In-Situ Synthesis and Formation Mechanism of Al₂O₃-Spinel(N) Composite in Nitrogen Atmosphere under Low Oxygen Partial Pressure

S. Tong[1], Y. Li[*1], J. Zhao[2], M. Yan[1], Y. Hong[1], Q. Zheng[1]

[1]School of Materials Science and Engineering, University of
Science and Technology Beijing, Beijing 100083, China
[2]Beijing Lier High-Temperature Materials Co., Ltd., Beijing 102200, China

Abstract

Al₂O₃-spinel-containing nitrogen element composite, abbreviated as Al₂O₃-spinel(N) composite, was prepared using white corundum, sintered magnesia and active α-Al₂O₃ powder as raw materials, with magnesium aluminate sol as a binder, and fired at 1600 °C for 4 h in a nitrogen atmosphere with low oxygen partial pressure. The prepared Al₂O₃-spinel(N) composite was characterized and analyzed by means of XRD, SEM, and EDS and the mechanism for the formation of the spinel(N) was further investigated. The results show that in nitrogen atmosphere with low oxygen partial pressure, Al₂O₃-spinel(N) composite is composed of alumina, spinel-containing nitrogen element and a little aluminum nitride; the spinel-containing nitrogen bonds the aggregates and matrix together, further realizing dense sintering of the Al₂O₃-spinel(N) composite. The mechanism for formation of the spinel(N) can be described as follows: in nitrogen atmosphere with low oxygen partial pressure, magnesia is unstable and decomposes into Mg(g). Mg(g) diffuses and transfers along the pores or gaps in Al₂O₃-MgO composites and reacts with corundum or spinel, forming gas aluminum at the same time. The gas metal aluminum then nitrides into aluminum nitride. The formed aluminum nitride further solid-solves into spinel, forming the spinel-containing nitrogen element.

Keywords: Magnesia aggregates, low oxygen partial pressure, Mg(g), spinel

I. Introduction

Magnesium aluminate spinel (MgAl₂O₄) is the only stable ternary compound in the MgO-Al₂O₃ binary system [1]. It has a high melting point (2135 °C), a low thermal expansion coefficient ($7.6 \times 10^{-6} K^{-1}$), good hot mechanical properties and excellent resistance to slag corrosion and penetration [1–4]. It is thus widely applied in high-temperature industries such as ceramics and refractories. In the refractories industry, MgAl₂O₄ has a large number of tetrahedron octahedron vacancies which can accommodate many oxides such as FeO, MnO, MgO and Al₂O₃ to form spinel solid solution, endowing MgO-Al₂O₃ materials with good corrosion resistance against steel melt [5–8]. Compared with pure alumina refractories, Al₂O₃-MgAl₂O₄-based materials exhibit better resistance against alkali and basic slag, which means less alkali slag and basic slag penetration and corrosion [9–11].

Refractories are composed of aggregates and matrix. Uniform distribution of aggregates and matrix is hard to achieve with mechanical mixing. It is therefore difficult to combine either the pre-synthesized spinel or the *in-situ*-formed spinel from MgO and Al₂O₃ in the matrix with the Al₂O₃ particles based on diffusion reactions and thereby further improve the slag resistance and slag penetration resistance of the material. Considering that in N₂ atmosphere with low oxygen partial pressure, MgO may transform into MgO(g) or Mg(g), the uniform distribution of spinel may be realized based on gas transfer of MgO(g) or Mg(g) [12–16]. The residual magnesia particles are minimized or even eliminated, avoiding the poor slag resistance caused by incomplete warping of alumina particles. Therefore, in this work, using fused corundum aggregates and powder, sintered magnesia aggregates and powder, and active alumina as starting materials, based on the solid-solid reaction between MgO and Al₂O₃ as well as the gas-solid reaction between Mg(g) and Al₂O₃, Al₂O₃-spinel-containing nitrogen refractories were prepared in nitrogen atmosphere with low oxygen partial pressure at 1600 °C, with the aim of realizing a close combination of the matrix and Al₂O₃ aggregates. In addition, the prepared specimens were characterized and analyzed by means of XRD, SEM and EDS, and the mechanism for the formation of the spinel-containing nitrogen element in low oxygen partial pressure was investigated.

