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Improvement of the corrosion resistance of alumina–chromia ceramic materials in molten slag

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Abstract

In the previous study, we found out that the corrosion of ceramic materials in molten slag depended strongly on the viscosity of the slag and the basicity gap between the ceramics and the slag. In this study, we propose experimental equation to predict the corrosion rate of a ceramic material in a molten slag as functions of the viscosity and the basicity gap on the basis of the corrosion tests. Cr_2O_3–Al_2O_3 ceramic materials were used for the tests in the SiO_2–CaO–B_2O_3 based model molten slag.

The obtained experimental equation is as follows:

$$\log\Delta D = 0.18^{*}\log\Delta B - 0.55^{*}\log\eta + C$$

where, ΔD is the depth of corrosion (μm), ΔB the basicity gap between the slag and specimen, η the viscosity of slag (Poise). C is the constant that depends on the conditions of the corrosion. The value is 2.7 for the testing temperature of 1573 K, holding time of 3600 s and rotating speed of specimen of 5.2 cm s^{-1} within this corrosion test.

Keywords: Al_2O_3; Corrosion resistance; Cr_2O_3; Refractories; Slag resistance

1. Introduction

It is important to improve the durability of the refractory materials in the combustion chamber, since the refractories in the combustion chambers are corroded seriously by the oxide melt originating from the cinders.[1–3]

In the steel production field, the corrosion resistant refractories have been developed as furnace liner materials against oxide melt.[4,5] The latest ones are the advanced non-oxide type refractories such as SiC type or MgO-C type.[6] However, these materials cannot be used in the strong oxidizing atmosphere such as in the combustion chamber. Thus the candidate materials for the combustion chamber refractories need to be selected from the oxides.

The dissolution mechanism of oxide ceramics into the molten oxide has been studied extensively.[7–10] Samaddar et al.[7] studied the dissolution mechanism of Al_2O_3 single crystal into CaO–SiO_2–Al_2O_3 molten oxide. They concluded that the dissolution rate of Al_2O_3 single crystal into the molten oxide is controlled by the rotating speed (rpm) of the specimen and viscosity of the slag. Ueda[8] also studied the dissolution mechanism of the sintered Al_2O_3 into the CaO–SiO_2–Al_2O_3 molten oxide. He also showed that the dissolution rate of Al_2O_3 was influenced by the rotating speed (rpm) of the specimen and the viscosity of the molten oxide. Kora[9] indicated that corrosion resistance of the basic oxide was higher than that of the acidic oxide in the basic slag. Taira et al.[10] studied the dissolution rate of the sintered Al_2O_3 into the CaO–SiO_2–Al_2O_3 molten oxide. Then, they concluded that the viscosity of the slag decreased along with increase of the CaO/SiO_2 ratio. They assumed that the decrease of viscosity has caused acceleration of corrosion.

Generally, the corrosion rate seems to be influenced by the properties of the molten slag such as the composition of oxide. However, the ceramic materials, which exhibit the superior stability in the molten slag, have been found out experientially or empirically, since the understanding about corrosion chemistry in a slag was still insufficient. In the previous study,[11] we investigated the corrosion behavior of Cr_2O_3–Al_2O_3 ceramics in the

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$CaO–SiO_2–B_2O_3$ model slag system. The obtained results suggest that the basicity and viscosity of slag were the critical factors, which control the corrosion behavior.

The aim of this study is to propose an equation to predict the corrosion rate of ceramic materials in molten slags for further study of corrosion chemistry to develop superior corrosion resistant ceramic materials.

2. Experimental procedures

2.1. $Cr_2O_3–Al_2O_3$ ceramics specimens

The starting powders to prepare the $Cr_2O_3–Al_2O_3$ ceramics were Cr_2O_3 (α-Cr_2O_3; purity, 99.4%; average particle size, 0.3 μm), Al_2O_3 (α-Al_2O_3; purity, 99.997%; average particle size, 0.25 μm), and TiO_2 (purity, 99.99%; average particle size, 0.27 μm). The composition of the mixed powders is 81.6 mol% Cr_2O_3–14.4 mol% Al_2O_3–4 mol% TiO_2. These powders were mixed with ball mill for 100 h using buthanol as solvent. The powder–buthanol mixture was dried in a rotary evaporator. The derived powder was pressed into the disks of about 70 mm in diameter and 10 mm in thickness. These compact bodies were sintered at the temperature of 1773 K for 10,800 s in a vacuum furnace. The sintered bodies have relative densities >95%. Cylindrical specimens for the corrosion experiment were cut out from the sintered bodies. The dimension of the specimen is 5 mm in diameter and 50 mm in length. The roughness of the specimen surface was about 20 μm.

