TECHNOLOGIES OF ALUMINA-MAGNESIA REFRACTORIES FOR STEEL LADLES PART I, BRICK DEVELOPMENT*

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Abstract

In this article, technologies of unburned Al_2O_3-MgO (UAM) refractories are demonstrated in terms of microstructure evolution. During operation, Mg^{2+} diffuses from MgO to Al_2O_3 through the liquid phase to form spinel ($MgAl_2O_4$) network. Molten slag tends to penetrate along the voids in the spinel network structure and spinel dissolves in the penetrated slag.

Therefore, maintaining a high degree of spinel saturation in the penetrated molten slag is important. In order to achieve the condition described above, suppression of overall mass transfer through penetrated slag is effective. This is achievable by evolution of complicated spinel network structure with small pore diameter, which increases the flow resistance of molten slag. Thus, optimization of refractory composition and fabricating conditions, with the aim of creating on improved spinel network, is essential.

The effectiveness of spinel network improvement was validated by commercial applications. According to the investigation of UAM brick after use, further densification due to heating under restrained conditions was recognized. Hence, it was concluded that the evolution of the spinel network structure in UAM refractories is essential technology needed to improve durability.

Keywords: Refractories; Brick; Steel ladle; Spinel

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1 INTRODUCTION

Traditionally, high alumina bricks or agalmatolite brick have been applied as refractories for the steel ladle metal line. However, recent intensive secondary steel refining treatment severely promotes wear of steel ladle refractories. Therefore, applications of MgO-C bricks and Al_2O_3-MgO-C bricks are increasing. In these cases, however, increases of heat loss as well as carbon pick up are concerned. In order to deal with these issues, utilization of Al_2O_3-MgO refractories is one of the solutions. Particularly in Japan, Al_2O_3-MgO castables have been widely applied to the steel ladle metal line in integrated steel mills.
Japanese integrated steel mills began to apply castable refractories to steel ladles in the 1980's according to the forecast that lack of skilled masons would become a serious issue. Since then, many castable refractory materials and castable installation technologies have been developed. Firstly, Al_2O_3-Spinel (Al_2MgO_4) castables exhibited successful results [1]-[6]. Then, Al_2O_3-MgO castables (hereinafter, referred to as AM castable) were substituted for them due to their high durability [7]. AM castables are the dominant materials for steel ladles used in integrated steel mills in Japan.
On the other hand, EAF-based mini mills still employ brick linings in steel ladles since a huge investment is necessary for castable-installing equipment. Hence, for the steel ladles used in mini mills, unburned Al_2O_3-MgO brick (hereinafter, referred to as UAM brick) was developed in the 2000's on the basis of castable technology [8]-[10]. As a result of UAM brick application, many advantageous results were recognized.
A key technology of Al_2O_3-MgO refractories is the suitable utilization of an in-situ spinel forming reaction. Both UAM brick and AM castables mainly consist of alumina and magnesia. Under high temperature conditions during operation, these two components react and form spinel (Al_2MgO_4) as expressed in Equation 1.

$$Al_2O_3 + MgO \rightarrow Al_2MgO_4 \quad (1)$$

Since the reaction is accompanied by volume expansion, joint openings and/or small cracks will be closed. While catastrophic fracture is worried for rapid volume expansion, adequate creep deformation releases the excessive stress.
Furthermore, thanks to brick structure reinforcement due to the in-situ spinel forming reaction, corrosion and slag penetration resistance of the brick is markedly improved. In terms of corrosion and slag penetration resistance, 7 mass% is considered to be the optimal MgO content.
According to the superior corrosion and slag penetration resistance, notable reduction in wear rate in comparison with traditional high alumina brick was recognized as shown in Figures 1 and 2.
Through laboratory experiments carried out to improve UAM brick in association with commercial applications, it was found that the porosity and microstructure after heating are essential elements for refractory durability. In this article, the technologies of Al_2O_3-MgO refractories are described focusing on the porosity and microstructure of UAM bricks.

