X. Cheng et al.: Low temperature and pressureless synthesis of MgAlON: qualitative analysis and formation evolution

Xiang Cheng^a, Lei Liu^a, Guibo Qiu^b, Zhitao Bai^b, Min Guo^a, Fangqin Cheng^c, Mei Zhang^{a,c}

^aState Key Laboratory of Advanced Metallurgy, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing, P.R. China

^bCentral Research Institute of Building and Construction Co., Ltd, MCC Group, Beijing, P.R. China

^cShanxi Collaborative Innovation Center of High Value-added Utilization of Coal-related Wastes in Shanxi University, Taiyuan, P.R. China

Low temperature and pressureless synthesis of MgAlON: qualitative analysis and formation evolution

By calculating the Gibbs free energy of a magnesium aluminium oxynitride (MgAlON) system, pure MgAlON was obtained by pressureless sintering at 1570 °C in a nitrogen atmosphere using Al, Al₂O₃, and MgO as raw materials. The formation mechanism of MgAlON and phase evolution of the Al–Al₂O₃–MgO–N₂ system were investigated. The aluminium was melted at approximately 660 °C and formed AlN in the range 740–1250 °C. The reaction of AlN, Al₂O₃, and MgO started to form a primary crystalline MgAlON phase at 950 °C, and as the temperature increased, the minerals continuously dissolved in the primary crystalline phase.

Keywords: MgAlON; Qualitative analysis; Low temperature; Pressureless synthesis; Formation evolution

1. Introduction

With the developments in the iron and steel industry, the quality requirements of ultra-low carbon steel are becoming much more stringent. Therefore, the impurity content in steel must be strictly controlled. Nowadays, magnesia carbon refractories are widely used as lining materials for electric furnaces, converters, and refining furnaces. However, magnesia carbon bricks increase the carbon content in mol-

ten steel, and this problem cannot be ignored. Magnesium aluminium oxynitride (MgAlON) is a solid solution of Al₂O₃, AlN, and MgO [1, 2]. It is possible to replace carbon-containing refractories with this new refractory for clean steel production because of its excellent mechanical properties such as good thermal stability at high temperatures, good slag corrosion resistance, low wettability to molten iron, and excellent peeling resistance [3–6].

Normally, MgAlON synthesis includes four common methods; namely, aluminothermy reduction, reactive sintering, carbothermal reduction and nitridation, and spark plasma sintering [7–11]. Yan et al. prepared MgAlON by aluminothermy reduction from Al, AlN, and MgO in a flowing nitrogen atmosphere at 1800 °C for 3 h. Willems et al. obtained MgAlON by the reactive sintering of Al₂O₃, MgO, and AlN at 1750 °C for 1 h with 3 bar of static nitrogen. Dai et al. prepared MgAlON using carbothermal reduction and nitridation from Al₂O₃, MgO, and C as well as spark plasma sintering from Al₂O₃, MgO, and AlN in nitrogen at 1700 °C. Zhang et al. synthesized single-phase MgAlON by spark plasma sintering of MgO · nAl₂O₃ (n > 1), Al₂O₃, and AlN at 1700 °C. However, the synthesis temperature of single-phase MgAlON is very high. In practice, production costs are significantly increased when the temperature exceeds 1700 °C, and a special furnace is required to achieve such high temperatures.

Qualitative analysis of MgAlON is difficult because MgAlON has the same crystal structure and similar lattice constants as magnesia-alumina spinel [12]. It has been reported that the position of the diffraction peak in the X-ray diffraction (XRD) pattern shifted to the right when the magnesia-alumina spinel was converted to MgAlON [13, 14]. The magnesia-alumina spinel and MgAlON must have the same molar percentage of Al_2O_3 and MgO prior to comparison. However, it is impossible to directly obtain the same molar percentage of Al_2O_3 and MgO in a solid solution because $\text{MgO} \cdot n\text{Al}_2\text{O}_3$ and MgAlON have a large solid-solution region. Therefore, an accurate and simple qualitative analysis of MgAlON in a solid solution needs to be explored.

