Synthesis of Magnesium Aluminum Oxynitride by Carbothermal Reduction and Nitridation Process

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Abstract: Carbothermal reduction and nitridation (CRN) process was utilized to prepare magnesium aluminum oxynitride (MgAlON) and the influence of reaction variables, such as heating temperature, soaking time and the source of carbon, on the formation of MgAlON was investigated. In addition, the density of samples prepared under different route was compared. The results show that volatile gases, Mg (g) in chief, lead to variation in lattice constant and chemical composition at high temperature, and decrease the sintering effect. Since high temperature and low CO partial pressure are favorable to the CRN reaction in view of thermodynamic reason and high temperature also favors the transport of gases, the rate of CRN reaction increases with the increasing temperature. Due to the difference in reactivity between graphite and carbon black, CRN reaction may be the rate controlling step when graphite is used and solid solution of AlN may be the controlling step when carbon black is utilized. CRN reaction can increase surface energy of reaction materials and results in higher final density. However, gases in the system retard the densification effect.

Key-words: Carbothermal reduction and nitridation (CRN), Magnesium aluminum oxynitride (MgAlON), Synthesis

1. Introduction

Magnesium aluminum oxynitride (MgAlON) is a cubic solid solution crystal material with excellent optical and mechanical properties and attracts lots of researchers’ interest after the introduction of Jack. Moreover, MgAlON and its oxidized material, magnesium aluminate spinel (MgAlO$_2$), and Al$_2$O$_3$ has high melting point and nitrogen in the material can increase the viscosity of slag to retard the further corrosion, respectively. It can be considered as a promising superior refractory. To prepare this material, the following synthesis methods were utilized: (1) solid phase reaction of AlN, Al$_2$O$_3$ and MgO; (2) reaction of Al, Al$_2$O$_3$ and MgO; (3) carbothermal reduction and nitridation (CRN) of Carbon, Al$_2$O$_3$ and MgO.

The MgAlON formation mechanism through solid phase reaction has been well investigated. MgO reacts with Al$_2$O$_3$ to form MgAlO$_{2n}$ above 1000°C. At higher temperatures, AlN and Al$_2$O$_3$ dissolve into MgAlO$_{2n}$ to form MgAlON. The maximal amount of AlN and Al$_2$O$_3$ dissolved into MgAlO$_{2n}$ increases with the increasing heating temperature and N diffusion is considered to be the rate controlling of MgAlON formation.

From the viewpoint of the purity of product, preparation of the raw materials and potential for large-scale production, the CRN process is considered to have advantages. However, the synthetic process and other details on preparing MgAlON through CRN were seldom discussed except for few reports proposed that AlON, prepared through CRN process, could be stabilized at low temperature by adding MgO or MgAlO$_{2n}$.

Since density is probably the most important parameter in the study of sintering and it relates to the sintering kinetics and correlates with many properties of sintering materials, the sintering characteristics of various routes could be surveyed by the comparison of the density of samples heated at the same condition.

In present investigation, CRN process was utilized to prepare MgAlON and the influence of reaction variables, such as heating temperature, soaking time and the source of carbon, on the formation of MgAlON was investigated. Moreover, density of the samples prepared by different route was compared. Based on the results, evaporation of MgAlON was analyzed, MgAlON formation mechanism through CRN process was discussed, and sintering characteristics of CRN process were surveyed.

2. Experimental procedure

2.1 Starting materials and synthesis procedure

Table 1 gives information about the starting materials used in present investigation. According to Table 2, the raw materials were meticulous weighted and then mixed by ball milling with alumina balls in ethyl alcohol. After evaporating the solvent in vacuum rotary, the mixtures were uniaxial pressed under 150 MPa. As described in Table 2, the green compacts were heated in a graphite furnace under various conditions. Gas pressure of the furnace was constant at 0.1 MPa and flow rate of N$_2$ gas (purity $>$ 99.999%) was 1 L·min$^{-1}$.

