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Effect of Addition of Non-oxides on the Slag Corrosion Resistance of MgO-Al_2O_3 Refractories

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Abstract. Various non-oxides, such as SiC, Si_3N_4 and AlN were added to MgO-Al_2O_3 refractory, and the effect on the slag corrosion resistance was investigated. The specimens were prepared by a spark plasma sintering (SPS) method. Slag corrosion tests were carried out using a button method under a reducing atmosphere. Improvement in corrosion resistance was confirmed for the SiC-added specimens, and the addition of nitrides, however, resulted in deterioration. Wettability was also examined, and the compositional dependence was not observed in contact angle. Quantitative relation was not found between contact angle and penetration depth.

1. Introduction

In the 1990's dioxins exhausted from waste incineration plants have been a serious social issue in Japan, and reducing the dioxin emissions has been instructed strictly. High temperature melting incineration systems have been developed to prevent the generation of endocrine disrupters such as dioxin. Municipal waste is discharged as aggregated molten slag, which have greatly contributed to the volume reduction of wastes and the improvement of the waste disposal capabilities. In the high temperature melting furnaces, Al_2O_3-Cr_2O_3 refractories have been often used because of their high corrosion resistance against the molten slags. However, another issue has been raised, that is, generation of poisonous hexavalent chromium ions by reacting with the molten slag. Therefore the development of chromium free refractories with high corrosion resistance is needed. It was reported that the corrosion resistance of MgO-C refractory was improved by adding non-oxides such as Al and B_4C, where the particles of non-oxides reacted with the molten-slag to form protecting layers of oxides [1]. In this study, various non-oxides, such as SiC, Si_3N_4 and AlN were added to MgO-Al_2O_3 refractory, and the effect on the slag corrosion resistance was investigated.

2. Experimental

Among the Cr-free refractories, $MgAl_2O_4$ was chosen. In the authors' group the corrosion resistance of $MgAl_2O_4$ and the effect of ZrO_2 addition have been examined [2]. The raw materials of reagent grade MgO, Al_2O_3 and non-oxide additives (SiC, Si_3N_4 and AlN) at 2, 5 and 10 vol% were thoroughly mixed in a ball-mill with ethanol solvent and dried. The specimens were prepared by a spark plasma sintering (SPS) method at 1,500°C under 20 MPa pressure holding for 5 minutes. Open porosity and bulk density were determined by the Achimedes method. The crystalline phases were identified by X-ray diffraction (XRD) measurement. Simulated waste slag was prepared from the reagents of SiO_2 :

Al_2O_3 : CaO : Fe_2O_3 : MgO : Na_2O : K_2O = 43 : 17 : 21 : 8 : 4 : 5 : 2 (mass%) by a melt-quenching method. Slag corrosion tests were carried out using a button method under a reducing (CO) atmosphere by heating to 1,500°C at a rate of 10°C per minute, holding for 6 hours and cooling at the same rate. A simulated waste slag synthesized was placed on the top surface of the specimen. After the corrosion test, the penetration depth was measured by microscopic observation, and XRD measurement was done for the depth direction. Wettability tests were carried out to determine the wettability of slag on the refractories. A piece of slag was placed on the pellet of the sintered bodies before heating. A CCD camera was used to monitor the shape of slag piece. The tube furnace was heated to 1,500°C at a rate of 10°C per minute, and the wetting behavior between slag and refractory was observed. Before the experiment, the sintered bodies and slag were ultrasonically cleaned in acetone.

3. Results and discussion

3.1. Open porosity

Table 1 shows the open porosity of sintered bodies. In most specimens, open porosities were less than 0.1%, indicating that dense sintered bodies were successfully prepared by using SPS method.

Table 1. Open porosity (%)

additive	amount of additive (vol%)			
	0	2	5	10
SiC	0.05	0.02	0.06	0.02
Si_3N_4	0.05	0.08	0.38	0.13
AlN	0.05	0.03	0.03	0.08

