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Effect of preformed and in situ spinels on microstructure and properties of a low cement refractory castable

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Abstract

Two types of magnesium-aluminate spinels, one commercially available as preformed powder and the other prepared from cheaper precursors by the sol–gel route as a semidried reactive mass, were characterized in terms of particle size distribution, XRD phase evolution and chemical composition. These two were incorporated in a high alumina based refractory castable in different concentrations and fired at elevated temperatures. Those preformed and in situ spinel bonded castables were characterized in terms of bulk density, apparent porosity, cold crushing strength, thermal shock resistance, volume shrinkage, flexural strength, XRD, SEM, EDS and slag corrosion resistance test to understand the effect of both kinds of spinel in the castable composition.

Keywords: A. Sol–gel processes; D. Spinel; High alumina castable

1. Introduction

With the advent of quality steel making processes, it became essential to opt for good quality refractories, especially monolithic castables suitable in the presence of molten slag and metal [1]. The growing demand and application of these castable materials encourage researchers and producers to investigate their physical, chemical and thermo-mechanical properties [2–5]. Magnesium aluminate spinel is now extensively applied in high performance refractory castables because of its unique combination of properties specially chemical resistance. This is very much desirable for steel ladles where the refractory lining has to withstand aggressive operational atmosphere of secondary refining process [6,7]. High alumina aggregates, preformed spinel grains and refractory cement bonds are the main constituents of a spinel-alumina castable, which is popularly used nowadays to improve slag corrosion and erosion resistances [8–11]. It is also known that preformed spinel grains rich in either MgO or Al_2O_3 or stoichiometric are commercially prepared after very high thermal treatment [10], of which the former one is not desirable to some applications due to the chances of hydration of second phase periclase. Alumina-spinel castables have also been developed with in situ spinel forming material where fine MgO powder taken in the batch reacts with Al_2O_3 fines to form spinel on firing [12–14]. However, other routes to prepare in situ spinel bonded castables have been little discussed. During the last few decades, many novel processing methods emerged in the area of ceramic fabrications, e.g. plasma spray decomposition, sol–gel synthesis, freeze-drying and so on, which paved the way for spinel preparation too [15,16]. So, a newer approach can be to prepare in situ $MgAl_2O_4$ hydrated spinel additive for application in refractory castable from a cost effective sol–gel route to benefit in terms of purity, homogeneity, time and temperature of heating [17–19].

In this work a commercially available preformed spinel, rich in Al_2O_3 was examined with respect to chemical analysis, particle size distribution (PSD), X-ray diffraction (XRD), and added in different concentrations to a high alumina based low cement castable. An in situ spinel was also prepared via the sol–gel route, characterized with respect to p^H, solid content, PSD, XRD and incorporated in different concentrations to the same castable. These two types of fired specimens were

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characterized and compared in terms of BD, AP, CCS, flexural strength, volume change and thermal shock resistance. The XRD analysis, scanning electron microscopy and energy dispersive spectroscopy (EDS) of some selected fired samples were performed to understand the mode of interaction of preformed and in situ spinels with the constituents of castables. To take account of the practical importance of those two types, the castables were subjected to slag corrosion test at severe conditions with blast furnace and converter slags.

2. Experimental

The characteristic features of preformed (R) and in situ (G) spinels have been shown in Table 1 (a) and (b), respectively. The preparation of hydrated $MgAl_2O_4$ via the sol–gel route for being used as in situ spinel has been mentioned in our previous papers [17,18] which corroborated the formation of spinel at significantly lower temperature (500–600 °C). The particle size distribution of G and R spinels was determined from MALVERN Autosizer II C and Mastersizer E Ver.1.2b instruments. Those two type of spinels, one in powder form (R) and the other in gel form (G), were incorporated in increasing concentrations (wt.%) in a castable composition and their effects in the thermo-mechanical properties of that refractory were studied. The results of chemical analysis of the raw materials used for the preparation of original spinel-free low cement castable has been given in Table 2, and Table 3 shows the batch

Table 1a
Characteristics of preformed spinel additives (R)

Chemical analysis (wt.%)	R
Al_2O_3	90.02
MgO	8.987
SiO_2	0.05
Fe_2O_3	0.08
Na_2O	0.15
CaO	0.23
Bulk density (g/cc)	3.29
Crystalline phases	Spinel, corundum
Particle size (μm)	<45
Amount added to castable (wt.%)	2, 4, 8%

Table 1b
Physicochemical properties of in situ spinel additive (G)

Characteristics	Sol gel spinel
Solid content	~10%
pH	3–4
Average particle size	11 nm
$MgAl_2O_4$ (wt.%) in calcined additive	>99.8%
Amount added to castable (wt.%)	0.5, 1.2

Table 3
Spinel free castable formulation and its physical properties after firing at 1500 °C firing for 2 h

Constituents	Content (wt.%)
White fused alumina	77
Microfine alumina	8
Microsilica	5
High alumina cement	6
White tabular alumina	4
SHMP (deflocculant)	0.05
Water	5–7%
Bulk density (g/cc)	2.97
Apparent porosity (%)	15
Cold crushing strength (at 1500 °C, kg/cm^2)	1400
PLC (%, 1500 °C, 2 h)	+0.2

Table 4
Chemical composition of (a) blast furnace and (b) converter slags

Constituents	Contents (wt.%)
(a) Blast furnace slag	
SiO_2	33.74
CaO	32.27
Al_2O_3	18.98
MgO	9.88
(b) Converter slag	
CaO	47.6
SiO_2	15.0
MgO	10.6
FeO	20.5
Al_2O_3	1.3
MnO	2.0

Table 2
Chemical analysis of raw materials of spinel free low cement castable

Type	Composition (wt.%)								
	Al_2O_3	CaO	SiO_2	Fe_2O_3	Na_2O	MgO	TiO_2	K_2O	LOI
White fused alumina	99.25	0.1	0.2	0.05	0.3				
Microfine alumina	99.1		0.02	0.01	0.26				0.5
Microsilica			98.0						0.8
High alumina cement	74.2	24.5	0.2	0.2	0.1	0.4	0.1	0.08	
White tabular alumina	99.4		0.05	0.04	0.3				

composition of the same castable along with its physical properties after being fired at 1500 °C with soaking for 2 h. It should be mentioned that the preformed (R) spinel was used in 2,4 and 8.0% in the spinel-free castables; but the amount of in situ spinel (hydrated gel mass G) added to the same castable was fixed to 0.5,1 and 2.0% because excess use of gel mass adversely affects the porosity and green strength of the castables and causes an installation problem due to migration of finer particles [3].