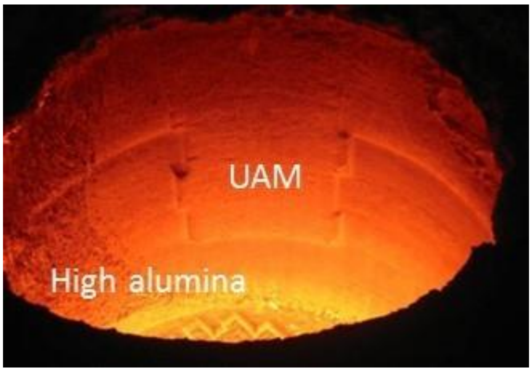

Figure 1. Application of UAM brick to steel ladle as alternative to high alumina brick.

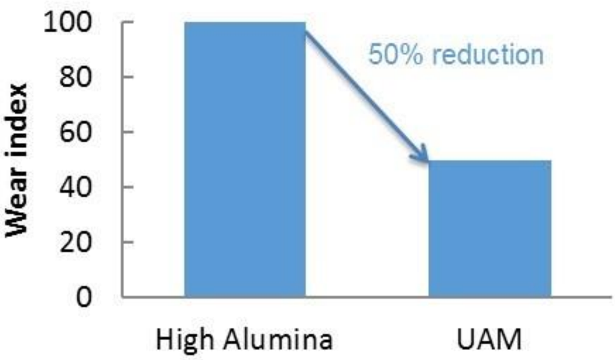

Figure 2. Wear rate of steel ladle metal line of EAF-based Japanese steel mill.

2 MATERIAL AND METHODS

2.1 Laboratory experiment

In this study, six UAM bricks, A and B1 to B5, were experimentally prepared. These five materials included 7 mass% of MgO. Table 1 provides the apparent porosities and modulus of ruptures of the bricks.

Table 1. Typical properties of UAM bricks evaluated in this study

I. D.	A	B1	B2	B3	B4	B5
MgO content / mass%	7	7	7	7	7	7
Apparent porosity / %	8.6	12.6	12.6	10.6	10.2	10.0
Modulus of rupture / MPa	11.3	5.2	13.3	10.1	8.8	8.7

A is characterized by the smallest porosity. Grain size distributions of B1 were arranged for the sake of sintering easiness. B2 to B5 is a series with basic grain size distributions equivalent to B1. Newly developed technologies such as small amount component addition, optimized fabricating conditions, and so on, were applied to B2 to B5 in order to improve sinterability and reduce porosity. These six materials were subject to the property evaluations summarized in Table 2.

2.2 Commercial applications

Since material B1 is standard product, it has been applied to many steel ladle of EAF-based Japanese steel mills. Thus, post use refractory samples were obtained from steel mill X followed by evaluation of apparent porosity, mineralogical

composition determination and microscopic observation. Archimedes method, XRD and EPMA were employed for the evaluations.
Material A has been successfully applied at steel ladle of Brazilian integrated steel mill Y. In that mill, the wear status after operation was inspected and potential life was estimated
At the steel ladle at EAF-based Japanese steel mill Z, at which B1 had been used for a long time, newly developed B5 was applied and the wear rate was evaluated. Additionally, cut surface observation and porosity evaluation were carried out for the specimen after use.

Table 2. Evaluation of experimentally prepared specimen properties

Evaluation	Specimens	Methodology
Permanent linear change	All	After heating at 1500 ºC for 10 h
M.O.R. after heating	All	Three point bending
Apparent porosity	All	After heating at 1500 ºC for 10 h Archmedes Method
Pore size measurement	All but B4	After heating at 1500 ºC for 10 h Merculy intrusion method
Thermal expansion	All but B4	R.T. to 1500 ºC, in Air
Thermal expansion under load	B1, 2, 3, 5	Load: 0.2 MPa R.T. to 1500 ºC, 3 h keeping, in Air
Corrosion resistance	All but B4	Without Pre-heating Rotary method, 1650 ºC for 5 h, Slag C/S=2.0, (FeO) = 15%
Microstructure observation after 10 h heating	A, B1, B5 B1	Optical microscope EPMA
Microstructure observation after 3 h heating	B1	EPMA
Microstructure observation after corrosion test	B1	EPMA

