

EVALUATION OF THE REFRACTORIES FOR APPLICATION TO THE RH DEGASSER

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Introduction

In the secondary refining of the steel, roughly divided two types of facilities are used. The distinction of them is whether vacuum treatment is applied or not. Regarding the vacuum treating system, one type is to treat the molten steel from a ladle and refine it in a degasser vessel, and the other type is to treat the molten steel in the ladle, which is covered by the vacuum system. The RH (Ruhrstahl-Heraus) is one of the typical examples of the sucking type degasser. Some of the researchers have worked so far on the wear of the refractories in the side wall of the RH degasser lower vessel.^{1)~4)} Especially, damage of the refractories used in the positions has been increased by the operation such as oxygen blowing and a powder blowing for refining to the purified high grade steel products.⁵⁾ The damage of the refractories is caused by the formation and penetration of the oxides of metals such as Fe, Si, and Al at the hot surface and also these oxides promote to lower the melting temperature of the refractories.

In the present investigation, the damage mechanism of the refractories against the both oxides of Al and Si was discussed in some detail since there are few reports focused on the damages due to the oxides formed in the hot surface.

Materials and experimental procedure

Erosion/corrosion test under molten steel flow

Erosion resistance of refractories against oxides in molten steel has been evaluated by rotating samples at high speed in the molten steel.⁶⁾ Schematic illustration of the erosion test system is shown in Fig. 1.

A high frequency induction furnace (50kW, 2.3 to 3.1kHz) in which a zirconia crucible (inner diameter 130mm, depth 195mm) was inserted was used for melting the steel. Approximately 10kg of low-carbon steel (C: 0.11%, Si: 0.22%,

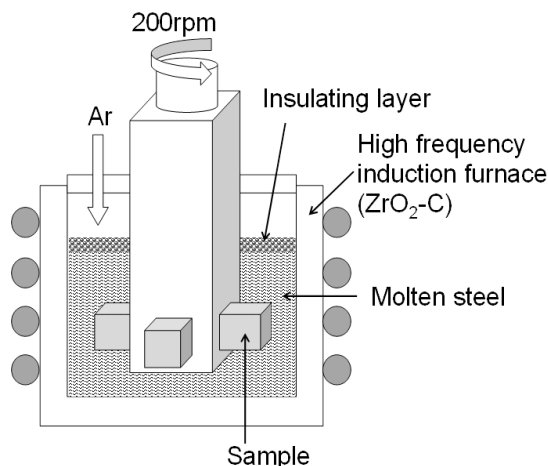


Fig.1 Schematic illustration of the erosion test system in the molten steel.

Mn: 0.55%) was heated to 1600°C and kept at the temperature in Ar flow in the crucible. After that, each Al and Si in an amount of 0.4% in terms of outer percentage was added into the molten steel. These are expected to react with oxygen in the molten steel and become oxides. After the Al and Si addition, about 50g of the sample was taken from the molten steel and the oxides were characterized as shown in Table 1.

Table 1 Chemical composition of Si and Al oxides

Oxide	Si	Al
Chemical composition /mass%		
SiO ₂	72	2
Al ₂ O ₃	6	90
FeO	22	8

A sample for evaluation (20 × 20 × 25mm) was attached to the tip of a zirconia prismatic refractory (40 × 40 × 180mm) in the circumferential direction at 90° pitch. The samples were preheated directly above the molten steel for 5min. And the samples were rotated in the molten steel at 200rpm (rim speed: 1.0m/s) for 120min to promote suspending of oxides and promoting the reaction between refractory samples and oxides. During the test, Ar gas of 1NL*/min was flowed between the lid of the furnace and the steel bath to suppress the rise of the oxygen concentration in the molten steel. The temperature of the molten steel was controlled to be from 1600 to 1650 °C.

The erosion/corrosion resistance was evaluated by measuring the change of samples' width between before and after the test.

The interface between the sample and the molten steel was analyzed and observed by the EPMA to evaluate the reactivity between oxides in the molten steel and the refractories.