The preformed and in situ spinel bonded LCC samples were also named as R and G to distinguish between the two types of additives. All the samples were cast by simple tapping method with cube (25.4 mm) and bar (75×12.5×12.5 mm) type moulds after properly estimating the compact particle packing (i.e., distribution modulus) from the granulometry of the original castable. These specimens were then cured under humid conditions for 24 h followed by 24 h of air-drying and oven drying at 110 °C for 3 days. Finally the samples were fired at 900, 1200 and 1500 °C with 2 h of soaking for each temperature. The two types of fired spinel bonded castables were subjected to various tests such as bulk density (BD), apparent porosity (AP), cold crushing strength (CCS), spalling or thermal shock resistance in terms of percent residual strength (%RS), flexural strength and slag corrosion resistance at elevated temperature. A comparison was carried out between two kinds of castables bonded with 2% of both R and G additives in terms of change in BD, AP, CCS and %RS with increasing temperature. The above changes in properties with temperature were again verified by altering the concentration other than 2% for both R and G types. A further comparison was done with respect to change of BD, AP, CCS and %RS of two castables fired at 1500 °C with increasing concentration of preformed and in situ spinels. BD, AP, CCS tests were done by standard methods. With the R and G type of bars previously fired at 1500 °C the experiment for flexural strength was performed with a Universal Testing machine INSTRON-1185 at 25 °C with cross head speed of 1.0 mm/min and a span of 50 mm. The thermal shock (i.e. spalling) resistance of R and G specimens previously fired at 1500 °C, was noted in terms of

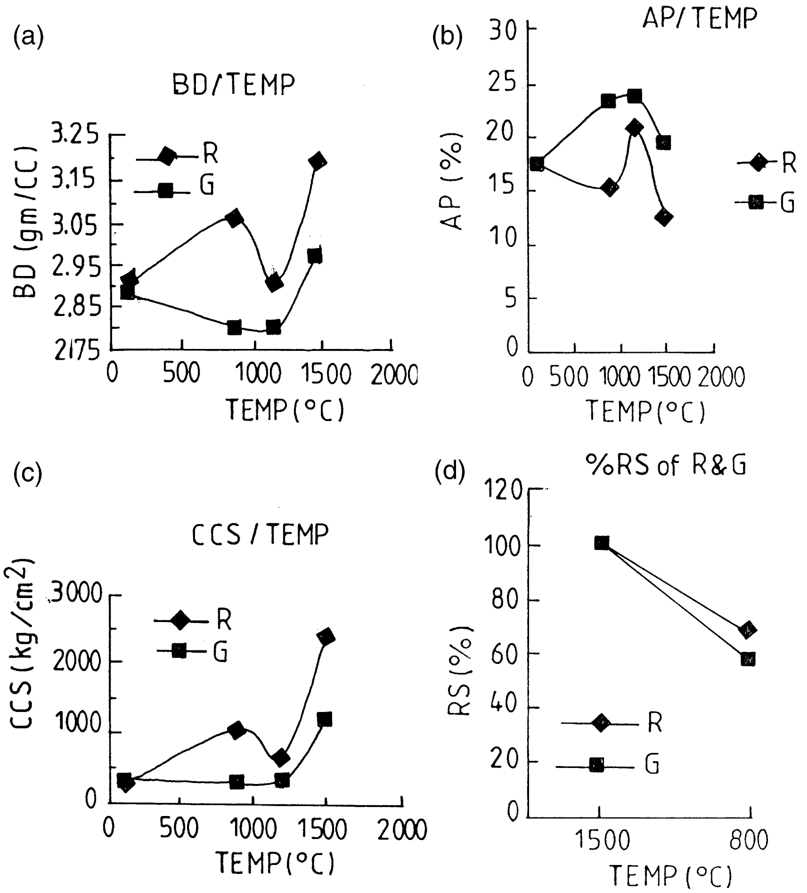

Fig. 1. Variation of (a) BD (b) AP (c) CCS and (d) %RS with temperature for 2.0% of two types of spinel bonded castables (R = preformed, G = in situ).

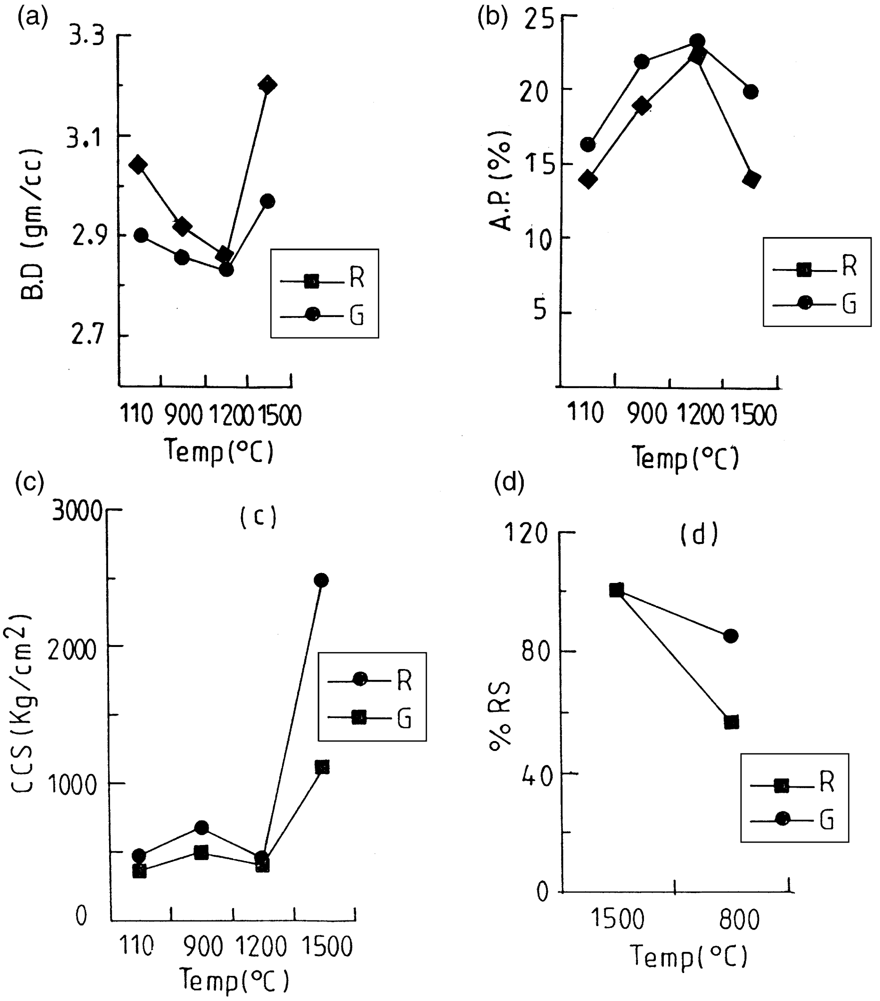

Fig. 2. Variation of (a) BD (b) AP (c) CCS and (d) %RS with temperature for 4.0% of preformed (R) and 0.5% of in situ (G) spinel bonded castables.

