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Effect of Spinel Content on Hot Strength of Alumina-spinel Castables in the Temperature Range 1000–1500°C

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Abstract

Hot modulus of rupture of Al_2O_3-spinel castables containing 5–15 wt% alumina-rich magnesia alumina spinel and 1·7 wt% CaO generally increases with increase in spinel content and temperature from 1000 to 1500°C. The magnitudes of hot modulus of rupture of castables containing 15 wt% spinel and 1·7 wt% CaO are 14·3 MPa at 1400°C and 15·6 MPa at 1500°C, while those of castables containing 20 wt% spinel and 1·7 wt% CaO are 12·5 MPa at 1400°C and 14·7 MPa at 1500°C. The former castables contained 15 wt% spinel of −75 μm size, while the latter contained 10 wt% spinel of +75 μm size and another 10 wt% spinel of −75 μm size. The bond linkage between the CA_6 and spinel grains in the matrix is believed to cause both the spinel content and temperature dependence of hot strength of Al_2O_3-spinel castables, as well as fine grain spinel even in amount less than coarser grain spinel to be more effective for enhancing hot strength. The trend of the magnitude of thermal expansion under load (0·2 MPa) above 1500°C of the castables is not necessarily indicative of the magnitude of hot modulus of rupture at 1400 or 1500°C. © 1999 Elsevier Science Limited. All rights reserved

Keywords: Al_2O_3-spinal castables, mechanical properties, strength, spinels, refractories.

1 Introduction

Alumina-spinel castables are being widely used as steel ladle linings to replace high alumina bricks due to the world wide shortage of bricklayers and increasing labor costs. Mori *et al.*[1] reported that addition of 10–30 wt% alumina-rich MgO-Al_2O_3 spinel confers superior slag resistant properties to alumina-spinel castables, whose life is twice as long as high-alumina brick. The mechanism of slag resistance of the castables was thoroughly and microscopically studied by Korgul *et al.*[2]

MacZura *et al.*[3] studied alumina-spinel castables containing 15 wt% alumina-rich MgO-Al_2O_3 spinel (78 wt% Al_2O_3), 15 wt% calcium aluminate cement and 70 wt% alumina and observed that the 1400 and 1500°C hot moduli of rupture (HMOR) are significantly higher than those of the high-alumina castable without addition of spinel. They attributed the hot strength enhancement to the strong interlocking bond between the CA_6 and corundum or spinel grains. Vance *et al.*,[4] previously, ascribed the hot strength enhancement to possible CA_2 or CA_6 linked corundum and spinel grains. Chan *et al.*[5] found that the modulus of rupture of Al_2O_3-spinel castables containing 20 wt% Al_2O_3-rich MgO–Al_2O_3 spinel and 1·36–2·04 wt% CaO generally increases with an increase in both CaO content and temperature from 1300 to 1500°C, but it remains virtually constant from 1000 to 1300°C; microscopic observation of the castable fired at 1500°C for 3 h reveals the growth of some CA_6 crystals out of the Al_2O_3-rich spinel grains in the bonding matrix of the castable; the bond linkage between the CA_6 and spinel grains in the matrix is believed to cause both the CaO content and temperature dependence of the hot strength of the Al_2O_3-spinel castables as well as the hot strength enhancement of high- Al_2O_3 castables with addition of Al_2O_3-rich spinel.

Spinel content dependence of hot strength of the Al_2O_3-spinel castables has not been systematically studied. Moreover, the work of MacZura *et al.*[3] dealt with castables whose CaO content is on the border between regular cement and low cement

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castables. In the past 15 years the low cement castables have become more popular. The purpose of the present work is to explore the influence of spinel content on the hot strength of typical low cement castables.

2 Experimental

2.1 Materials

The chemical composition of raw materials is listed in Table 1. Aggregates used were white fused alumina, while fine and ultra fine aluminas were of calcined type. The alumina cement contained 17 wt% CaO and the sintered alumina-rich spinel contained 90 wt% Al_2O_3. Three Al_2O_3-spinel castables containing 5–15 wt% spinel and 1·7 wt% CaO and one high- Al_2O_3 castable containing 1·7 wt% CaO, without addition of spinel, were prepared.