2.2. Molten oxide system

The corrosive oxide mixture was composed of SiO_2, CaO, B_2O_3; detailed compositions were shown in Fig. 1.

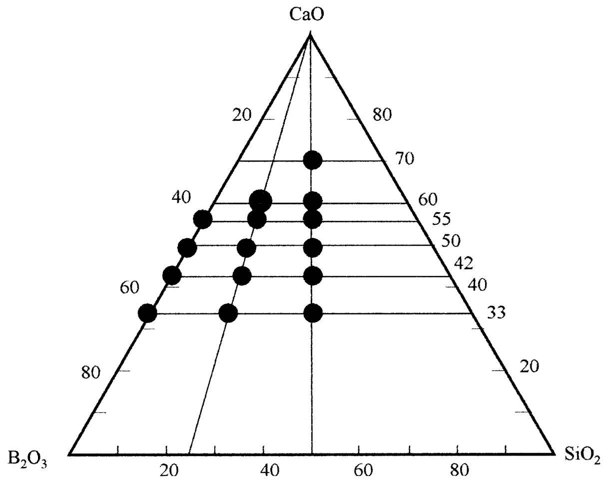

Fig. 1. Chemical composition of the oxide mixture for corrosion test (mol%).

The starting powders used were SiO_2, $CaCO_3$ and H_3BO_3. They were mixed to obtain 40 g of final molten oxide. The mixture was heated in a platinum crucible at 1573 K for 600 s to make a homogenous molten oxide.

2.3. B parameter

In this study, B parameter[12] was used as an index for evaluating the basicities of molten oxide and also the ceramic specimen. According to the definition, the B parameter is estimated as follows:

$$B = \Sigma n_i B_i \tag{1}$$

$$B_i = \frac{\left(\frac{(r_i + 1.40)^2}{Z_i \times 2}\right) - 0.405}{1.023} \tag{2}$$

where, n_i is the fraction of cation i against the number of all cations, r_i and Z_i are the ionic radius and the valence of the cation i, respectively.

This parameter reflects the degree of localization of the lone pair electrons. This parameter could express the basicity of the completely molten oxide if the bond between cation and anion in the slag is assumed to be ionic.

2.4. Viscosity measurement of the molten oxide

The viscosity of the molten oxide was measured by platinum sphere pulling-up method. The platinum sphere of 8 mm in diameter was soaked into the molten slag in the platinum crucible of 70 cm^3. Then, the sphere was taken out from the molten oxide at the rate of 0.833 mm s^{-1}. The viscosity of the melt was calculated from the load applied to the platinum sphere according to the equation of Stokes.

2.5. Corrosion test in the molten oxide

Cylindrical $Cr_2O_3–Al_2O_3$ ceramic specimens for the corrosion experiment were cut out from the sintered bodies. The dimension of the specimen is 5 mm in diameter and 50 mm in length. The roughness of the specimen surface was about 20 μm. Fig. 2 shows the corrosion test equipment. Specimens were set at the bottom of the rod made of high-purity Al_2O_3; 10 mm in diameter and 500 mm in length. Specimens were soaked into the molten oxide at specified temperature; 1573 K, and then rotated. The rotation rate measured by a tachometer, was 5.2 cm s^{-1}. Corrosion time was 3600 s. The tested specimens were cut perpendicularly to the rotating axis and the cross section was polished. Fig. 3 shows the cross section of specimen before and after the corrosion test. The depth of corrosion damage was measured through these optical micrographs.

