Effect of spinel on the properties of alumina-spinel-magnesia refractory castables for steel-ladle bottom

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ABSTRACT

Al_2O_3-spinel (AS) and Al_2O_3-MgO (AM) castables are generally used for the bottom of steel ladle depending on the operating and facility environment. AS castable has excellent thermal stability; however, structural spalling by slag erosion can occur. AM castable possesses good corrosion resistance; however, there are some problems associated with thermal spalling due to the differences in spinel production. In this study, the influence of spinel on the properties of Al_2O_3-spinel-MgO (ASM) castables was investigated to compensate for the limitations associated with AS and AM castables. Controlling the rate of linear change is crucial in ASM castables for controlling the particle size and content of spinel. In the case of spinel, the higher the fine particle ratio and the higher the overall content, the lower the expansion rate. Therefore, it was possible to compensate for the problems of the two castable types by controlling the rate of linear change with proper spinel particle size and content control. Field test results showed that there were no troublemakers due to spalling compared to those in AS castable, and that the average lifespan was improved by approximately 20%.

INTRODUCTION

Al_2O_3-spinel (AS) and Al_2O_3-MgO (AM) castable are widely used for steel-ladle lining owing to their excellent thermal properties[1]. Compared to high Al_2O_3 castable, the AS castable possesses high strength at high temperature obtained by adding pre-formed spinel to high Al_2O_3 castable. Moreover, the AS castable reduces the rate of slag penetration when it comes into contact with a slag, because Fe^{+} of the slag is entrapped on the cation lattice defect of spinel[2]. In contrast, the AM castable produces in-situ spinel by adding MgO to the high Al_2O_3 castable. Produced at high temperatures, in-situ spinel expands due to the difference in density between Al_2O_3 and MgO. When used in steel ladles, its expansion is suppressed to yield reduced porosity and improved corrosion resistance[3]. AS castable has better thermal stability than AM castable but has lower slag corrosion resistance, while slag penetration causes structural spalling. AM castable causes thermal spalling when volume expansion occurs during in-situ spinel formation. Figure 1 shows a damaged state during filed use of a AS castable and AM castable. The AS castable had many fine cracks in the impact zone and had a high erosion rate. AM castable had many large cracks by thermal spalling.

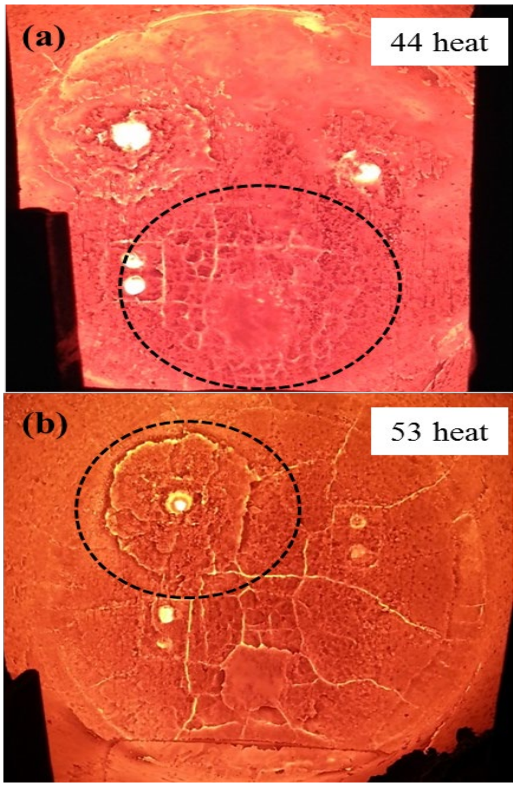


Fig. 1. Damage state during field use: (a) AS castable and (b) AM castable.

ASM castable, the hybrid system, was developed by adding MgO to AS castable and combining the characteristics of AS castable and AM castable[4)]. ASM castable forms in-situ spinel at high temperature but has a small permanent linear change than AM castable and high slag resistance than AS castable. Because spinel plays a key role in controlling the permanent linear change and improving slag penetration and corrosion resistance within the ASM castable, the disadvantages associated with AS and AM castables can be overcome by adjusting the spinel content and particle size to increase the lifespan.