2.2 Procedure

Castables were cast with water (6 wt% solids) with the aid of a vibrating table. Flowability of the castables was measured by using a vibrating flow table immediately after mixing.[6] Castables were cured in air at ambient temperature for 24 h and then dried at 110°C for at least 16 h before firing. Specimens 160 by 40 by 40 mm were cast for measuring physical properties including hot modulus of rupture (HMOR). Physical properties such as apparent porosity, bulk density, permanent linear change, cold modulus of rupture and cold crushing strength of the castables fired at 1500°C for 3 h were measured based on JIS.[6] All physical properties were determined on three specimens with the average value taken.

The specimens for hot modulus of rupture measurements were heated at a rate of 100°C min^{-1} from ambient temperature to 100°C, and, for tests at higher temperatures, further on at a rate of 5°C min^{-1} from 1000 to 1250°C and 3°C min^{-1} from 1250°C up to the final testing temperature. The specimens were held at 1000, 1300, 1400 and 1500°C for 3 h before measurement at temperature was made. Strength at temperature was determined using a three-point bending method. The span and loading rate used in measuring the strength were 100 mm and 0·49 MPa s^{-1}, respectively. Strength at temperature was determined using three specimens with the average value taken.

A cylindrical specimen, 50 mm in height and 50 mm in diameter, was cast for the refractoriness-under-load test. A differential technique was employed for measuring the deformation. The specimen was heated at a constant rate of 6°C min^{-1} below 1000°C and 3°C min^{-1} above 1000°C, at a fixed load of 0·2 MPa. Deformation under load versus temperature was recorded from ambient temperature up to 1640°C. The high temperature load testing machine (model HW-10K, EKO, JAPAN) was used for carrying out the measurements.

Table 1. Chemical analysis of raw materials and particle size of oxides

Type	*Composition (wt%)*						
	MgO	*Al_2O_3*	*CaO*	*Fe_2O_3*	*SiO_2*	*Na_2O*	*Particle size*
Sintered spinel	10·0	89·4	0·1	0·1	0·1	–	< 1 mm
Fused alumina	–	99·7	–	0·013	0·016	0·15	< 30 mm
Calcined alumina	–	99·7	–	0·01	0·02	0·27	< 15 μm
Reactive alumina	–	99·6	–	0·01	0·02	0·26	< 10 μm
Cement	–	81·0	17	0·05	0·70	1·00	

3 Results and Discussion

3.1 Microscopic observation of castables fired at 1500°C for 3 h

Figure 1 reveals that some CA_6 crystals have grown out of the spinel grains in the bonding matrix of castable containing 2·04 wt% CaO and 20 wt% spinel. Identification of CA_6 was established by energy dispersive spectroscopy (EDS), based chemical analysis and the EDS spectra of the points, as shown in Table 2 and Fig. 1. Diffusion is, of course, necessary for the CaO to react with the corundum in the Al_2O_3-rich spinel for the formation of CA_6 to set up the bond linkage between CA_6 and spinel grains in the bonding matrix. Notably, such CA_6 crystals are not observed to have grown out of the fused corundum grains in the bonding matrix of the castables. This is probably a result of fused corundum being more inert than the sintered spinel.

The probability of bond linkage between the CA_6 and spinel grains in the bonding matrix of the castable increases with increased temperature, CaO and spinel contents, as well as number of spinel grains.

3.2 Changes in physical properties after firing at 1500°C for 3 h

Table 3 reveals that there is no significant difference in the magnitudes of apparent porosity and permanent linear change (PLC) for castables containing 5–15 wt% spinel and 1·7 wt% CaO. The positive permanent linear change is caused by the growth of CA_6 crystals.[7] The growth of CA_6 crystals in alumina grains leading to complete disintegration of the grains[8] can result in apparent

