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In situ spinel bonded refractory castable in relation to co-precipitation and sol–gel derived spinel forming agents

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Abstract

This paper deals with the preparation and characterization of two types of in situ spinel bonded low cement high alumina based castable refractories. Semidried magnesium aluminate mass was prepared from cheaper precursors via coprecipitation and sol–gel routes for application in a refractory castable composition in different concentrations. The pH, average particle size, solid content, DTG analysis and XRD patterns of those two additives were observed. After being fired at elevated temperatures those two kinds of in situ spinel bonded castables were characterized and compared in terms of bulk density, apparent porosity, cold crushing strength, flexural strength, volume shrinkage, spalling resistance, and XRD phase analysis. Scanning electron microscopy of some selected fired samples was done to analyse the mode of interaction of in situ spinel bonds in castable microstructure. The corrosion resistance of the castables was estimated by heating with blast furnace and converter slags.

Keywords: A. Sol–gel processes; D. Spinels; E. Refractories

1. Introduction

Evolution of castable refractories aimed at building up of a refractory construction which itself is a single unit and the present day scenario shows a remarkable increase in the use of various kinds of castables [1–5]. With the changes in time and technology, the service condition has become more severe and it became necessary to search for high performance castable particularly suitable in the presence of molten slag and metal [6,7]. It is well known that magnesium aluminate spinel possesses a unique combination of thermal, mechanical and chemical properties at high temperature [8,9] and refractory alumina-spinel castables are being widely used in steel ladle linings due to certain advantages they offer especially in comparison with the shaped alumina bricks [10–13]. A common practice to fabricate high alumina cement bonded alumina-spinel castables is with self-forming spinels, where fine magnesia powder taken in the batch reacts with alumina to form in situ spinel during service [13–15]. Very often small amount of microsilica is added to the in situ spinel bonded castable to promote hydration resistance [15–17] and spinel formation. But the other varieties of in situ spinel bonded castables are not much found in literature.

The conventional method of the preparation of $MgAl_2O_4$ spinel is solid state sintering between high purity MgO and Al_2O_3 where the temperature needed is normally around 1600 °C for commercial practice. Over the last few decades, a variety of new techniques have been used to prepare $MgAl_2O_4$ spinel which include hydrothermal synthesis, coprecipitation, plasma spray decomposition, sol–gel methods, freeze drying and decomposition of organometallic compounds etc. [18–25]. In these processes, good quality of the spinel product is expected primarily due to the purity of the precursor materials used and chemical homogeneity obtained from the synthesis route [26–28].

Therefore an entirely novel approach may be to prepare magnesium aluminate hydrated spinel additives from sol–gel and coprecipitation routes (by taking the benefit of time, temperature and reactivity) and to apply these materials as in situ spinel forming agents in a castable composition. In this work, those two kinds of spinels were prepared and examined in terms of pH, solid content, average particle size, differential thermogravimetric analysis and X-ray diffraction patterns at different temperatures. Then these additives were used in different concentrations in a high alumina based low

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cement castable material. The two types of fired castable specimens were characterized and compared with respect to B.D., A.P., CCS, volume shrinkage, flexural strength and thermal shock resistance. The XRD analysis and scanning electron microscopy of some selected fired samples were performed to understand the interaction of in situ spinel bonds with the constituents of castable. Some samples were subjected to slag corrosion test at aggressive condition with blast furnace and converter slags and the nature of slag penetration was investigated.

2. Experimental

In the present study, semi-dried (25 °C) magnesium aluminate hydrated mass was prepared from coprecipitation and sol–gel routes [18–25,29] for application in a low cement castable as self-forming additives. Fig. 1 shows the steps (schematic) followed for the preparation of stoichiometric spinel additives from two chemical routes. The pH value, solid content, average particle size and amount of these additives used in this wok are reported in Table 1. It should be mentioned that a bimodal nature of particle size distribution was observed for the coprecipitated additive with some particles having submicron average size of 0.2 μm while the majority of particles possessed the size around 6 micron. The solid content was determined from the well known ignition method. The particle size was measured with the help of MALVERN-Autosizer IIC and MALVERN-Mastersizer 2000 instruments. The TG analysis was conducted at a rate of 5 °C/min. The X-ray diffraction had instrumental parameters Ni-filtered Cu K_{α}., 40 kV, 20 and 30 mA.

In the second phase of the experiment, these two spinel additives were incorporated in the castable composition in increasing concentration (0.5, 1 and 2% by wt) and their effect in the thermomechanical properties of castable was investigated. The report 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 composition of the same castable along with its physical properties after being fired at 1500 °C for 2 h. The spinel bonded LCC samples were named as C and G respectively to distinguish between the coprecipitated and sol–gel derived additives. All the samples were cast by simple tapping technique with cube (25.4 mm) and bar (75×12.5×12.5 mm) type moulds after properly fixing the granulometry

Table 1
Physicochemical properties of two types of in situ spinel additives

Characteristics	Co-ppt spinel	Sol gel spinel
Solid content	~10%	~10%
pH	6–7	3–4
Average particle size	6 μm	11 nm
$MgAl_2O_4$ (wt.%) in calcined additive	>99.8%	>99.8%
Amount added to castable (wt.%)	0.5, 1, 2.	0.5, 1, 2.