II. Experimental

In this work, fused corundum aggregates and powder (Xingyang Jinbo Refractory Abrasive Co. Ltd., China, 99.5 % purity), sintered magnesia aggregates and powder (Beijing Lier High-Temperature Materials Co., Ltd.,

China, 97.8 % purity), active alumina (Shandong Aopeng New Materials Technology Co., Ltd., China, 99.4% purity) were adopted as the main raw materials, batched according to Table 1, mixed for 30 min, and pressed into specimens (40 mm × 40 mm × 120 mm) under 300 MPa. The green specimens underwent different heat treatment: one specimen was fired in a corundum pipe heater at 1600 °C for 4 h in air, this is denoted specimen A_0; another specimen was placed in a covered graphite crucible and fired in a corundum pipe heater at 1600 °C for 4 h in N_2 atmosphere with low oxygen pressure, this is denoted specimen A_1; the N_2 flow used had a pressure of 0.1 MPa, a purity of 99.99 vol% and an oxygen content of 5×10^{-3} vol%.

The phase composition and microstructure were characterized and analyzed by means of XRD (PANalytical, X'Pert Powder, working voltage: 40 kV; working current: 40 mA; CuKα radiation; steps: 0.013 °; counting time: 2 min, scanning range: 10 – 90 °), SEM (FEI, X-3500N), and EDS.

Table 1: Formulation of the experiment.

Raw materials	Size	A_0	A_1
Fused corundum aggregates	5 – 3 mm	5	5
3 – 1 mm		35	35
1 – 0 mm		25	25
Sintered magnesia aggregates	1 – 0 mm	6	6
Tabular corundum powder	44 μm	17	17
Active fine α-Al_2O_3 powder	≤ 5 μm	6	6
Sintered magnesia powder	74 μm	6	6
Magnesium aluminate colloid	G3297BX	4	4

III. Results and Discussion

Fig. 1 shows the XRD patterns of specimens A_0 and A_1 after firing. It can be seen that specimen A_0 fired in air at 1600 °C is composed of Al_2O_3, MgO, and spinel. In contrast, specimen A_1 fired in N_2 atmosphere with low oxygen partial pressure is composed of Al_2O_3, AlN and

spinel; besides, compared with those of A_0, in A_1 the diffraction peaks of MgO disappear, the peaks of Al_2O_3 become weaker while those of spinel shift. With a comparison of three strong diffraction peaks of spinel in specimens A_0 and A_1, namely (113), (004), and (044), it is found that for specimen A_1, the diffraction peaks shift slightly to small angles and the peaks split (Fig. 2), which indicates that when sintered in nitrogen atmosphere with low oxygen partial pressure (specimen A_1), the magnesia aggregates and powder react and exhaust, forming spinel with crystal parameters shifting towards the small angles.
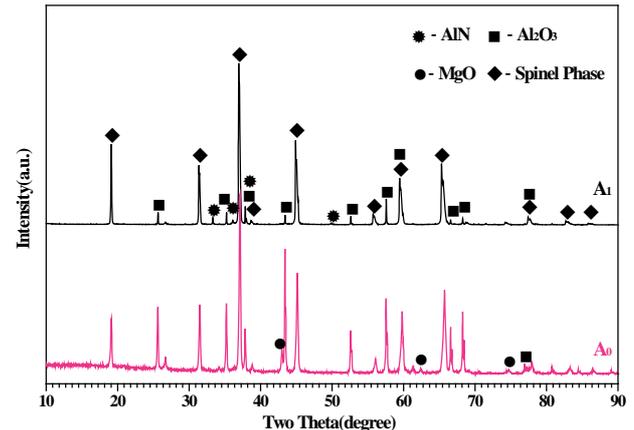
Fig. 1: XRD patterns of specimens A_0 and A_1 after firing.
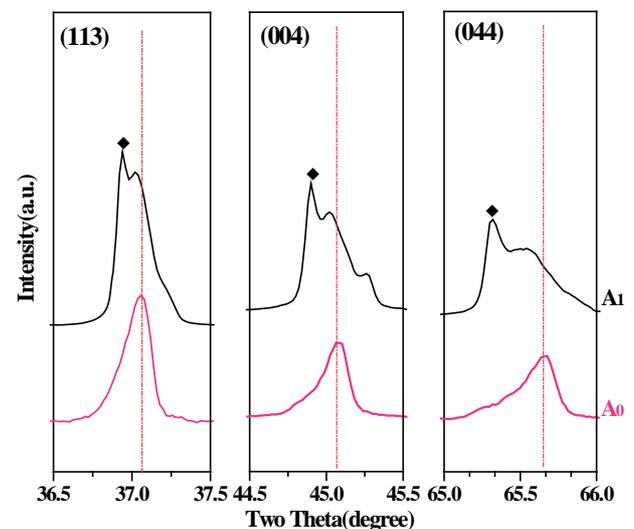
Fig. 2: Enlarged XRD patterns of three diffraction peaks of spinel in Fig. 1.