The formation mechanism of MgAlON has been widely studied [15–19]. Researchers have found that the formation of MgAlON has three synthesis mechanisms. The first formation mechanism is the reaction of Al_2O_3 with MgO to form an intermediate solid solution $\text{Mg}_{1-x}\text{Al}_{2+2x/3}\text{O}_4$, and with an increase in the temperature, MgAlON is generated by Al_2O_3 and AlN dissolving in spinel. The second mechanism is the generation of AlON through the reaction of MgO and AlN and then, dissolving of MgO into AlON at 1 160 °C to form MgAlON. The third mechanism is the diffusion of AlN into Al_2O_3 and MgO particles to obtain MgAlON at 1 100 °C. Hence, there is still nonconformity in the formation mechanism of MgAlON.

In this study, the Gibbs free energy of a MgAlON system was calculated to preliminarily determine the synthesis parameters of MgAlON. According to the thermodynamic calculation results, pure MgAlON was synthesized by pressureless sintering. Qualitative analysis of MgAlON in a solid solution was performed and a formation mechanism of MgAlON was developed.

2. Experimental procedure

2.1. Raw materials and preparation process

In this work, the raw materials were aluminium powder (wt. Al > 99.6 %), alumina micro-powder (wt. Al_2O_3 > 99.3 %), and fused magnesite (wt. MgO > 95.2 %). The chemical composition of raw materials is shown in Table 1. Figure 1 shows SEM images of the morphologies of the raw materials. As shown in Fig. 1a, the aluminium powder consisted of large particles of 15–30 μm and small particles of 0.1–3 μm . The particle size of alumina micro-powder was 0.2–5 μm (Fig. 1b). As shown in Fig. 1c, the magnesite consisted of large particles of approximately 60 μm and small particles of 0.2–10 μm .

Table 2 lists the composition of the green bodies in mass ratio and heating conditions. According to the mass ratio of the listed raw materials, the starting materials were accurately weighed and mixed by ball milling with an agate ball for 3 h in absolute alcohol. Subsequently, the mixture was uniaxially pressed at 20 MPa to form cylindrical samples of $\varnothing 20 \times 4$ mm. All the green bodies were placed in a corundum crucible, which was placed in another corundum crucible with active carbon powder on the bottom. The active carbon was designed to reduce the partial pressure of oxygen in the system, ensuring the nitridation of aluminium and preventing the oxidation of the reaction products. The green bodies A_{N_2} and A_{air} were sintered at 1 570 °C and held for 3 h in air and nitrogen atmospheres, respectively. The A_{vary} was sintered at temperatures ranging from 850 to 1 450 °C in steps of 100 °C at 30-min intervals. The samples B_0 , $B_{0.25}$, $B_{0.5}$, and $B_{0.75}$ with different aluminium contents were heated at 1 620 °C for 4 h in a high-temperature furnace with continuously flowing nitrogen. The heating rate was 10 K min^{-1} from room temperature to 1 000 °C, 5 K min^{-1} from 1 000 to 1 400 °C, and 3 K min^{-1} from 1 400 °C to the soak-

Table 1. Chemical composition of raw materials.

Raw materials	Chemical composition (wt.%)						
	Al	Al_2O_3	MgO	Na_2O	CaO	SiO_2	Fe_2O_3
aluminum powder	99.67	–	–	–	–	–	0.24
alumina micro-powder	–	99.39	–	0.40	–	–	–
fused magnesite	–	0.31	95.27	–	1.28	2.29	0.57

Fig. 1. SEM images of the morphologies of the raw materials (a) Al, (b) Al_2O_3 , and (c) MgO; the inserts are the corresponding enlarged images.

ing temperature. The cooling rate was 5 K min⁻¹ from soaking temperature to 1400 °C and 6.5 K min⁻¹ from 1400 to 700 °C, and then the furnace cooled naturally.

2.2. Characterization

A preliminary determination of the phase composition was investigated by XRD (MAC-M21XRHF, Japan) using Cu-K α radiation. X-ray fluorescence (XRF) (XRF-1800, Japan) was used for the elemental analysis. The microstructure of the specimens was studied by means of field-emission scanning electron microscopy (SEM) (Zeiss, SUPRA 55, Germany). Prior to the SEM analysis, the sintered samples were cut, and the section was carbonized. X-ray photoelectron spectroscopy (XPS) (Kratos AXIS Ultra DLD, Japan) was used to identify the presence of nitrogen in the samples. ²⁷Al solid-state nuclear magnetic resonance (NMR) (Bruker Avance III, Switzerland) was used to distinguish the presence of MgAlON and MgAl₂O₄. To characterize the weight losses and thermal behaviour of samples at high temperatures, thermal gravimetric and differential scanning calorimeter (TG-DSC) analysis (S60, SETARAM, France) were

performed to continuously measure the heating process from room temperature to 1500 °C at a rate of 10 K min⁻¹ with flowing nitrogen.