Therefore, in this study, the effect of spinel on the ASM castable to select the optimized ratio was investigated, and applied the result to the castable for steel-ladle bottom to improve the life compared to the AS castable and AM castable.

EXPERIMENTAL PROCEDURE

In the first test of this study, a mount of magnesia (seawater magnesia, MgO 95 mass%, Korea) with size of 75 µm or less was fixed. Tests were performed by adjusting the content of spinel (AR-78, Almatis, Netherlands) with size of 90 µm or less, and the content of tabular alumina (Almatis, Netherlands) with size 45 µm or less. Table I shows the composition of raw materials according to the spinel content.

Table I. Raw material composition according to spinel content

Raw materials	C1	C2	C3
Sintered spinel 20 µm >	α		
Sintered spinel 90 µm >	β	1.2β	1.4β
Tabular alumina 45 µm >	γ	0.8γ	0.6γ

In the second test was conducted by adjusting the ratio of spinel (AR-78, Almatis, Netherlands) with the size of 20 µm or less and that of spinel with size of 90 µm or less, using 4 different specimens with varying the particle sizes. Table II shows the composition of raw materials according to the spinel particle size.

Table II. Raw material composition according to particle size of spinel

Raw materials	P1	P2	P3	P4
Sintered spinel 20 µm >	0.6α	0.8α	α	1.2α
Sintered spinel 90 µm >	1.8β	1.6β	1.4β	1.2β
Tabular alumina 45 µm >	0.6γ			

Each test sample was cast to a size of 40 mm × 40 mm × 160 mm, cured at 25 °C and 40% relative humidity for 24 h, and then dried at 110 °C for another 24 h. To check the permanent linear change, heat treatment was performed at 1,500 and 1,600 °C thrice for 3 h. The cold crushing strength(CCS), cold modulus of rupture(CMOR), porosity, and bulk density were measured with dried sample and one time heat-treated sample at 1,500 and 1,600 °C for 3h. Thermal expansion was observed when heated to 1,500 °C three times using a dilatometer (DIL 402C, Netzsch, Germany). Subsequently, to compare the thermal properties according to the spinel particle size, an erosion test was performed using a ladle slag with CaO/SiO_2 = 6.05 on a rotary corrosion tester. The spalling test was then conducted at 1,400 °C for 50 min and air-cooled for 10 min until the test specimens was fractured

X-ray diffraction (XRD) analysis was performed using X'pert PRO (PANalytical, Netherland) to confirm the spinel and CA_6 crystal phases at 1,600 ° C.

RESULTS AND DISCUSSION

EFFECT OF CONTENT OF SPINEL

Adjusting the permanent linear change of the ASM castable is one of the most important factor for stable use at high temperatures. Figure 2 shows the permanent linear change when the heat treatment was performed three times with the spinel content of 90 μm or less. It is evident from the figure that the permanent linear change decreases at 1,500 and 1,600 °C as the spinel content increases (C1 → C3).

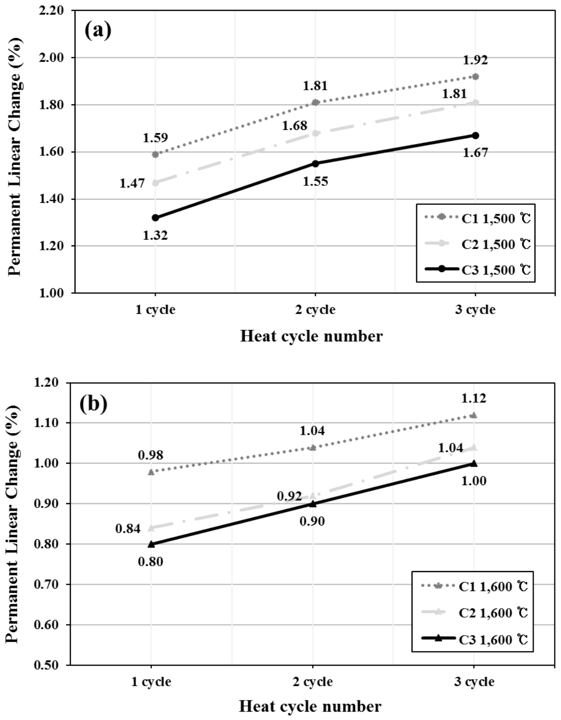


Fig. 2. Permanent linear change according to spinel content (three cycles): (a) 1,500 and (b) 1,600 °C