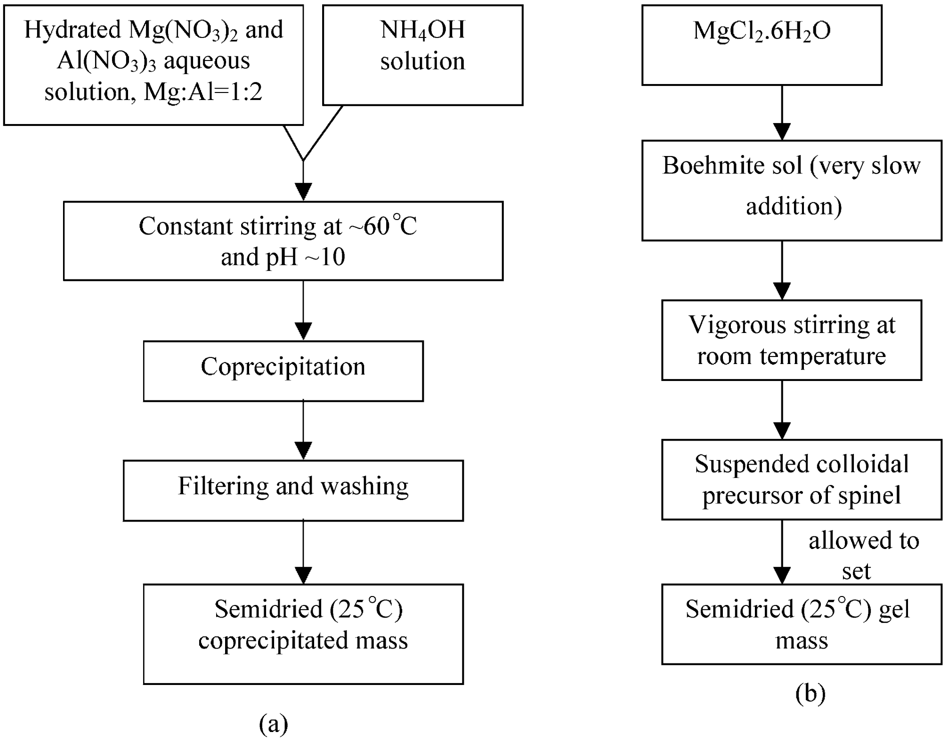


Fig. 1. Flowchart for the preparation of (a) co-precipitated and (b) sol–gel derived spinel additives.

Table 2
Chemical analyses 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						0.88
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				

Table 3
Spinel free castable formulation and its physical properties 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 (MPa)	140
PLC (%)	+0.2
Flexural strength (MPa)	30

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

of the original castable from the distribution modulus (i.e. q-value) calculation as shown in Fig. 2. Those specimens were then cured under humid condition 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 various temperatures (900, 1200 and 1500 °C) with 2 h of soaking time. To get a clear comparative study of the interaction of castable with two additives in different concentrations, the fired (1500 °C) castable specimens were subjected to various tests such as bulk density (BD), apparent porosity (AP), cold crushing strength (CCS), thermal shock resistance, slag corrosion resistance at elevated temperature and flexural strength at room temperature. A further comparison was carried out in terms of BD, AP, CCS and spalling resistance with respect to firing temperatures of both C and G type castables prepared with the highest dose of additives showing the best result among the three different concentrations. BD, AP and CCS tests were done by standard methods. With 1500 °C fired

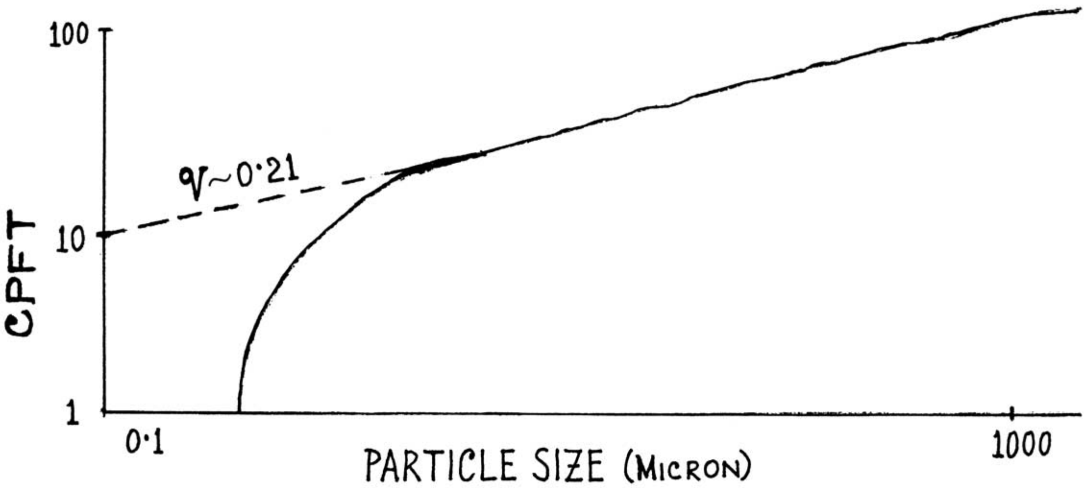


Fig. 2. Distribution modulus (q value) of spinel free castable.