3. Results and discussion

3.1. Thermodynamic analysis

Equations (1–3) [12] describe the Gibbs free energy of MgAlON with different compositions, where $\Delta_f G^\theta$ and T represent Gibbs free energy and temperature, respectively. Figure 2 shows

$$\Delta_f G^\theta(\text{Mg}_{0.1}\text{Al}_{1.6}\text{O}_{2.2}\text{N}_{0.2}) = -1308073.75 + 258.66T \text{ (J mol}^{-1}\text{)} \quad (1)$$

$$\Delta_f G^\theta(\text{Mg}_{0.2}\text{Al}_{1.45}\text{O}_{2.15}\text{N}_{0.15}) = -1287344.2 + 256.41T \text{ (J mol}^{-1}\text{)} \quad (2)$$

Table 2. Composition of the green bodies in mass ratio and heating conditions.

Sample No	Aluminum powder: Alumina micro-powder: Fused magnesite (mass ratio)	Reaction parameter		
		soaking temperature (°C)	atmosphere	soaking time (h)
A _{vary}	1 : 8 : 1.5	850–1450	N ₂	0.5
A _{N2}	1 : 8 : 1.5	1570	N ₂	3
A _{air}	1 : 8 : 1.5	1570	Air	3
B ₀	0 : 8 : 2.5	1620	N ₂	4
B _{0.25}	0.25 : 8 : 2.5	1620	N ₂	4
B _{0.5}	0.50 : 8 : 2.5	1620	N ₂	4
B _{0.75}	0.75 : 8 : 2.5	1620	N ₂	4

Fig. 2. The phase stability diagrams of the MgAlON system under (a) different nitrogen content (1873 K), and (b) different temperatures ($\text{Mg}_{0.3}\text{Al}_{1.3}\text{O}_{2.1}\text{N}_{0.1}$).

$$\Delta_f G^0(\text{Mg}_{0.3}\text{Al}_{1.3}\text{O}_{2.1}\text{N}_{0.1}) = -1266614.64 + 255.6T \text{ (J mol}^{-1}\text{)} \quad (3)$$

the phase stability diagrams of the MgAlON system under different temperatures and nitrogen contents. As shown in Fig. 2a, the partial pressure of oxygen required for the synthesis of $\text{Mg}_{0.3}\text{Al}_{1.3}\text{O}_{2.1}\text{N}_{0.1}$, $\text{Mg}_{0.2}\text{Al}_{1.45}\text{O}_{2.15}\text{N}_{0.15}$, and $\text{Mg}_{0.1}\text{Al}_{1.6}\text{O}_{2.2}\text{N}_{0.2}$ must be separately controlled at $1.5 \times 10^{-18} - 3.5 \times 10^{-8}$, $3 \times 10^{-18} - 6.2 \times 10^{-12}$, and $6.1 \times 10^{-18} - 2.6 \times 10^{-14}$ MPa, respectively, at 1873 K and 0.1 MPa. It was revealed that the solid-solution region of the MgAlON gradually shrank with an increase in the nitrogen content of the solid solution at the same temperature. Figure 2b shows the predominance area diagrams of $\text{Mg}_{0.3}\text{Al}_{1.3}\text{O}_{2.1}\text{N}_{0.1}$ synthesis at four different temperatures (1823, 1873, 1973, and 2073 K). Accordingly, the partial pressures of oxygen required for the synthesis of $\text{Mg}_{0.3}\text{Al}_{1.3}\text{O}_{2.1}\text{N}_{0.1}$ were $4.5 \times 10^{-19} - 7.1 \times 10^{-9}$, $1.5 \times 10^{-18} - 3.5 \times 10^{-8}$, $1.4 \times 10^{-17} - 6.5 \times 10^{-7}$, and $1.0 \times 10^{-16} - 9.2 \times 10^{-6}$ MPa. It was indicated that the partial pressure of oxygen decreased with an increase in the temperature for the same dissolved nitrogen content; however, a change in the area of the solid-solution region was not obvious. According to the thermodynamic analysis, the partial pressure of oxygen should be controlled at $1.0 \times 10^{-16} - 7.1 \times 10^{-9}$ MPa for the synthesis of MgAlON in the temperature range of 1823–2073 K.