3 RESULTS AND DISCUSSION

3.1 Laboratory experiment

3.1.1 Physical properties after heating

Table 3 shows properties evaluated after heating at 1500 ºC for 10 h. While slight deviations were recognized for permanent linear change and modulus of rupture, no notable fluctuation was detected. Therefore, the tendency of porosity difference of as-received materials shown in Table 2 was almost maintained after heating at 1500 ºC for 10 h. Although the porosities of series B after heating decreased thanks to the developed technology application, material A still exhibited the lowest porosity after heating. However, material A showed considerably large pore diameter.

Table 3. Properties of UAM bricks after heating at 1500 ºC for 10 h

I. D.	A	B1	B2	B3	B4	B5
Permanent linear change / %	3.0	3.2	2.8	3.3	3.7	3.4
Modulus of rupture / MPs	21.3	17.5	22.6	22.5	18.1	20.3
Apparent porosity / %	17.0	21.4	19.0	18.2	18.5	18.1
Median pore diameter / μm	23.0	5.4	6.6	3.8	-	6.3

Figure 3 shows the thermal expansion curves with and without load. While the expansion behaviors showed slight deviation, it is empirically predicted that all materials are applicable to commercially operated steel ladles.

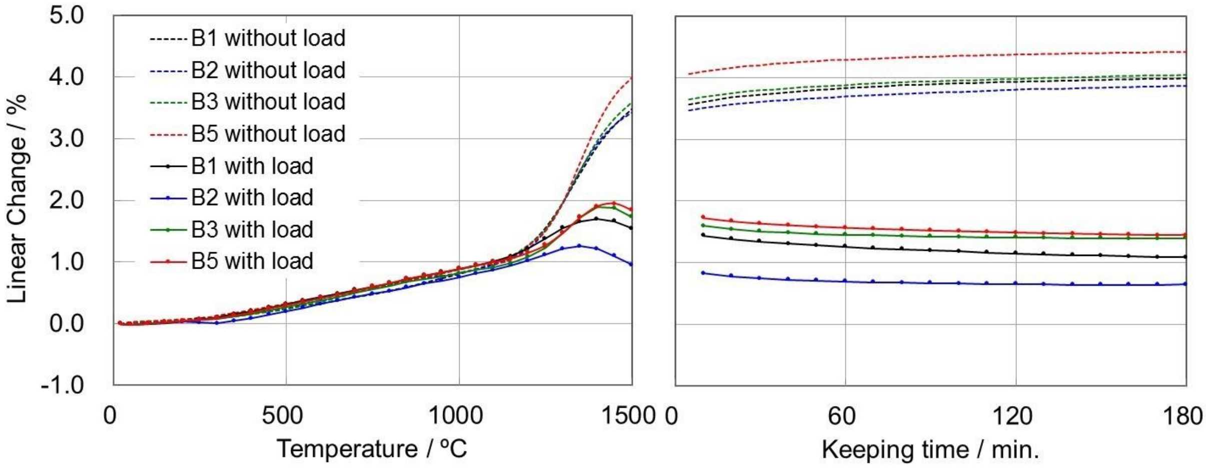

Figure 3. Thermal expansion behaviors of materials.

3.1.2 Corrosion resistance and microstructure

Figure 4 shows influence of porosity after being heated at 1500 ºC for 10 h on slag corrosion resistance. As shown in material series B in Figure 4, a good correlation between corrosion rate and porosity after heating was obtained. On the contrary, material A, that exhibited lowest porosity after heating, showed the poorest corrosion resistance. That is considered attributable to pore size.

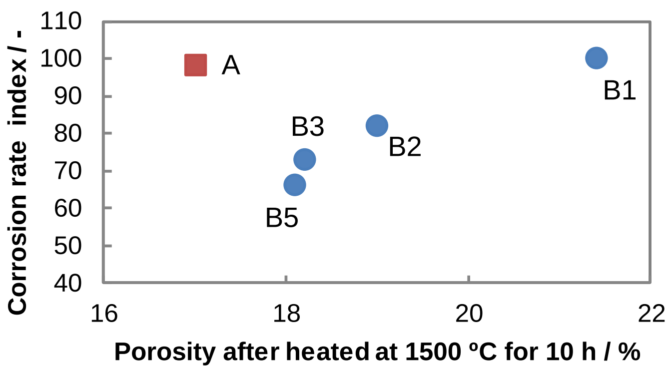

Figure 4. Variation in corrosion rate index as a function of porosity after heating.