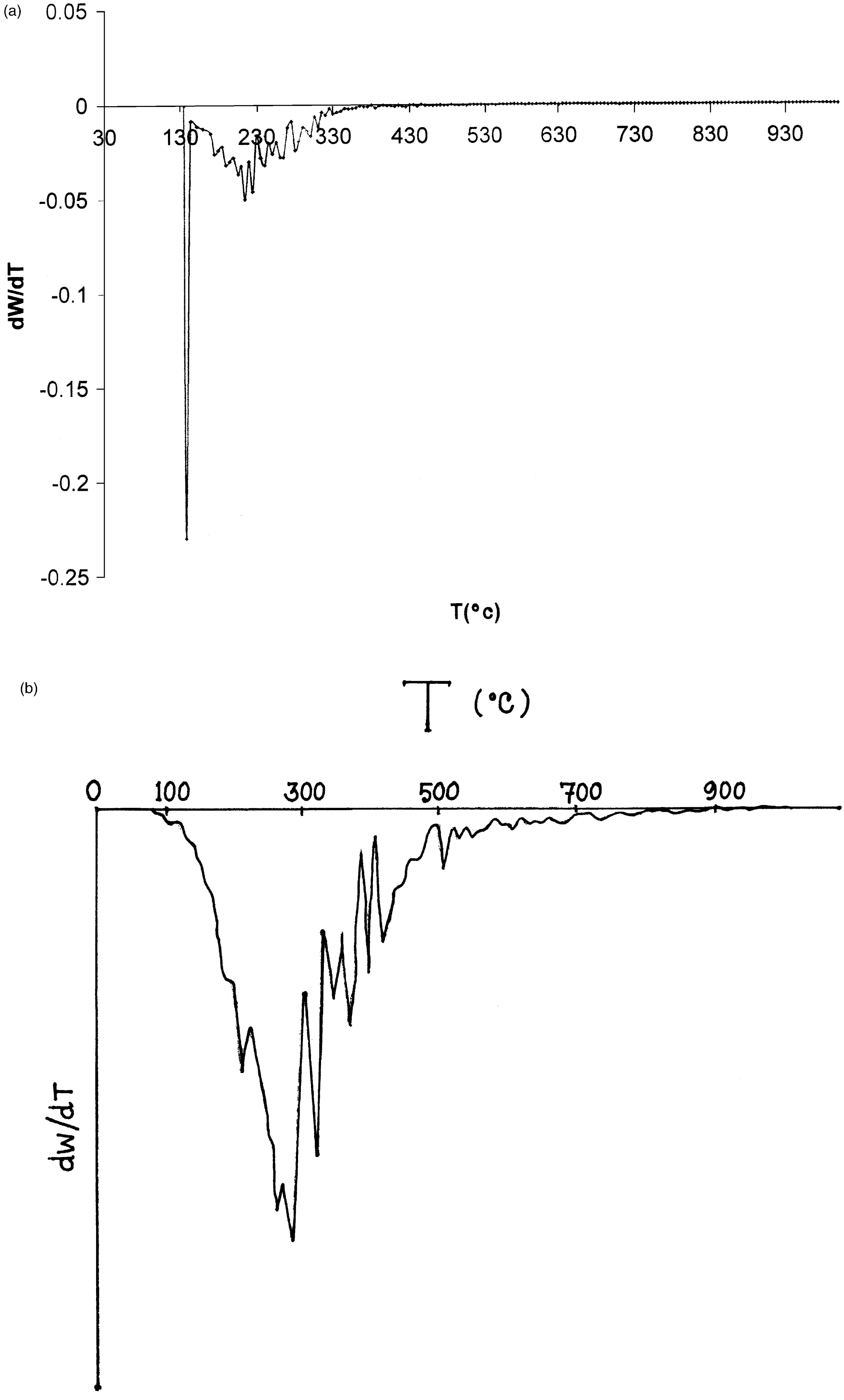


Fig. 3. DTGA reports of spinel additives (a) coprecipitated (b) sol gel derived.

LCC samples prepared with the highest amount of both kinds of additives, XRD and SEM tests were also performed to emphasize the role of those additives. With the C and G type of bars previously fired at 1500 °C the experiment for flexural strength was done with a Universal Testing machine INSTRON-1185 at 25 °C with a cross-head speed of 1.0 mm per minute and a span of 50 mm. The thermal shock resistance (i.e. spalling test) of C and G specimens previously fired at 1500 °C, was noted in terms of 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. To evaluate the practical importance of both kinds of in situ spinel bonded castables the test for slag corrosion resistance was conducted. For this purpose the cubes were prefired at 1200 °C after making a cylindrical groove of the same

