specimens M<sub>2</sub> and M<sub>3</sub> have some cyclic structures dispersed in their matrix and some complete octahedral particles around the cyclic structures.

Table 4 shows the EDS results of the matrix in specimens M<sub>1</sub>, M<sub>2</sub>, and M<sub>3</sub>. These results indicate that specimen M<sub>1</sub> is composed of Mg, Al, and O, whereas specimens M<sub>2</sub> and M<sub>3</sub> consist of Mg, Al, O, and N. The Mg content in different areas varies. In combination with the XRD results in Fig. 1, we observed that, after heat treatment at 1700°C, MgO and Al<sub>2</sub>O<sub>3</sub> in the matrix of specimen M<sub>1</sub> diffuse and migrate into each other, react, and form MgAl<sub>2</sub>O<sub>4</sub>. By contrast, when aluminum is added, MgO and Al<sub>2</sub>O<sub>3</sub> in the matrix of specimens M<sub>2</sub> and M<sub>3</sub> are nitridized into MgAlON and AlN-polytypoids. Because AlN can solid-solve some MgO [24] and because the atomic numbers of Mg and Al as well as those of N and O are similar, distinguishing MgAlON and AlN-polytypoids in SEM images (Figs. 3(d) and 3(f)) is difficult. In addition, EDS results of octahedral particles in specimens M<sub>3</sub> are shown in Fig. 4. The MgAlON phase is well known to form as octahedral particles under good crystal growth conditions.

### 3.3. Reaction mechanism

The melting point of aluminum is 660°C. When temperatures are higher than 660°C, the nitridation reaction of Al is restrained. Thus, soaking at 580°C for 8 h was carried out to allow more aluminum be nitridized into AlN, avoiding the transformation to Al(g), Al<sub>2</sub>O(g), or Al<sub>2</sub>O<sub>3</sub> at high temperatures [25], which will influence the synthesis of MgAlON or AlN-polytypoids.

Therefore, after the soaking stage at 580°C for 8 h, aluminum is nitridized into AlN and the original Al–Al<sub>2</sub>O<sub>3</sub>–MgO system transforms to an AlN–Al<sub>2</sub>O<sub>3</sub>–MgO system. As temperature rises, Al<sub>2</sub>O<sub>3</sub> diffuses and migrates into AlN crystal lattices, forming AlN-polytypoids such as 12H, 21R, and 27R [26]. The reaction equation can be expressed as  $\text{Al}_2\text{O}_3 \xrightarrow{\text{AlN}} 2\text{Al}_{\text{Al}} + 3\text{ON}' + \text{V}'_{\text{Al}}$  (· represents 1 unit positive charge, ' represents 1 negative charge). When the temperature rises higher, AlN diffuses and migrates into Al<sub>2</sub>O<sub>3</sub>, forming  $\gamma$ -AlON; the reaction equation in this case is expressed as  $\text{AlN} \xrightarrow{\text{Al}_2\text{O}_3} 2\text{Al}_{\text{Al}} + 3\text{N}'_{\text{O}} + \text{Al}'_{\text{i}}$  (i represents interstitial). The chemical formula of  $\gamma$ -AlON is  $\text{Al}_{64+x}(\text{VAl})_{8-x}\text{O}_{32-x}\text{N}_x$ , where VAl is a cation vacancy

in the spinel structure,  $0 \leq x \leq 8$  [27–28]. Meanwhile, as the temperature increases, because  $\text{Al}_2\text{O}_3(\text{s}) + \text{MgO}(\text{s}) = \text{MgAl}_2\text{O}_4(\text{s})$ ,  $\Delta G = -23604 - 5.91T$ ,  $\Delta G < 0$ , MgO reacts with Al<sub>2</sub>O<sub>3</sub>, forming MgAl<sub>2</sub>O<sub>4</sub>; thus, under increasing tem-

perature, the  $\text{MgAl}_2\text{O}_4$  spinel content increases. The  $\gamma$ -AlON and  $\text{MgAl}_2\text{O}_4$  are both oxide spinels. At high temperatures, they can solid-solve together, forming a new spinel phase, MgAlON [29]. Thus, when the  $\text{AlN-Al}_2\text{O}_3\text{-MgO}$  system is soaked at  $580^\circ\text{C}$  and fired at  $1700^\circ\text{C}$ ,  $\text{Al}_2\text{O}_3$  reacts with AlN or MgO to form AlN-polytypoids,  $\gamma$ -AlON, or  $\text{MgAl}_2\text{O}_4$ . The formed  $\gamma$ -AlON and  $\text{MgAl}_2\text{O}_4$  further react, resulting in the formation of spinel-structured MgAlON. Differently, AlN-polytypoids solid-solve some MgO, forming Mg-containing AlN-polytypoids. Given that Mg-containing AlN-polytypoids