*NL: Amount of flow in normal condition (0°C, 1atm, 0.1013MPa and 0% humidity); L = NL × (0.1013 / (0.1013 + Applied pressure [MPa])) × (273 + Applied temperature [°C]) / 273

Test materials

Chemical composition and properties of refractory samples for the erosion test are shown in Table 2. In this experiment, a direct-bonded magnesia-chrome brick (labeled as A) and a magnesia-carbon brick (labeled as B), generally used in the RH degasser lower vessel, were tested. The magnesia-carbon brick was fired at 1400 °C for 3 h in reducing atmosphere.

Table 2 Chemical composition and properties of samples for the erosion test

Sample	A	B
Chemical composition /mass%		
MgO	55	93
Cr ₂ O ₃	30	
C		5
Al ₂ O ₃	6	
Bulk density/ g/cm ³	3.25	3.13
Apparent porosity/ %	16.8	4.4

Results

Wear characteristics of refractories

Figure 2 shows the results of the molten steel stirring test of the samples A and B for both Si and Al oxides. The direct-bonded magnesia-chrome brick (sample A) showed superior erosion resistance against both oxides to the magnesia-carbon brick (sample B). The erosion rate of the both samples by the Al oxides was lower than that by the Si oxides.

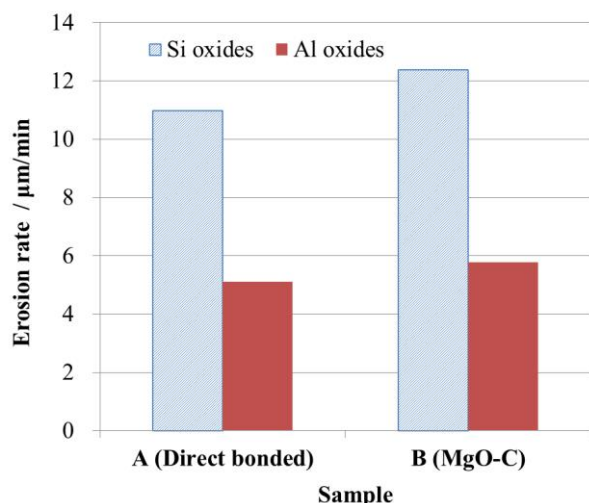


Fig.2 Results of the erosion test for both samples in the molten steel against both types of oxides.

Characterization of hot surface after erosion test

Magnesia-chrome brick

The hot surface of the direct-bonded magnesia-chrome brick after the molten steel stirring test was observed and analyzed by the EPMA. **Figure 3** compares the state of the hot surface after the test by both oxides in the molten steel. In the case of Si oxides, MgO-SiO₂ based reaction layer was formed on the hot surface, and SiO₂ penetrated into the brick. In the case of Al oxides, MgO-Al₂O₃ based reaction layer with 0.5mm thickness was formed in the hot surface. Very little chromic oxide was noted in the reaction layer, and the original chrome containing grains retained almost their entire original shape.

Magnesia-carbon brick

The hot surface of the magnesia-carbon brick after the test was also observed and analyzed by the EPMA. Figure.4 shows the state of the hot surface after the erosion test by both oxides in the molten steel. In the case of Si oxides, MgO-SiO₂ based reaction layer containing no carbon was formed on the hot surface. On the other hand, the penetration of SiO₂ into the brick which was observed in the case of magnesia-chrome brick was suppressed. In the case of Al oxides, MgO-Al₂O₃ based reaction layer containing no carbon was also formed on the hot surface. The penetration of Al₂O₃ into the brick was not observed.

Chemical composition of the reaction layer

From the above described results, it was found that any refractories react with the oxide in the molten steel and form a reaction layer. It was considered that the formed reaction layer had an effect on the erosion of the refractories, and investigated this reaction layer. Thus, analyzed chemical compositions of the reaction layers formed by the Si and Al oxides are shown in **Tables 3 and 4**, respectively. The layer formed by the Si oxides was mainly composed of MgO and SiO₂ for both refractories. In addition, small amount of the oxides like manganese oxide derived from the steel component were detected. The layer formed by the Al oxides was mainly composed of MgO and Al₂O₃ for both refractories. As in the case of the Si oxides, the manganese oxide was also detected. In the meanwhile, chromium oxide derived from magnesia-chrome brick, which