Figure 5 compares microstructure of materials A, B1 and B5 after heated at 1500 ºC for 10 h. As is obvious, network structure evolution was recognized for materials B1 and B5 while poor inter-particle connecting structure was observed for material A. As a result of the analysis, it was clarified that the network structure consists of spinel. Hence, difference in pore diameter can be attributed to the microstructure.

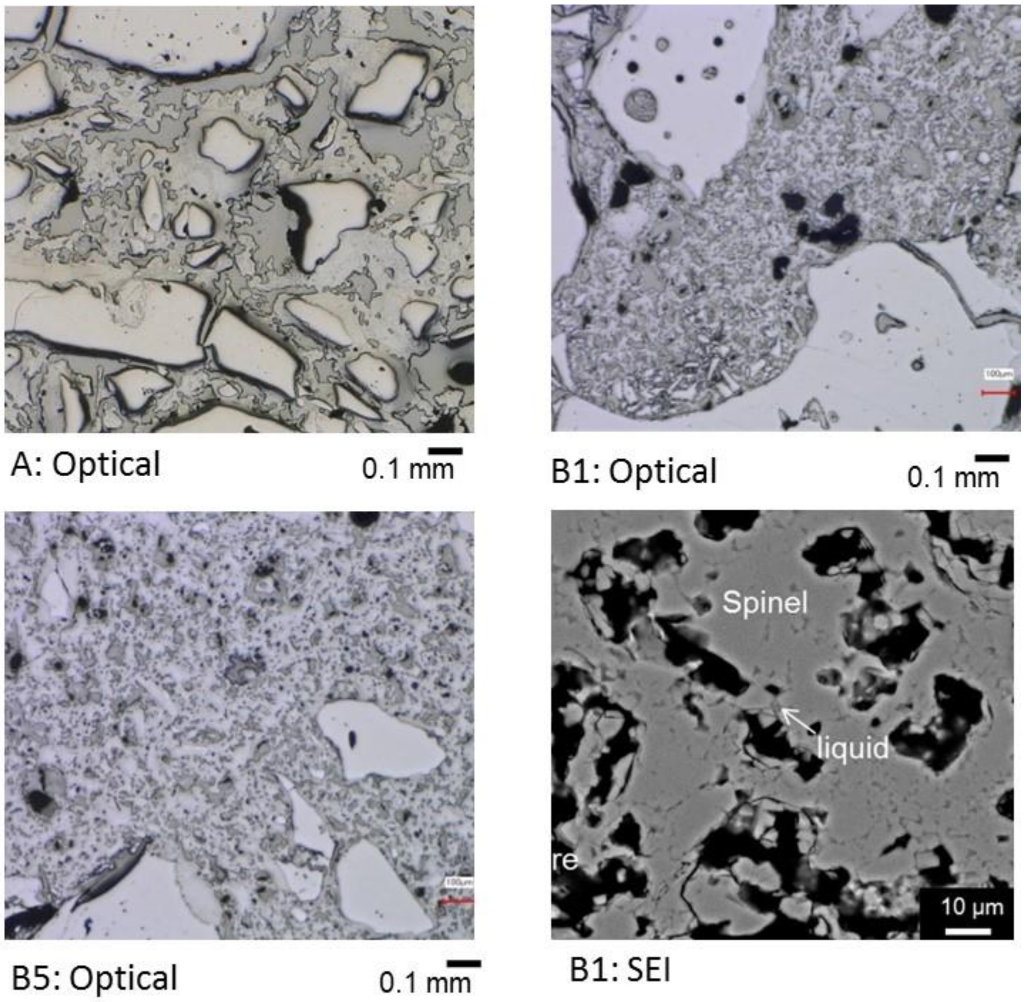

Figure 5. Microstructure of specimens after heating at 1500 ºC for 10 h.