Table 2: Chemical composition of the used raw materials.

Raw materials	Chemical composition					
	MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3	R_2O
Active fine α-Al_2O_3 powder	—	99.40	0.19	—	0.02	0.12
Tabular corundum powder	—	99.5	0.05	—	—	0.08
Sintered magnesia aggregates/powder	97.8	—	0.5	1.34	—	—
Fused corundum aggregates	—	99.4	0.13	—	0.13	0.15

SEM images of specimen A$_1$ after firing are shown in Fig. 3. In Fig. 3(a-d), it is shown that in N$_2$ atmosphere with low oxygen partial pressure, the corundum aggregates and the matrix are well sintered, realizing complete transformation of spinel in the magnesia powder and corundum powder. Besides, the magnesia aggregates disappear and a clear ring structure appears in large or medium magnesia particles. Small particles less than 100 μm in size transform into spinel completely. A hydration test was conducted on the fired specimen A$_1$ and the section images are shown in Fig. 3(e-f). As can be seen from Fig. 3(e-f), flake crystals are observed on the surface of the synthesized spinel. With a combination of the XRD results and the hydration of AlN, the flake crystals are confirmed as aluminum nitride. The EDS results show that the spinel in the matrix and around the corundum is Al-rich and contains nitrogen element. Nitrogen ions (0.146 nm) have larger diameter than O ions (0.14 nm). What is more, MgO in the system turns into spinel completely. Thus, the spinel synthesized in N$_2$ atmosphere with low oxygen partial pressure has a larger crystal parameter than that synthesized in air, which is also confirmed by the XRD results in Fig. 1.

The particle size of the sintered magnesia powder used in this work was < 74 μm; the starting synthesis temperature of spinel is 1050 °C – 1200 °C [17], so 1100 °C was adopted as the synthesis temperature. A comparison of the XRD and SEM results of specimens A$_0$ and A$_1$ shows that complete spinel transformation of both magnesia aggregates and powder are realized in nitrogen atmosphere with low oxygen partial pressure, indicating that the aggregates and powder react with alumina by different means.