Figure 3 shows a thermal expansion according to spinel content. Similar to figure 2, the thermal expansion decreases as the spinel content increases. This can be attributed to the differences in calcium hexaluminate (CA_6) formation. In ASM castable, CA_6 is produced through the reaction of alumina and lime in the liquid phase, and the CA_6 production decreases as the amount of liquid phase produced increases. At this time, a pre-formed spinel in ASM castable, becomes a liquid phase at 1,300 °C or higher, so the amount of liquid phase produced increases as the content of spinel increases, and the amount of CA_6 produced decreases[5)]. According to the thermal expansion result at 1,400 °C or higher, the expansion decreases as the spinel content increases due to the decrease in the amount of CA_6 produced.

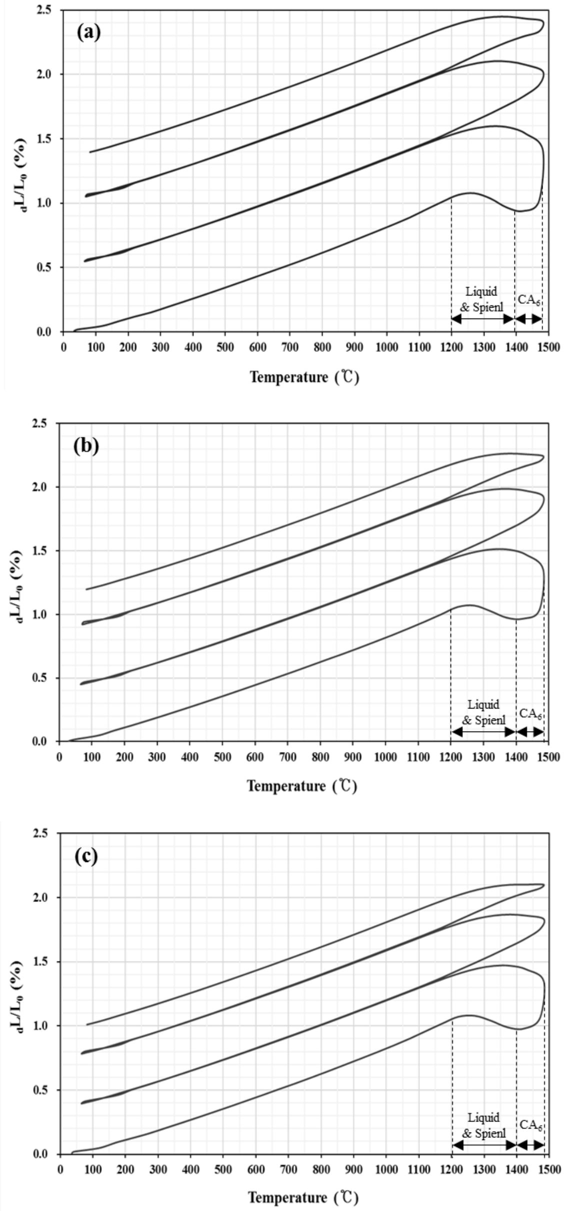


Fig. 3. Thermal expansion according to spinel content (three cycles): (a) C1, (b) C2, and (c) C3

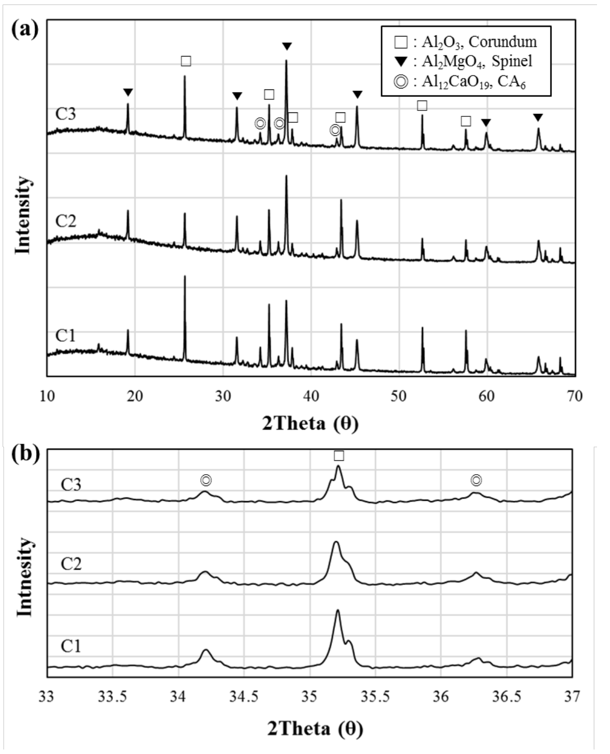


Fig. 4. XRD analysis results by spinel content after heat treatment at 1,600 °C: (a) 2θ = 10–70° and (b) 2θ = 33–37°