Since material A possesses considerably large pores after heating, the activated overall mass transfer through penetrated slag that promotes refractory wear will occur. On the other hand, a lower overall mass transfer rate is expected for materials B1 and B5 due to the complex structure that increases flow resistance. Therefore, poor corrosion resistance of lowest porosity material A is explainable by the assumption described above. Thus, in the case of UAM brick, improvement of sinterability is equivalent to increase in evolution degree of spinel networking structure.

Figure 6 is the microstructure of B1 after being heated at 1500 ºC for 3 h. In this time duration, the spinel forming reaction (Equation 1) has not completed. According to Figure 6, spinel network evolution is assumed to be caused by the diffusion of Mg^{2+} through the liquid phase.

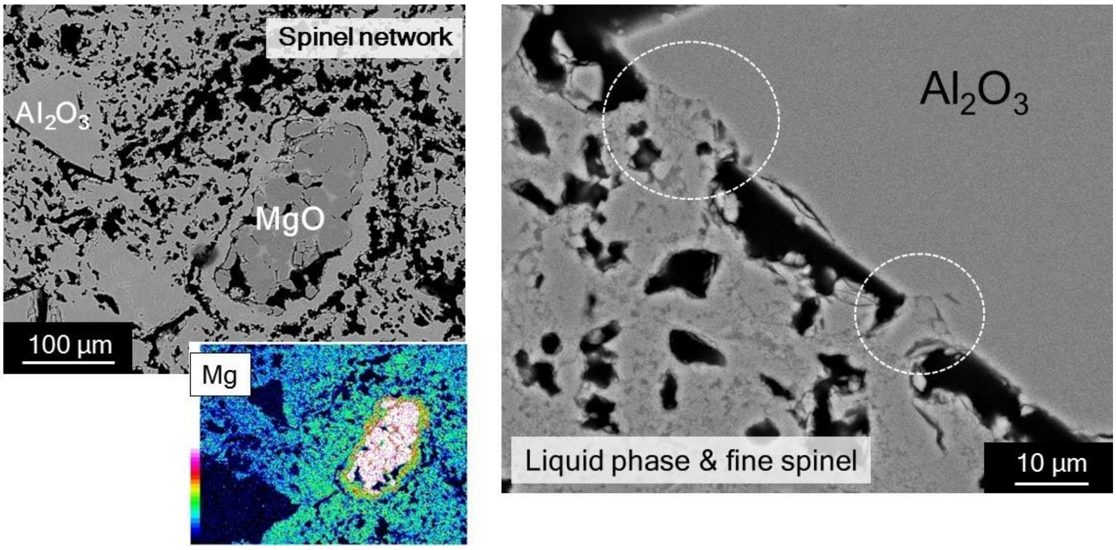

Figure 6. Microstructure of material B1 after heating at 1500 ºC for 3 h.

Figure 7 shows cut surface of material B1 after corrosion experiment. Smooth wear surface and thin slag penetrated layer were observed.

Figure 7. Cut surface of material B1 after corrosion experiment.

Figure 8 shows microstructure of B1 after the corrosion experiment. Penetration of CaO and FeO through spinel network structure was recognized. Assuming the poor degree of network structure evolution, slag penetration and linking of penetrated slag might occur much easier. Thus, it is reasonable to assume that reduction in porosity of suitably engineered microstructure is important for improving corrosion resistance.
Figure 9 shows phase relation of the system SiO_2-CaO-Al_2O_3-MgO [11]. MgO 10 mass% plane is demonstrated. In accordance with slag penetration, slag composition is considered to change straight toward Al_2O_3 since Al_2O_3 is supplied from UAM brick. According to the diagram, spinel is a stable solid phase in the penetrated slag.
Since the matrix network structure is comprised of spinel, the network structure is hard to dissolve in the penetrated slag. Thus, the continuous easy mass transfer that maintains sufficient solubility of spinel would promote the network dissolution. In order to achieve the situation, smooth exchange of molten slag according to active flow is necessary. Inversely, a complex structure with narrow fluid path is predicted to increase flow resistance, resulting in inhibition of refractory dissolution. Therefore, it was hypothesized that the formation of a suitably engineered complex spinel network with a small pore diameter microstructure would effectively improve the corrosion resistance of UAM bricks