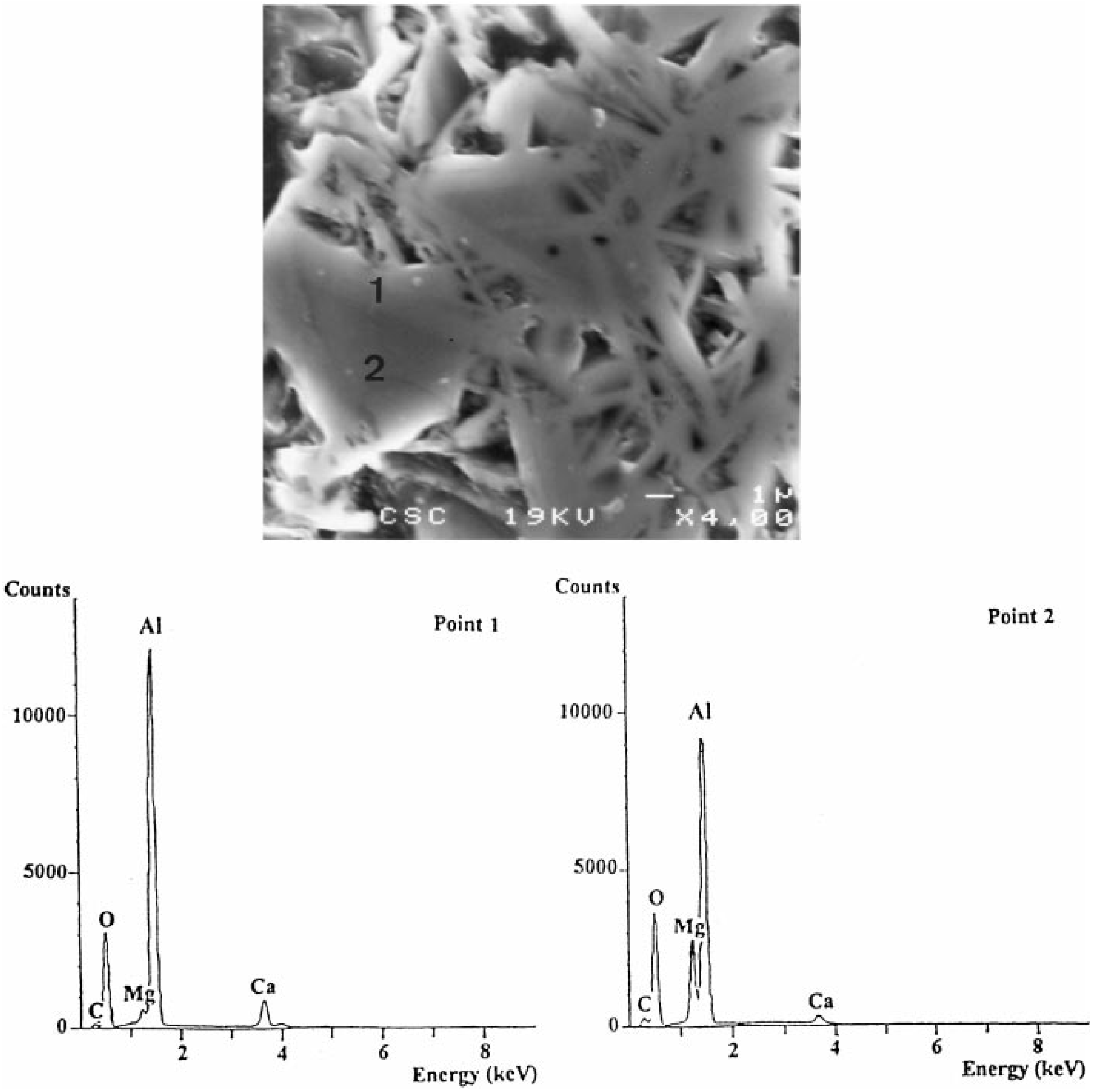

Fig. 1. SEM micrograph and EDS spectra of the bonding matrix of the Al_2O_3-spinel castable containing 2·04 wt% CaO and 20 wt% spinel after being fired at 1500°C for 3 h. Points 1 and 2 were, respectively, identified as CA_6 and spinel, based on the chemical analyses of the points as shown in Table 2.

Table 2. EDS chemical analysis of the points as shown in Fig. 1

Point	*Composition (wt%)*		
	Al_2O_3	*CaO*	*MgO*
1	91·05	7·23	1·56
2	83·16	1·21	15·43

porosity increase. These castables containing the same amount of CaO fired at 1500°C for 3 h are expected to have a similar amount of CA_6. Consequently, there is no significant difference in the magnitudes of apparent porosity and permanent linear change.