3.2. Slag corrosion test

Table 2 shows the cross sections of the sintered bodies after slag corrosion tests, which were observed through a stereoscopic microscope. Penetrated layers generated due to the infiltration of slag into the sintered bodies are confirmed. The depth was evaluated as a measure of the slag corrosion resistance of specimens in this experiment. In Si_3N_4-added specimens, a number of cracks are observed. In the blank test, where the sintered bodies without slag were fired at 1,500°C under the reducing atmosphere, such the cracks and discoloration were never observed. It is therefore concluded that the changes found in the sintered-bodies after slag corrosion tests are caused by the penetration of slag into the sintered bodies. Table 3 shows the penetration depth after slag corrosion tests. By the additions of Si_3N_4, AlN and 5 vol% of SiC, the penetration depth increases as compared with the additive-free specimen. However, the additions of 2 and 10 vol% of SiC lead to decrease in the penetration depth, suggesting that the corrosion resistance of MgO-Al_2O_3 material is improved by the addition of SiC.
Figure 1 shows the XRD pattern of the sintered bodies of MgO-Al_2O_3 after the slag corrosion tests, where the surface was polished and removed repeatedly. Only $MgAl_2O_4$ spinel phase is confirmed in the slag-penetrated layers. In the unpenetrated layer of Si_3N_4-added MgO-Al_2O_3, small peaks are also confirmed, which are probably derived from Si_3N_4, and these peaks are not observed in the penetrated layers. It is also the case in the specimens with SiC and AlN addition. It is consequently concluded that the crystalline phases originated from non-oxides react with the penetrated slag to form glassy phases.

3.3. Wettability test

Figure 2 shows the change in contact angle as a function of temperature. A common trend is observed in the specimens with SiC and AlN added, where the contact angle decreases with increasing temperature. At 1,500°C, the contact angle of these specimens reduces to almost 0°, and at lower temperatures, the specimens with different additive amount indicate different contact angle, in which

Table 2. Cross section of the sintered bodies of $MgO-Al_2O_3$ after slag corrosion tests under a reducing atmosphere

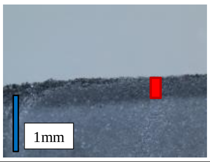
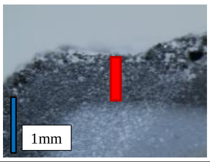
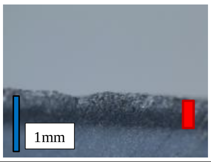
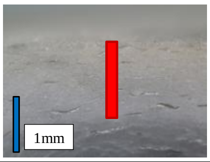
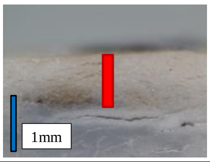
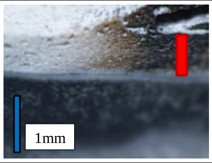
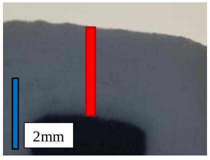
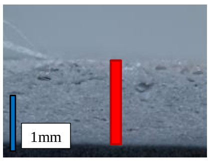
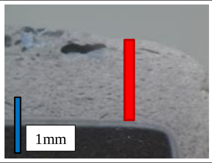
additive	amount of additive (vol%)		
	2	5	10
SiC			
Si_3N_4			
AlN			

Table 3. Penetration depth (mm) after slag corrosion tests

additive	amount of additive (vol%)			
	0	2	5	10
SiC	0.50	0.36	0.73	0.49
Si_3N_4	0.50	1.34	0.93	0.71
AlN	0.50	2.74	1.50	1.50

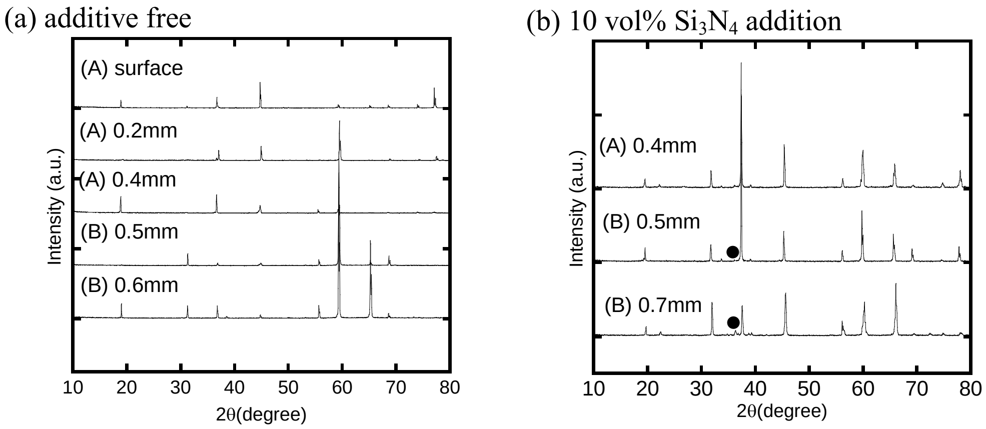


Figure 1. XRD pattern of the depth direction after slag corrosion tests of (a) additive free $MgO-Al_2O_3$ and (b) $MgO-Al_2O_3$ + 10 vol% Si_3N_4 All the peaks other than marked ● are assigned to $MgAl_2O_4$. *(A) penetrated layer (B) unpenetrated layer.

no systematic change over additive amount is not seen. As for the specimens with Si_3N_4 added, the change in contact angle is different from other specimens with SiC and AlN added. At lower temperature, the contact angle decreases and turns into increase at around 1,300°C. Even at 1,500°C, the molten slags remain as droplet, and the specimens with higher Si_3N_4 content have larger contact angle.