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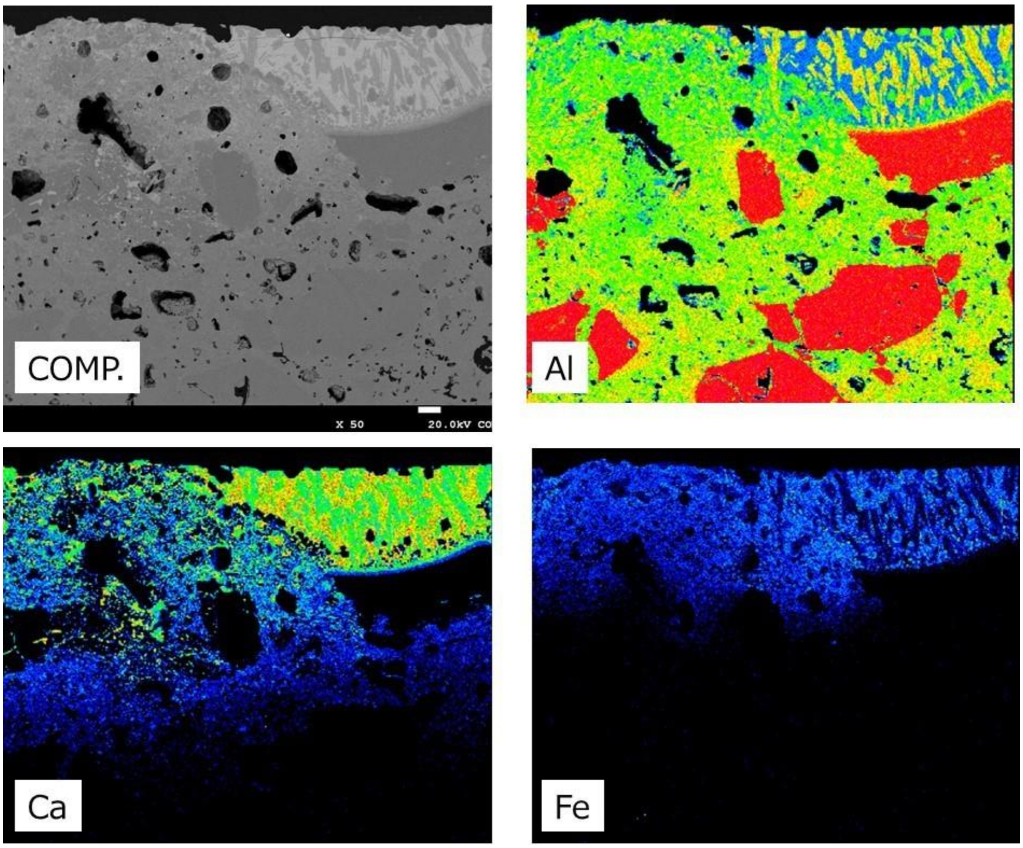

Figure 8. Microstructure of material B1 after corrosion experiment.