have similar elemental compositions and that their crystal boundaries can be partly fused together, they are impossible to distinguish in SEM images, as confirmed by the XRD results in Fig. 1, SEM images in Fig. 3, and the EDS results in Table 4. In Figs. 3(d) and 3(f), some cyclic structures are observed, which are deduced to be aluminum metal. Aluminum powder easily aggregates because of its small particle size and high surface energy. This aggregation leads to an incomplete nitridation at  $580^\circ\text{C}$ . At higher temperatures, Al(s) transforms into Al(g) and  $\text{Al}_2\text{O}_3(\text{g})$  and escapes.

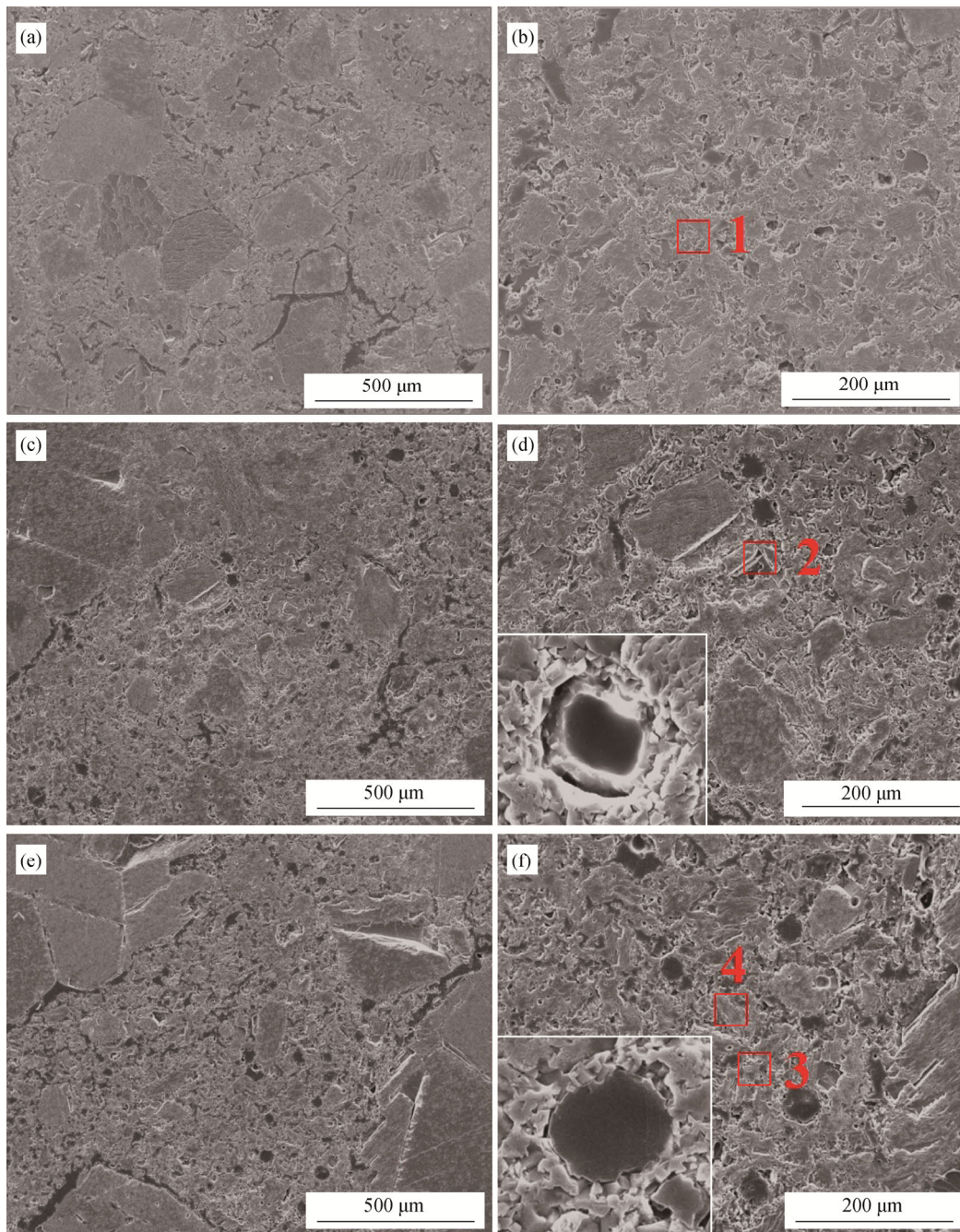
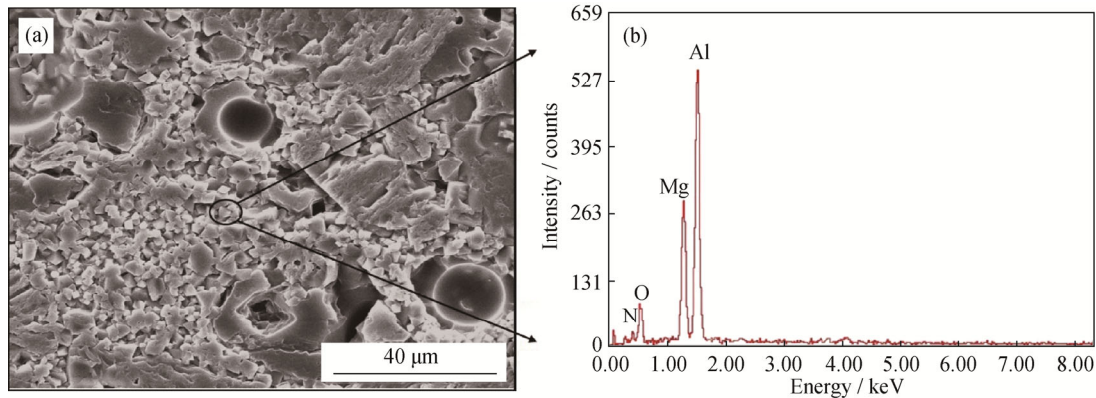