2.2 Characterization

In present work, Bulk density and apparent porosity were measured by SGM-6 automatic gravimeter, true density was analyzed by IONICS multi pycnometer, and specific surface area was tested by IONICS monosorb. The phase composition...
was identified by RINT2200 X-ray diffraction (XRD) and the relative intensity of the random $i$ phase ($R_i$) was calculated according to the following equation,

$$R_i = \frac{I_i}{I_1 + I_2 + \ldots + I_i + \ldots} \times 100\%$$

where the subscripts represent the detected phases, $I_i$ is the intensity of the strongest peak of $i$ phase.

To analyze formation process in quantity, chemical composition of intermediate product should be concerned. However, it is difficult to determine composition of MgAl$_2$O$_4$ss and MgAlION only by chemical analysis when Al$_2$O$_3$ exists in the sample. In present work, chemical composition of MgAl$_2$O$_4$ss and MgAlION is calculated by the combination of chemical composition and lattice constant. As lattice constant of MgAl$_2$O$_4$ss and MgAlION, designated as $a_{\text{MgAl}_2\text{O}_4\text{ss}}$ and $a_{\text{MgAlION}}$, can be calculated through the following equations,

$$a_{\text{MgAl}_2\text{O}_4\text{ss}} = a_{\text{Mg}_3\text{Al}_2\text{O}_6} = 0.7900 \text{ nm}$$

$$a_{\text{MgAlION}} = a_{\text{MgAlION}} = 0.7900 \text{ nm}$$

with $[\text{MgO}]$ or $[\text{AlN}]$ in mol% of each component. Chemical composition of MgAl$_2$O$_4$ss could be calculated from Eqs. (4)–(6) on the condition that entire Mg exists in MgAl$_2$O$_4$ss struc-

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<th>Table 1. Some Information of Staring Materials</th>
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<td>M1</td>
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<td>Purity (wt%)</td>
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<td>Particle size (μm)</td>
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<td>Specific surface area (m$^2$/g)</td>
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*1 The materials for chemical analysis were preheated at 1000℃. The ignition loss of M1 and M2 was 3.6% and 8.2%, respectively, and it was considered during the weighting.

*2 Amorphous

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<th>Table 2. Composition of the Compacts in Molar ratio and Heating Conditions</th>
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ture,

\[
[Mg]_{MgAlON}\% = \frac{(\alpha_{MgAlON} - 0.7900) \times 80}{(15 - (\alpha_{MgAlON} - 0.7900) \times 240)} \times 100\% \\
(4)
\]

\[
[Al]_{MgAlON}\% = \frac{6 - (\alpha_{MgAlON} - 0.7900) \times 160}{(15 - (\alpha_{MgAlON} - 0.7900) \times 240)} \times 100\% \\
(5)
\]

\[
[O]_{MgAlON}\% = 1 - [Mg]_{MgAlON}\% - [Al]_{MgAlON}\% \\
(6)
\]

When entire N and Mg exist in MgAlON structure, chemical composition of MgAlON can be figured out in the following equations:

\[
[Mg]_{MgAlON}\% = \frac{(\alpha_{MgAlON} - 0.7900) \times (Mg)_{\%}}{(2.5575 \times (Mg)_{\%} + 2.445 \times (N)_{\%} - \alpha_{MgAlON} \times (Mg)_{\%} + (N)_{\%}) \times 3)} \times 100\% \\
(7)
\]

\[
[Al]_{MgAlON}\% = \frac{(1.655 \times (Mg)_{\%} + 0.82 \times (N)_{\%} - (Mg)_{\%} \times 2 + (N)_{\%} \times \alpha_{MgAlON})}{(2.5575 \times (Mg)_{\%} + 2.445 \times (N)_{\%} - \alpha_{MgAlON} \times (Mg)_{\%} + (N)_{\%}) \times 3)} \times 100\% \\
(8)
\]

\[
[N]_{MgAlON}\% = \frac{(\alpha_{MgAlON} - 0.7900) \times (N)_{\%}}{(2.5575 \times (Mg)_{\%} + 2.445 \times (N)_{\%} - \alpha_{MgAlON} \times (Mg)_{\%} + (N)_{\%}) \times 3)} \times 100\% \\
(9)
\]