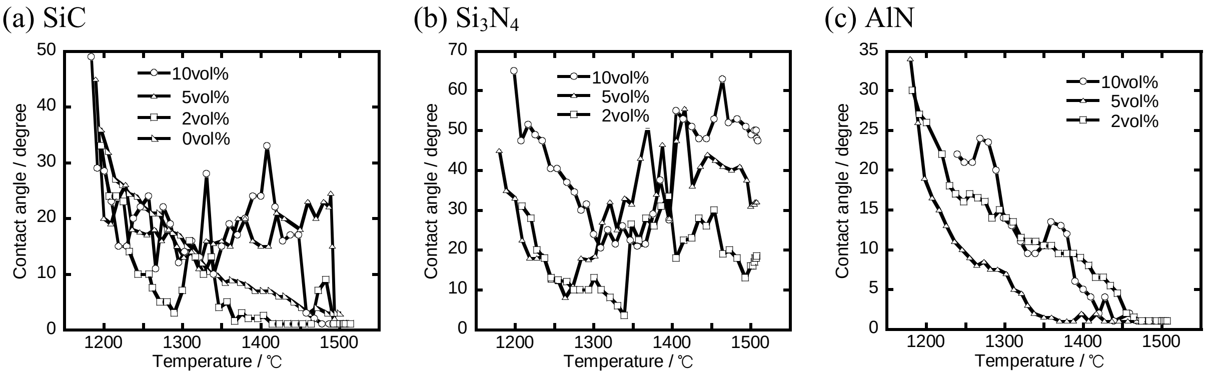


Figure 2. Contact angle for molten slag on the sintered-bodies of $MgO-Al_2O_3$ including (a) SiC, (b) Si_3N_4, and (c) AlN

As shown in Fig. 2, fluctuations in contact angle are observed in most specimens. In these specimens, fluctuations in size of molten slags were also observed during the measurements. Such the fluctuations in contact angle and size of molten slags were not found in the additive-free specimen. Similar fluctuation in contact angle was reported for SiO_2-MnO-TiO_2-FeO_x slag on graphite [3], in which it was considered that the fluctuation was caused by gas generation by the following reaction of FeO_x and carbon.

$$FeO_x(s) + x\,C(s) \rightarrow Fe(s) + x\,CO(g)$$
$$FeO_x(s) + x\,CO(g) \rightarrow Fe(s) + x\,CO_2(g)$$

The generated gases accumulate in the molten slag and inflate the slag. Once the gases are released, the molten-slag contract. The repetitive inflation and contraction due to the gas generation result in the fluctuation in contact angle. In the present study, the fluctuations in contact angle are observed only in the specimens containing non-oxides, and it is hence supposed that the gases are originated from non-oxides in $MgO-Al_2O_3$. As for SiC, gaseous SiO is known to be formed from SiC in reducing atmosphere [4].

No correlation is found between the contact angle and corrosion resistance in the present study, and further investigation is therefore needed. Only in the Si_3N_4-added specimens, however, the contact angle does not converge on 0° at 1,500°C, indicating that the Si_3N_4-added specimens are less wettable to the molten slag compared with other specimens. In the Si_3N_4-added specimens, however, cracks are confirmed after the slag corrosion test, probably resulting in the deeper penetration of molten slag. It is consequently expected that higher slag corrosion resistance is attainable if the crack formation in the Si_3N_4-added specimens is prevented.

4. Conclusion

Various non-oxides, such as SiC, Si_3N_4 and AlN were added to $MgO-Al_2O_3$ refractory, and the effect on the slag corrosion resistance was investigated. By SiC addition, a decrease in the penetration depth was observed, and the deterioration in slag corrosion resistance was found in the specimens with Si_3N_4 and AlN added. The wettability of molten slag was also evaluated, and the quantitative relation was however not confirmed between wettability and penetration depth.

References

[1] Zhang S and Lee W E 2001 *J. Eur. Ceram. Soc.* **21** 2393
[2] Fujita M, Kita H, Igabo K, Sakida S, Benino Y, Nanba T, Miura Y and Yamaguchi A *Taikabutsu* (submitted).
[3] Shen P, Fujii H and Nogi K 2009 *Mater. Chem. Phys.* **114** 681
[4] Yamaguchi A 2006 *Tansoganyuutaikabutsu* (Okayama Ceramics Research Foundation) pp 68-69