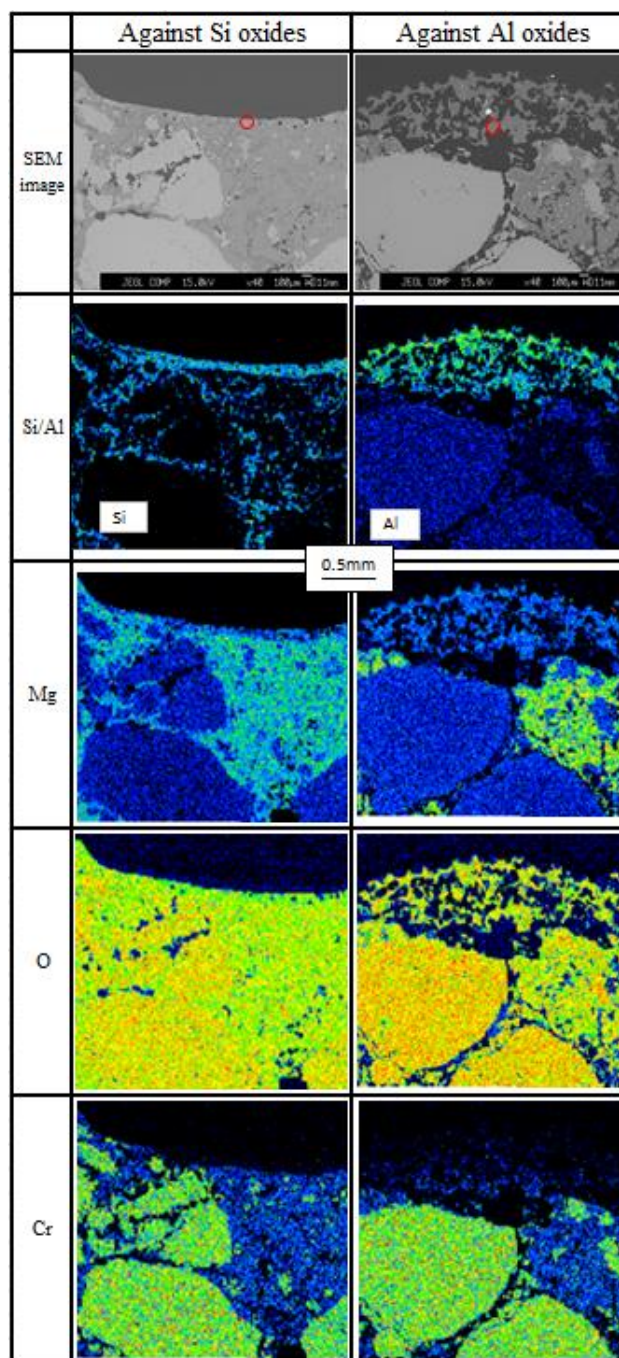


Fig.3 EPMA analysis of direct bonded brick's hot surface tested in Si oxides and Al oxides in molten steel.

was hardly confirmed in the reaction layer formed by the Si oxides, was also detected.

Discussion

Liquid phase formation at hot surface

The amount of wear of refractories by both Si and Al oxides in the molten steel was counted in both samples of magnesia-chrome brick (A) and magnesia-carbon brick (B). The wear of the sample B was larger than the sample A for both oxides. In addition, the wear rate of two samples by the Si oxide was larger than that by Al oxide.

Both refractories were considered to react with the oxide in the molten steel and formed a reaction layer at the hot surface. Based on the analytical results of the reaction layer formed at the hot surface, shown in the **Tables 3 and 4**, **Fig.5** shows the results of calculation for both samples A and B against Si and Al oxides, respectively. The liquid phase ratio at the surface contacted to the molten steel was calculated by the

