Oxidation kinetics of magnesium aluminum oxynitride–boron nitride (MgAlON–BN) composites

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The oxidation behaviour of MgAlON–BN composite was investigated under the air atmosphere using thermogravimetry (TG), scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques in the present articles. Non-isothermal experimental results indicated that the rate of oxidation can be neglected at low temperature and, with further increasing temperatures, an increase of the oxidation was observed. While BN addition promoted the oxidation above 1100 K, and the weight gain was observed to decrease due to the fast evaporation of boron oxide as the temperature was beyond 1580 K. Isothermal studies also clearly indicated the decrease of weight gain due to evaporation after a certain oxidation time. The oxidation mechanism was investigated, and the results showed the oxidation products were γ-Al2O3 at low temperature and transformed to α-Al2O3 as the temperature was above 1100°C. BN addition promoted the transformation from γ-Al2O3 to α-Al2O3. From the isothermal oxidations, the kinetics of oxidation and evaporation were evaluated, and the overall kinetics of oxidation and evaporation were studied, and the activation energy for evaporation of B2O3 and for the oxidation of MgAlON was above 1100°C. BN addition promoted the transformation from silicon.4) Magnesium aluminum oxynitride (MgAlON) has been necessary to develop some oxynitride that does not contain the pose by the dissolution of silicon into molten steel, it is therefore quite attractive as a high-performance ceramic material in view of their unique combination of high hot strength, high thermal shock resistance and high corrosion resistance,1) in view of their unique combination of high hot strength, high thermal shock resistance and high corrosion resistance.3–5) However, some nitride or oxynitride containing silicon may decompose by the dissolution of silicon into molten steel, it is therefore necessary to develop some oxynitride that does not contain the silicon.3–5) Magnesium aluminum oxynitride (MgAlON) has been quite attractive as a high-performance ceramic material in view of its promising optical, mechanical and chemical properties, thus having the potential as a superior ceramic material at high temperature.3–5) A number of investigations have shown that graphite-based refractories incorporating some MgAlON could improve the resistance to slag and steel corrosion.10,11) This indicates that MgAlON can be expected find application as high performance refractories. To use ceramics as high performance refractories, it is necessary to give a high durability for thermal shock and erosion, together with appropriate strength and toughness. In general, to improve the thermal shock resistance, materials need to have high thermal conductivity and low thermal expansion coefficient. Hexagonal boron nitride (h-BN) which demonstrates excellent thermal shock resistance and machinability may fulfil above-mentioned requirements in addition to its non-reactive nature.12,13) These indicate that BN is a suitable candidate in developing a material with high resistance to oxidation and chemical attack as well as high thermal shock resistance by incorporation into other materials. Thus, MgAlON–BN composites are expected to find application in special refractory components.1,2) The present paper provides a way to deal with oxidation of composites containing evaporating component.

Key-words : Magnesium aluminum oxynitride, Boron nitride, Thermogravimetry, Oxidation, Activation energy

1. Introduction

Nitride and oxynitride are widely used as refractory materials in view of their unique combination of high hot strength, high thermal shock resistance and high corrosion resistance.1–3) However, some nitride or oxynitride containing silicon may decompose by the dissolution of silicon into molten steel, it is therefore necessary to develop some oxynitride that does not contain the silicon.1–3) Magnesium aluminum oxynitride (MgAlON) has been quite attractive as a high-performance ceramic material in view of its promising optical, mechanical and chemical properties, thus having the potential as a superior ceramic material at high temperature.1–3) A number of investigations have shown that graphite-based refractories incorporating some MgAlON could improve the resistance to slag and steel corrosion.4,5) This indicates that MgAlON can be expected find application as high performance refractories. To use ceramics as high performance refractories, it is necessary to give a high durability for thermal shock and erosion, together with appropriate strength and toughness. In general, to improve the thermal shock resistance, materials need to have high thermal conductivity and low thermal expansion coefficient. Hexagonal boron nitride (h-BN) which demonstrates excellent thermal shock resistance and machinability may fulfil above-mentioned requirements in addition to its non-reactive nature.6–9) These indicate that BN is a suitable candidate in developing a material with high resistance to oxidation and chemical attack as well as high thermal shock resistance by incorporation into other materials. Thus, MgAlON–BN composites are expected to find application in special refractory components.1,2) The present paper provides a way to deal with oxidation of composites containing evaporating component.