Figure 4 shows the result of the XRD analysis by the spinel content. According to this figure, the CA_6 peak decreases as the spinel content increases, similar to the result of the thermal expansion analysis. Thus, the amount of CA_6 produced decreased and a small permanent linear change was obtained at 1,400 °C or higher as the spinel content increased.

EFFECT OF PARTICLE SIZE OF SPINEL

To examine the characteristics, this tests were conducted by adjusting the ratio of spinel of 20 µm or less and spinel of 90 µm or less by changing the particle size of the spinel.

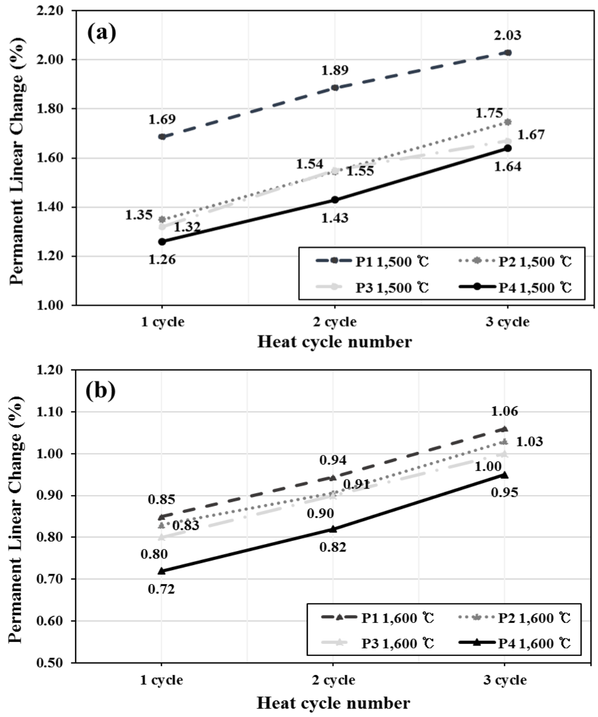
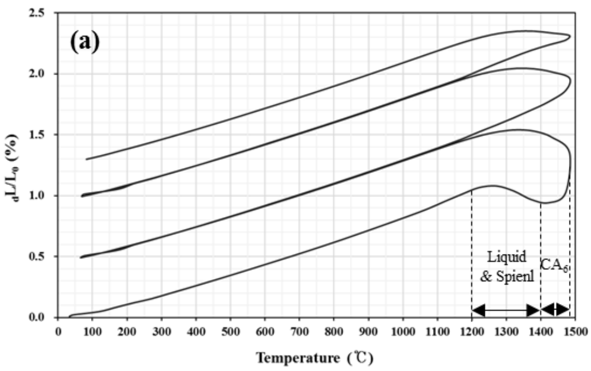


Fig. 5. Permanent linear change according to spinel particle size (3cycle): (a) 1,500 °C and (b) 1,600 °C

Figure 5 shows the permanent linear change when the heat treatment was performed three times according to the spinel particle size. As shown in the figure, finer the spinel particle size (P1 → P4), smaller is the permanent linear change.