Figure 2 clearly shows that cold crushing strength of the castables can be correlated linearly with spinel content. Although there is a huge scatter of cold modulus of rupture measurements as shown in Fig. 3, cold modulus of rupture can also be correlated almost linearly with spinel content. The huge scatter of the measurements is believed to be caused by using 10–30 mm size aggregates in the mix grading for preparation of the specimen, 160 by 40 by 40 mm. Fracture surface of the fired castables after hot and cold moduli of rupture measurements showed a mixed character of transgranular and intragranular fractures. Visual inspection of the fracture surface of the specimens revealed that transgranular fracture frequently took place if 10–30 mm size aggregates were incidentally located across the cross section at the center of a beam specimen. The transgranular fracture of particularly large aggregates resulted in higher strength and a wide scatter of the measurements.

The magnitudes of cold modulus of rupture, cold crushing strength and porosity of castables containing 15 wt% spinel and 1·7 wt% CaO, fired at 1500°C for 3 h, are 21·2, 83·8 MPa and 23·2%, respectively, for the present work, while those of castables containing 15·0 wt% spinel and 2·55 wt%

Table 3. Physical properties of castables fired at 1500°C for 3 h

Castable type	*Spinel content (wt%)*	*Bulk density (g/cm³)*	*Apparent porosity (%)*	*Permanent linear change (%)*
AS05	5·0	2·98	22·9	0·14
AS10	10·0	2·99	22·5	0·08
AS15	15·0	2·95	23·2	0·10
High-alumina	0	2·99	23.2	0.106

AS05: alumina-spinel castable containing 5 wt% spinel and 10 wt% cement.
AS10: alumina-spinel castable containing 10 wt% spinel and 10 wt% cement.
AS15: alumina-spinel castable containing 15 wt% spinel and 10 wt% cement.

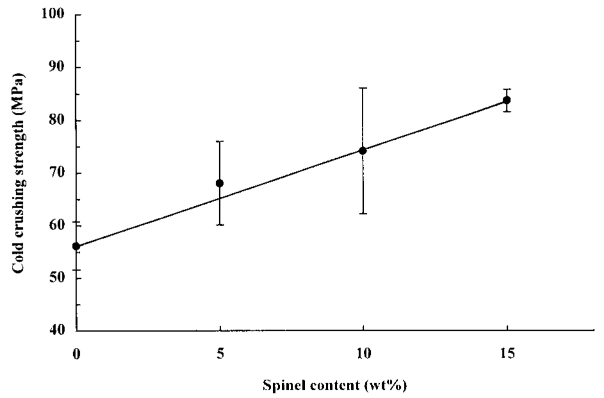

Fig. 2. Effect of spinel content on cold crushing strength of Al_2O_3-spinel castables fired at 1500°C for 3 h.

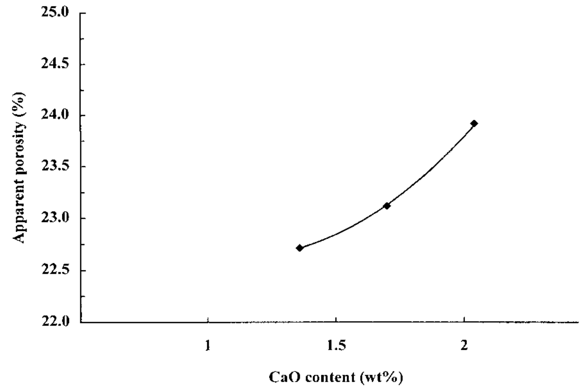

Fig. 4. Effect of CaO content on apparent porosity of Al_2O_3-spinel castables containing 20 wt% spinel.

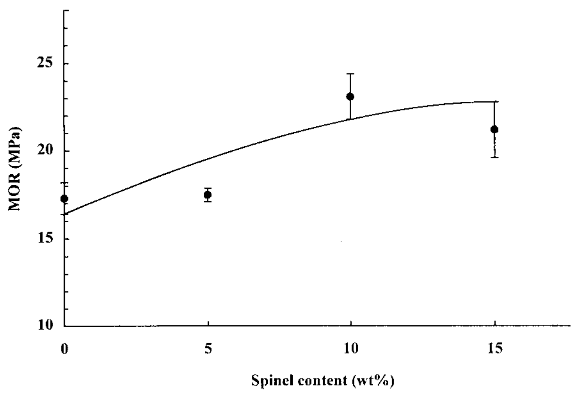

Fig. 3. Effect of spinel content on cold modulus of rupture of Al_2O_3-spinel castables fired at 1500°C for 3 h.