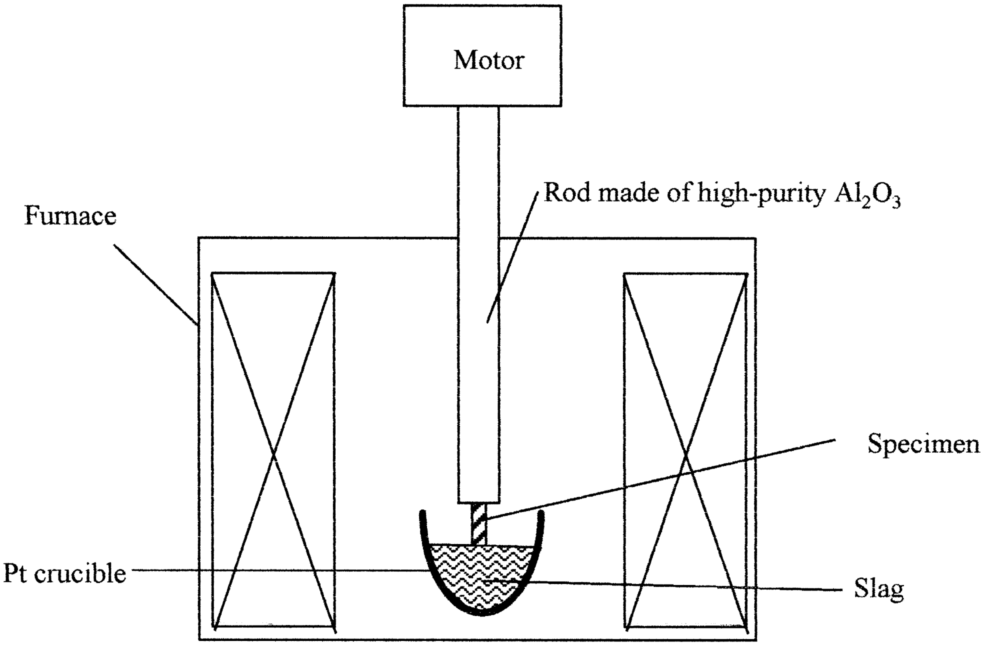

Fig. 2. Schematic diagram of the corrosion test equipment.

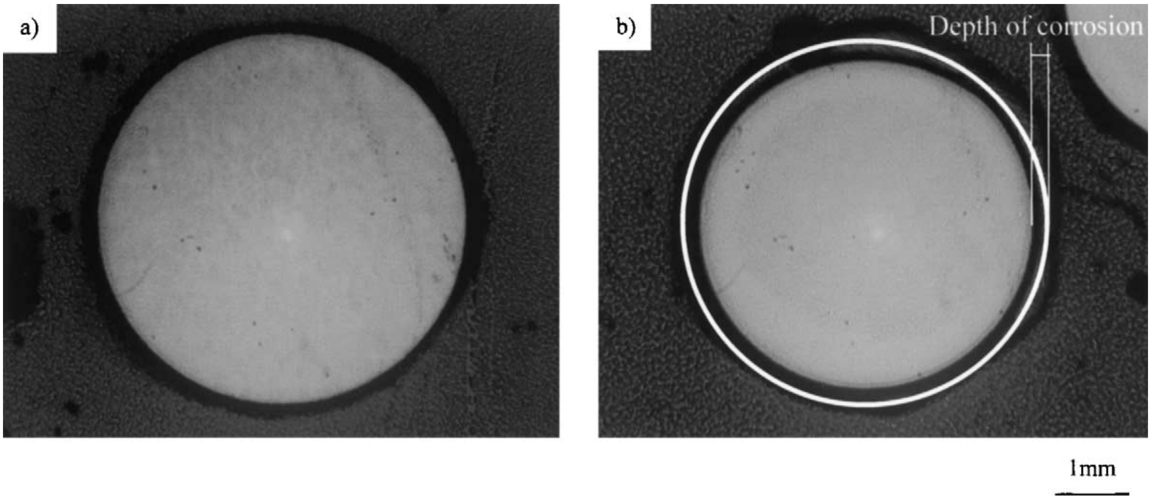

Fig. 3. Cross section of specimen. (a) Before testing; (b) after testing.

2.6. *Prediction of corrosion depth in the molten oxide*

An equation that shows the relationship between the depth of corrosion and the viscosity and basicity of slag is obtained through the multi-variable analysis and has the following form; $\log(\Delta D) = a^{*}\log(\Delta B) + b^{*}\log(\eta) + c$.

The symbols of ΔD, ΔB and η in this equation are the depth of corrosion, basicity gap and viscosity respectively. Also, the symbols of a, b and c are the constants.

2.7. *The estimation of corrosion resistance of MgO–Cr_2O_3–Al_2O_3 ceramics specimens*

We estimate the effect of adding MgO for Cr_2O_3–Al_2O_3 ceramics on improvement of corrosion resistance. The composition of the specimen is xMgO-(1−x)(81.6 mol% Cr_2O_3–14.4 mol% Al_2O_3–4 mol% TiO_2). The contents of MgO,x, are 10, 20 and 30 mol%. Corrosion tests were carried out by the method shown in Section 2.5.

3. Results and discussion

Fig. 4 shows the relationship between the corrosion depth of Cr_2O_3–Al_2O_3 ceramics specimen and CaO content of the molten CaO–SiO_2–B_2O_3 system. From Fig. 4, the depth of corrosion increases with increasing CaO content. At the same CaO content, the depth of corrosion increases with decreasing SiO_2 contents. Fig. 5