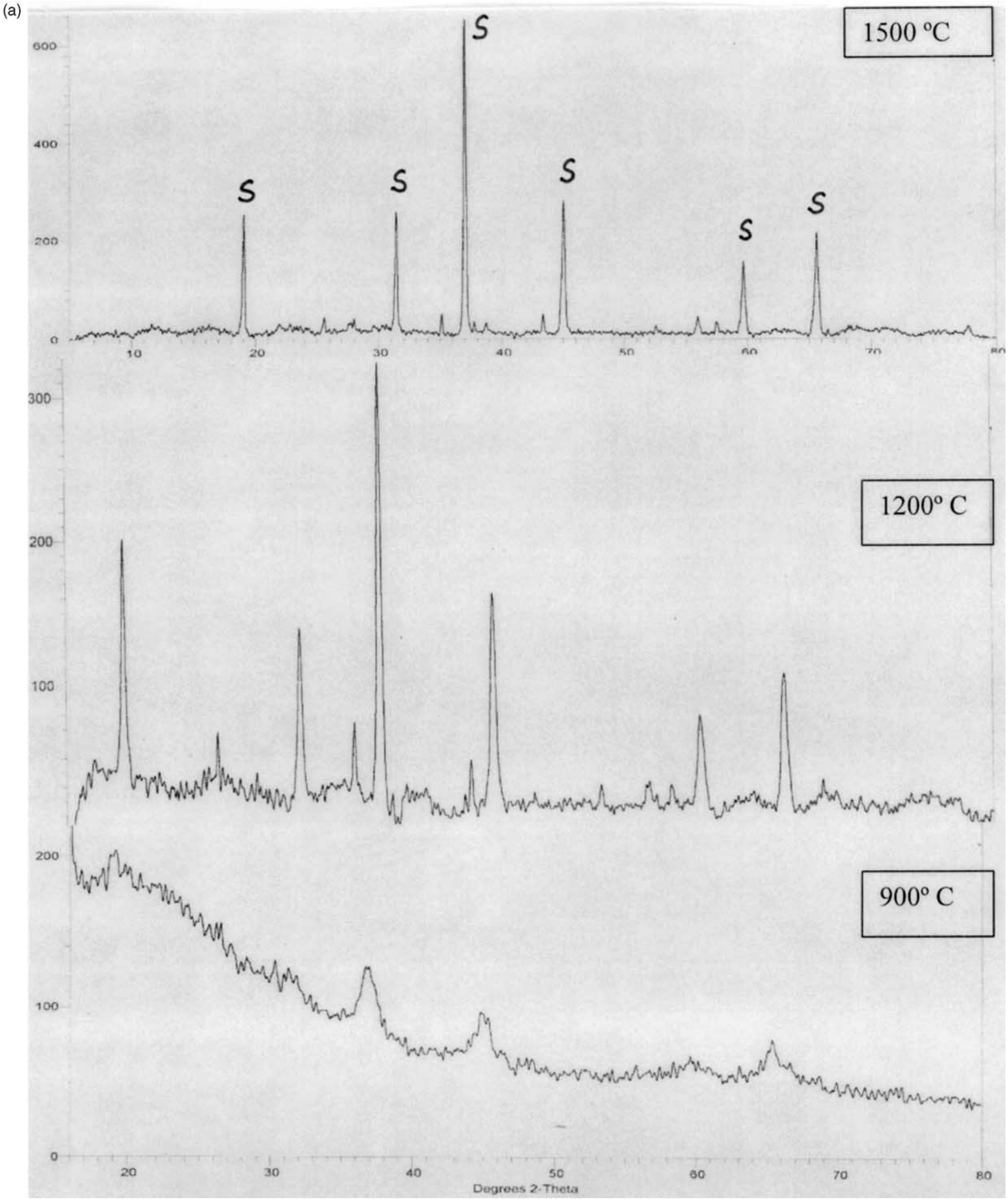


Fig. 4. XRD patterns of spinel additives with increasing temperature (a) coprecipitated (b) sol gel derived. [S = Spinel.]

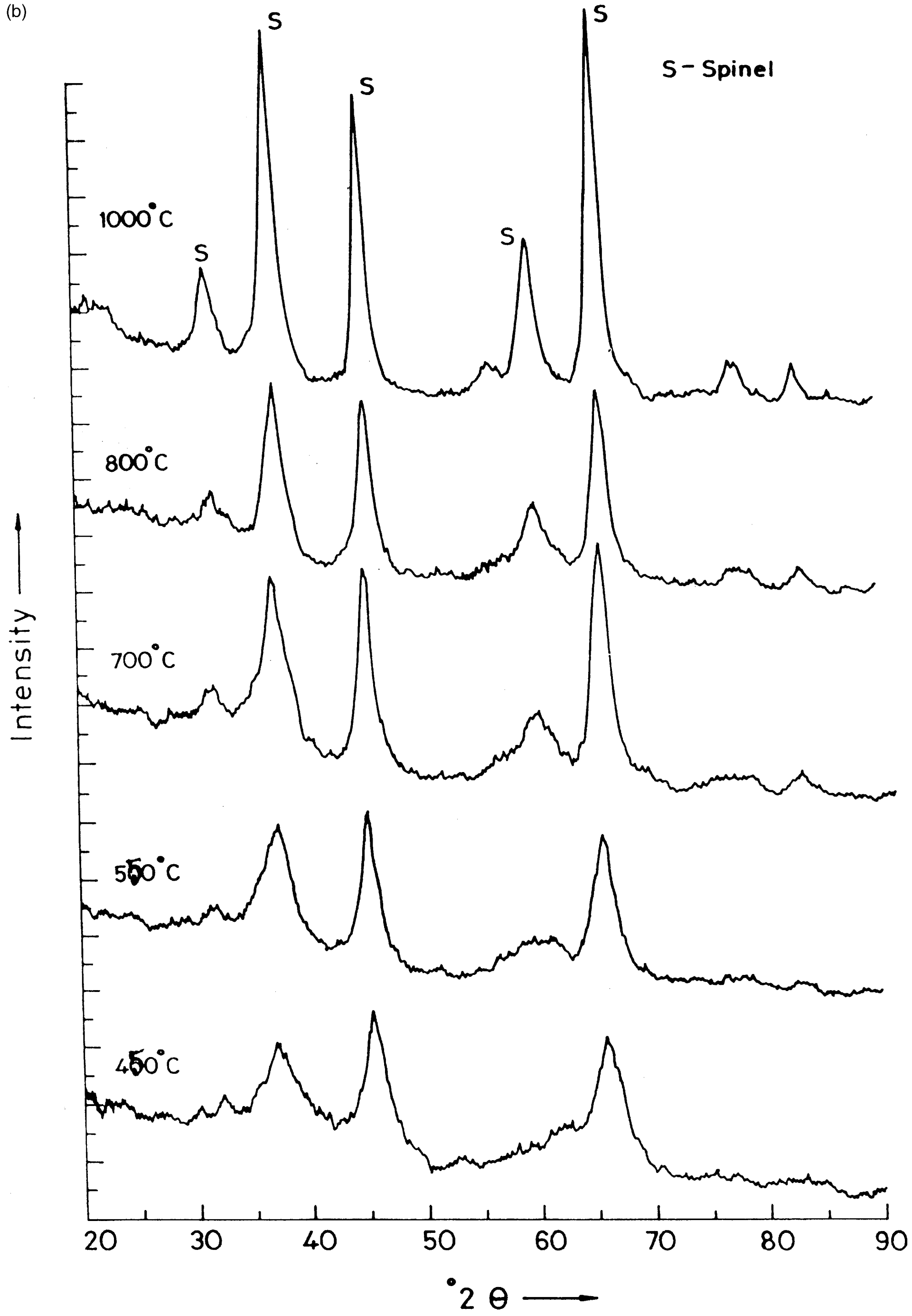


Fig. 4 (*continued*).

size at the centre of all the cubes. The grooves were then filled up with two types of slags (Blast Furnace and Converter slags supplied from TISCO and VSL, India respectively) given in Table 4, and the cubes were heat treated at 1500 °C for 2 h. After cooling, the samples were cut across the middle and the extent of slag penetration was studied to interpret the performance of in situ spinels. The SEM study of selected 1500 °C fired samples was done in the instrument Jeol JSM- 5200 model.