With the condition of mild flowing nitrogen (0.1 MPa; partial pressure P$_{O_2}$ = 5 ×10^{-3} P$^\theta$), in the Al$_2$O$_3$-MgO system, as the CO equilibrium reactions take place in the graphite crucible process, the oxygen partial pressure decreases, the following Mg-C-O thermodynamic reactions may happen [18]:

$$C(s)+0.5O_2(g) \rightarrow CO(g)$$
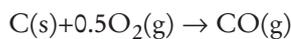
$$\Delta_r G_1 = -114400 - 85.77T + 2.303RT \lg \frac{P_{CO(g)}}{P^\theta} - 0.5 \times 2.303RT \lg \frac{P_{O_2(g)}}{P^\theta} /J \cdot mol^{-1} \quad (1)$$

$$\lg \frac{P_{O_2(g)}}{P^\theta} = -\frac{228800}{2.303RT} - \frac{171.54}{2.303R} + 2\lg \frac{P_{CO(g)}}{P^\theta}$$

$$MgO(s) \rightarrow Mg(g) + 0.5O_2(g)$$

$$\Delta_r G_2 = 714420 - 193.72T + 2.303RT \ln \frac{P_{Mg(g)}}{P^\theta} + 0.5 \times 2.303RT \ln \frac{P_{O_2}(g)}{P^\theta} /J \cdot mol^{-1} \quad (2)$$

$$\lg \frac{P_{Mg(g)}}{P^\theta} = -\frac{714420}{2.303RT} + \frac{193.72}{2.303R} - 0.5 \lg \frac{P_{O_2(g)}}{P^\theta}$$

$$MgO(s) + C(s) \rightarrow Mg(g) + CO(g)$$
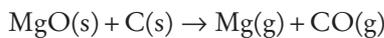
$$\Delta_r G_3 = 60020 - 279.49T + 2.303RT \lg \frac{P_{Mg(g)}}{P^\theta} + 2.303RT \lg \frac{P_{CO(g)}}{P^\theta} /J \cdot mol^{-1} \quad (3)$$

$$\lg \frac{P_{Mg(g)}}{P^\theta} = \frac{-600020}{2.303RT} + \frac{279.49}{2.606R} - \lg \frac{P_{CO(g)}}{P^\theta}$$
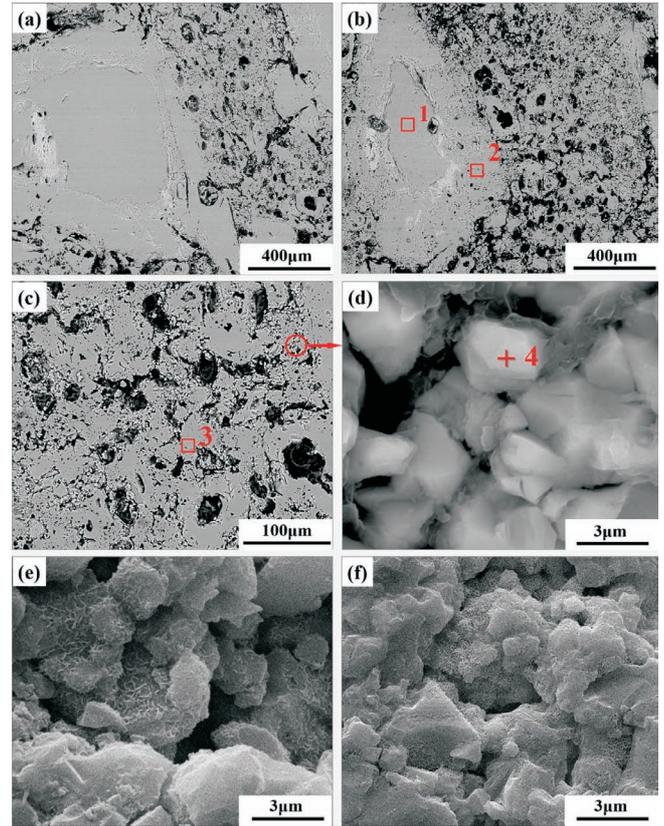
Fig. 3: SEM images of specimen A$_1$ after firing, backscattered electron images: (a), (b), (c), and (d), secondary emission images: (e) and (f).