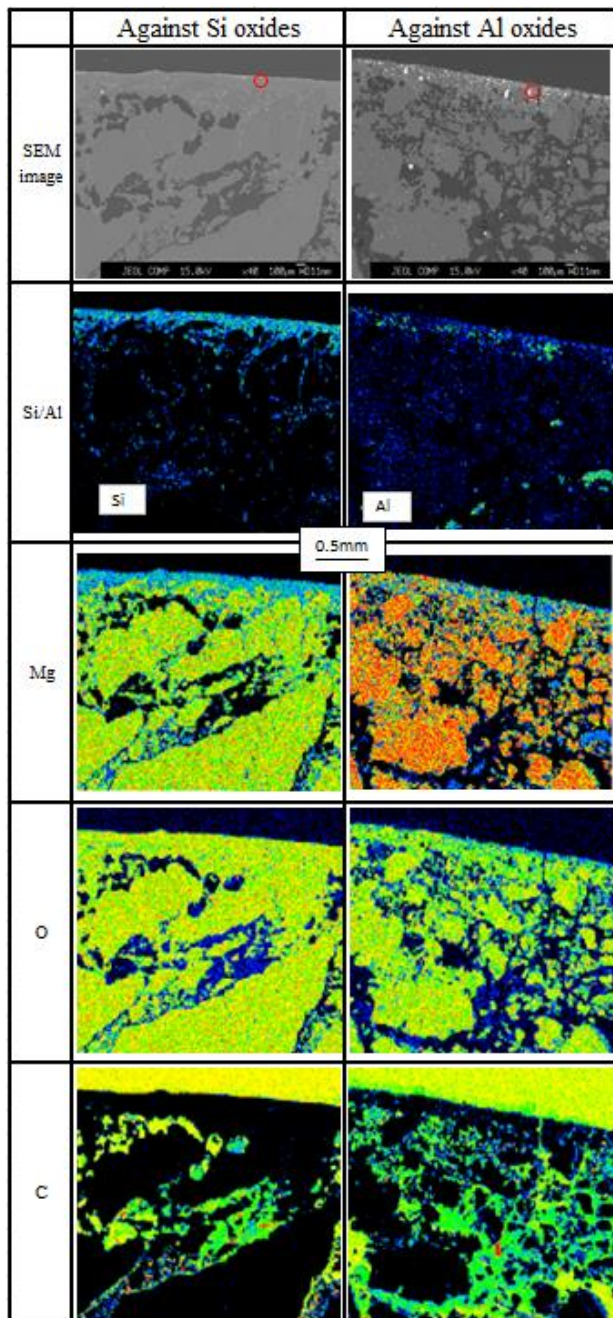


Fig.4 EPMA analysis of MgO-C brick's hot surface tested in Si oxides and Al oxides in molten steel.

software (FactSage) assuming the temperature of 1650 °C. The liquid phase ratio of the reaction layer formed by the Si oxides was 100% for both samples A and B, so that the formation layer at the hot surface enhanced the erosion (wear-off) of the samples. On the other hand, the liquid phase ratio of the reaction layer formed by the Al oxides is less than 10% for both samples. It means that the reaction layer formed by the Al

Table 3 Chemical composition of the reaction layer by the Si oxides

Sample	MgO	SiO ₂	Cr ₂ O ₃	Others
A	56.2	42.8	0.2	0.8
B	57.1	42.0	0.1	0.9

Table 4 Chemical composition of the reaction layer by the Al oxides

Sample	MgO	Al ₂ O ₃	Cr ₂ O ₃	Others
A	27.2	58.2	10.3	4.3
B	27.9	69.3	0.1	2.7

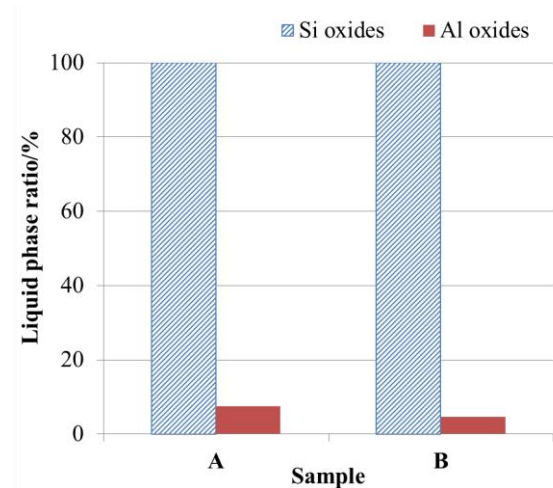


Fig.5 Liquid phase ratio of the reaction layer.

oxides has higher resistance to the erosion than that by the Si oxides. Since the liquid phase ratio of the reaction layer formed by the Si oxides at the hot surface was higher than by the Al oxides, it was conceivable that the wear rate was increased.