3. Results and discussion

3.1. DTG and XRD patterns

The DTG patterns of C and G bonds (Fig. 3) reveal that a lot of volatiles are released below 400 °C which when used in LCC may deteriorate the green strength of the castable by generating considerable quantities of micro bubbles in the microstructure. For the coprecipitated bond the major part of decomposition includes

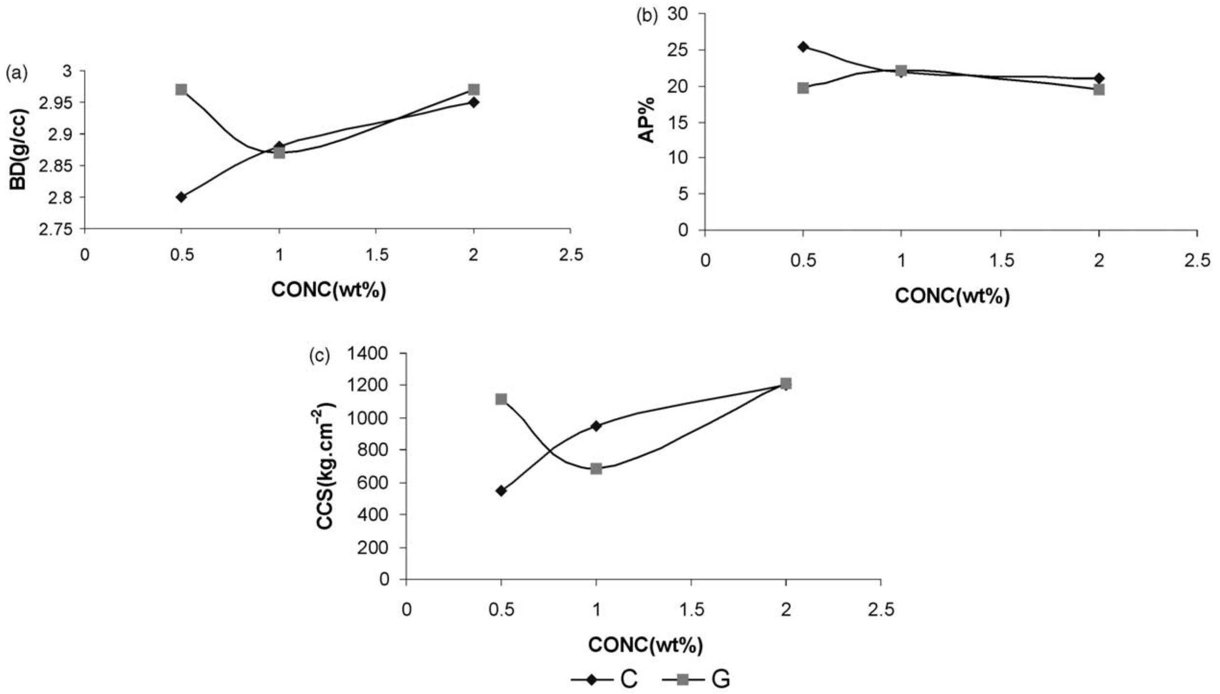


Fig. 5. Physical properties of two types of in situ spinel bonded castables fired at 1500 °C in relation to the amount of spinel additives (a) B.D. (b) A.P. (c) C.C.S.

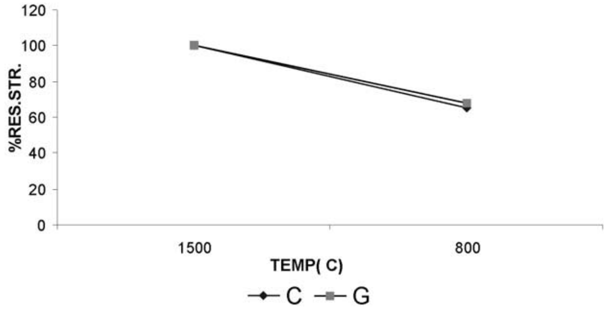


Fig. 6. Plot of % residual strength of castable specimens prepared with 2% of two types of spinel additives.

release of free water, rupture of mixed hydroxide interlayers and evolution of CO_2 [19]. For the sol–gel bond the DTG pattern suggests the progressive dehydrations and dechlorination [29] as reported earlier. The XRD patterns (Fig. 4) of C and G bonds showed that the spinelization takes place quite early at 900 and 600 °C respectively. The XRD patterns (Fig. 9) of the C and G bonded castables show the conspicuous presence of spinel, hibonite and corundum phases. The corundum phase appears due to fused alumina taken in sufficient quantity in the batch. The spinel phase appears because of low temperature spinellisation of the two additives used in the castable. The formation of hibonite (calcium hexa aluminate) in castable after 1300 °C has been discussed later.

3.2. BD, AP, CCS, flexural and residual strength

For the gel bond castable G, fired at 1500 °C (Fig. 5), 1% concentration of additive shows a failure in BD, AP, CCS and an improvement in spalling resistance. The expansion-contraction mismatch between spinel and the rest part of castable may be maximum at this concentrtion. We also suggest this optimum amount contains reactive stoichiometric sol–gel spinel that takes up fine alumina from the matrix to extend the spinel solid solution [15]. For this dissolution the microstructure becomes disjointed at different places and properties deteriorate. But when gel additive is increased to 2%, the extra amount of gel forms the CMAS ($CaO–MgO–Al_2O_3–SiO_2$) phases that produce necks and bridges [15] to improve the properties and microstructure. For 1% G the large number of pores possibly helped in crack closure and upgraded the residual strength (Fig. 8). But for C bond with smaller surface area, being not so reactive like G, the increase of amount from 0.5 to 2% only causes a simple increase of solid spinel fines to fill up the voids and enhance the bond linkage resulting in a gradual increase in properties (Fig. 5).