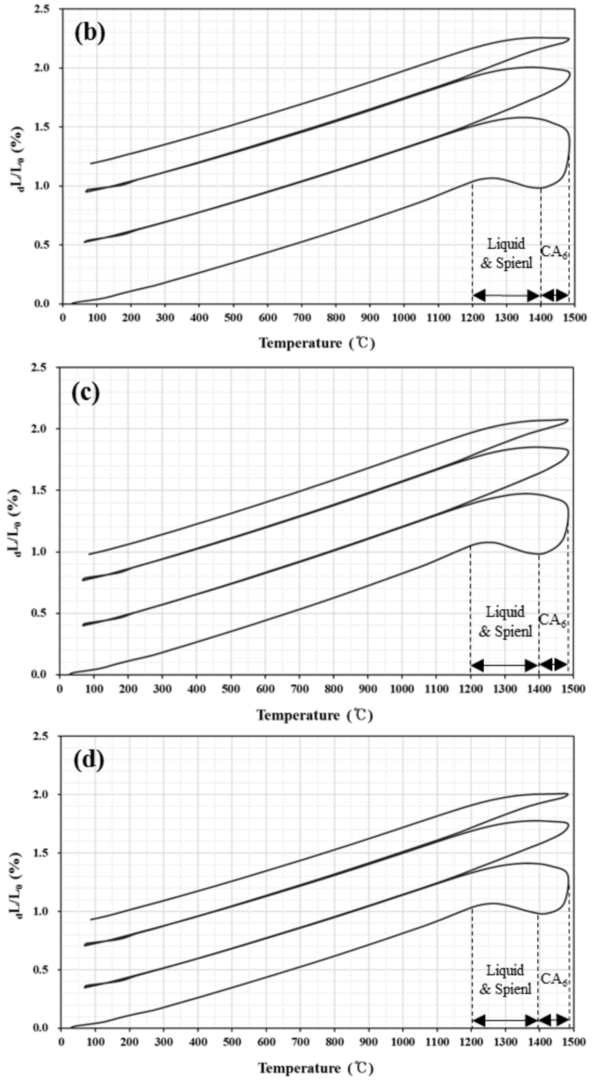


Fig. 6. Thermal expansion according to spinel particle size (3cycle): (a) P1, (b) P2, (c) P3 and (d) P4

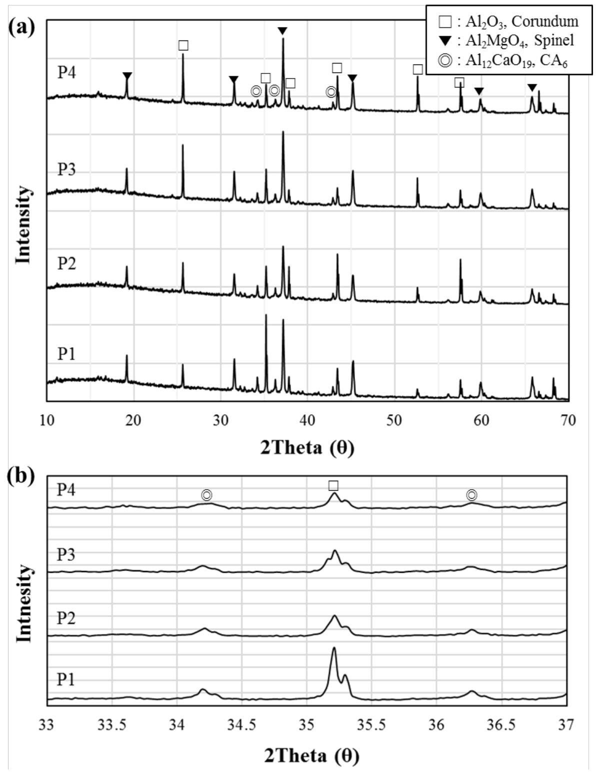


Fig. 7. X-ray diffraction analysis results by spinel particle size after heat treatment at 1,600 °C: (a) 10-70θ and (b) 33-37θ

Figure 6 shows the thermal expansion according to the spinel particle size. The result showed that the thermal expansion had the same tendency as the permanent linear change. The finer the spinel particle size is, the larger is the specific surface area of the spinel distributed in the matrix, resulting in increased liquid formation and reduced CA_6 production. These results can be confirmed from the XRD results shown in Figure 7. Furthermore, the more densely matrix is formed when the fine spinel content increases, and the sintering property increases at high temperatures thus showing tendency to shrink.