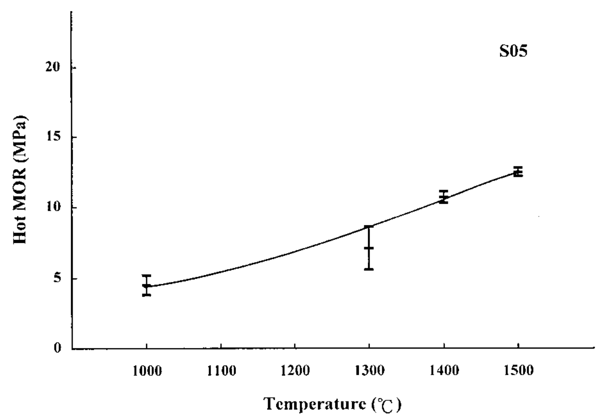

Fig. 5. Hot modulus of rupture of castables containing 5 wt% spinel and 1·7 wt% CaO.

CaO, fired at 1500°C for 5 h, are 32·8, 141 MPa and 25%, respectively, as published by MacZura *et al.*[3] The disparity in the magnitudes of strengths and porosity, reported by the present work and MacZura *et al.*,[3] is most probably caused by the difference in CaO contents of the castables, based on the findings that cold modulus of rupture and cold crushing strength of Al_2O_3-spinel castables fired at 1500°C for 3 h increase with increased CaO content[5] and Fig. 4.[9]

3.3 Hot modulus of rupture

Figures 5–7 show that hot modulus of rupture of castables containing 5–15 wt% spinel and 1·7 wt% CaO generally increases with increasing spinel content and temperature, from 1000 to 1500°C. Figure 8 demonstrates that hot modulus of rupture of high-Al_2O_3 castables containing 1·7 wt% CaO, without addition of spinel, increases very slightly with increasing temperature.

As can be seen from Fig. 7, the magnitude of hot modulus of rupture of castables containing 15 wt% spinel and 1·7 wt% CaO increases slightly from 14·3 MPa at 1400°C to 15·6 MPa at 1500°C, while that of castables containing 15 wt% spinel and 2·55 wt% CaO increases slightly from 21·6 MPa at 1400°C to 22·2 MPa at 1500°C, as published by MacZura *et al.*[3] It is believed that the higher magnitudes of hot modulus of rupture are mainly caused by the higher CaO content of castables, which results in the increased bond linkage between CA_6 and spinel grains in the bonding matrix of castables. A comparison of Figs 7 with 9 shows that the magnitudes of hot modulus of rupture of castables containing 15 wt% spinel and 1·7 wt% CaO are 14·3 MPa at 1400°C and 15·6 MPa at 1500°C, while those of the castables containing 20 wt% spinel and 1·7 wt% CaO are 12·5 MPa at 1400°C and 14·7 MPa at 1500°C. The former castables contained 15 wt% spinel of $-75\,\mu$m size, while the latter contained 10 wt% spinel of $+75\,\mu$ size and another 10 wt% spinel of $-75\,\mu$m size. Apparently, fine grain spinel even in amount less than coarser grain spinel can be more effective for enhancing the hot strength of Al_2O_3-spinel castables.

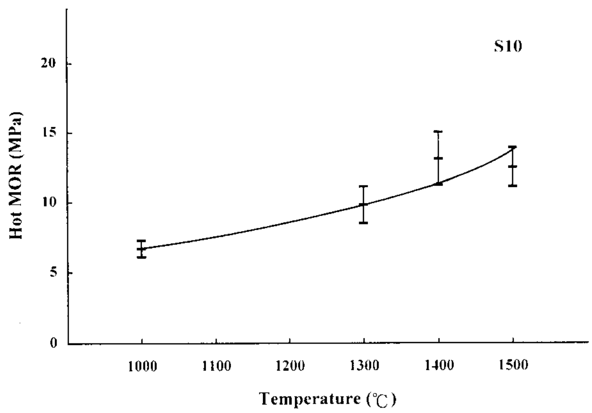

Fig. 6. Hot modulus of rupture of castables containing 10 wt% spinel and 1·7 wt% CaO.