As the average particle size of gel is very much less than that of the co-precipitated spinel therefore the specific surface area of spinel gel is much higher with high reactivity. As a result the green and fired bulk density of the gel bonded castable (G) prepared with 2% additive are greater (Fig. 7a) than that of the coprecipitated spinel bonded castable (C). It may be

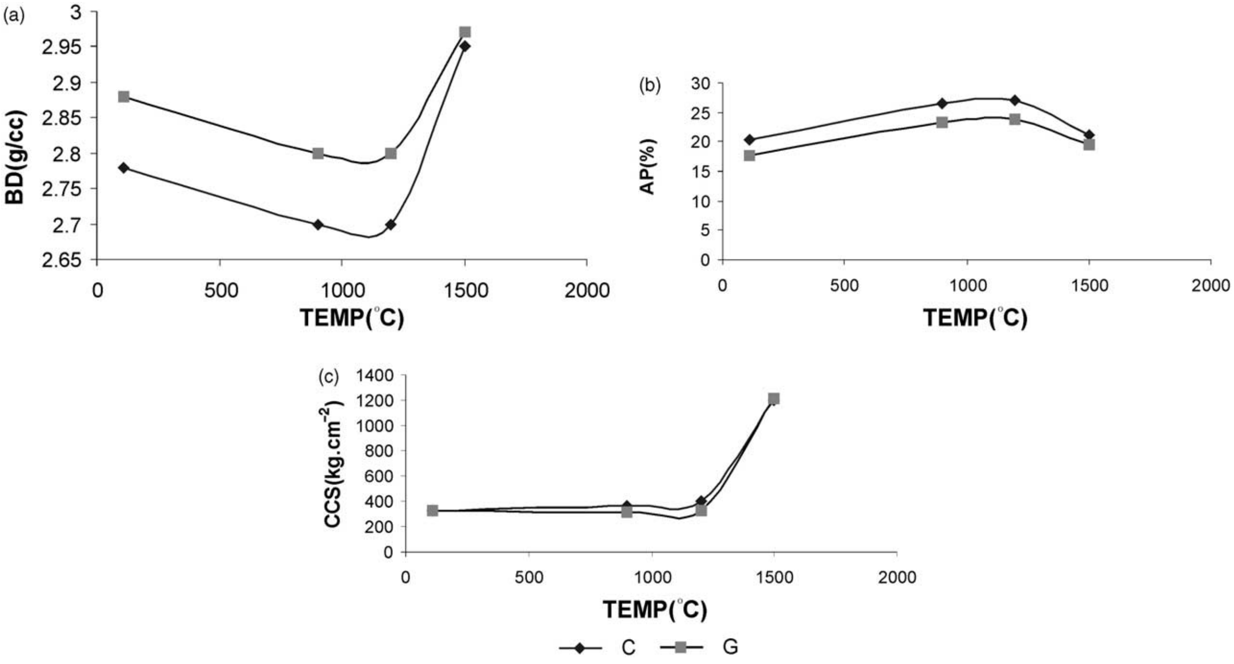


Fig. 7. Variation of (a) B.D. (b) A.P. (c) C.C.S. with temperature for in situ spinel bonded castables prepared with 2% of two types of spinel additives.

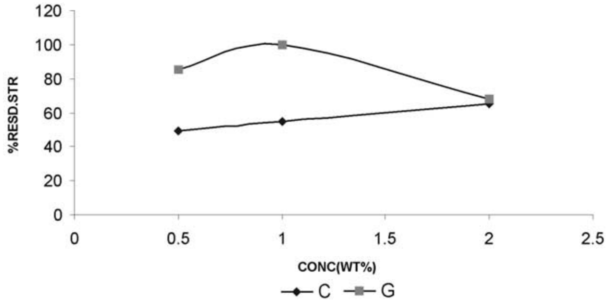


Fig. 8. Plot of residual strength of C and G type castables spalled at 800 °C with 0.5, 1 and 2% of each additive.

safely suggested that the finer particles of spinel gel assisted the homogeneous distribution of particles due to better flow properties and increased the particle packing to yield a compact structure. For the same reason the apparent porosity (Fig. 7b) of G is less than that of C. The cold crushing strength of both C and G (Fig. 7c) are comparable. The residual strength of G type castable, as evident from Figs. 6 and 8, is better than the other type.

It is also very clear from Fig. 7 that both G and C type castables (prepared with 2% additives) showed a general decrease of properties (BD, AP, CCS) between 900 and 1200 °C because it is known that this is a common feature of cement bearing castable to degrade in that range due to complete dehydration. It is also suggested that the reactive self-forming spinels in castable contribute to excessive expansion within that temperature range due to three different mechanisms [30–32], namely, the increase of molar volume from reaction, development of reaction layers of spinel at Al_2O_3–MgO interface and Kirkendall effect, which may affect the properties. Besides that it is also quite likely that the reactive C and G bonds react with plenty of micro silica present in the batch to produce CMAS phases together with low melting gehlenite (C_2AS) [33] with an interconnected silicate network that may act as a crack propagation path to degrade the quality of castable. However, above 1200 °C, it is observed that both G and C exhibited an improvement of properties may probably be due to the links and bridges formed by gradual increase of that CMAS phase which intensively bonded MA phases [15]. Above 1300 °C the interlocking, platy crystals of hibonite (CA_6) appeared largely to bond the grains and matrix with a net like continuity as supported too from the XRD patterns. This phase resulted in a remarkable increase in the properties [12,15,34]. Some literature recently pointed out that the spinel bonded castables exhibit a quasi brittle behaviour at around 1000 °C due to a large number of localized and diffused damages [35]. The flexural strength values of C and G castables prepared with 2% of additives had been observed to be greater than 30 MPa that might be possibly due to the intensive interlocking of spinel and hibonite.