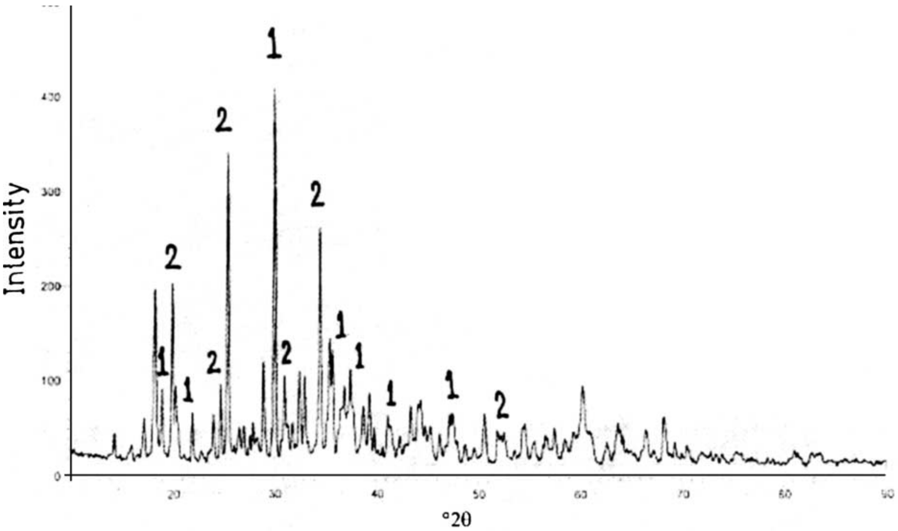

Fig. 3. XRD curve of refractory high alumina cement used in batch composition of castable (1 = $CaO.Al_2O_3$, 2 = $CaO.2Al_2O_3$).

residual strength after 5 cycles of thermal shock, each cycle was completed by putting the fired samples in a furnace at 800 °C for 10 min followed by immersing them in water at room temperature for another 10 min. For all these tests, an average result of four samples was taken at each temperature and each concentration for both kinds of castables. For the test of slag corrosion resistance, the cubes were pre fired at 1200 °C after

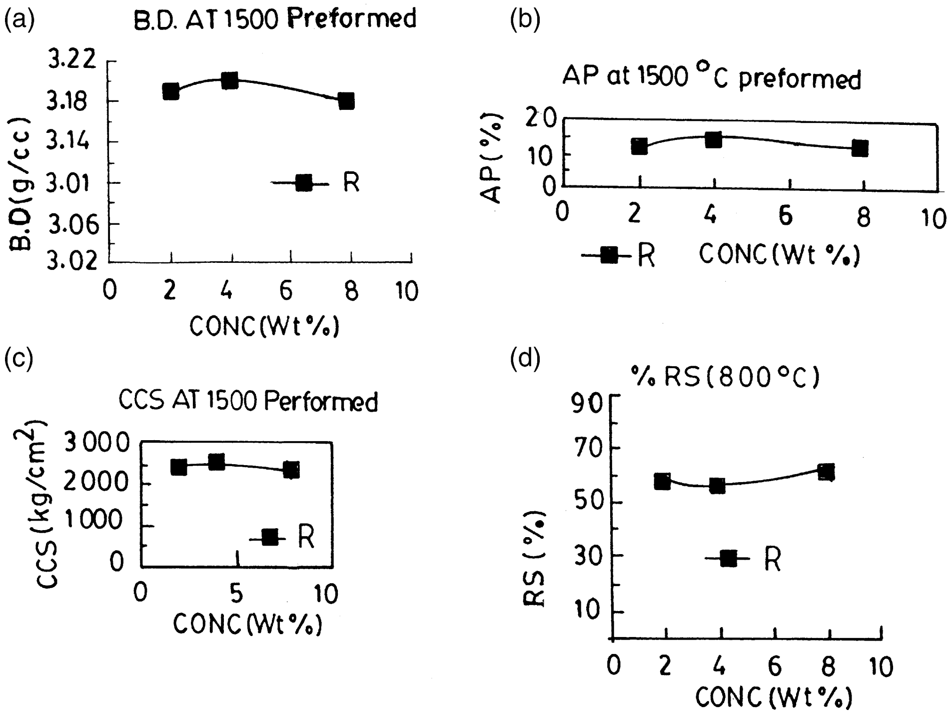

Fig. 4. Physical properties of preformed spinelbonded castable (R) fired at 1500 °C in relation to increasing concentration of spinel additives, Variation of (a) BD (b) AP (c) CCS and (d) %RS.

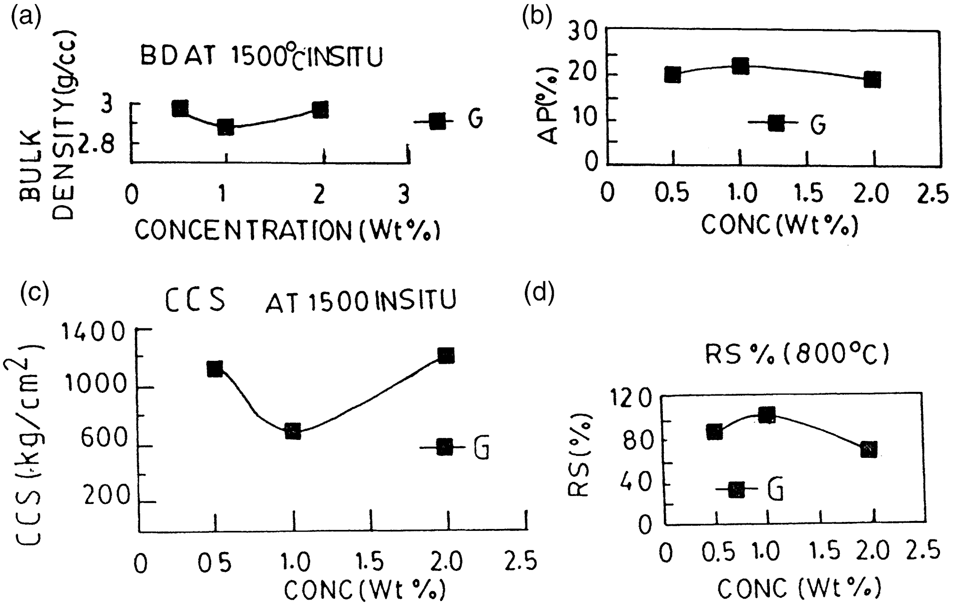

Fig. 5. Physical properties of in situ spinel bonded castable (G) fired at 1500 °C in relation to increasing concentration of spinel additives, Variation of (a) BD (b) AP (c) CCS and (d) %RS.

making cylindrical groove of the same size at the centre of all cubes; the grooves were then filled up with Blast furnace and Converter slags (supplied from TISCO and VSL, India respectively) given in Table 4, and the cubes were fired at 1500 °C for 2 h. After cooling, cubes were cut across the middle and the extent of slag penetration was studied. SEM, EDS and XRD of selected samples fired at 1500 °Cwere performed to envisage the interaction of two kinds of spinels in the castables. The SEM study was done in the instrument JEOL JSM-5200 model; EDS study had the system resolution 187 eV and X-ray diffraction patterns were taken from the instrument with Ni filtered CuK_α, 40 kV, 20 mA and 30 mA.