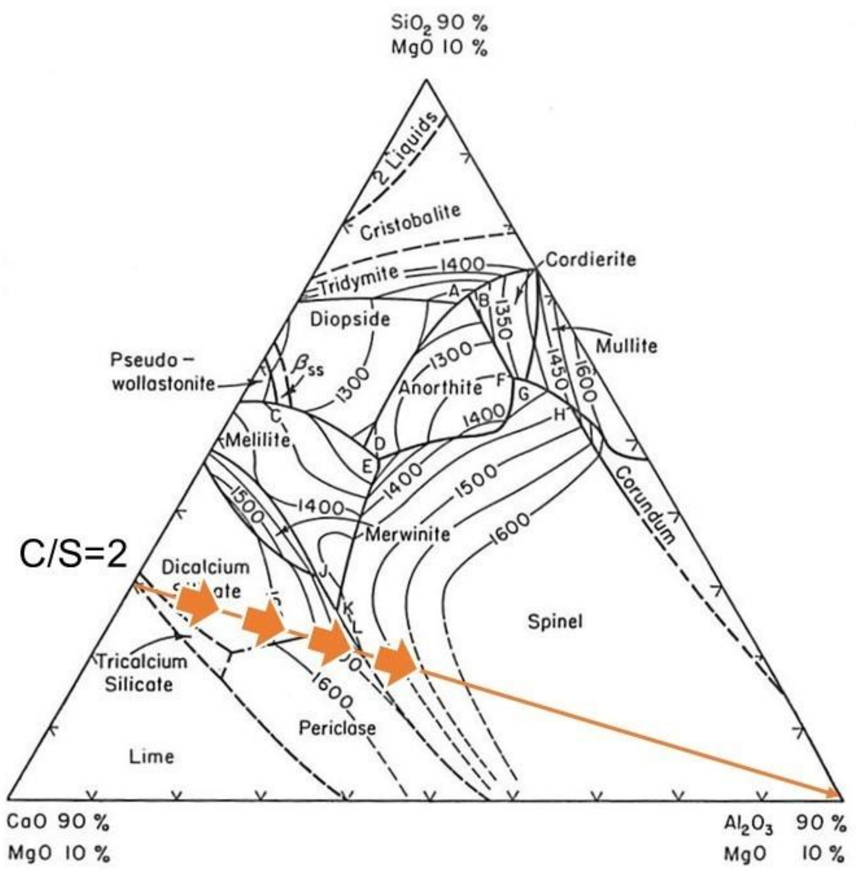

Figure 9. Phase diagram of the system SiO_2-CaO-Al_2O_3-MgO [11].

3.2 Commercial applications

3.2.1 Investigation of material B1 after use

Cut surface of the material B1 after commercial application to steel ladle of EAF-based Japanese steel mill X is shown in Figure 10. A thin slag penetrated layer is recognizable. Smoothness of the cut surface is evidence of a firm structure.

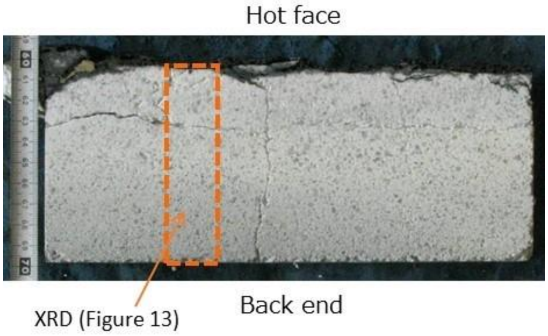

Figure 10. Cut surface of material B1 after use.

The microstructures of material B1 after use are shown in Figure 11. Slag penetration in the matrix was observed. Comparing microstructure of the sintered layer to the microstructure of B1 shown in Figure 6, a much thicker network structure and lower pore fraction were recognized.

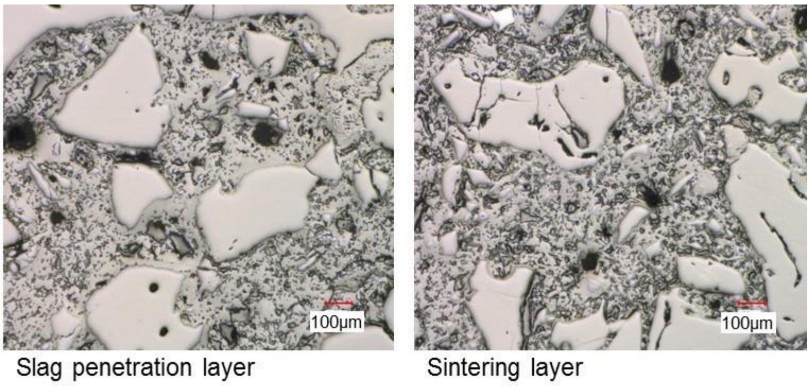

Figure 11. Microstructure of B1 after use.