3.3. SEM reports (microstructure)

As the sol–gel additives released a substantial amount of micro bubbles [36], the porosity of C and G type castables are larger ($>15\%$) than spinel free castable. This porosity is also evident from the respective microstructures (Figs. 10 and 11), which may affect the slag

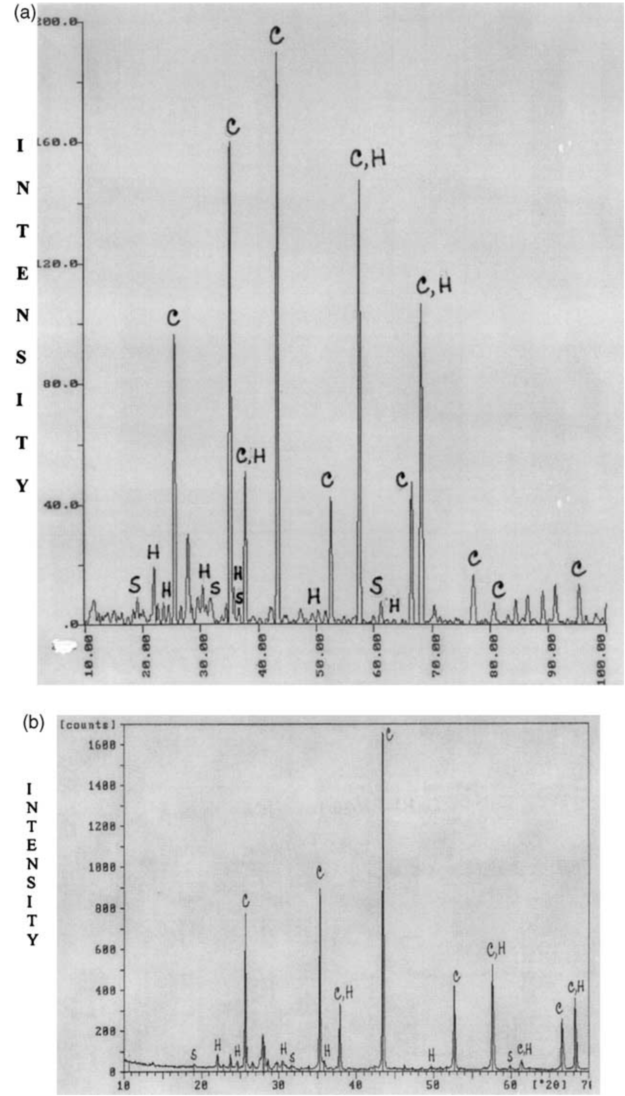
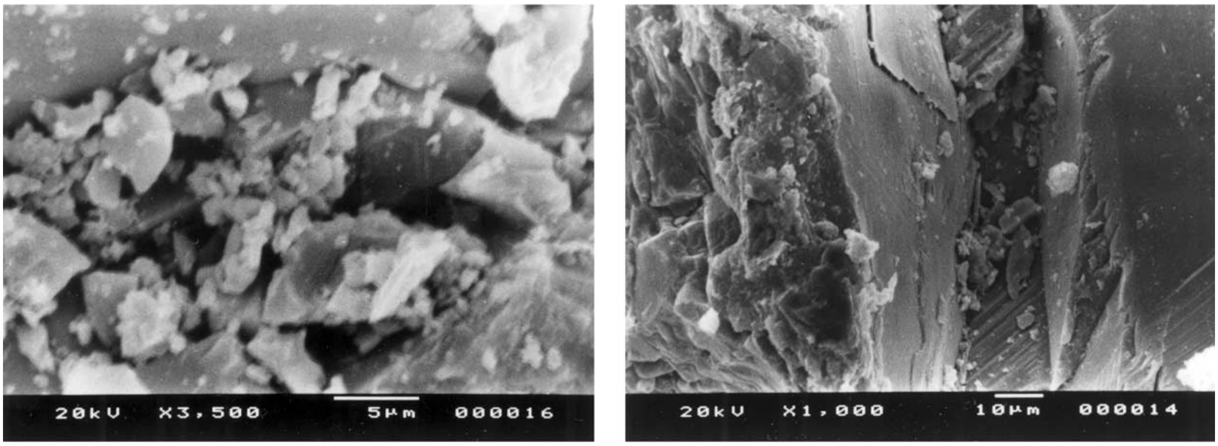


Fig. 9. XRD patterns of in situ spinel bonded castable (fired at 1500 °C) prepared with 2% of (a) coprecipitated (b) sol gel derived spinel additives. [S = Spinel, C = Corundum, H = Calcium hexa-aluminate.].

corrosion. However finer particles in G type helped more pronounced flow properties and better homogeneity with improved thermo-mechanical properties, by forming necks and bridges between the medium and large sized grains. In some parts of the microstructures, polygonal and columnar type dual nature of spinel crystallites was also found [37]. It is suggested that some liquid phase sintering probably took place from reactive gel that intensively bonded the corundum phase with siliceous glassy CMAS matrix [15]. It is also noted that the loosening of structure in some regions in some compositions at 1500 °C was there might be due to the dissolution of some part of fine alumina in the reactive stoichiometric spinel by extending the spinel solid solution as mentioned earlier. It has been already reported that early spinelization causes a considerable volume expansion [29,30] with highly stressed regions resulting in fissures which is also corroborated here (Figs. 10 and 11). Another third and important phase (from XRD) was also detected in the matrix with a net like morphology consisting of tabular, platy crystals of hibonite (CA_6) that provided a firm interlocking bond to link fused aggregates with the spinel bonded matrix [15,34].