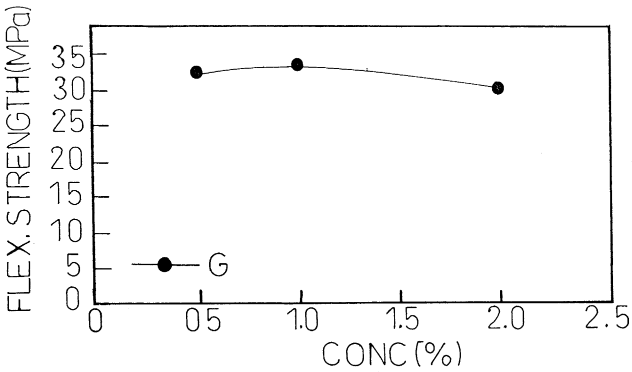

Fig. 6. Plot of flexural strength (at 25 °C) of fired (1500 °C) in situ spinel bonded castable (G) with increasing concentration of spinel additive.

3. Results and discussion

3.1. Properties of castables

Fig. 1(a–d) shows the comparison of change in properties with temperature between 2% of preformed and in situ spinel bonded castables, which indicate that R type excels over G type in terms of BD, AP, CCS, while the spalling resistance is better in G. When the concentration of R is changed to 4% and G to 0.5% (Fig. 2) the trend of changes in those properties remain almost the same. It is also very conspicuous from Figs. 1 and 2 that R type castable shows a noticeable decrease in property at around 1000–1200 °C while at 1500 °C, a remarkable improvement is observed for the same properties. It has been mentioned in Table 1 (a) that XRD pattern of R comprises both spinel and corundum phases. Actually, the MgO–Al_2O_3 phase diagram shows that spinel forms a solid solution at high temperature with excess of both Al_2O_3 and MgO, but these non-stoichiometric solid solutions are metastable at room temperature so that the cooling rate from sintering or fusion temperature is an important factor for preparing preformed spinels. Consequently, some commercial spinels contain some second phase [10] as we see for R type here. During the onset of sintering and ceramic bond formation, these extra aluminas possibly show a thermal expansion mismatch with spinel fines and deteriorate the properties of castables by creating some flaws. However this extra alumina reacts later with calcium-aluminates from cement (Fig. 3) to form sufficient amount of CA_6 [C = CaO, A = Al_2O_3] above 1300 °C. This hexa aluminate provides an excellent bond linkage between grains in the matrix by an inter-locking morphology [11,25],

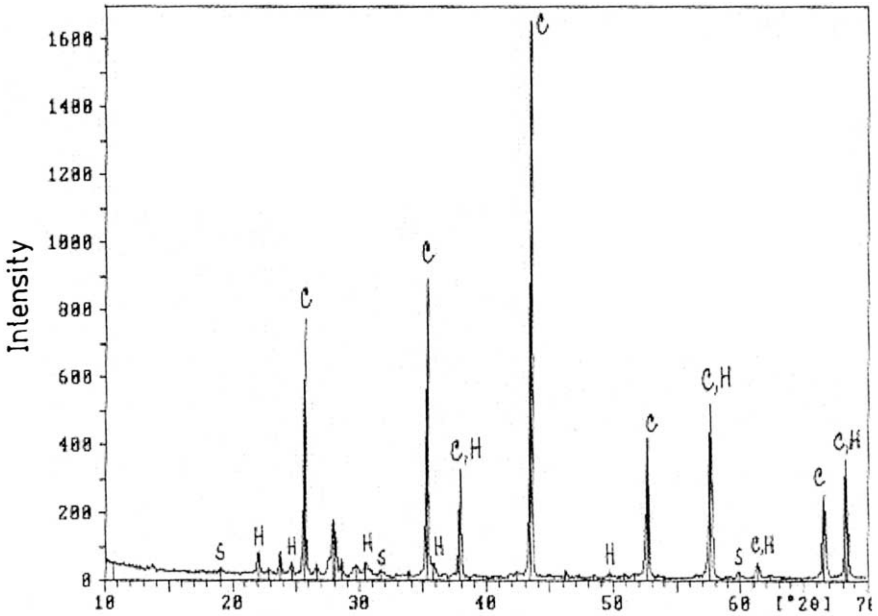

Fig. 7. XRD pattern of in situ spinel bonded castable (G) fired at 1500 °C/2 h (S = Spinel, C = Corundum, H = Calcium Hexa aluminate).

which upgrades the properties at 1500 °C. The fall in property of G type castable at the intermediate temperature range is also observed (Fig. 1 and 2), which can be attributed to the complete dehydration of cement [24] and due to the quasi-brittle nature of castable around 1000 °C [11] having a lot of diffused and localized damages. This kind of damage also takes place for R type castables in that temperature range in addition to what has been mentioned earlier.

It is also interesting to note that for G type castables, in situ spinel formation takes place at a lower temperature [17], which is energetically and economically favourable. But it poses two problems which degrade the properties of G compared to R type. Firstly, a lot of volatiles are released from the gel mass [17–19], which generate micro-bubbles in the castable and make the structure porous. Secondly, the in situ spinel formation is associated with a considerable volume expansion [19]

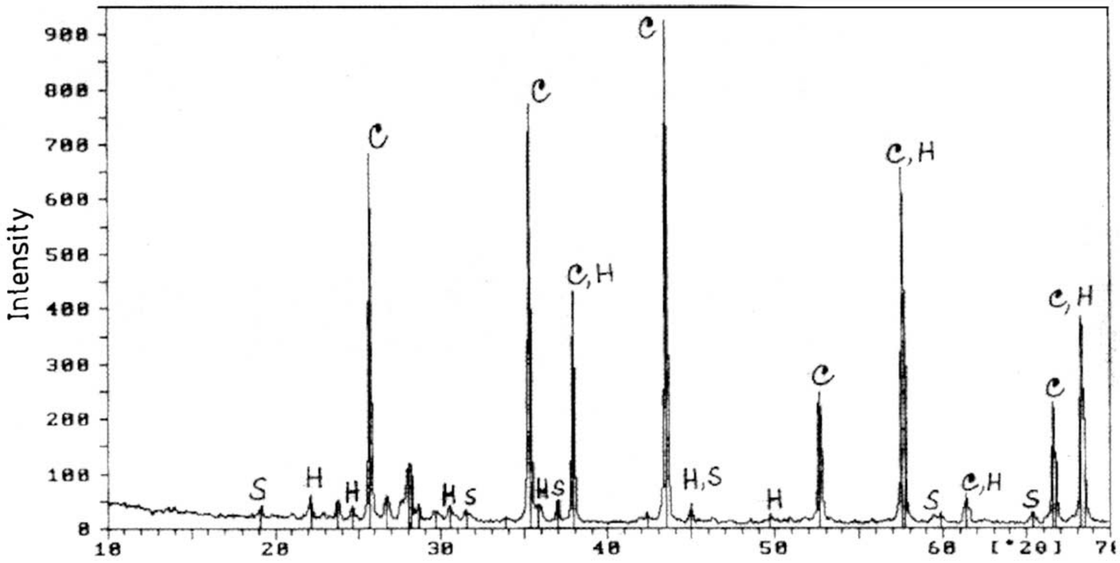

Fig. 8. XRD pattern of preformed spinel bonded castable (R) fired at 1500 °C/2h (S = Spinel, C = Corundum, H = Calcium Hexa aluminate).