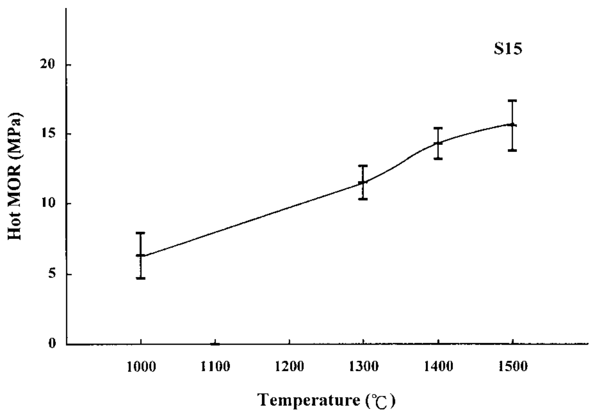

Fig. 7. Hot modulus of rupture of castables containing 15 wt% spinel and 1·7 wt% CaO.

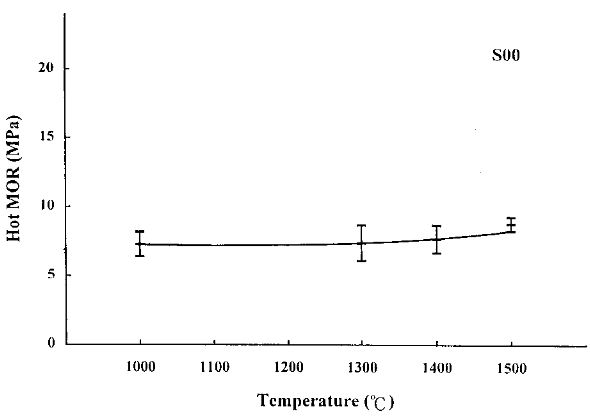

Fig. 8. Hot modulus of rupture of high-Al_2O_3 castables containing 1·7 wt% CaO without addition of spinel.

The probability of bond linkage between the CA_6 and spinel grains in the bonding matrix of the castable increases with increased temperature, CaO and spinel contents, and number of spinel grains in the matrix based on Fig. 1. This explains why hot modulus of rupture of these castables increases with increased temperature and spinel content, and fine grain spinel even in amount less than coarser grain spinel can be more effective for hot strength enhancement.

3.4 Refractoriness under load

In order to prevent thermal spalling, the amount of fines ($-75\,\mu$m) was carefully controlled to be less than 35 wt% castable in the present work. Reactive and calcined aluminas in particular were maintained constant in these castables. Consequently, the amount of fine fused alumina ($-75\,\mu$m) in the castables is inversely proportional to the amount of spinel in the castables. Grain composition of castables is given in Table 4.

One gram of CaO needs 10·93 g of Al_2O_3 for formation of CA_6 stoichometrically. One hundred grams of castables contain 10 wt% cement. Ten grams of cement contain 8·3 g of Al_2O_3, and 1·7 g of CaO, which need 18·58 g of Al_2O_3 for complete formation of CA_6. Hence, there is a need of additional 10·28 g of Al_2O_3 for CA_6. Referring to

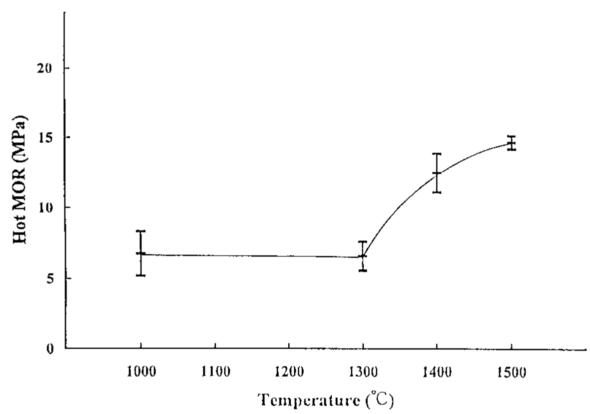

Fig. 9. Hot modulus of rupture of castables containing 20 wt% spinel and 1·7 wt% CaO.[5]

Table 4. Grain composition of castables (wt%)

Castable type	*Aggregates*	*Matrix*		
	Alumina > 0·075 mm	*Alumina < 0·075 mm*	*Spinel < 0·075 mm*	*Cement*
AS05	69	16	5	10
AS10	69	11	10	10
AS15	69	6	15	10

AS05: alumina-spinel castable containing 5 wt% spinel and 10 wt% cement.
AS10: alumina-spinel castable containing 10 wt% spinel and 10 wt% cement.
AS15: alumina-spinel castable containing 15 wt% spinel and 10 wt% cement.