Fig. 3. SEM images of specimens  $M_1$ ,  $M_2$ , and  $M_3$ : (a) (b) SEM images of  $M_1$ ; (c) (d) SEM images of  $M_2$ ; (e) (f) SEM images of  $M_3$ .

Table 4. EDS results of the marked areas in Fig. 3

Specimen	Marked areas	Atomic number percentage / %			
		Mg	Al	O	N
M <sub>1</sub>	1	19.65	44.56	35.79	—
M <sub>2</sub>	2	5.81	39.25	25.26	29.68
	3	18.79	41.13	31.58	8.50
M <sub>3</sub>	4	7.35	37.83	21.22	33.60
	5	18.72	31.14	30.83	19.30

Fig. 4. SEM image (a) and EDS spectrum (b) of the fracture in specimen M<sub>3</sub>.

#### 4. Conclusions

In this work, Al–Al<sub>2</sub>O<sub>3</sub>–MgO composites (MgAlON as a bonding phase) were prepared at 1700°C for 5 h under a nitrogen atmosphere using fused magnesia, α-Al<sub>2</sub>O<sub>3</sub>, tabular alumina, metal aluminum, and sintered magnesia as raw materials. The composites after calcination were characterized and analyzed by XRD, SEM, and EDS. The results are summarized as follows:

(1) Specimen M<sub>1</sub> was composed of MgO and MgAl<sub>2</sub>O<sub>4</sub>. Compared with specimen M<sub>1</sub>, specimens M<sub>2</sub> and M<sub>3</sub> contained MgAlON, whose content increased with increasing aluminum addition.

(2) Under a nitrogen atmosphere, MgO, Al<sub>2</sub>O<sub>3</sub>, and Al in the matrix of specimens M<sub>2</sub> and M<sub>3</sub> reacted to form MgAlON and AlN-polytypoids, which combined the particles and the matrix together and imparted the composite with a dense structure.

(3) The mechanism of MgAlON synthesis is described as follows. Under an N<sub>2</sub> atmosphere, the partial pressure of oxygen is quite low; thus, when the Al–Al<sub>2</sub>O<sub>3</sub>–MgO system was soaked at 580°C for an extended period, aluminum metal was transformed into AlN. With increasing temperature, Al<sub>2</sub>O<sub>3</sub> diffused into AlN crystal lattices and formed AlN-polytypoids; by contrast, MgO reacted with Al<sub>2</sub>O<sub>3</sub> to form MgAl<sub>2</sub>O<sub>4</sub>. When the temperature was greater than (1640 ± 10)°C, AlN diffused into Al<sub>2</sub>O<sub>3</sub> and formed spi-

nel-structured AlON. *In situ* MgAlON was then acquired through a solid-solution reaction between AlON and MgAl<sub>2</sub>O<sub>4</sub> at high temperatures because of their similar spinel structures.

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