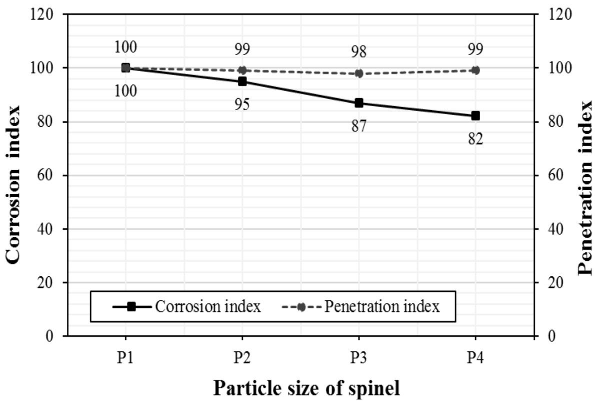


Fig. 8. Rotational erosion test results with spinel particle size

The result of the rotary erosion test according to the spinel particle size is shown in Figure 8, to explain the thermal property according to the spinel particle size. The penetration index was at the same level regardless of the spinel particle size owing to the in-situ spinel produced in the ASM castable. There was a difference in the corrosion index: a finer spinel particle size corresponded to a larger corrosion resistance. It is also known that the finer the spinel particle size, the smaller is the CA_6 production. In ASM castable, CA_6 is present around the aggregate and in the matrix, and physicochemically protects the reaction with slag. Nevertheless, the reason the corrosion resistance increased as the spinel particle size became finer is that when the specific surface area of the pre-formed spinel increased, not only did it have a more densely matrix but the contact area between the slag and the spinel also increased. Consequently, As the contact area between the slag and the spinel increases, Fe^{+} in the slag more easily entrapped into the Mg^{+} site that exists as a vacancy in the spinel and the viscosity of slag increase thus reducing the corrosion rate of slag. Figure 9 shows a cross-sectional photograph of the sample after the rotary erosion test.

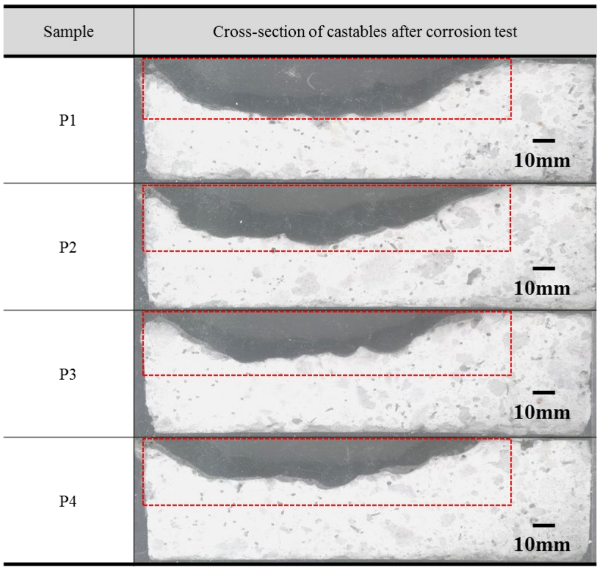


Fig. 9. Rotational erosion test piece cross section with spinel particle size

Figure 10 shows the results of the spalling test according to the spinel particle size. The thermal shock resistance (spalling resistance) increased as spinel particle size increased. The reason for the decrease in spalling resistance — despite the decrease in the thermal expansion with the spinel particle size becoming finer — is that the modulus of elasticity increases as the matrix becomes finer. The modulus of elasticity increases when increases compressive stress. This is shown in the CCS results in Figure 11. Compressive strength increases at 1,500 and 1,600 °C as the particle size of spinel decrease. Spalling resistance follows the following equation:

$$\text{Thermal shock resistance} = \sigma_f k / E \alpha \quad (1)$$

where σ is the fracture strength, k is the thermal conductivity, E is the modulus of elasticity, and α is the coefficient of thermal expansion

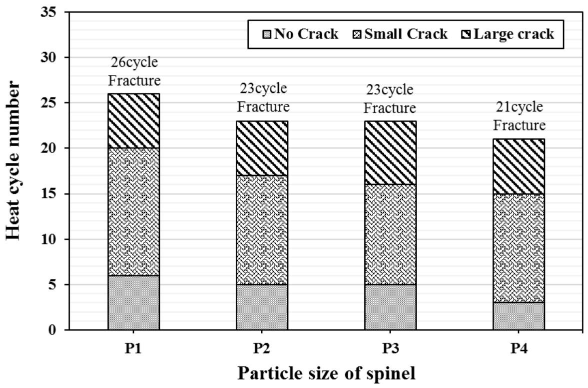


Fig. 10. Spalling test results according to spinel particle size (Crack width 1 mm ≤: Small crack and Crack width 5 mm ≤: Large crack)

Figure 11 shows CMOR and CCS by spinel particle size. Although the specimens have the same strength value at 110 °C, a finer spinel particle size corresponds to a denser matrix at 1,500 °C and 1,600 °C, which leads to the increase in CMOR and CCS.