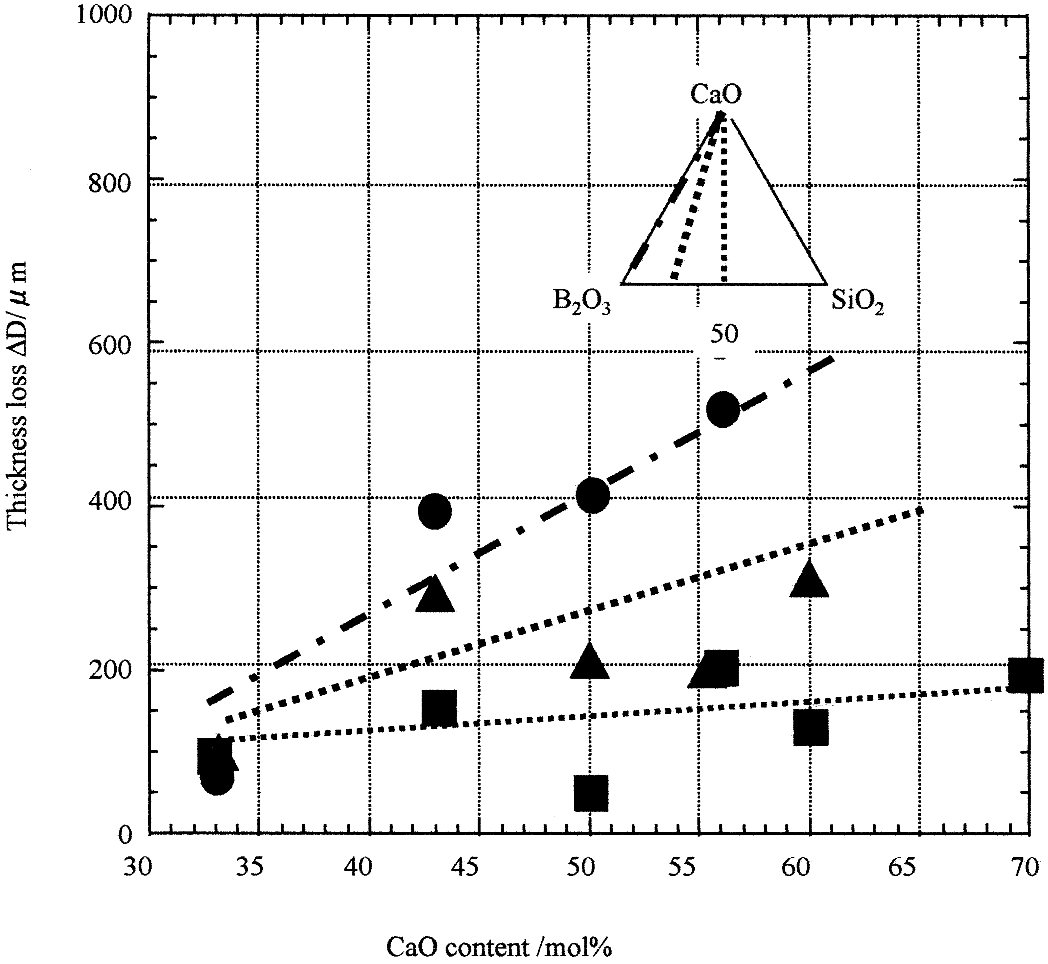

Fig. 4. Relationship between the corrosion depth of specimens and CaO content in the CaO–B_2O_3–SiO_2 molten oxides.

shows the relationship between the basicity and composition of the slag. From Fig. 5, the basicity of slag increase with the increase of CaO content, since CaO is one of the basic oxides. Fig. 6 shows the relationship between the viscosity of this slag and CaO content. The viscosity increases with decreasing CaO content and with increasing SiO_2 content.

In a previous study,[11] we showed that the corrosion depth depends on the basicity and viscosity of slag. Here we propose the equation for prediction of corrosion depth as functions of the basicity gap and the viscosity of slag. To derive the following equation, the data on Figs. 4–6 were treated with multi-variable analysis method:

$$\log\Delta D = 0.18^{*}\log\Delta B - 0.55^{*}\log\eta + C \qquad (3)$$

where, ΔD is the depth of corrosion (μm), ΔB is the basicity gap between the slag and specimen with B-parameter, η is the viscosity of slag (Poise). The constant C has the value 2.7 when the slag system, temperature, holding time and rotating rate of specimen were the CaO–SiO_2–B_2O_3 slag system, 1573 K, 3600 s and 5.2 cm s^{-1} respectively.

Kawai et al.[13] shows that the dissolution rate of oxide ceramics to the slag is controlled by the diffusion rate of the ceramic composition through the boundary layer at the surface of the specimen. They also showed that the corrosion rate, J, was expressed with the following equation.

$$J \propto D \bullet (Ci - C\infty)/\delta \ldots \qquad (4)$$

(J: corrosion rate, D: diffusion coefficient of composition of specimen, Ci: Solubility of specimen, $C\infty$: concentration of composition of the specimen, δ: thickness of boundary layer)

They showed that the parameters of D and δ in the Eq. (4) depended on the viscosity of the slag. The corrosion rate seems to depend on the viscosity of slag through these parameters as we shows in the Eq. (3).