2. Experimental procedure

2.1 Materials

Single phase MgAlON samples were prepared by mixing Al2O3, AlN and MgO powders. Based on previous works, a mixture with a molar ratio of Al2O3/AlN/MgO = 7/2/1 was...
selected to synthesize MgAlON.\textsuperscript{8,9} Then, BN was added into the mixture to obtain the MgAlON–15 vol.% BN composite. The weighed powders were mixed by a ball mill and using an ethanol medium for 12 h and then dried. The mixtures were prepared into cylindrical compacts. These cylindrical compacts, covered with boron nitride, were hot-pressed at 1800°C under 20 MPa for 2 h. X-ray diffraction analysis of the sample was carried out to confirm the formation of the MgAlON–15 vol.% BN composite, as shown in Fig. 1. Pieces with the size of an approximate 20\*6\*1 mm\(^3\) were used for the oxidation experiments, which were carefully polished with diamond grains down to a size <1 \(\mu\)m. Before oxidation, the samples were cleaned with toluene and acetone, and then dried at 110°C for 10 h.

During the oxidation experiments, argon gas was used to protect the system from oxidation. The argon gas was purified by passing through columns of silica gel and dehydrate \([\text{Mg(ClO}_4\text{)}_2]\) to remove moisture, through ascarite to remove carbon dioxide, and through tube furnaces containing copper and magnesium at 773 and 673 K respectively to remove residual oxygen. It was shown that the gas after purification had an oxygen partial pressure less than \(10^{-13}\) Pa as measured by a calcia-stabilized zirconia galvanic cell mounted in the exit gas route.\textsuperscript{8,9} The air was used as the oxidation atmosphere, which was passed through silica gel and dehydrate to remove the moisture and through ascarite to remove carbon dioxide.

### 2.2 Apparatus and procedure

The oxidation experiments were carried out in a SETARAM TGA 92 (France), as shown in Fig. 2, which had a detection limit of 1 \(\mu\)g. The system was controlled by an IBM PC\textsuperscript{8} through a CS92 controller. The plate samples were suspended in the even temperature zone of the furnace by Pt wire. During the non-isothermal oxidation experiments, the reaction tube was first evacuated for 5 min, and then filled with air atmosphere at a fixed flow rate above the starvation rate. The furnace was then heated from room temperature to a given temperature at a fixed heating rate of 20 K/min. Different oxidation temperatures were adopted according to the non-isothermal oxidation results. The furnace was heated up to the presetted oxidation temperature in an argon atmosphere, and kept stable for 5 min; argon gas was replaced with air gas. At the end of the oxidation experiment, air atmosphere was replaced by argon gas to restrain the reaction.

The oxidized surfaces of plate samples after oxidation were analysed by X-ray diffraction (XRD) to determine the oxidation products. The cross sections of plate samples after oxidation were examined using Scanning Electron Microscopic (SEM) detection.

### 3. Results and discussions

#### 3.1 Nonisothermal oxidation of composites

In order to confirm the oxidation characteristics and choose the oxidation temperature range, non-isothermal experiments were carried out under the air atmosphere. Figure 3 shows the oxidation curves of MgAlON as well as MgAlON–15 vol.% BN composite plate. For MgAlON sample, the oxidation can be negligible under 1250 K, then the weight gain increases with increasing oxidation temperature. While for MgAlON–15 vol.% BN composite, the non-isothermal oxidation showed different behaviours. It can be seen from the curve, the oxidation of MgAlON–15 vol.% BN composite plate was found to be initiated at about 1100 K and the weight gain increased with increasing temperature. With further increasing temperature, the weight gain started decreasing at about 1580 K. The occurrences of the decreasing weight gain seem to be due to the evaporation of boron oxide. Initially, MgAlON and BN were oxidized to form the oxides and the evaporation rate was relatively slow at low temperatures, resulting in the increase of weight gain. With the oxidation proceeding, an oxidation layer was formed and the oxidation rate was correspondingly decreased due to the
oxidation layer formation. While, the evaporation rate of boron oxide increased with increasing temperature, which led to the decrease of weight gain at 1580 K.