As shown in the phase stability diagrams (Fig. 2b), the partial pressure of oxygen required for the synthesis of MgAlON at 1550 °C (1823 K) must be controlled within

4.5×10^{-19} and 7.1×10^{-9} MPa. The purity of the nitrogen gas selected in this experiment was 99.999 %, and the partial pressure of oxygen at one atmospheric pressure was 10^{-6} MPa, which was much higher than 4.5×10^{-19} and 7.1×10^{-9} MPa. This experiment was designed to sharply reduce the partial pressure of oxygen of the system by carbon powder. Equations (4) and (5) [20] were chosen to calculate the partial pressure of oxygen of the system after carbon sequestration. The partial pressures of oxygen in the system at 1570 and 1620 °C were 4.792×10^{-11} and 5.272×10^{-11} MPa, respectively, indicating that the partial pressure of oxygen of the entire system met the requirement of MgAlON synthesis by using the carbon powder.

3.2. Preparation of pure MgAlON

The same-composition A_{N_2} and A_{air} samples were sintered at 1570 °C for 3 h in nitrogen and air atmospheres, and Fig. 3a shows the corresponding XRD patterns. The XRD spectra of the A_{N_2} and A_{air} samples were different; the sintered product of A_{N_2} was only the spinel phase, and the calcined products of A_{air} were the spinel phase and Al_2O_3 . According to the previous thermodynamic analysis, MgAlON must be synthesized under a nitrogen atmosphere. Hence,

Fig. 3. (a) The XRD pattern of A_{N_2} and A_{air} with same composition sintered at 1570 °C for 3 h in nitrogen and air atmosphere, respectively. (b) The XRD results of B_0 , $\text{B}_{0.25}$, $\text{B}_{0.5}$, and $\text{B}_{0.75}$ calcined at 1620 °C for 4 h in flowing nitrogen.

Table 3. Comparison of three major XRD diffraction peaks of samples B_0 , $\text{B}_{0.25}$, $\text{B}_{0.5}$, and $\text{B}_{0.75}$ with different aluminum contents.

(h k l)	B_0	$\text{B}_{0.25}$	$\text{B}_{0.5}$	$\text{B}_{0.75}$
(3 1 1)	36.800	36.919	36.860	36.801
(4 0 0)	44.782	44.900	44.859	44.801
(4 4 0)	65.319	65.401	65.342	65.321

the calcined products of A_{air} were Al_2O_3 (PDF#89-7717) and MgAl_2O_4 (PDF#73-1959). The sintered product of sample A_{N_2} was speculated to be MgAlON because, combined with the thermodynamic analysis, the A_{N_2} and A_{air} samples had the same spinel-phase peak position and the sample A_{N_2} was sintered in nitrogen.

3.3. Qualitative analysis of MgAlON

To solve the qualitative problem of MgAlON, samples B_0 , $B_{0.25}$, $B_{0.5}$, and $B_{0.75}$ with different aluminium contents were calcined at 1620 °C for 4 h in a flowing nitrogen atmosphere. As shown in the XRD results of Fig. 3b, the sintered products of B_0 , $B_{0.25}$, $B_{0.5}$, and $B_{0.75}$ were all spinel; namely, MgAlON or MgAl_2O_4 . According to the thermodynamic calculations of Eqs. (6 and 7) [20], Al_2O_3 and MgO cannot be nitrated in a nitrogen atmosphere at 1620 °C; therefore, the sintered product of sample B_0 was MgAl_2O_4 . In addition,

Ye et al. [13] reported that with an increase in the nitrogen content in the spinel phase, the peak positions of XRD gradually shift to the right. A comparison of three major XRD diffraction peaks ((3 1 1), (4 0 0), and (4 4 0)) of samples B_0 , $B_{0.25}$, $B_{0.5}$, and $B_{0.75}$ with different aluminium contents

is shown in Table 3. In the case of the same mass ratio of MgO and Al_2O_3 , the characteristic peaks of samples B_0 , $B_{0.25}$, $B_{0.5}$, and $B_{0.75}$ did not show the same shift with an increase in the amount of aluminium powder added. It may be that a low amount of nitrogen dissolved in the spinel results with an undetectable trace shift. Therefore, the sintered products of $B_{0.25}$, $B_{0.5}$, and $B_{0.75}$ cannot be directly determined as MgAlON from XRD analysis.