Fig. 7 show that the relationship between the solubility of Cr_2O_3 to the slag and the CaO content of CaO–B_2O_3 slag. The solubility increases with increasing the CaO content. Fig. 5 shows that the basicity of slag also increases with increasing the CaO content. The basicity of Cr_2O_3–Al_2O_3 shown in Fig. 5 is almost the same as that of 30 mol% CaO–70 mol% B_2O_3 slag. The basicity

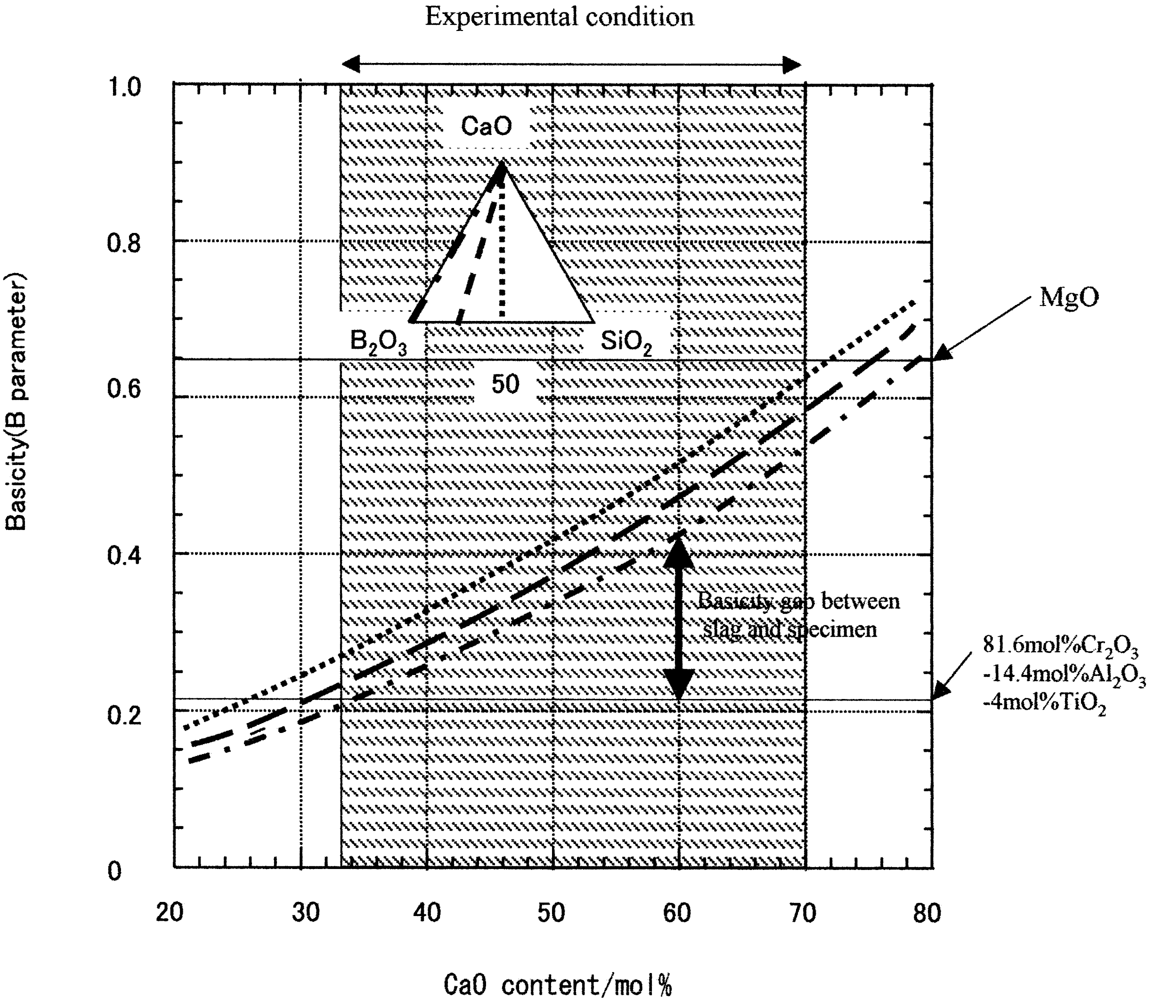

Fig. 5. Relationship between the basicity and CaO content of the molten oxide. (Basicity is represented with parameter *B*.)

gap between the Cr_2O_3–Al_2O_3 specimens and CaO–B_2O_3 slag increases with increasing CaO content of CaO–B_2O_3 slag. Fig. 8 shows the relationship between the solubility of Cr_2O_3 and the basicity gap between the slag and the specimen. We derived the following Eq. (5) from Fig. 8.

$$\log Ci = 0.25 + 0.2\log \Delta B \tag{5}$$

(Ci: the solubility of Cr_2O_3, ΔB: basicity gap)

If it assumes that $C\infty$ in the Eq. (4) is 0, the corrosion rate depends on the solubility of composition, Ci. When Eq. (5) is substituted for the Eq. (4), the relation shown with Eq. (3) will be obtained. This result seems to mean that the corrosion rate depends on the basicity gap between the specimen and slag.