Table 4, calculation indicated that castables containing 15 wt% spinel are deficient in 4·28 g of fine alumina in the matrix for formation of CA_6, while castables containing 10 wt% spinel have an slightly excessive amount of 0·72 g of fine alumina in the matrix and castables containing 5 wt% spinel have an amply excessive amount of 5·72 g of fine alumina in the matrix. The small amount of these fine aluminas associated with formation of liquid at elevated temperature is ignored.

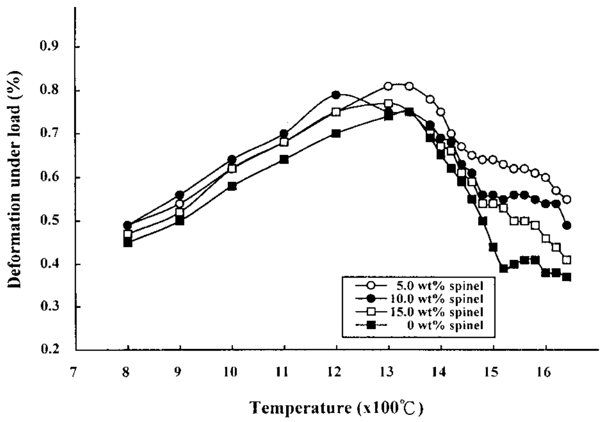

Fig. 10. Refractoriness-under-load of Al_2O_3-spinel and high-Al_2O_3 castables.

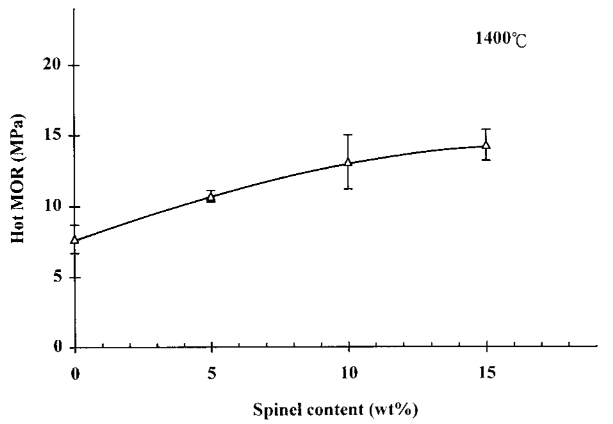

Fig. 11. Effect of spinel content on hot modulus of rupture of Al_2O_3-spinel castables containing 1·7 wt% CaO at 1400°C.

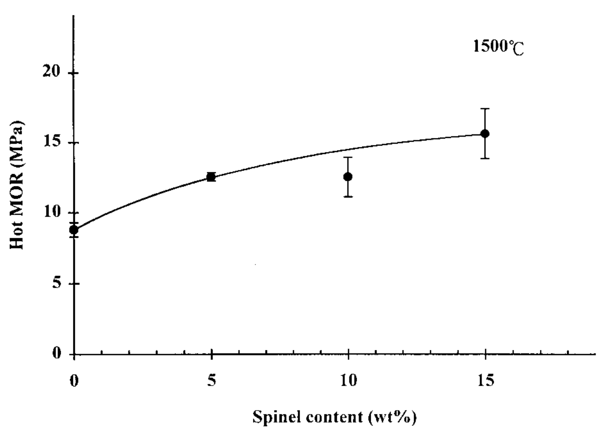

Fig. 12. Effect of spinel content on hot modulus of rupture of Al_2O_3-spinel castables containing 1·7 wt% CaO at 1500°C.

Iida *et al.*[7] found that the growth of CA_6 results in permanent volume expansion of the fired Al_2O_3 and Al_2O_3-spinel castables. Eto *et al.*[10] observed that CA_6 was identified in the Al_2O_3-spinel castables fired at 1500°C and higher temperatures, but no CA_6 was identified at 1300°C. As can be seen in Fig. 10, in castables containing 5 wt% spinel the growth of CA_6 becomes obvious at around 1440°C, at which the slope of the expansion curve changes notably, and the magnitude of thermal expansion under load above 1500°C is greatest because of ample availability of fine grain alumina in the matrix, which facilitates growth of CA_6, while in castables containing 10 and 15 wt% spinel growth of CA_6 also becomes obvious at around 1500°C, at which the slopes of the expansion curves also change notably, and the magnitude of thermal expansion under load above 1500°C of castables containing 10 wt% spinel is greater than that containing 15 wt% spinel due to the former having more fine grain alumina in the matrix than the latter. The high- Al_2O_3 castable, without addition of spinel, has more fine grain alumina than any others, but the magnitude of thermal expansion under load above 1500°C is the least as shown in Fig. 10. This is most probably caused by lack of bond linkage in the matrix between the CA_6 and spinel grains. In summary, the trend of the magnitude of thermal expansion under load of the castables above 1500°C is dictated by the combined action of growth of CA6 and bond linkage between the CA_6 and spinel grains in the matrix.