The apparent porosity of material B1 after use was evaluated as 15.9 %. That is much smaller than the value evaluated after heating, i.e., 21.4 % (See Table 3). It is attributable to heating under the restrained conditions of an actual steel ladle. According to the adequate creep property as shown in Figure 3, further densification of the structure was expected for practical application. The smallness of the apparent porosity and microstructure after use are evidence of the above mentioned assumption.
Figure 12 shows the variation in the peak intensities of the spinel ($MgAl_2O_4$) and periclase (MgO) of material B1 after use as a function of distance from the hot face. The area indicated by the dotted open rectangular shown in Figure 10 was cut into a small peace and analyzed.
According to Figure 12, it was validated that the spinel forming reaction as shown in Equation 1 is completed in the vicinity of hot face. Thus, it was confirmed that evaluation of the specimen after sufficient heating is reasonable. In addition,

investigation of properties after heating under restrained conditions is desirable if it is possible.

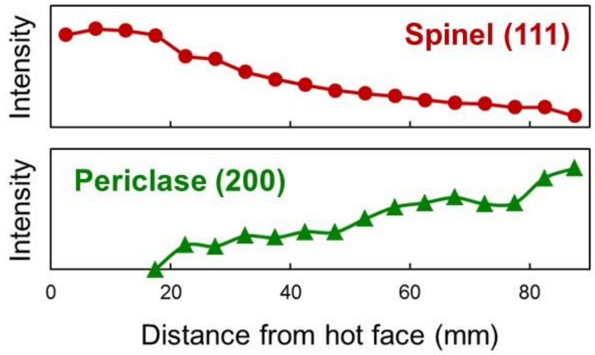

Figure 12. Variation of XRD peak intensities of spinel and periclase of B1 after use.

3.2.1 Application of material A to steel ladle of Brazilian steel mill

Figure 13 shows the appearance of a post-operation steel ladle at Brazilian steel mill Y to which low porosity UAM brick A was applied. While thin peeling was recognized, residual thickness was sufficient and a satisfactory long service life was assessed.

Figure 13. Snap shots of a steel ladle after use at a Brazilian steel mill in which UAM brick is applied.

3.2.3 Application of material B5 to a steel ladle at Japanese steel mill

The wear rates of newly developed B5 and standard material B1 are compared in Figure 14. Both of them were evaluated by steel ladle of EAF-based Japanese steel mill Z, Obviously, a considerable reduction in wear rate was achieved

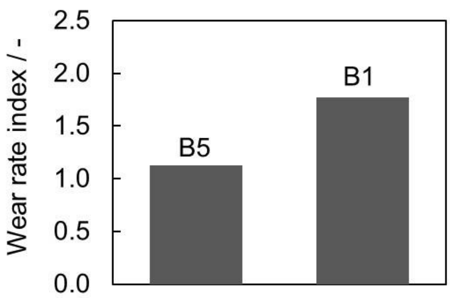

Figure 14. Wear rate of UAM bricks installed in steel ladle at Japanese mill Z.

Apparent porosity of B5 after use was 13.1%. It is also extremely small compared to the value evaluated after heating, i.e. 18.1%. Furthermore, it is smaller than the value evaluated for material B1 after use, i.e., 15.9 %. Hence, it was verified that reduction of apparent porosity after heating is effective for practical steel ladles that tend to be heated under restrained conditions.

4 CONCLUSION

Improvement in the durability of Unburned Al_2O_3-MgO (UAM) refractories for the steel ladle was achieved by focusing on microstructure engineering and porosity. According to laboratory experiments and practical application, it was found that reduction in apparent porosity with effective formation of spinel network structure during heating is important. In other words, low apparent porosity material with insufficient spinel network evolution shows poor corrosion resistance.

Spinel network evolution is accompanied by the pore size reduction that increases molten slag flow resistance, resulting in inhibition of smooth mass transfer through penetrated slag. As a result, the overall dissolution rate of refractory substances is lowered.

On the bases of the investigation of UAM brick after use, reduction in apparent porosity after heating is effective for practical steel ladles that tend to be heated under restrained conditions.

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