Rapp et al.[14] have investigated the relationship between the solubility specimen and the corrosion rate. They also have investigated the dependence of basicity of specimen and Na_2SO_4 based molten salts on the solubility of specimen. They used the activity of Na_2O as an index for estimating the basicity. They showed that the corrosion rate increase with increasing solubility. They also showed a possibility that solubility increase with increasing basicity gap. In this study, we show that the same relationship between the basicity gap and corrosion rate is realized in the molten oxide.

In developing high corrosion resistant refractories, it has been made important that the basicity of the specimen is brought close to the basicity of slag.[6] For example, since the high basic slags are generated in the converter, MgO refractories, which show the high basicity, have been used. In the steel making field, the CaO/SiO_2 ratio have been used as an index showing the basicity. However, it is not able to exhibit the basicity of slag that does not include CaO and SiO_2 with the CaO/SiO_2 ratio. It is also not able to exhibit the specimen. It is possible that the basicity of specimen is brought close to the basicity of even slag of what ingredient using B parameter as the index.

From Fig. 5, the basicity of Cr_2O_3–Al_2O_3 ceramics is smaller compared to that of 60 mol% CaO–(25 mol% SiO_2–B_2O_3) slag. Adding the oxide of higher basicity to Cr_2O_3–Al_2O_3 ceramics seems to improve the corrosion resistance. The basicity of MgO indicated in Fig. 5 is higher than that of Cr_2O_3–Al_2O_3. Fig. 9 shows the

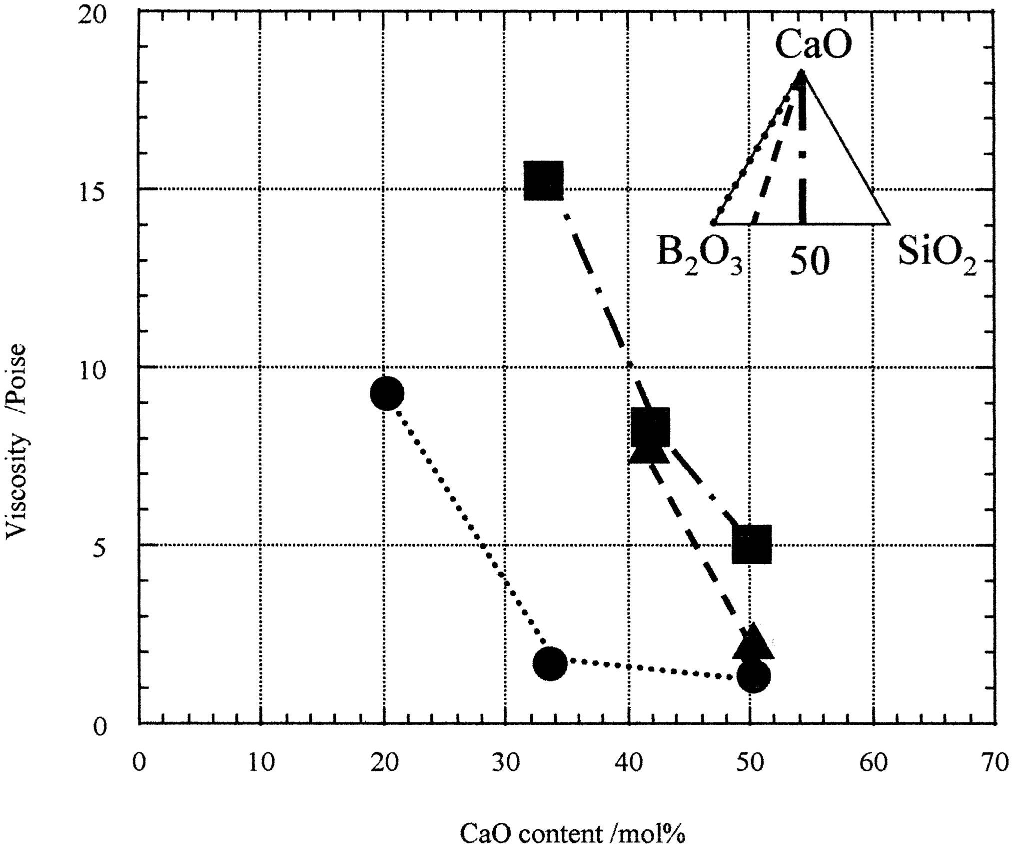

Fig. 6. Relationship between the viscosity and CaO content of the molten oxide. (Temperature: 1573 K.)