3.2 Isothermal Oxidation of the Composites
Considering the non-isothermal oxidation results, the isothermal oxidation experiment was carried out in the temperature of 1273 to 1573 K. The isothermal oxidation results are shown in Fig. 4. From the Fig. 4(a), the oxidation rate of MgAlON increased quickly with increasing oxidation temperature, while the oxidation rate decreased at a long time intervals due to the formation of oxidation layer, indicating the significant effect of the mass transfer behaviour suppressing the reaction. Figure 4(b) shows the isothermal oxidation curves of MgAlON–15 vol.% BN composite plates. It is seen that the reactions can be divided into two stages, the weight gain increases with increasing oxidation time, and then the weight gain started decreasing with further increasing oxidation time. It is also noted that the transiting time decreases with increasing oxidation temperature. The reason caused may be because that the evaporation rate of boron oxide is very low at low temperatures, resulting in the weight gain by the oxidation dominate the overall reactions. With increasing oxidation temperatures, both the oxidation and evaporation rates increases but the evaporation rate dominate the reactions at later stages of oxidation, resulting in the decrease of weight gain. It is also noted that the oxidation curves show a linear relation with time at the later stage of reactions. The reason will be discussed in the following sections.

3.3 Oxidation product analyzed by XRD and SEM
In order to determine the product of oxidation, XRD analyses of the samples MgAlON and MgAlON–15 vol.% BN composite after oxidation were carried out, as shown in Fig. 5. It can be seen that the oxidation products are dependent on the oxidation temperatures according to XRD patterns. At lower temperature, such as 1100°C, after oxidation for 2 h, XRD results showed that the oxidation products of MgAlON were composed of spinel or $\gamma$-Al$_2$O$_3$, and no $\alpha$-Al$_2$O$_3$ was observed. It should be pointed out that the XRD patterns among $\gamma$-Al$_2$O$_3$, MgAl$_2$O$_4$ and MgAlON are very similar, it is hard to distinguish them through XRD peaks. With increasing oxidation temperature, the $\alpha$-Al$_2$O$_3$ was formed. This is consistent with the reported result that the MgAlON was oxidized to form spinel and $\gamma$-Al$_2$O$_3$ when the oxidation temperature is lower than 1200°C, and the oxidation products are spinel and $\alpha$-Al$_2$O$_3$ when the oxidation temperature is higher than 1200°C.$^{21}$ The addition of BN promoted the oxidation, and the (Al$_2$O$_3$)$_9$(B$_2$O$_3$)$_2$ was found at 1100°C [Fig. 5(b)], and $\gamma$-Al$_2$O$_3$ and spinel were also found at higher oxidation temperature, such as 1300°C, due to kinetic condition. After the oxidation, the cross sections of oxidized plates were examined by SEM, as shown in Fig. 6. It can be seen that the product layer was very dense without any cracks when the temperature was 1100°C [Fig. 6(a)], this is
because that the density of MgAlON is very similar with γ-Al2O3 and MgAl2O4. With increasing oxidation temperature, some cracks were observed due to the formation of θ-Al2O3 with high density. The thickness of oxidation layers are around 5 and 12 micros for MgAlON and MgAlON–BN composites, respectively.