The XPS analysis was first adopted for qualitative analysis of samples $B_{0.25}$, $B_{0.5}$, and $B_{0.75}$. The N 1s XPS spectra of samples B_0 , $B_{0.25}$, $B_{0.5}$, and $B_{0.75}$ are given in Fig. 4. Figure 4a shows that the N 1s XPS spectra of sample B_0 did not have a peak, indicating that sample B_0 was MgAl_2O_4 . As shown in Fig. 4b–d, the N 1s binding energy of sample $B_{0.25}$ was 395.7 eV and that of samples $B_{0.5}$ and $B_{0.75}$ were 395.44 and 397.12 eV and 395.69 and 397.8 eV, respectively. Therefore, the calcined product of samples $B_{0.25}$, $B_{0.5}$, and $B_{0.75}$ should be MgAlON. In addition, a new peak appeared at approximately 397.8 eV when the nitrogen content increased to a certain extent. Baraldi et al. [21] proposed that the peak N 1s of NO absorbed on Rh at 320 K in XPS spectra was 397.3 eV. Hagio et al. [22] determined that the peak N 1s in AlN was 396.7 eV. Therefore, the peak near 395.7 eV may be related to the bond between the nitrogen and aluminium atoms, while the peak near 397.8 eV is related to the bond between the nitrogen and oxygen atoms. Hence, the nitrogen in MgAlON with a low nitrogen content combines only with Al atoms ($B_{0.25}$, Fig. 4b), whereas the nitrogen in MgAlON with high nitrogen content combines with Al and O atoms ($B_{0.5}$ and $B_{0.75}$, Fig. 4c and d). As shown in Fig. 4e, the N 1s XPS spectra became stronger and wider with an increase in the dissolution

Fig. 4. The N 1s XPS spectra of specimens (a) B_0 , (b) $B_{0.25}$, (c) $B_{0.5}$, (d) $B_{0.75}$, and (e) the N 1s XPS spectra comparison of B_0 , $B_{0.25}$, $B_{0.5}$, and $B_{0.75}$.

Fig. 5. The ^{27}Al solid-state NMR spectra of the A_{N_2} and A_{air} samples sintered in nitrogen and air atmosphere, respectively.

Fig. 6. SEM images of the fracture surfaces and EDS mapping analysis of (a and b) MgAl_2O_4 (B_0) and (c and d) MgAlON ($B_{0.75}$).

of nitrogen. This result is consistent with the experimental design. In summary, the XPS nitrogen analysis confirmed sample B₀ was MgAl₂O₄ and B_{0.25}, B_{0.5}, and B_{0.75} were MgAlON.

In addition, ²⁷Al solid-state NMR analysis was also used to solve the qualitative problem of MgAlON. The ²⁷Al solid-state NMR spectra of A_{N2} and A_{air} are shown in Fig. 5; the two samples had peaks at 15 and 68 ppm, and a new peak at 116.6 ppm emerged in the A_{N2}. Previous research [23–27] has reported that chemical shifts of α-Al₂O₃, γ-Al₂O₃, AlN, AlON (5AlN:9Al₂O₃), and MgAl₂O₄ occurred at 11.5; 8 and 66; 113; 12, 65 and 114; 5 and 70 ppm, respectively. This proves that the peaks around 5 and 70 ppm were related to AlO₆ octahedra and AlO₄ tetrahedra, respectively, while the peak near 113 ppm was related to AlN₄ tetrahedra. The spectra of A_{N2} and A_{air} share some commonalities: a narrow peak in the range 10–20 ppm is in agreement with the octahedral <AlO₆> sites, and a characteristic peak located at 60–70 ppm is related to AlO₄ tetrahedra. Nevertheless, the ²⁷Al solid-state NMR spectra of the A_{N2} sample showed a weak peak at 116.6 ppm attributed to the Al atoms in a nitrogen tetrahedral system. This is consistent with another report [28], indicating that the spinel phases in A_{N2} and A_{air} are MgAlON and MgAl₂O₄, respectively.