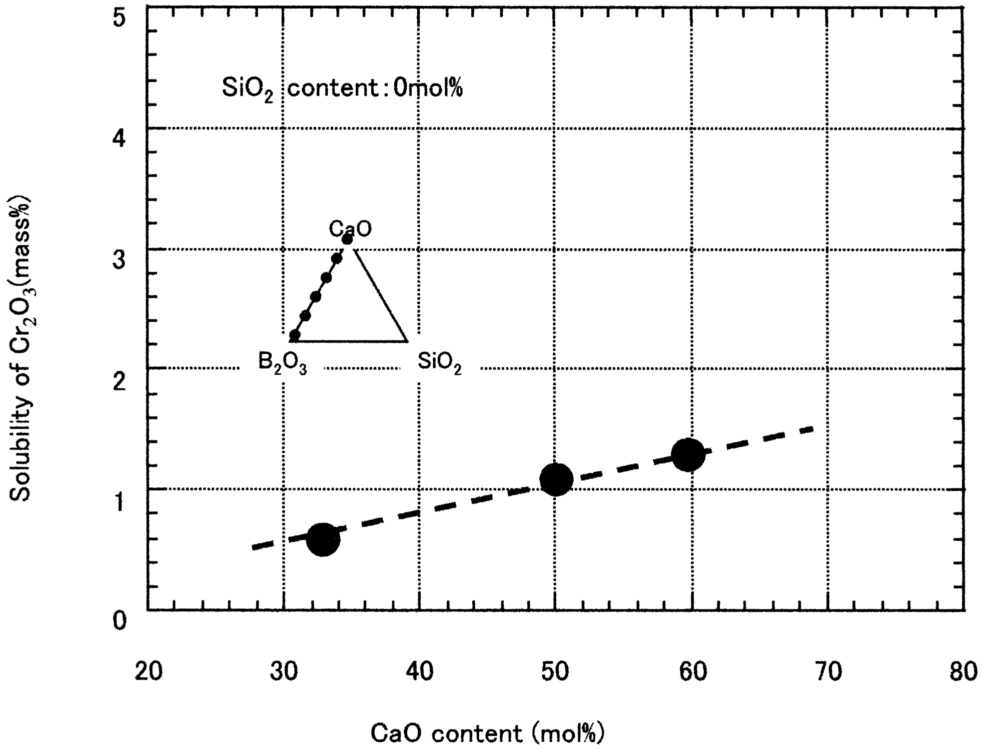

Fig. 7. The relationship between solubility of Cr_3O_3 and CaO content (CaO–B_2O_3 based slag).

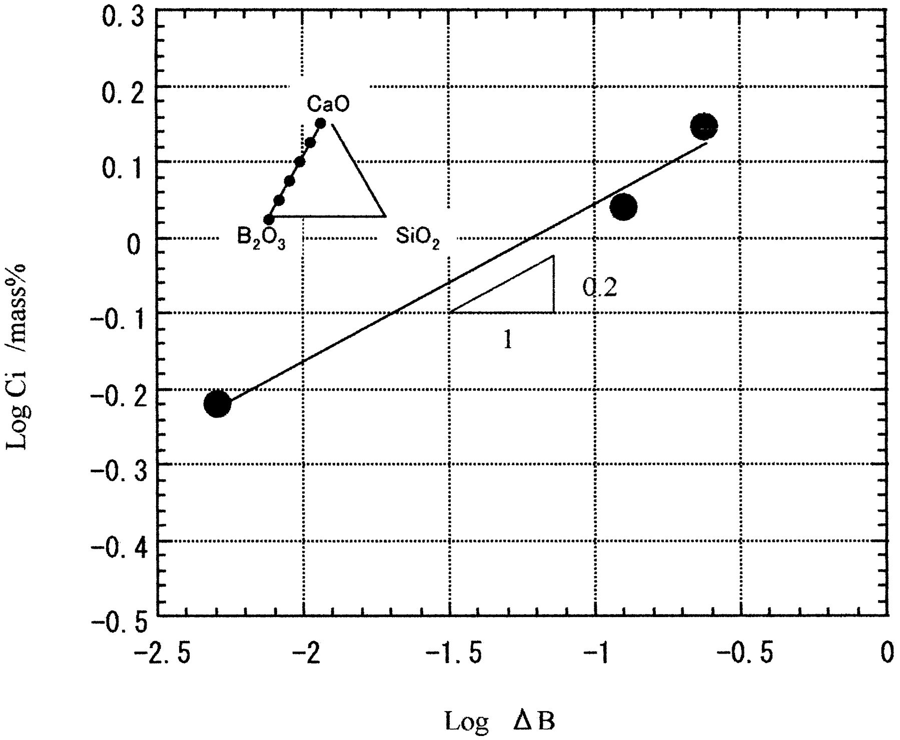

Fig. 8. The relationship between the solubility and the basicity gap between the specimen and the slag.