3.4 Kinetics of Oxidation

General speaking, the oxidation of MgAlON–BN composite is a complicated process, which is involved with two steps, the oxidation of MgAlON as well as the oxidation of BN. As aforementioned, MgAlON was oxidized to form γ-Al2O3 and spinel when the oxidation temperature is lower than 1200°C, and the oxidation reaction can be described as follows,

\[
\text{MgAl}_{16}O_{22}N_2(s) + 1.5O_2(g) = 7\gamma - Al_2O_3(s) + MgAl_2O_4(s) + N_2(g) \quad T \leq 1200 ^\circ C \quad (1)
\]

With further increasing temperature, the oxidation products are composed of α-Al2O3 and spinel, and under this conditions the oxidation reaction was shown as,

\[
\text{MgAl}_{16}O_{22}N_2(s) + 1.5O_2(g) = 7\alpha - Al_2O_3(s) + MgAl_2O_4(s) + N_2(g) \quad T \geq 1200 ^\circ C \quad (2)
\]

In the case of MgAlON–15 vol%BN oxidation, BN will be oxidized as,

\[
\frac{4}{3} \text{BN(s)} + \frac{2}{3} O_2(g) = \frac{2}{3} \text{B}_2\text{O}_3(l) + \frac{2}{3} N_2(g) \quad (3)
\]

The BN was initially oxidized as B2O3 as a primary phase. It should be pointed out that B2O3 is a liquid phase at about 650°C, which may evaporate at the elevated temperatures. And some B2O3 may react with the formed Al2O3 to form 9Al2O3·2B2O3 compound.22)

When MgAlON or MgAlON–BN composite are exposed to the oxygen containing atmosphere at elevated temperature, it may be oxidized. The overall process involves mass transfer of oxygen from bulk gas to the composite surface, dissociation of oxygen as well as the inward diffusion of oxygen or outward diffusion element through oxide layer. Thus, the oxidation rate-limiting step may be one of these steps.

1. Oxygen transfer from the bulk of gas flow through gas–solid boundary layer to the sample surface,
2. Oxygen transfer from the surface to the interface by diffusion through the product layer,
3. Oxygen reacts with MgAlON or BN to produce oxides and nitrogen,
4. Nitrogen transfer from interface to the sample surface,
5. Nitrogen transfer from surface of sample through gas–solid boundary layer to the gas flow.

As mentioned earlier, the experiments were conducted at the flow rates higher than the starvation rate for the reaction. Hence, under the present experimental conditions, the reaction step (1), viz. the oxygen transfer from the bulk gas flow may be fast and is not likely to influence the reaction rate. During the proceeding oxidation of MgAlON and BN, the sample will have a weight gain, while the evaporation of B2O3 resulted in the weight loss.

Initially, oxidation of MgAlON or MgAlON–BN plate would occur on the surface, and the thickness of oxidation layer can be negligible. Therefore, the reaction rate in the case of chemical reaction can be expressed as,17,18)
\[
\frac{\Delta W_{\text{Init}}}{A_0} = k_{\text{Init}} \cdot t
\]  \hspace{1cm} (4)

Where \(\Delta W_{\text{Init}}\) is the weight change due to the oxidation at the initial stage, \(A_0\) is the surface area, \(k_{\text{Init}}\) is the reaction rate constant at the initial stage and \(t\) is the oxidation time. It can be seen from reaction (4), the weight change per unit area shows a linear relationship with oxidation time. Once the oxides are formed, it should consider the evaporation of B\(_2\)O\(_3\) because that B\(_2\)O\(_3\) is the liquid phase at about 723 K and its boiling temperature is 2338 K, and it will evaporate when the oxidation temperature is lower than the boiling temperature.\(^{22}\) It is reasonable to assume that the evaporation rate is constant at the constant temperature and pressure. Thus, the weight loss due to the evaporation of B\(_2\)O\(_3\) can be expressed as,

\[
\frac{\Delta W_{\text{Evap}}}{A_0} = -k_{\text{Evap}} \cdot t
\]  \hspace{1cm} (5)

Where \(\Delta W_{\text{Evap}}\) is the weight change due to evaporation and \(k_{\text{Evap}}\) is the evaporation reaction rate constant. Considering the weight change due to oxidation and evaporation, the overall weight change can be obtained,

\[
\frac{\Delta W_{\text{Ox}}}{A_0} = (k_{\text{Init}} - k_{\text{Evap}}) \cdot t
\]  \hspace{1cm} (6)

