In situ reaction mechanism of MgAlON in Al–Al₂O₃–MgO composites at 1700°C under flowing N₂

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(Received: 9 December 2016; revised: 6 April 2017; accepted: 10 April 2017)

Abstract: The Al–Al₂O₃–MgO composites with added aluminum contents of approximately 0wt%, 5wt%, and 10wt%, named as M₁, M₂, and M₃, respectively, were prepared at 1700°C for 5 h under a flowing N₂ atmosphere using the reaction sintering method. After sintering, the Al–Al₂O₃–MgO composites were characterized and analyzed by X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The results show that specimen M₁ was composed of MgO and MgAl₂O₄. Compared with specimen M₁, specimens M₂ and M₃ possessed MgAlON, and its production increased with increasing aluminum addition. Under an N₂ atmosphere, MgO, Al₂O₃, and Al in the matrix of specimens M₂ and M₃ reacted to form MgAlON and AlN-polytypoids, which combined the particles and the matrix together and imparted the Al–Al₂O₃–MgO composites with a dense structure. The mechanism of MgAlON synthesis is described as follows. Under an N₂ atmosphere, the partial pressure of oxygen is quite low; thus, when the Al–Al₂O₃–MgO composites were soaked at 580°C for an extended period, aluminum metal was transformed into AlN. With increasing temperature, Al₂O₃ diffused into AlN crystal lattices and formed AlN-polytypoids; however, MgO reacted with Al₂O₃ to form MgAl₂O₄. When the temperature was greater than (1640 ± 10)°C, AlN diffused into Al₂O₃ and formed spinel-structured AlON. In situ MgAlON was acquired through a solid-solution reaction between AlON and MgAl₂O₄ 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 possess 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 investigate non-oxide–oxide systems without carbon.

In 1959, Yamguchi and Yanagida [10] reported the possibility of a spinel-type phase in the Al₂O₃–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 MgAl2O4 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–Al2O3 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 Al2O3–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, α-Al2O3 micropowder, fused magnesite micropowder, and sintered magnesia powder were used as the raw materials, and thermostetting phenolic resin was used as the binder. The ratio of aggregate to matrix was 65:35, and the formulations of M1, M2, and M3 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 (M1, M2, and M3) 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–Al2O3–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

| Specimen | M1 | M2 | M3 |
|----------|----|----|----|
| Fused magnesite particles | 5–3 mm | 5 | 5 | 5 |
| Tabular alumina | 1–0 mm | 6 | 6 | 6 |
| α-Al2O3 micropowder | ≤5 μm | 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 M1, M2, and M3

| Specimen | Al2O3 | AlN | MgO |
|----------|-------|-----|-----|
| M1 | 0.12 | 0 | 0.88 |
| M2 | 0.11 | 0.17 | 0.72 |
| M3 | 0.10 | 0.33 | 0.57 |

Table 3. Particle size and chemical composition of raw materials

| Raw material | Particle size | Chemical composition / wt% |
|--------------|--------------|---------------------------|
| Fused magnesite | ≤48 μm | MgO: 97.5, Al2O3: —, Al: —, SiO2: —, CaO: —, Fe2O3: —, K2O: —, Na2O: — |
| α-Al2O3 micropowder | ≤5 μm | MgO: —, Al2O3: 99.40, Al: —, SiO2: —, CaO: 0.19, Fe2O3: —, K2O: 0.02, Na2O: 0.04 |
| Tabular alumina | 1–0 mm | MgO: —, Al2O3: —, Al: 99.50, SiO2: —, CaO: —, Fe2O3: 0.05, K2O: —, Na2O: 0.06 |
| Metal aluminum powder | 325 mesh | MgO: —, Al2O3: —, Al: 99.3, SiO2: —, CaO: —, Fe2O3: —, K2O: —, Na2O: — |
| Sintered high-purity magnesia | 200 mesh | MgO: 97.8, Al2O3: —, Al: —, SiO2: 0.50, CaO: 1.34, Fe2O3: —, K2O: —, Na2O: — |

3. Results and discussion

3.1. Phase composition

Fig. 1 shows the XRD patterns of specimens M1, M2, and M3 after firing. As observed in Fig. 1, specimen M1 is composed of MgO and spinel, whereas specimens M2 and M3 consist of MgO, AlN-polytypoids (Al2O3N6 and Al10N2O), 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 M₁, those in the XRD patterns of specimens M₂ and M₃ shift toward larger angles and their diffraction intensity increases with increasing aluminum addition. Therefore, the spinel phase in specimens M₂ and M₃ 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 MgAl₂O₄ and its diffraction peaks shift toward those of MgAl₂O₄. 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 M₂ and M₃ are completely nitridized into AlN, which then further reacts with Al₂O₃ and MgO to form MgAlON and AlN-polytypoids (containing some MgO) after being soaked at 580°C and fired at 1700°C.