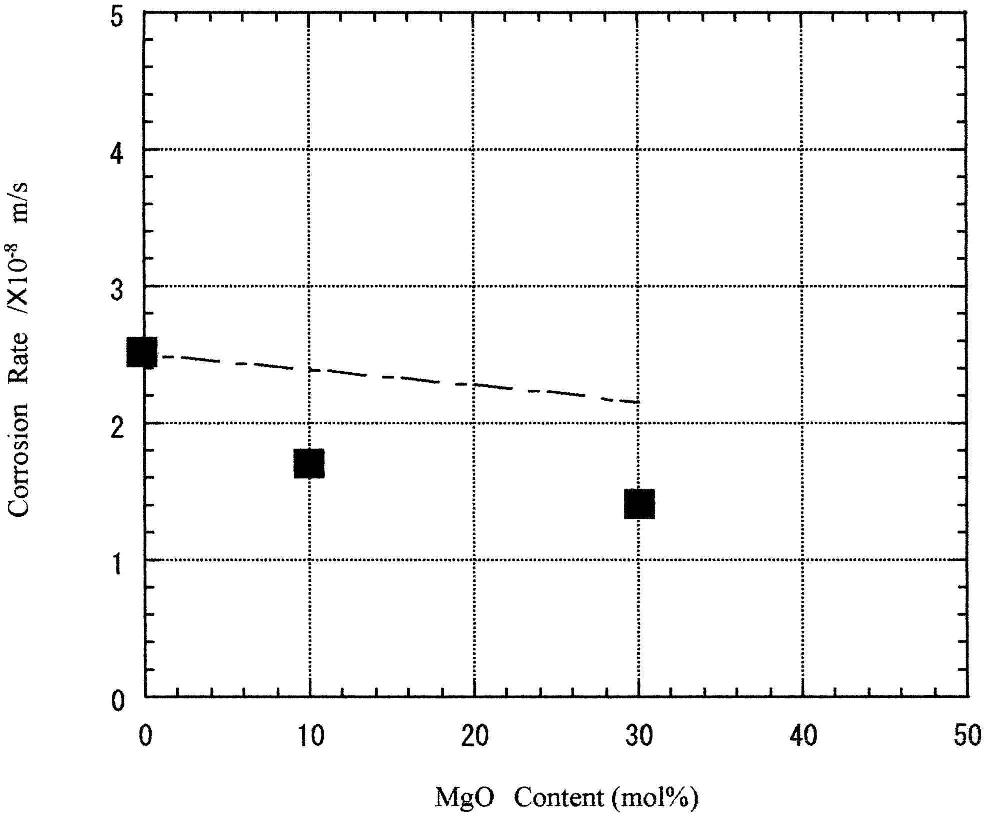

Fig. 9. The relationship between corrosion rate and MgO content in the MgO–(81.6Cr_2O_3–14.4Al_2O_3–4TiO_2) ceramics. (Testing temperature: 1573 K, time: 3.6 ks, rotating rate: 0 cm s^{-1}.)

dependence of corrosion rate of $MgO–Cr_2O_3–Al_2O_3$ ceramics in 60 mol %CaO–(25 mol% $SiO_2–B_2O_3$) slag on MgO content. The corrosion rate of $MgO–Cr_2O_3–Al_2O_3$ ceramics decreases with increasing MgO content. We can choose the high corrosion resistance materials by using B parameter as the index of basicity and decreasing the basicity gap between the slag and the specimen.

4. Conclusion

1. The depth of corrosion can be predicted from the basicity and the viscosity of the slag.
2. The depth of corrosion is described as follows:

   $$\log\Delta D = 0.18^{*}\log\Delta B - 0.55^{*}\log\eta + \mathrm{C}$$

   Where ΔD is the depth of corrosion (μm), ΔB is the basicity gap between slag and specimen with *B*-parameter, η is the viscosity of slag (Poise). The constant *C* derived from condition of corrosion test has the value 2.7 when the slag system, temperature, holding time and rotating rate of the specimen were the $CaO–SiO_2–B_2O_3$ slag system, 1573 K, 3600 s and 5.2 cm s^{-1} respectively.
3. From Eq. (3), the viscosity of the molten slag is rather the dominating factor for the corrosion than the basicity.
4. Basicity gap between the slag and specimen influences the corrosion rate because it affects the solubility of specimen to the slag.
5. The corrosion resistance of $Cr_2O_3–Al_2O_3$ ceramics is improved by adding MgO in the high basicity slag.

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