Where \(\Delta W_{\text{Ox}}\) is the overall weight change at the initial stage. As the oxidation proceeds, the product layer will become thicker, resulting in the increase of resistance to diffusion of the reactant and product gases through the oxidation layer. After some time interval, diffusion through the product layer becomes the rate-controlling step. The weight change due to oxidation can be expressed as,\(^{17,18}\)

\[
\frac{\Delta W_{\text{Flat}}}{A_0} = k_{\text{Flat}} \cdot t^2
\]  \hspace{1cm} (7)

Where \(\Delta W_{\text{Flat}}\) is the weight change due to the oxidation at the later stage, \(A_0\) is the surface area, \(k_{\text{Flat}}\) is the reaction rate constant at the later stage and \(t\) is the oxidation time. Considering the evaporation of B\(_2\)O\(_3\), the overall weight change is shown as follows,

\[
\frac{\Delta W_{\text{Fr}}}{A_0} = k_{\text{Flat}} \cdot t^2 - k_{\text{Evap}} \cdot t
\]  \hspace{1cm} (8)

Where \(\Delta W_{\text{Fr}}\) is the overall weight change at later stage. Derivation of Eq. (8), the following equation can be obtained,

\[
\left(\frac{\Delta W_{\text{Flat}}}{A_0}\right)' = k_0 - \frac{k_{\text{Evap}}}{2\sqrt{t}}
\]  \hspace{1cm} (9)

As Eq. (9) is equal 0, the isothermal weight change would show the maximum value. Assuming the oxidation time is long enough, the following equation can be approximately obtained.

\[
\left(\frac{\Delta W_{\text{Flat}}}{A_0}\right)' = -k_{\text{Evap}}
\]  \hspace{1cm} (10)

According to Eq. (10), the oxidation rate for a long time can be approximately obtained as,

\[
\frac{\Delta W_{\text{Flat}}}{A_0} = -k_{\text{Evap}} \cdot t
\]  \hspace{1cm} (11)

It can be seen from Eq. (11), the overall weight gain is approximately equal the evaporation rate caused by the evaporation, i.e., the overall weight gain is linear with oxidation time for a long time. This is consistent with the TG curves shown in Fig. 4(b). Therefore, \(k_{\text{Evap}}\) can be attained from the slope of oxidation curves after a long time interval at different temperatures. Thus, the weight gain by oxidation can be re-calculated at different temperatures and the results are shown in Fig. 7.

According to the results from Fig. 4 and Eq. (4), the reaction rate constant at the initial stage, \(k_{\text{Init}}\) was obtained, and the activation energy for pure MgAlON can be therefore calculated as 94.1 kJ/mol. Assuming the evaporation rate is small initially, the activation energy for MgAlON–15 vol%BN composite was thus calculated as 170.4 kJ/mol at initial stage. The difference may be caused by the effect of BN addition and evaporation of boron oxides.

After a long time interval, diffusion was the reaction limited-step, and the evaporation rate was equal with the overall weight gain at this stage, the activation energy for evaporation was therefore obtained as 115.4 kJ/mol. The activation energy for MgAlON–15 vol%BN at this stage based on Fig. 7 was also calculated as 196.1 kJ/mol.

4. Conclusions

(1) At lower temperatures, MgAlON and MgAlON–15 vol%BN composite show the good resistance to oxidation. But at higher oxidation temperatures, MgAlON shows good resistance to oxidation, and the addition of BN promote the oxidation.

(2) The results showed that the reaction rate was likely to be chemically controlled in the initial stages and the diffusion was the controlling step after a long time interval due to the formation of thickness of oxidation layer.

(3) The oxidation products were determined by XRD, and the results indicated that the oxidation products of MgAlON at 1100 and 1200°C consist of γ-Al\(_2\)O\(_3\) and spinel, while γ-Al\(_2\)O\(_3\) transformed to α-Al\(_2\)O\(_3\) at 1300°C. The activation energy for evaporation of B\(_2\)O\(_3\) and for the oxidation of MgAlON–15 vol%BN at the later stage are 115.4 and 196.1 kJ/mol, respectively.

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