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

Marked areas	Atomic mole percentage/%			
	Mg	Al	O	N
1	—	62.56	37.44	—
2	7.42	31.44	50.61	10.53
3	3.15	60.86	9.96	26.03
4	7.35	45.83	23.22	23.60

Two extreme situations were considered. First, CO reactions are always in equilibrium: thermodynamic reaction (3) was established based on reactions (1) – (2) (The reaction does not exist and is just an expression addition for calculation convenience). The second, CO reactions are not in equilibrium all the time: the oxygen partial pressure equals the oxygen content in the N$_2$ flow, namely P$_{O_2}$ = 5 × 10^{-3} P$^\theta$. Thermodynamic reactions (2) and (3) based on the two extreme situations show the thermodynamic relationship between the Mg(g) partial pressure and the temperature in Fig. 4. As shown, as the temperature increases, the partial pressure of Mg(g), P$_{Mg(g)}$ keeps increasing. At 1873 K (1600 °C), the equilibrium partial pressure P$_{Mg(g)}$ reaches the maximum based on the two extreme situations. When the CO equilibrium is established, $\lg \frac{P_{Mg(g)}}{P^\theta}$ = -0.134. If equilibrium is not achieved and P$_{O_2}$ = 5 × 10^{-3} P$^\theta$, $\lg \frac{P_{Mg(g)}}{P^\theta}$ = -8.75. So it is analyzed that the decrease in the oxygen partial pressure caused by CO reactions can make the magnesia particles decompose into

Mg(g), providing there is means for gas transfer in magnesia aggregates and powder in N_2 atmosphere with low partial pressure. Thus, in N_2 atmosphere with low oxygen partial pressure, spinel forms in Al_2O_3-MgO composites based on solid-solid transferring and gas-solid transferring.
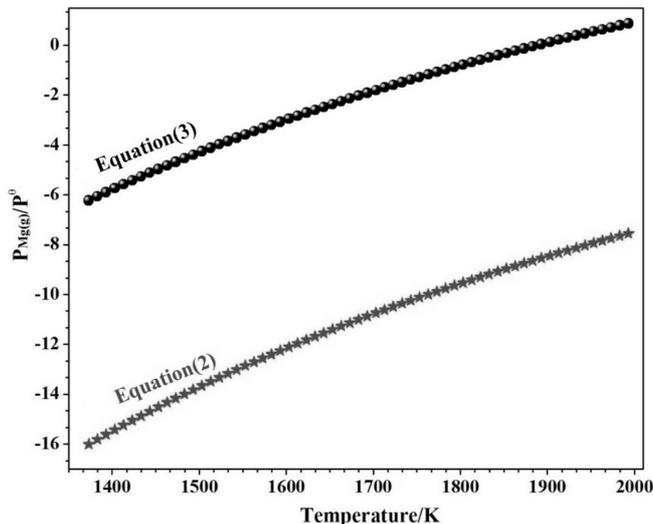
Fig. 4: Relationship between Mg(g) partial pressure and temperature.

(1) Solid-solid reaction mechanism of spinel before CO equilibrium is established

Before CO equilibrium is established, when the oxygen partial pressure is not enough to make the magnesia decompose into Mg(g), spinel is formed by solid-solid mass transfer between MgO and Al_2O_3. Under the high-temperature surface tension, the magnesia aggregates and powder contact and react with corundum aggregates and powder. Mg^{2+} and Al^{3+} mutually diffuse, forming MgO-$MgO\cdot Al_2O_3$ and Al_2O_3-$MgO\cdot Al_2O_3$ interfaces on the sides of magnesia and corundum. The ratio of the theoretical spinel formation on the magnesia side vs on the corundum side is 3:1. Besides, the Al_2O_3-$MgO\cdot Al_2O_3$ interface has a higher solid solving degree to Al_2O_3. The formation of spinel can be considered as the diffusion of MgO towards Al_2O_3, which forms a spinel layer on the surface of Al_2O_3 particles. When the spinel formation based on the diffusion of MgO to Al_2O_3 finishes, since the spinel can accommodate more Al_2O_3, during later sintering, $2Al^{3+}$ in the alumina particles diffuses towards the spinel crystal lattice and occupies the site of $2Mg^{2+}$, turning the stoichiometric spinel into Al-rich spinel. Meanwhile, to keep an electric balance, 1 V''_{Mg} vacancy is generated in the spinel, increasing the vacancy concentration. In addition, $3Mg^{2+}$ from the spinel diffuses into alumina particles and reacts with $4Al_2O_3$, thus forming spinel and thickening the spinel layer. As this goes on, the spinel layer gets thicker and thicker and the stoichiometric spinel becomes Al-rich.