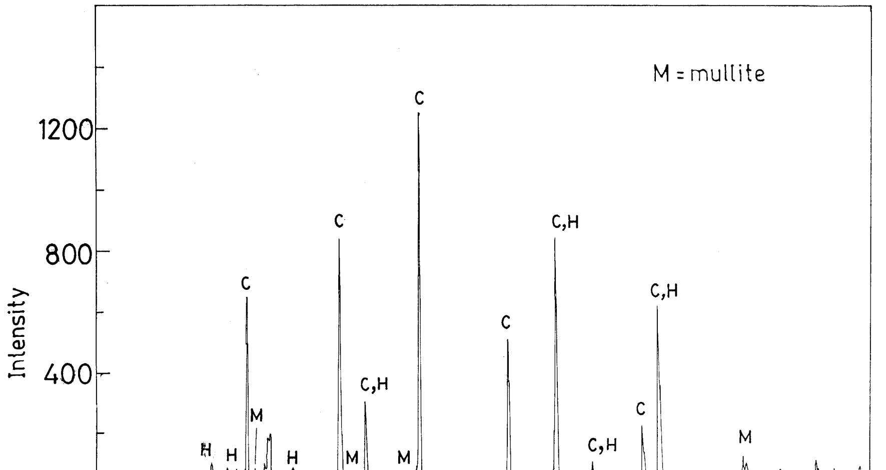

Fig. 9. XRD pattern of spinel free castable fired at 1500 °C/2 h (M = Mullite).

as explained by three different mechanisms [20], which adversely affects the microstructure of G type. But it is evident from Fig. 1 and 2 that the pores can help crack closure and therefore %RS of G is better than R.

The finer particle of G type (Table 1b) has a positive effect because this sol gel spinel with high surface area has high reactivity to combine with microsilica and lime present in the batch to produce CMAS phase [M = MgO, S = SiO_2] which intensively bonds MA and corundum phases by forming link and bridges [13] to upgrade the strength of castables at elevated temperature. But at the same time some extra low melting glassy phases like gehlenite (C_2AS) and anorthite (CAS_2) are generated [13,18] which may act as crack propagation paths and degrade the hot properties of castables [21]. It is therefore very much important to keep the microsilica content below a certain level in spinel bonded alumina castables; otherwise it would enhance the formation of detrimental liquid phases [21–23] and may also lead to damage during corrosion.

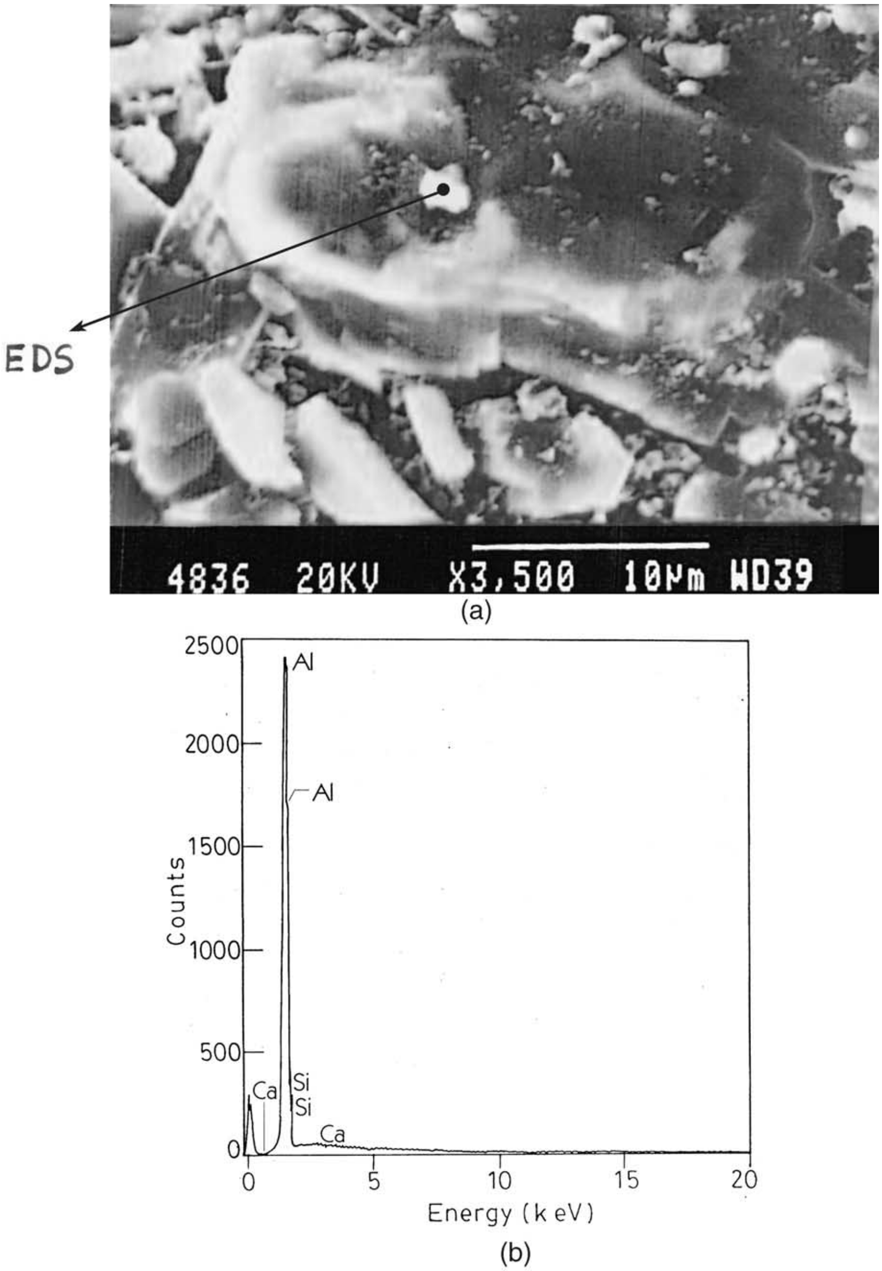

Fig. 10. (a) SEM photomicrograph of spinel free castable fired at 1500 °C/2 h. (b) EDS pattern of C–A–S phase present in spinel free castable.