3.4. Microstructures

To observe the microstructural difference between MgAl₂O₄ and MgAlON, Fig. 6a and b and Fig. 6c and d present SEM images of the fracture surfaces and EDS mapping analysis of the B₀ (MgAl₂O₄) and B_{0.75} (MgAlON) samples sintered at 1620 °C in a nitrogen atmosphere, respectively. Figure 6a and b show that the microstructure of MgAl₂O₄ exhibited a densified structure and integrated grains. As shown in Fig. 6c and d, the sintered product MgAlON consisted of many small grains. The particle size of MgAlON was consistent with that of the raw materials in Fig. 1. Ma et al. [29] reported that the fracture surfaces of MgAlON synthesized by pressureless sintering at 1840 °C for 10 h and hot isostatic pressing at 1880 °C for 2 h showed that MgAlON behaved as a perfect crystal. Therefore, sintering temperature and sintering pressure affect the development of crystal grains. Sample B_{0.75} was obtained by pressureless sintering at 1570 °C, resulting in MgAlON with a smaller grain size. As shown in the EDS analysis of Fig. 6b and d, Al, Mg, O, and C were detected in B₀ (MgAl₂O₄) and B_{0.75} (MgAlON). Nitrogen was not detected in MgAlON by

Fig. 7. (a) The TG-DSC result of A_{TG}. (b) The XRD patterns of sample A_{vary} sintered at various temperatures and A_{N2} sintered at 1570 °C.

Fig. 8. Formation evolution of MgAlON in Al–Al₂O₃–MgO–N₂ system.

EDS because nitrogen is a light element; moreover, the nitrogen content of MgAlON is very low.

3.5. Formation evolution of MgAlON

The thermal analysis and thermogravimetric change of the nitriding reaction of the sample A_{TG} (Al:Al₂O₃:MgO = 1:8:1.5 mass ratio) were measured by TG-DSC analysis from room temperature to 1500 °C at a heating rate of 10 K min⁻¹. The TG-DSC result is shown in Fig. 7a. The mass reduction below 600 °C was the result of the evaporation of water. The endothermic peak at 660 °C indicated the melting of aluminium powder, while the nitriding reaction of aluminium had not yet begun. There was a strong exothermic peak located at 780 °C, which resulted from the nitriding reaction of aluminium accompanied by a large gain in mass. With a further increase in the temperature, the mass change became very weak, meaning that nitrogen was basically no longer involved in the reaction. After 850 °C, the value of heat flow increased with an increase in the temperature, indicating that the exothermic reaction had not been completed until a temperature of 1500 °C had been attained.

Therefore, to further study the formation mechanism of MgAlON, sample A_{vary} was sintered at 850, 950, 1050, 1150, 1250, 1350, and 1450 °C for 40 min in a nitrogen atmosphere, and the corresponding XRD patterns are shown in Fig. 7b. The formation evolution of MgAlON is shown in Fig. 8. The weight of sample A_{TG} (Fig. 7a) increased from 750 to 1250 °C, and Fig. 7b shows that AlN was always present in this temperature range (Fig. 8b and c); therefore, the nitriding reaction of aluminium was not completed until 1250 °C. The peak intensity of Al₂O₃, AlN, and MgO decreased in the temperature range 850–950 °C, and the spinel phase appeared at 950 °C. This result demonstrates that Al₂O₃, AlN, and MgO simultaneously started the solid-solution reaction at approximately 950 °C to form MgAlON (Fig. 8c). Then, as the temperature increased, Al₂O₃, AlN, and MgO continuously dissolved in the spinel (Fig. 8d). The peak of MgO disappeared at 1350 °C, proving clearly that MgO had been completely exhausted before 1350 °C. The AlN was fully dissolved into spinel at approximately 1450 °C (Fig. 8e). The Al₂O₃ was being continuously dissolved in the MgAlON until the end of the reaction (Fig. 8f and g). The formation evolution of MgAlON obtained by pressureless sintering from Al, Al₂O₃, and MgO at 1570 °C in a nitrogen atmosphere in this work was consistent with the research of Wang et al. [19]. On the basis of thermodynamic calculations, MgAlON can be directly synthesized by strictly controlling the reaction temperature and partial pressure of oxygen. This is possible because the liquid phase formed by the fusion of aluminium promotes the development of a solid-solution reaction, and the AlN formed by the nitriding reaction of aluminium shows good reactivity.