Table 4 shows the EDS results of the matrix in specimens M₁, M₂, and M₃. These results indicate that specimen M₁ is composed of Mg, Al, and O, whereas specimens M₂ and M₃ 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 Al₂O₃ in the matrix of specimen M₁ diffuse and migrate into each other, react, and form MgAl₂O₄. By contrast, when aluminum is added, MgO and Al₂O₃ in the matrix of specimens M₂ and M₃ 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 M₃ 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), Al₂O(g), or Al₂O₃ 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–Al₂O₃–MgO system transforms to an AlN–Al₂O₃–MgO system. As temperature rises, Al₂O₃ diffuses and migrates into AlN crystal lattices, forming AlN-polytypoids such as 12H, 21R, and 27R [26]. The reaction equation can be expressed as \(\text{AlN} \rightarrow 2\text{Al}_3\text{O}_3 + 3\text{ON}^- + V_{\text{Al}}^-\) (\(V_{\text{Al}}^-\) represents 1 negative charge). When the temperature rises higher, AlN diffuses and migrates into Al₂O₃, forming \(\gamma\)-AlON; the reaction equation in this case is expressed as \(\gamma\)-AlON. The chemical formula of \(\gamma\)-AlON is \(\text{Al}_{6+x}(\text{VA})_{8-x}\text{O}_{32-},\text{N}_x\), where \(\text{VA}\) is a cation vacancy in the spinel structure, \(0 \leq x \leq 8\) [27–28]. Nonetheless, as the temperature increases, because \(\text{Al}_2\text{O}_3 + \text{MgO} = \text{MgAl}_2\text{O}_4\), \(\Delta G = -23604 - 5.91T\), \(\Delta G < 0\), MgO reacts with Al₂O₃, forming MgAl₂O₄; thus, under increasing tem-
perature, the MgAl₂O₄ spinel content increases. The γ-Al₂O₃ and MgAl₂O₄ are both oxide spinels. At high temperatures, they can solid-solve together, forming a new spinel phase, MgAlON [29]. Thus, when the AlN–Al₂O₃–MgO system is soaked at 580°C and fired at 1700°C, Al₂O₃ reacts with AlN or MgO to form AlN-polytypoids, γ-Al₂O₃, or MgAl₂O₄. The formed γ-Al₂O₃ and MgAl₂O₄ 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°C. At higher temperatures, Al(s) transforms into Al(g) and Al₂O(g) and escapes.

Fig. 3. SEM images of specimens M₁, M₂, and M₃: (a) (b) SEM images of M₁; (c) (d) SEM images of M₂; (e) (f) SEM images of M₃.
4. Conclusions

In this work, Al–Al$_2$O$_3$–MgO composites (MgAlON as a bonding phase) were prepared at 1700°C for 5 h under a nitrogen atmosphere using fused magnesia, α-Al$_2$O$_3$, 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$_1$ was composed of MgO and MgAl$_2$O$_4$. Compared with specimen M$_1$, specimens M$_2$ and M$_3$ contained MgAlON, whose content increased with increasing aluminum addition.

(2) Under a nitrogen atmosphere, MgO, Al$_2$O$_3$, and Al in the matrix of specimens M$_2$ and M$_3$ 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$_2$ atmosphere, the partial pressure of oxygen is quite low; thus, when the Al–Al$_2$O$_3$–MgO system was soaked at 580°C for an extended period, aluminum metal was transformed into AlN. With increasing temperature, Al$_2$O$_3$ diffused into AlN crystal lattices and formed AlN-polytypoids; by contrast, MgO reacted with Al$_2$O$_3$ to form MgAl$_2$O$_4$. When the temperature was greater than (1640 ± 10)°C, AlN diffused into Al$_2$O$_3$ and formed spinel-structured AlON. In situ MgAlON was then acquired through a solid-solution reaction between AlON and MgAl$_2$O$_4$ at high temperatures because of their similar spinel structures.

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