Fig. 4 shows that for R type castable fired at 1500 °C, the properties remain almost uniform with the variation of concentrations of spinel (2.0, 4.0 and 8.0 wt.%). It was already reported before that preformed spinels show shrinkage on firing [20] while the growth of CA_6 causes a permanent volume expansion. We may suggest that this expansion–contraction balance is not remarkably disturbed in those percentage ranges. But for the G type castable (Fig. 5) 1% concentration shows a failure in BD, AP, CCS and an increase in spalling resistance. This can be due to the dissolution of some part of fine alumina from matrix to the reactive stoichiometric in situ gel, which may give rise to loosening of structure [13] in some parts. But for 2% addition of the same, the problem is compensated may be by CMAS formation which has been discussed in our earlier communication [18,19]. Fig. 6 shows that the flexural strength of G at different concentrations of additive lie above 30 MPa which is better than spinel free castable (Table 3). This happens may be due to a more interlocking network between spinel and CA_6 [9,11,14] as it is observed that those two phases are present in the respective XRD pattern (Fig. 7). Figs. 8 and 9 show the XRD patterns of preformed spinel bonded castable and spinel free castable respectively, which also support the existence of hibonite (CA_6) phases; the only difference is the appearance of spinel in the former and mullite in latter. As mentioned earlier Fig. 3 shows the XRD pattern of high alumina cement used in the batch composition of

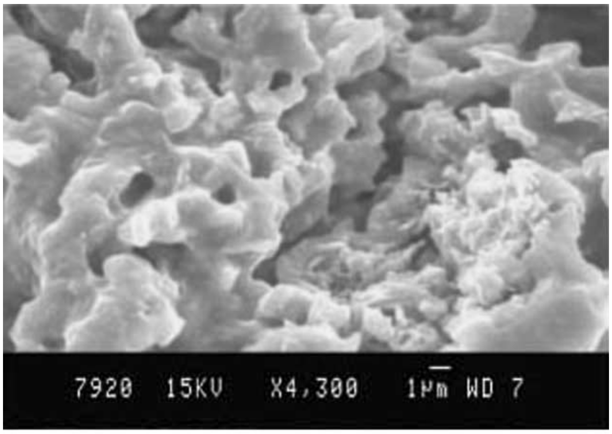

Fig. 11. SEM photomicrograph of the matrix part of spinel free castable fired at 1500 °C/2 h.

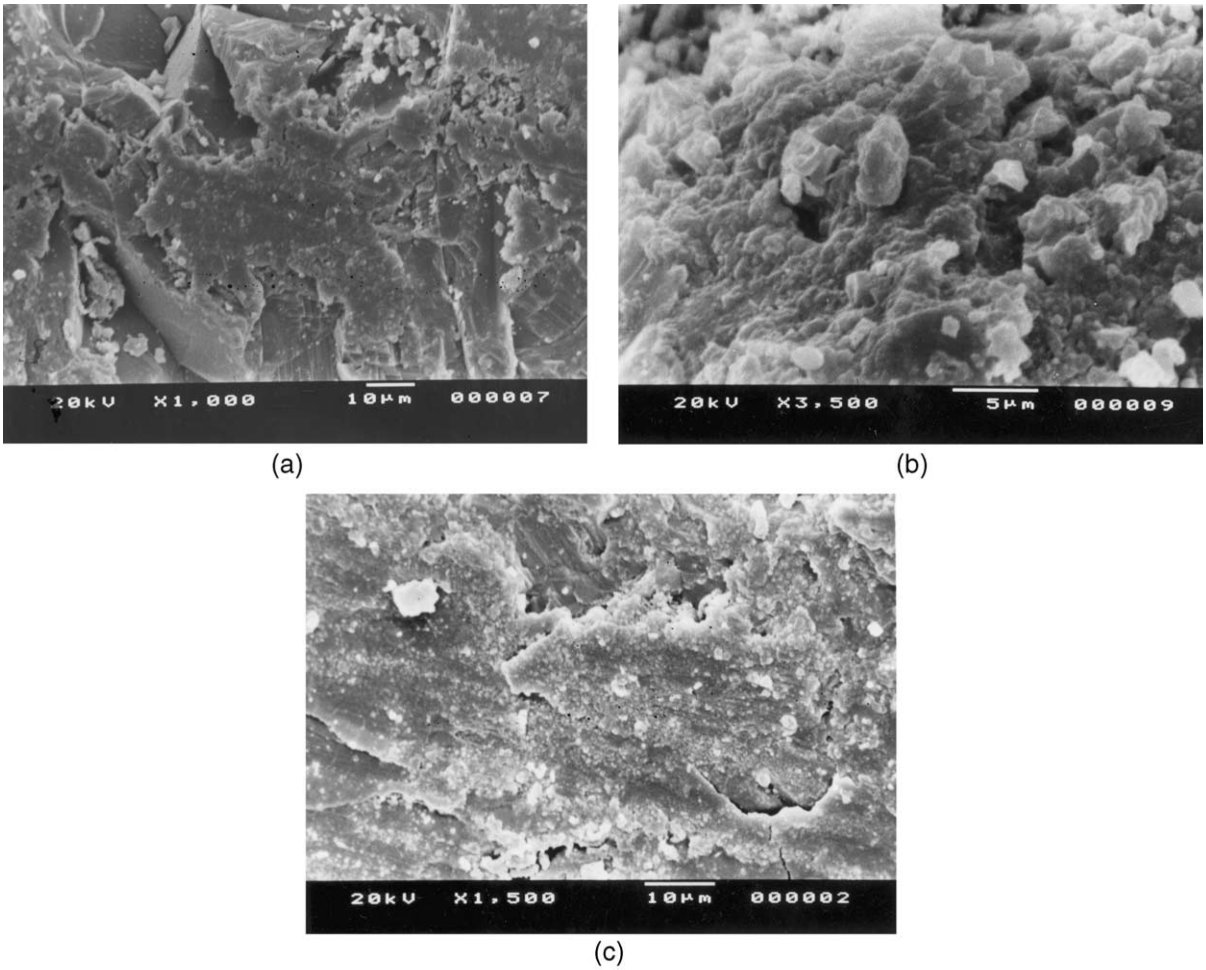

Fig. 12. SEM photomicrographs of preformed spinel bonded castable (R) fired at 1500 °C/ 2h, (a) ×1000 (b) ×3500 (c) ×1500.

both the castables. It shows that plenty of CA and CA_2 phases are present, which render the green strength of castables by helping the formation of hydrated phases [24]. At above 1300 °C these phases take up alumina from the matrix to form interlocking card like CA_6 phase [25], which has been discussed earlier. Those CA and CA_2 phases are also responsible to form a silicate phase (glassy) in presence of microsilica, which can affect the high temperature properties of castables.