4. Conclusions

Thermodynamic analysis of MgAlON indicates that as the nitrogen content increases, the solid-solution region of MgAlON gradually shrinks, when a constant sintering temperature is maintained. However, the partial pressure of oxygen required for the synthesis of MgAlON is reduced at the same dissolved nitrogen content by increasing the sintering temperature.

The XPS analysis of MgAlON indicated that the N 1s XPS spectra became stronger and wider with an increase in the dissolution of nitrogen. A comparison of the ²⁷Al solid-state NMR spectra of MgAl₂O₄ and MgAlON indicated that the additional characteristic peak located at 116.6 ppm corresponded to the AlN₄ tetrahedral. Hence, MgAlON can be accurately determined by XPS analysis or by ²⁷Al solid-state NMR analysis combined with XRD analysis.

The formation mechanism of MgAlON using Al, Al₂O₃, and MgO as initial materials is as follows: the aluminium is first melted at approximately 660 °C; second, the nitriding reaction of aluminium occurs from 740 to 1250 °C. Then, AlN, Al₂O₃, and MgO begin to react with each other to form MgAlON at 950 °C. They continuously dissolve into MgAlON with an increase in the sintering temperature. The MgO, AlN, and Al₂O₃ complete the solid-solution reaction at approximately 1350–1570 °C.

The National Natural Science Foundation of China (Nos. 51972019, 51672025, 51572020), and Major Projects of Science and Technology in Shanxi Province (MC2016-03) are duly acknowledged for their financial support.

References

- [1] H.X. Zhang, Y.R. Hong, Y. Huang, J.L. Sun: *J. Mater. Sci. Technol.* 21 (2005) 277. DOI:10.3321/j.issn:1005-0302.2005.02.030
- [2] W.Y. Sun, L.T. Ma, D.S. Yan: *Chin. Sci. Bull.* 35 (1990) 1189. DOI:10.1360/sb1990-35-14-1189
- [3] C.J. Deng, Y.R. Hong, X.C. Zhong, J.L. Sun: *Int. J. Min. Met. Mater.* 7 (2000) 96.
- [4] Z.T. Zhang, L.D. Teng, W.C. Li: *J. Eur. Ceram. Soc.* 27 (2007) 319. DOI:10.1016/j.jeurceramsoc.2006.04.184
- [5] Z.T. Zhang, T. Matsushita, W.C. Li, S. Seetharaman: *Metall. Mater. Trans. B.* 38 (2007) 231. DOI:10.1007/s11663-007-9038-1
- [6] Z.T. Zhang, T. Matsushita, W.C. Li, S. Seetharaman: *Metall. Mater. Trans. B.* 37 (2006) 421. DOI:10.1007/s11663-006-0027-6
- [7] M.W. Yan, Y. Li, H.Y. Li, Y. Sun, H.Y. Chen, C.H. Ma, J.L. Sun: *Ceram. Int.* 44 (2018) 3856. DOI:10.1016/j.ceramint.2017.11.174
- [8] H.X. Willems, G. de With, R. Metselaar: *J. Eur. Ceram. Soc.* 12 (1993) 43. DOI:10.1016/0955-2219(93)90069-4
- [9] H.X. Zhang, N.S. Zhou, J.L. Sun, J.Y. Zhang, W.D. Xue, Y.R. Hong: *China's Refractories.* 36 (2002) 128.
- [10] W.B. Dai, W. Lin, A. Yamaguchi, J. Ommyoji, J.K. Yu, Z.S. Zou: *J. Ceram. Soc. Jpn.* 115 (2007) 42. DOI:10.2109/jcersj.115.42
- [11] W.B. Dai, A. Yamaguchi, W. Lin, J. Ommyoji, J.K. Yu, Z.S. Zou: *J. Ceram. Soc. Jpn.* 115 (2007) 525. DOI:10.2109/jcersj.115.525
- [12] X.D. Wang, F.M. Wang, W.C. Li: *J. Inorg. Mater.* 18 (2003) 83. DOI:10.1177/0883911503018001005
- [13] G.T. Ye, J.L. Shang, D.R. Zhang, M. Liang, Y.S. Chen: *J. Am. Ceram. Soc.* 93 (2010) 322. DOI:10.1111/j.1551-2916.2009.03408.x
- [14] Y. Sun, S.J. Chen, L. Tian, G.H. Li: *China's Refractories.* 50 (2016) 428. DOI:10.3969/j.issn.1001-1935.2016.06.007
- [15] J. Weiss, P. Greil, L.J. Gauckler: *Commun. Amer. Ceram. Soc.* (1982) C68. DOI:10.1111/j.1151-2916.1982.tb10435.x
- [16] A. Granon, P. Goeuriot, F. Thevenot, J. Guyader, P. L'Haridon, Y. Laurent: *J. Eur. Ceram. Soc.* 13 (1994) 365. DOI:10.1016/0955-2219(94)90012-4
- [17] H.F. Li: Msc thesis, MgAlON Fabrication and properties of MgAlON and composite refractories, Wuhan University Of Science And Technology, China (2002).
- [18] S. Bandyopadhyay, G. Rixecker, F. Aldinger, H.S. Maiti: *J. Am. Ceram. Soc.* 87 (2004) 480. DOI:10.1111/j.1551-2916.2004.00480.x
- [19] X.T. Wang, H.Z. Wang, B.G. Zhang, Y.R. Hong, J.L. Sun: *Rare. Metal. Mat. Eng.* 34 (2005) 42. DOI:10.3321/j.issn:1002-185X.2005.z1.012
- [20] D.L. Ye, J.H. Hu: *Thermodynamic Data Directory of Inorganic Matter, Metallurgical Industry Press, Beijing* (2002).
- [21] A. Baraldi, V.R. Dhanak, M. Kiskinova, R. Rosei: *Appl. Surf. Sci.* 78 (1994) 445. DOI:10.1016/0169-4332(94)90068-X