Wear of the magnesia-chrome brick

It is considered that the wearing form of magnesia-chrome brick by the oxides occurred as follows. First, the magnesia-chrome brick and the oxides in the molten steel bring into contact with each other and form a reaction layer. The liquid phase ratio when the magnesia-chrome reacted with the oxides in the molten steel was calculated using the FactSage, assuming that the homogeneity of components in the brick. The calculated liquid phase ratio is plotted against the reaction rate of the brick component and the oxides in the steel at 1650 °C with the range from 0 to 40% in Fig.6. It is understood that the liquid phase ratio is very low when the reaction proceeds with the Al oxide compared to the Si oxide. The higher liquid phase ratio in the Si oxide is considered to enhance the higher rate of erosion.

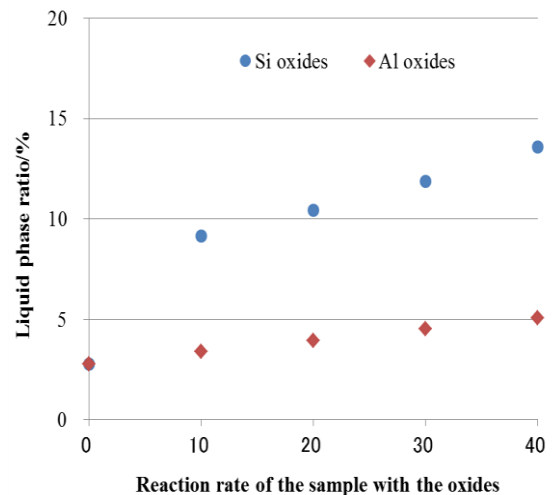


Fig.6 Analytical relation between the liquid phase ratio and the reaction rate of the magnesia-chrome brick with both oxides.

Figure 7 shows the relation between the calculated compositions of the magnesia and the chromium oxide in the liquid phase and the reaction rate of the sample with the Si oxide. Comparing both magnesia and chromium oxide, it is found that the proportion of the magnesia contained in the liquid phase is extremely high. From this calculation result and analysis result of the reaction layer shown in the Table 3, the major component of the layer was MgO and SiO₂. It is considered that the wear of the magnesia-chrome brick is

controlled by the elution of the MgO which is likely to generate the liquid phase by the Si oxides.

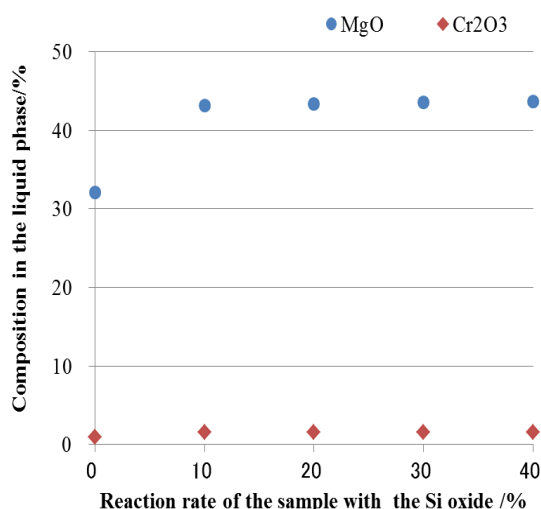


Fig.7 Analytical relation between the composition in the liquid phase and the relation rate of the magnesia-chrome brick with the Si oxide.

Figure 8 shows the relation between the calculated composition of the magnesia and the chromium oxide in the liquid phase and the reaction rate of the sample with the Al oxide. Comparing both magnesia and chromium oxide, it is found that the proportion of magnesia contained in the liquid phase is very high. From this calculation result and analysis result of the reaction layer shown in the **Table 4**, the major component of the layer was MgO and Al_2O_3 . It is considered that the wear of the magnesia-chrome brick is controlled again by the elution of the MgO which is likely to generate the liquid phase by the Al oxides.