Moreover, Fig. 10 shows that the trend of the magnitude of thermal expansion under load above 1500°C increases with decreasing spinel content in the castables, while Figs 11 and 12 show that hot modulus of rupture at 1400 and 1500°C increases with increasing spinel content. It is worth noting that the trend of the magnitude of thermal expansion under load above 1500°C of the Al_2O_3-spinel castables is not necessarily indicative of the magnitude of hot modulus of rupture at 1400 or 1500°C.

4 Conclusions

1. Hot modulus of rupture of Al_2O_3-spinel castables generally increases with increase in spinel content and temperature from 1000 to 1500°C.
2. The magnitudes of hot modulus of rupture of castables containing 15 wt% spinel and 1·7 wt% CaO are 14·3 MPa at 1400°C and 15·6 MPa at 1500°C, while those of castables containing 20 wt% spinel and 1·7 wt% CaO are 12·5 MPa at 1400°C and 14·7 MPa at 1500°C. The former castables contained 15 wt% spinel of −75 μm size, while the latter

contained 10 wt% spinel of +75 μm size and another 10 wt% spinel of −75 μm size.

3. The bond linkage between CA_6 and spinel grains in the matrix results in temperature and spinel content, as well as number of spinel grains dependence of hot strength of Al_2O_3-spinel castables.
4. The trend of the magnitude of thermal expansion under load above 1500°C of the castables is not necessarily indicative of the magnitude of hot modulus of rupture at 1400 or 1500°C.

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References

1. Mori, J., Watanabe, N., Yoshimura, M., Oguchi, Y., Kawakami, T. and and Matsuo, A., Material design of monolithic refractories for steel ladle. *Bull. Am. Ceram. Soc.*, 1990, **69**, 1172–1176.
2. Korgul, P., Wilson, D. R. and Lee, W. E., Microstructural analysis of corroded alumina-spinel castable refractories. *J. Eur. Ceram. Soc.*, 1997, **17**, 77–84.
3. MacZura, G., Madono, M., Kriechbaum, G. W. and Sewell, B., Low moisture regular corundum/spinel castables with superior properties. In *Proc. Unified Int. Tech. Conf. on Refractories*, Kyoto, Japan, 1995, vol. 3, pp. 179–186.
4. Vance, M. W., Kriechbaum, G. W., Henrichsen, R. A., MacZura, G., Moody, K. J. and Munding, S., Influence of spinel additives on high-alumina/spinel castables. *Bull. Am. Ceram. Soc.*, 1994, **73**, 70–74.
5. Chan, C. F. and Ko, Y. C., Effect of CaO content on the hot strength of alumina-spinel castables in the temperature range of 1000–1500°C. *J. Am. Ceram. Soc.*, 1998, **81**, 2957–2960.
6. JIS Refractories, R2521-1995, Refractories Manual '97, The Technical Association of Refractories, Japan, 1997, pp. 372–385.
7. Iida, M., Mori, J., Ishii, H., Yoshimura, M., Oguchi, Y. and Kawakami, T., Permanent linear change of alumina-spinel castables. *Taikabutsu*, 1990, **42**, 273–274.
8. Fuhrer, M., Hey, A. and Lee, W. E., Microstructural evolution in self-forming spinel/calcium aluminate-bonded castable refractories. *J. Eur. Ceram. Soc.*, 1998, **18**, 813–820.
9. Ko, Y. C., China Steel Corporation, Kaohsiung, Taiwan, R.O.C., unpublished research, 1997.
10. Eto, S., Jono, K., Mori, J., Hirota, T., Hitomi, S., Tanaka, S. and Mafune, T., Effect of CaO content on the properties of alumina-spinel castable for steel ladle. In *Proc. Unified Int. Tech. Conf. on Refractories, Sao Paulo, Brazil*, 1993, pp. 1289–1300.