(2) Gas-solid reaction mechanism of spinel before and after CO equilibrium

As oxygen is consumed by C and the CO reactions move to the equilibrium, the oxygen partial pressure continues to decrease and the magnesia decomposes, forming Mg(g):

$MgO(s) \rightarrow Mg(g)+0,5O_2(g)$. Then Mg(g) diffuses along the gaps or pores to the matrix and corundum aggregates. On one side, Mg(g) diffuses to the Al-rich spinel in the matrix and replaces Al in the spinel, forming Al(g); Al(g) is further nitrided into aluminum nitride and adheres to the surface of the spinel. Mg(g) enters the spinel lattice and increases the Mg content. On the other hand, similarly, Mg(g) diffuses to the corundum particles and reacts with alumina, forming spinel, which further constructs a spinel ring structure on the surface of the corundum particles based on solid-solid reactions. Then Mg(g) enters spinel lattice and enhances the Mg content of spinel, which provides a persistent Mg source to wrap alumina particles and further enhance the transformation of alumina to spinel.

Because of the diffusion and replacement reaction process for transformation of Mg(g) into spinel, magnesia is consumed gradually and spinel forms continually, which thicken the Al-rich spinel layer around alumina aggregates, gradually increasing the Mg content of the *in-situ* formed spinel in the matrix, and enlarging the crystal parameters of the Al-rich spinel. So the corresponding XRD diffraction peaks shift towards the small angles. Besides, at high temperatures, AlN can solid-solve into Al-rich spinel partly, resulting in spinel-containing N, which further enhances the lattice diameter of the spinel. The XRD patterns of the fired specimens A_0 and A_1 in Fig. 1 confirm this and indicate that the spinel Mg/Al ratio in the spinel around alumina aggregates is different to that in the matrix, while these ratios are both higher than those of the specimen fired in air. Fig. 3(e-f) shows that the aluminum nitride generated by the replacing reaction adheres to the spinel surface.

IV. Conclusions

Al_2O_3-spinel(N) composite was prepared using white corundum, sintered magnesia and active α-Al_2O_3 powder as raw materials, with magnesium aluminate sol as binder. The prepared samples were characterized and analyzed by means of XRD, SEM and EDS to investigate the mechanism for the formation of spinel(N). The results show:

1) Specimen A_0 fired in air at 1600 °C is composed of Al_2O_3, MgO, and spinel. In contrast, specimen A_1 fired in N_2 atmosphere with low oxygen partial pressure is composed of Al_2O_3, AlN and spinel-containing N.

2) The spinel-containing N bonds the aggregates and matrix together, realizing the close combination of matrix and Al_2O_3 aggregates.

3) The formation mechanism of spinel(N) can be described as follows: in nitrogen atmosphere with low oxygen partial pressure, MgO is unstable and decomposes into Mg(g). Mg(g) diffuses and transfers along the pores or gaps in the material and reacts with corundum or spinel, forming gas aluminum. The gas metal aluminum then nitrides into aluminum nitride. The formed aluminum nitride further solid-solves into spinel, forming spinel-containing N.

References

[1] du Merac, M.R., Kleebe, H.-J., Müller, M.M., Reimanis, I.E.: Fifty years of research and development coming to fruition;

  unraveling the complex interactions during processing of transparent magnesium aluminate (MgAl$_2$O$_4$) spinel, *J. Am. Ceram. Soc.*, **96**, 3341 – 3365, (2013).