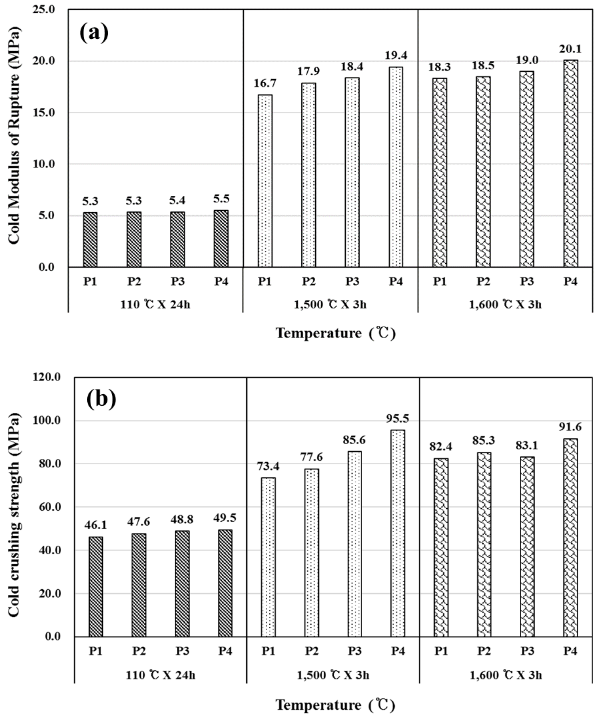


Fig. 11. CMOR (a) and CCS (b) test results by spinel particle size

Figure 12 shows the results of bulk density and apparent porosity. The tendency was similar to that of the previous experiments: the finer the spinel particle size, the denser was the matrix; hence, the porosity decreases while the bulk density increases at 1,500 °C and 1,600 °C.

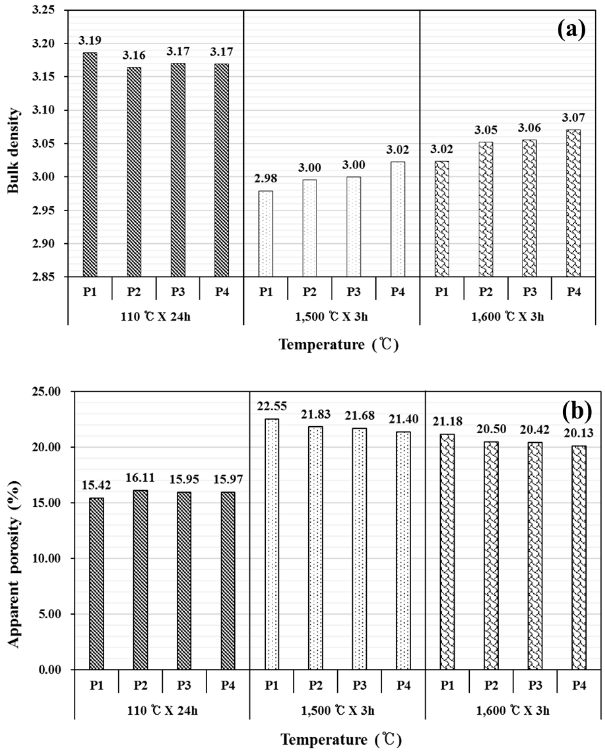


Fig. 12. Bulk density (a) and apparent porosity (b) test results by spinel particle size

Based on these experiments, the optimal condition that complemented the shortcomings of AS castable and AM castable was determined to be P3, which was applied to the field to confirm the damage morphology during use (shown in Figure 13). As a result, the service life was used up to an average of 60 heat, which was approximately 20% higher than the average service life of 50 heat for AS castable. Although no noticeable difference was found between the average service life of AM castable from that of ASM castable (60 heat), ASM castable was more stable due to a reduced thermal spalling.