- [22] T. Hagio, A. Takase, S. Umebayashi: J. Mater. Sci. Lett. 11 (1992) 878. DOI:10.1007/BF00730493
- [23] R. Dupree, M.H. Lewis, M.E. Smith: Philos. Mag. A. 53 (1986) L17. DOI:10.1080/01418618608242816
- [24] R. Dupree, M.H. Lewis, M.E. Smith: J. Appl. Crystallogr. 21 (1988) 109. DOI:10.1107/S0021889887010069
- [25] H. Maekawa, S. Kato, K. Kawamura, T. Yokokawa: Am. Mineral. 82 (1997) 1125. DOI:10.2138/am-1997-11-1210
- [26] N. Kashii, H. Maekawa, Y. Hinatsu: J. Am. Ceram. Soc. 82 (1999) 1844. DOI:10.1111/j.1151-2916.1999.tb02007.x
- [27] V. Montouillout, D. Massiot, A. Douy, J.P. Coutures: J. Am. Ceram. Soc. 82 (1999) 3299. DOI:10.1111/j.1151-2916.1999.tb02243.x
- [28] O. Morey, P. Goeuriot: J. Eur. Ceram. Soc. 25 (2005) 501. DOI:10.1016/j.jeurceramsoc.2004.01.023
- [29] B.Y. Ma, W. Zhang, Y.Z. Wang, X.M. Xie, H.Z. Song, C. Yao, Z.B. Zhang, Q. Xu: Ceram. Int. 44 (2018) 4512. DOI:10.1016/j.ceramint.2017.12.023

(Received October 9, 2019; accepted April 1, 2020; online since June 22, 2020)

Correspondence address

Mei Zhang, PhD
Full Professor
State Key Laboratory of Advanced Metallurgy
School of Metallurgical and Ecological Engineering
University of Science and Technology Beijing
No. 30 Xueyuan Road
Beijing 100083
P.R. China
Tel: +86-10-6233-4926
Fax: +86-10-6233-4926
E-mail: zhangmei@ustb.edu.cn

Bibliography

DOI 10.3139/146.111916
Int. J. Mater. Res. (formerly Z. Metallkd.)
111 (2020) 7; page 537–545
© Carl Hanser Verlag GmbH & Co. KG
ISSN 1862-5282