3.2. Microstructures of castables

Fig. 10(a) is the micrograph of spinel free castable which conspicuously shows that detrimental glassy C–A–S phases are present as confirmed by the EDS pattern of the indicated point [Fig. 10(b)]. However, desirable corundum and mullite phases, with good continuity and homogeneity are also present in the spinel free castable as observed from Fig. 11, the SEM photomicrograph of only the matrix part (fired) of the same castable. Figs. 12 and 13 show the microstructures of R and G type castables respectively. It is clear from Fig. 12 (a), (b) and (c) that a dense and compact microstructure exists for R type, that possesses tabular and platy crystals of hibonite (CA_6) which creates an intensive bonding between grains and matrix with a high degree of interweaving network [8,9,11]. Fig. 13(a)–(c) clearly reveals more porous, cracked platelets and flaky morphology of the G type castable. The exceedingly high volume expansion and liberation of substantial amount of volatiles of in situ spinel may be the reason behind it. Although the reactive spinel results in a glassy matrix of CMAS phase which firmly holds corundum phases, but simultaneously some regions in the microstructure becomes disjointed may be due to the dissolution of fine alumina in reactive spinel [13]. Furthermore the

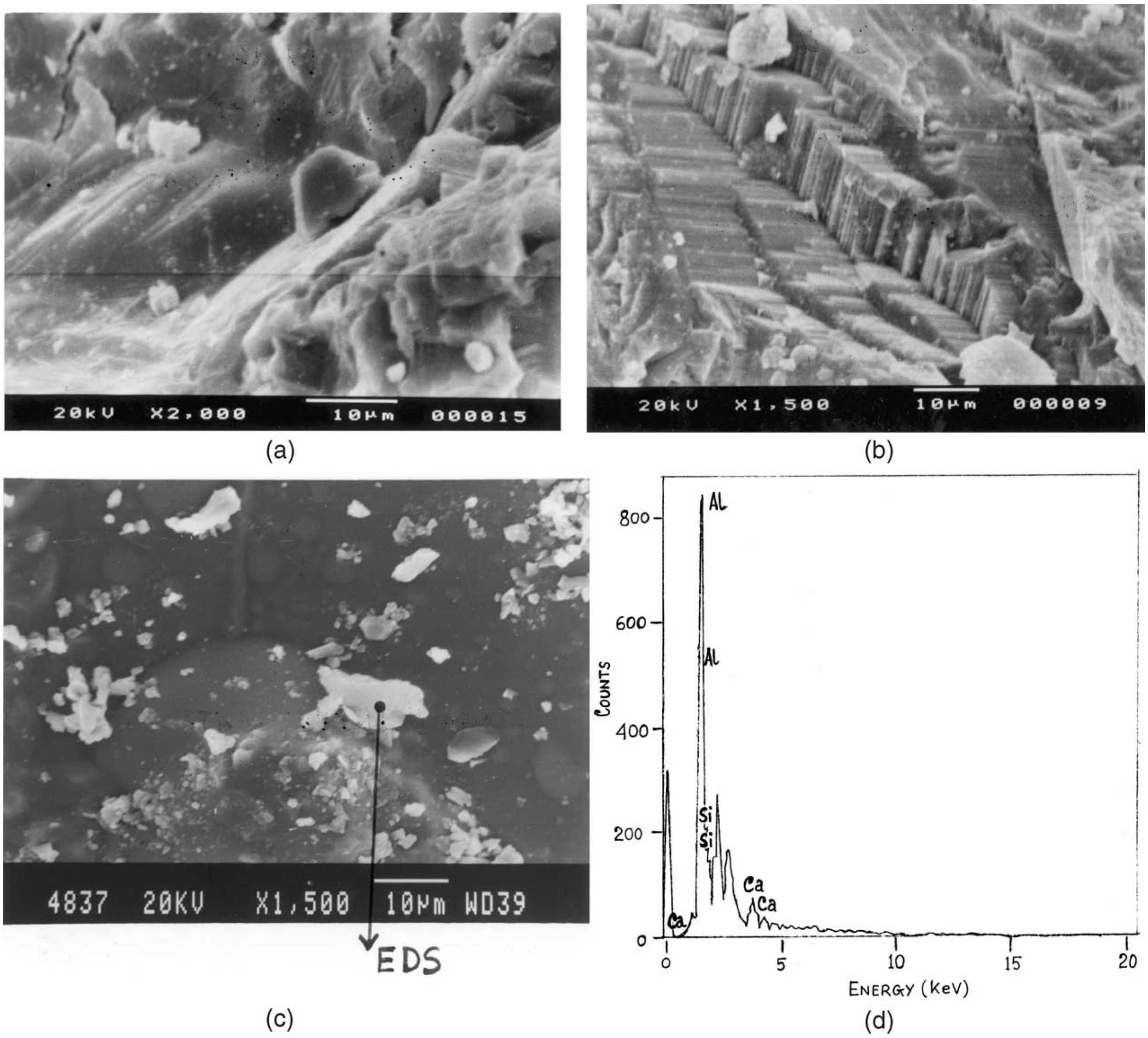

Fig. 13. SEM photomicrographs of in situ spinel bonded castable (G) fired at 1500 °C/ 2h, (a) ×2000 (b) ×1500 (c) ×1500 and (d) EDS pattern of C–A–S phase shown in (c).

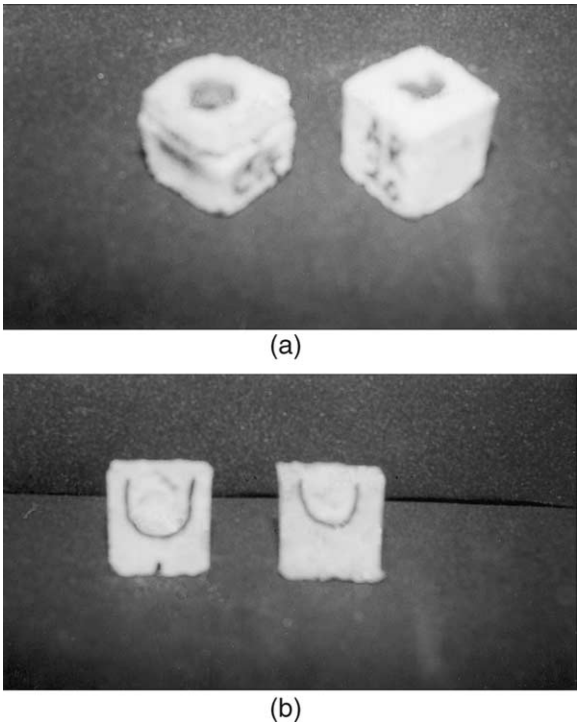

Fig. 14. (a) Photograph of two types of spinel bonded castable specimens fired at 1500 °C for 2 h with converter slag (LHS: G type, RHS: R type). (b) Photograph of blast furnace slag attack towards R type (LHS) and spinel free (RHS) castables fired at 1500 °C for 2 h soaking.

cementitious phase reacts with excess microsilica in batch to result in undesirable low melting C–A–S phase, which is confirmed, from the EDS pattern of Fig. 13(d). Fig. 14(a) shows that corrosion resistance of R type castable in presence of converter slag is better than G, but the performance of R is not so good in contact with blast furnace slag [Fig. 14(b)], which is likely may be due to the difference in basicity (CaO/SiO_2) between the two slags.