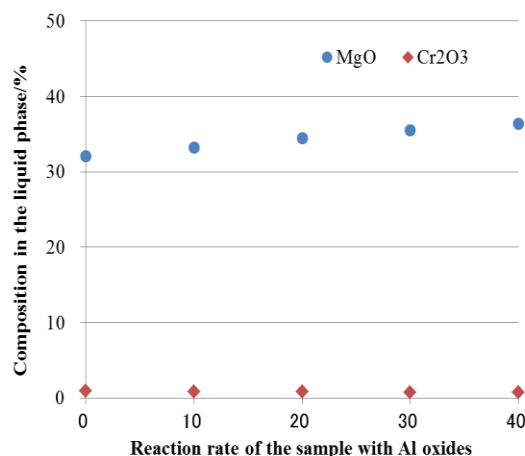
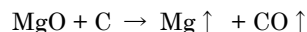


Fig.8 Analytical relation between the composition in the liquid phase and the reaction rate of the magnesia-chrome brick with the Al oxides.

Wear of magnesia-carbon brick

The following reaction occurs in the magnesia-carbon bricks in the molten steel,



MgO generates Mg gas by the occurrence of de-magnesium phenomenon of the MgO when it contacts with carbon at the molten steel temperature. It is said that the reaction becomes $P_{\text{Mg}} + P_{\text{CO}} \geq 1 \text{ atm}$ when the temperature exceeds 1750°C and this reaction can be suppressed by confining the generated gas within brick⁷⁾. In this experiment, it is considered that a negative pressure generated by the molten steel flow promoted the reaction in which the Mg gas is released from the sample actively occurred at the molten steel temperature. It is assumed that the Mg gas moves to the interface between the molten steel and brick, it reacts with both oxides and formed the reaction layer at the hot surface. It is considered that the wear of the brick is caused by the reaction layer generating a liquid phase and eluting.

Conclusions

We focused on the wear of the refractories for the RH by Al and Si oxides in the molten steel and investigated the damage mechanism of refractories for the RH by the oxides in the molten steel under the condition of molten steel stirring test system. The following conclusions were obtained.

- 1) The amount of wear of both refractories tested which are the magnesia-chrome brick and the magnesia-carbon brick by Si and Al oxides in the molten steel was smaller in the former brick than the latter against both the oxides of Si and Al.
- 2) The wear rate of the both refractories by the Si oxides was higher than that by the Al oxides due mainly to the higher liquid phase ratio at 1650°C in the molten steel containing the Si oxides.
- 3) It is considered that both refractories formed reaction layers with the oxides of Si and Al in the molten steel, and the wear mechanism of the refractories was closely related with the elution of the reaction layers formed at the hot surface.

References

- [1]Calkins DJ. Wear of basic refractories in RH and RH-OB degassers. Proceedings of the UNITECR1989 Nov.1-4; Anaheim, USA p695-707.
- [2]Kuwayama M, Nishikawa H, Kanatani T, Sudo F. and Mizushima Works. Reduction of refractory consumption in BOF shop using oxygen top blowing method for vacuum degasser. Proceedings of the UNITECR 1991 Sep.23-26; Aachen, Germany p26-9.
- [3]Cordonnier T, Hiot B, Blumenfeld P. How to select magnesia-chromite bricks for RH-degasser applications. Proceedings of the 53rd International Colloquium on Refractories; 2010 Sept.8-9; Aachen, Germany. 2010. p.155-8.
- [4]Ha CS, Jeong DH. Wear behavior of $\text{MgO-Cr}_2\text{O}_3$ brick in RH process. Proceedings of the UNITECR 2011 Oct.30-Nov.2; Kyoto, Japan. 2011 1-B1-3
- [5]Ishii A, Goto K. Refractory degradation in secondary Steelmaking. Taikabutsu. 1992 44(4):245-50.
- [6]Koga S, Amano J, Morikawa K, Asano K. The effect of the refractory composition on erosion resistance of refractories for continuous casting. Taikabutsu. 2005 57(9):326-33.
- [7]Nagafune M, Ishii H, Tsuchiya I, Oguchi Y, Kawakami T. Reaction between magnesia and carbon at high temperature. Taikabutsu. 1989 41(8):410-18.