\[
[O]_{MgAlON}\% = 1 - [Mg]_{MgAlON}\% - [Al]_{MgAlON}\% \\
- [N]_{MgAlON}\% \\
(10)
\]

where \([Mg], [Al] and [O]_{MgAlON}\% or [Mg], [Al], [O] and [N]_{MgAlON}\% are mol\% of elements in these two phases. \((Mg)_{\%} and (N)_{\%}\) are mol\% of Mg and N in the sintered sample. In present investigation, lattice constant of MgAlO_{4ss} and MgAlON was determined by XRD by using high purity silicon \((\text{purity} > 99.999\text{ mass}\%\) as internal standard material, and the content of Mg and Al was measured by Simultix12 X-ray fluorescence spectroscope (XRFS), O, N by EMGA650 oxygen and nitrogen analyzer, and Carbon by EMIA810 carbon analyzer.

3. Results and discussion

3.1 Influence of heating temperature

The content of residual carbon in the samples of A_1–A_10 is plotted in Fig. 1. At temperatures below 1300°C, the content of residual carbon in these samples \((3.16\text{ mass}\%)\) approximated to that in the raw material \((3.19\text{ mass}\%)\) and when above it, especially above 1400°C, the rate of graphite consumption increased with the increasing temperature.

Figure 2 reveals the relative intensities of detected phases in the samples of A_1–A_{10}. MgO could not be detected in samples even as low as 1100°C, because entire MgO reacted with Al_2O_3 to form MgAlO_{4ss}. In view of lattice constant of MgAlO_{4ss} decreased from 0.8079 nm at 1100°C to 0.8050 nm at 1300°C, as shown in Fig. 3, chemical composition of MgAlO_{4ss} calculated by equations \((4)-(6)\) could be represented as Mg_2Al_8O_{17.76} (1100°C) and MgAl_9O_{22.75} (1300°C) respectively. Since the amount of Al_2O_3 dissolved into MgAlO_{4ss} increased with the increasing temperature and the molar weight of graphite and MgAlO_{4ss} had not obvious change below 1300°C, the relative intensity of Al_2O_3 decreased, while that of graphite and MgAlO_{4ss} increased from 1100°C to 1300°C. By making use of chemical analysis and XRD detection, it was confirmed that MgAlON was formed in the samples heated above 1350°C. Based on the result of lattice constant, as shown in Fig. 3 chemical composition of the synthesized MgAlON could be calculated by Eqs. \((7)-(9)\) and some of them were Mg_2Al_{1.6}O_{22.29}N_{0.00} \((1350°C)\), Mg_2Al_{17.68}O_{29.00}N_{7.6} \((1450°C)\) and Mg_2Al_{27.6}O_{41.4}O_{2.93} \((1600°C)\). When over 1650°C, monophase MgAlON was obtained and chemical composition of these samples was calculated by making use of chemical analysis and these were Mg_2Al_{33.72}O_{46.7}N_{5.12} \((1650°C)\), Mg_2Al_{32.20}O_{47.60}N_{5.11} \((1700°C)\) and Mg_2Al_{32.76}O_{48.44}N_{5.16} \((1800°C)\) respectively. It is indicated that Mg content decreased with the increasing temperature and as a consequence, lattice constant of MgAlON decreased according to equation \((9)\). Through the further discussion in Section 3.5, it is known that volatile gases of MgAlON caused the variation.

3.2 Effect of the soaking time

In the sample of B_1, which was heated at 1500°C for 96 h, AlN, Al_2O_3 and MgAlON were detected and the residual car-
the samples B, relative density was different with the synthesis route. Among less than 0.03 mass \% for different soaking time, the content of residual carbon was 0.11 mass \%. It's composition was close to the sample of B. Evaporation of MgAlON at high temperature leads to it and the decrease caused variation in lattice constant detected and the content of residual carbon was 0.03 mass \% and only MgAlON detected. According to the result of chemical analysis, their chemical composition could be expressed as Mg$_{29.87}$Al$_{32.20}$O$_{47.60}$N$_{47.53}$ (3 h), Mg$_{23.45}$Al$_{30.04}$O$_{25.48}$N$_{29.78}$ (3 h), Mg$_{24}$Al$_{33.55}$O$_{49.53}$N$_{33.51}$ (9 h), respectively.