4. Conclusions

From the present study, it may be concluded that,

(1) Although the properties of in situ spinel castable discussed here are quite satisfactory as evaluated from laboratory scale results, but preformed spinel bonded castables reveal every significant improvement in terms of BD, AP, CCS, flexural strength and microstructure. However, reduction of microsilica below a certain level holds a strong indication of further improvement of both types of castables.

(2) The desired spinel phase of in situ castable is generated from cheaper precursors at remarkably low temperature indicating a possibility of cost and energy saving than preformed spinel preparation, which needs exceedingly higher temperature. But in situ spinel bonded castable exhibits the adverse effects of excessive volume expansion, micro-bubble formation and deleterious glassy phases in microstructures, although its spalling resistance is better than the other.

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References

[1] W.E. Lee, R.E. Moore, Evolution of in situ refractories in the 20th Century, J. Am. Ceram. Soc. 81 (6) (1998) 1385–1410.
[2] M.D.M. Innocentini, A.R. Studart, R.G. Pileggi, V.C. Pandolfelli, PSD effect on the permeability of refractory castables, Am. Ceram. Soc. Bull. 80 (5) (2001) 31–36.
[3] A.R. Studart, F.S. Ortega, M.D.M. Innocentini, V.C. Pandolfelli, Gel casting high alumina refractory castable, Am. Ceram. Soc. Bull. 81 (20) (2002) 42.
[4] J. Mori, W. Watanabe, M. Yoshimura, Y. Oguchi, T. Kawakami, Material design of monolithic refractory for steel ladle, Am. Ceram. Soc. Bull. 69 (7) (1990) 1172–1176.
[5] J. Madias, R.E. Caligaris, L. Zamboni, Postmortem study of alumina-spinel castables of an electrical arc furnace roof, Interceram 49 (5) (2000) 348–351.
[6] Y. Sato, H. Joguchi, N. Hiroki, Test results of alumina-spinel castables for steel ladle, Taikabutsu Overseas 12 (1) (1992) 10–14.
[7] H. Kato, T. Takahashi, T. Kondo, Y. Ogura, Application of alumina spinel castable refractory in ladle bottoms, Taikabutsu Overseas 16 (3) (1996) 22–27.
[8] P. Korgul, D.R. Wilson, W.E. Lee, Microstructural analysis of corroded alumina-spinel castable refractories, J. Eur. Ceram. Soc. 17 (1997) 77–84.
[9] G. Maczura, M. Madono, G.W. Kriechbaum, B. Sewell, Low moisture regular corundum/spinel castables with superior properties, in: Proc. UNITECR 1995, Kyoto, Japan, Vol. 3, pp. 179–186.
[10] C.F. Chan, Y.C. Ko, A study of commercial magnesia–alumina spinels for alumina-spinel castables, Interceram 47 (6) (1998) 374–378.
[11] F. Simonin, C. Olagnon, S. Maximilien, G. Fantozzi, Thermomechanical behaviour of high alumina refractory castables with synthetic spinel additions, J. Am. Ceram. Soc. 83 (10) (2000) 2481–2490.
[12] C. Parr, T.A. Beir, M. Vialle, C. Revais, An approach to formulate spinel forming castables, in: Proc. UNITECR, Berlin, 6–9 September, 1999, pp. 19–21.
[13] M. Fuhrer, A. Hey, W.E. Lee, Microstructural evolution in self forming spinel/calcium aluminate bonded castable refracroties, J. Eur. Ceram. Soc. 18 (1998) 813–820.
[14] Y.C. Ko, Influence of the characteristics of spinels on the slag resistance of Al_2O_3–MgO and Al_2O_3-spinel castables, J. Am. Ceram. Soc. 83 (9) (2000) 2333–2335.

[15] R.J. Bratton, Coprecipitates yielding $MgAl_2O_4$ spinel powders, Am. Ceram. Soc. Bull. 48 (8) (1969) 759–762.

[16] J.C. Devsikdar, Preparation of transparent non-crystalline stoichiometric magnesium aluminate gel monolith by the sol gel process, J. Mater. Sci. 20 (12) (1985) 4454.

[17] S. Mukhopadhyay, S. Ghosh, M.K. Mahapatra, R. Majumdar, P. Barick, S. Guptaand, S. Chakraborty, Easy-to-use mullite and spinel sols as bonding agents in a high alumina based ultra low cement castable, Ceram. Int. 28 (7) (2002) 719–729.

[18] S. Mukhopadhyay, S, Sen, T. Maiti, M. Mukherjee, R.N. Nandy, B.K. Sinhamahapatra, In situ spinel bonded refractory castable in relation to coprecipitation and sol gel derived spinel forming agents, Ceram. Int. 29 (8) (2003) 857–868.

[19] S. Ghosh, R. Majumdar, B.K. Sinhamahapatra, R.N. Nandy, M. Mukherjee, S. Mukhopadhyay, Micro structures of refractory castables prepared with sol gel additives, Ceram. Int. 29 (6) (2003) 671–677.

[20] K.H. Hwang, K.D. Oh, R.C. Bradt, In situ spinel bond formation (expansion/contraction) during firing, in: Proc. UNITECR, New Orleans, 4–7 November, Vol. 3, 1997, p. 1575.

[21] C.F. Chan, F.J. Huang, Y.C. Ko, Refractoriness under load of alumina-spinel castables, Interceram 46 (2) (1997) 86–89.

[22] M.R. Rao, Liquidus relations in the quaternary subsystem $CaAl_2O_4$–$CaAl_4O_7$–$Ca_2Al_2SiO_7$–$MgAl_2O_4$, J. Am. Ceram. Soc. 51 (1) (1968) 50–54.

[23] Y.C. Ko, Influence of microsilica addition on the properties of alumina-spinel castables, in Proc. UNITECR, Berlin, 6–9 September 1999, pp. 22–25.

[24] K.M. Parker, J.H. Sharp, Refractory calcium aluminate cements, Trans. Brit. Ceram. 81 (1982) 35–42.

[25] N.M. Khalil, M.F.M. Jawrah, Improvement of physico-mechanical properties of self-forming MA spinel castables, Trans. Brit. Ceram. 100 (3) (2001) 110–114.