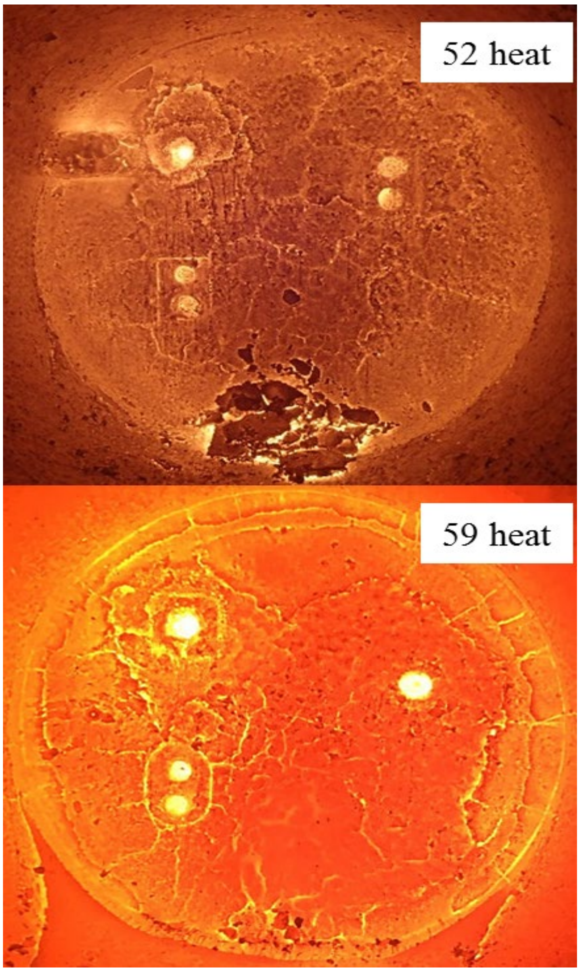


Fig. 13. ASM castable field damage during use

CONCLUSION

In this study, the effect of spinel was confirmed in order to use ASM castable with high lifespan in the field by supplementing the shortcomings of AS castable and AM castable. When the spinel content was increased in the ASM castable, the pre-formed spinel transited to liquid phase above 1,300 °C and reduce CA_6 formation, which then reduced the permanent linear change at 1,500 °C and 1,600 °C. When the particle size of the spinel was changed, not only did the CA_6 production decrease as the spinel particle size became finer but the permanent linear change also decreased as the matrix became dense. As for the thermal property, the finer the spinel particle size, the higher is the corrosion resistance, which is also affected by the more densely matrix. Moreover, as the specific surface area of the spinel increased, the contact area between the slag and the spinel also increased; consequently, the Fe^{+} within the slag was entrapped to the spinel cation lattice defects and reduced the corrosion rate. In spite of permanent linear change decreased at 1,500 °C and 1600 °C, the spalling resistance decreased as the spinel particle size became finer because of modulus of elasticity increased. Based on these results, a field test was conducted under the optimal spinel content conditions to show that the service life for improved by approximately 20% compared to AS castable. Furthermore, unlike the AM castable, the thermal spalling was reduced to enable a stable operation.

REFERENCES

1. S. K. Chen, M. Y. Cheng, S. J. Lin and Y. C. Ko, "Characteristics of Al_2O_3–MgO and Al_2O_3–spinel castables for steel ladles", Ceramics Int., 28 [7] 811-817 (2002).

2. M. K. Cho and G. G. Hong, "Effects of MgO content of spinel on the reaction of spinel with CaO-Al2O3-SiO2 slag", J. of the Kor. Ceram. Soc., 36 [4] 410-416 (1999).

3. M. K. Cho and G. G. Hong, "Corrosion behavior of spinel clinkers by ladle slag", J. of the Kor. Ceram. Soc., 36 [10] 1035-1039 (1999).

4. C. Wohrmeyer. C. Parr, H.Fryda, J. M. Auvray and S. Li, "Castables with improved corrosion resistance based upon a novel calcium aluminate cement", Refractories worldforum**,** 4 [3] 99-105 (2012).

5. E. Y. Sako, M. A. L. Braulio and V. C. Pandolfelli, "Insights on in situ $MgAl_2O_4$ formation mechanism and its correlation with the corrosion resistance of spinel-containing refractory castables", Refractories worldforum, 6 [1] 79-83 (2014).