It implies that Mg content decreased with the soaking time and the decrease caused variation in lattice constant (Fig. 4). Evaporation of MgAlON at high temperature leads to it and the reason was further discussed in Section 3.5.

### 3.3 Effect of the source of carbon
In the sample of C, which was made from carbon black and heated at 1500°C for 96 h, MgO, Al$_2$O$_3$, and AlN, had the highest density. However, due to volatile gases of MgAlON at high temperature, which was discussed in Section 3.5, closed pores were formed in the matrix and full dense samples could not be obtained in present condition without any auxiliary means, such as spark plasma.

**3.4 Density of samples prepared by different route**
In present investigation, all the samples heated at 1700°C for 6 h were monophase MgAlON and the chemical composition was close to each other. However, as shown in Fig. 5, the relative density was different with the synthesis route. Among the samples B$_1$, C$_1$, D, and E, which were made from coarser MgO and Al$_2$O$_3$, the sample of B$_1$, which was made from graphite by CRN process, had the highest density and that of C$_1$, which was made from carbon black, was the most porous one. As to the samples made from finer MgO and Al$_2$O$_3$ (F, G, H, and J), the density was much higher than that of samples made from coarser materials. The density of samples F and G, which was prepared by CRN process, was lower than that of others and the sample of H, which was made from MgO, had the highest density and that of others and the sample of H, which was made from MgO, Al$_2$O$_3$, and AlN, had the highest density. However, due to volatile gases of MgAlON at high temperature, which was discussed in Section 3.5, closed pores were formed in the matrix and full dense samples could not be obtained in present condition without any auxiliary means, such as spark plasma.

**3.5 Evaporation of MgAlON**
Based on the thermodynamics data,$^{5,6,11}$ equilibrium partial pressure of gases of Mg$_{23}$Al$_{33}$O$_{49}$N$_{33}$ at 1727°C in nitrogen atmosphere are calculated and plotted in Fig. 6. These gases, Mg (g) in chief, may be entrained by the flowing nitrogen gas and then evaporation occurs at high temperature. In this way, as mention in Sections 3.1 and 3.2, Mg content in the sample decreased and lattice constant was also decreased according to Eq. (3). Moreover, the volatile gases lead to closed pores formed in the matrix and it is difficult to obtain full dense MgAlON sample in present condition without any auxiliary means, such as spark plasma.$^{4}$

**3.6 MgAlON formation mechanism by CRN process**
As mentioned in Section 3.1, entire MgO react with Al$_2$O$_3$ to form MgAl$_2$O$_4$ below 1100°C. The reaction is considered as the first step and similar to solid phase reaction system. In the CRN process, it is certain that nitride, AlN, must be provided before its solid solution reaction. Hence, in the second step, AlN supplies by the following overall reaction.

$$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{AlN} + 3\text{CO} \quad \text{(11)}$$

Figure 7 shows the equilibrium partial pressure of CO of
The process of carbothermal reduction and nitridation (CRN) on the synthesis of magnesium aluminum oxynitride (MgAlON) was investigated in present investigation. Being the volatile gases of MgAlON, Mg (g) in chief, there was variation in lattice constant and chemical composition at high temperature. In addition, these gases resulted in closed pores formed in the matrix and decreased the density of sample. Considering that high temperature and low CO partial pressure are favorable to the CRN reaction in view of thermodynamics reason and high temperature also favors the transport of gases, increasing the heating temperature is an efficient means to increase CRN reaction rate. Because of the difference in reactivity between graphite and carbon black, CRN reaction was the rate controlling step when graphite was used and solid solution of AlN was the controlling step when carbon black was utilized. CRN reaction could increase surface energy and lead to higher final density. However, gases in the system tended to decrease the final density.

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References