[2] Reimanis, I., Kleebe, H.J.: A review on the sintering and microstructure development of transparent spinel (MgAl$_2$O$_4$), *J. Am. Ceram. Soc.*, **92**, 1472 – 1480, (2009).

[3] Chen, S.K., Cheng, M.Y., Lin, S.J., Ko, Y.C.: Thermal characteristics of Al$_2$O$_3$-MgO and Al$_2$O$_3$-spinel castables for steel ladles, *Ceram. Int.*, **28**, 811 – 817, (2002).

[4] Alper, A.M., Mcnally, R.N., Ribbe, P.H., Doman, R.C.: The system MgO-MgAl$_2$O$_4$, *J. Am. Ceram. Soc.*, **45**, 263 – 268, (1962).

[5] Ko, Y.C.: Role of spinel composition in the slag resistance of Al$_2$O$_3$-spinel and Al$_2$O$_3$-MgO castables, *Ceram. Int.*, **28**, 805 – 810, (2002).

[6] Naigai, B., Matsumoto, O., Isobe, T., Nishiumi, Y.: Wear mechanism of castable for steel ladle by slag, *Taik. Ov.*, **12**, 15 – 20, (1992).

[7] Yamamura, T., Kubota, Y., Kaneshige, T., Nanba, M.: Effect of spinel clinker composition on properties of alumina-spinel castable, *Taik. Ov.*, **13**, 39 – 45, (1994).

[8] Ko, Y.C.: Effect of microsilica addition on the properties of alumina-spinel castables, *Ceram. Int.*, **6**, 51 – 56, (2002).

[9] Mori, J., Watanabe, N., Yoshimura, M., Oguchi, Y., Kawakami, T., Matsuo, A.: Material design of monolithic refractories for steel ladle, *Am. Ceram. Soc. Bull.*, **69**, 1172 – 1176, (1990).

[10] Braulio, M.A.L., Rigaud, M., Buhr, A., Parr, C., Pandolfelli, V.C.: Spinel-containing alumina-based refractory castables, *Ceram. Int.*, **37**, 1705 – 1724, (2011).

[11] Braulio, M.A.L., Martinez, A.G.T., Luz, A.P., Liebske, C., Pandolfelli, V.C.: Basic slag attack of spinel-containing refractory castables, *Ceram. Int.*, **37**, 1935 – 1945, (2011).

[12] Chen, Y., Li, J., Han, Y., Yang, X., Dai, J.: The effect of mg vapor source on the formation of MgO whiskers and sheets, *J. Crystal. Growth.*, **245**, 163 – 170, (2002).

[13] Mehdi, A.N., Hirasawa, M., Sano, M.: Deoxidation of iron melt with immersed MgO-C porous tube, *Isij. Int.*, **36**, 1366 – 1372, (1996).

[14] Yang, J., Yamasaki, T., Kuwabara, M.: Behavior of inclusions in deoxidation process of molten steel with *in situ* produced mg vapor, *Isij. Int.*, **47**, 699 – 708, (2007).

[15] Yuasa, S., Kou, S., Aizawa, S., Kitagawa, K.: Combustion characteristics of Mg vapor jet flames in CO$_2$ atmospheres, *P. Combust. Inst.*, **31**, 2037 – 2044, (2007).

[16] Hashimoto, S., Yamaguchi, A.: Synthesis of MgAl$_2$O$_4$ whiskers by an oxidation-reduction reaction, *J. Am. Ceram. Soc.*, **79**, 491 – 494, (1996).

[17] Braulio, M.A.L., Castro, J.F.R., Pagliosa, C., Bittencourt, L.R.M., Pandolfelli, V.C.: From macro to Nanomagnesia: designing the *in situ* spinel expansion, *J. Am. Ceram. Soc.*, **91**, 3090 – 3093, (2008).

[18] Chen, Z.Y.: Chemical thermodynamics of refractories, Metallurgical Industry Press, Beijing, 2005.