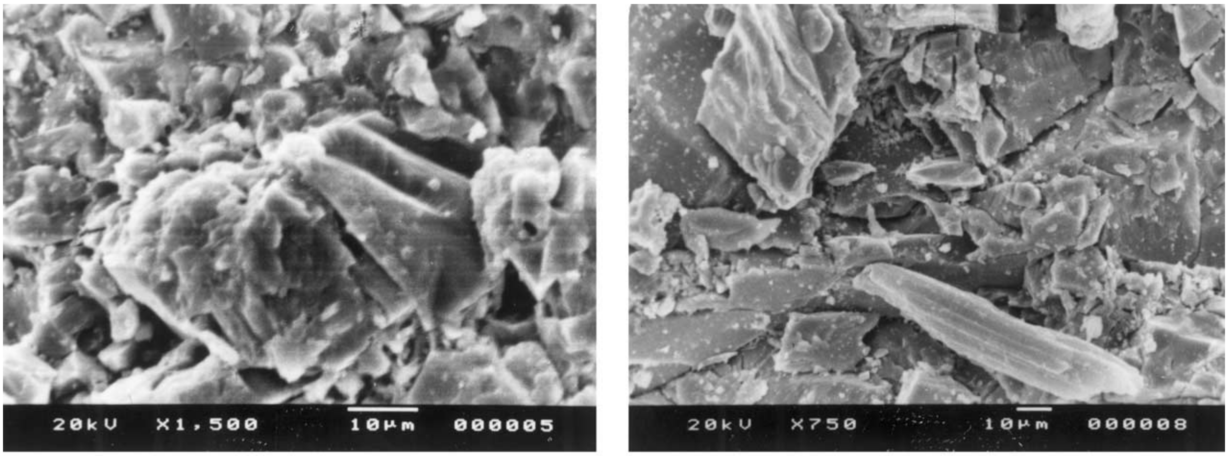
3.4. Slag corrosion resistance

As the basicity (CaO/SiO_2 ratio) is widely different in two slags (Table 4) it may be anticipated that they would behave differently towards both kinds of spinels. The same is very clear from the photographs in Figs. 12a and b that each of C and G type exhibits good resistance towards a specific slag. The corrosion resistance of the castables can be improved if microsilica content is reduced below a certain limit [33,35]. Because for spinel bonded alumina castable it forms low viscosity glassy phase which is detrimental for the RUL value too [38]. Here the reactive C and G bonds assisted in forming CMAS phase together with low melting anorthite



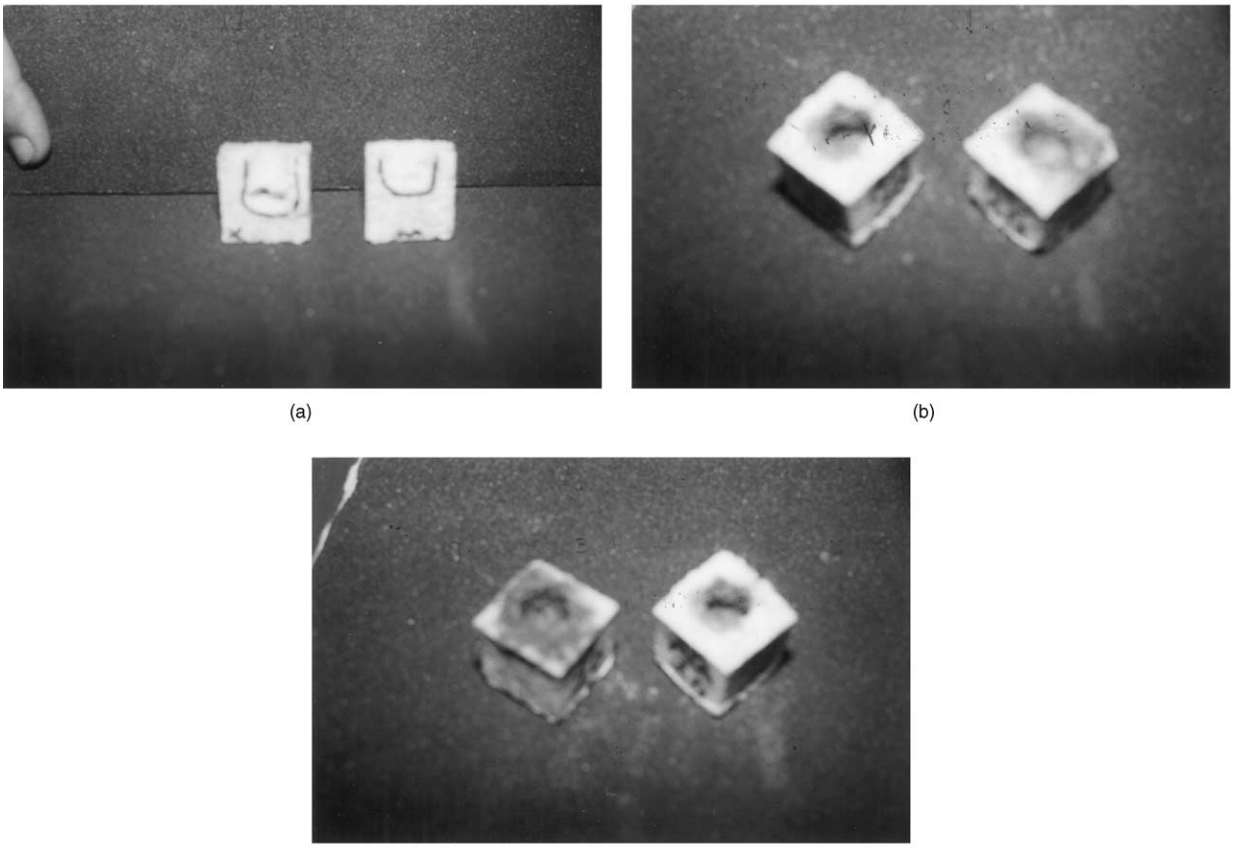
(a) (b)

Fig. 10. SEM photographs of in situ spinel bonded castable (fired at 1500 °C) prepared with coprecipitated spinel additives (a) ×3500 (b) ×1000.



(a) (b)

Fig. 11. SEM photographs of insitu spinel bonded castable (fired at 1500 °C) prepared with sol gel derived spinel additives (a) ×1500 (b) ×750.



(a) (b) (c)

Fig. 12. Photographs of two types of in situ spinel bonded castable specimens fired at 1500 °C for 2 h with (a) blast furnace and (b) converter slags. L.H.S—G type, RHS–C type. (c) Photograph of converter slag attack towards G type (RHS) and spinel free (LHS) castables fired at 1500 °C for 2 h.

(CAS_2) and gehlenite (C_2AS) phases that might lead to wetting during corrosion [39]. However Fig. 12c reveals that the attack of converter slag in G type castable is not so severe as in spinel free castable because the reactive spinel gel can arrest Mn^{2+} and Fe^{3+} ions from slag [11], forming complex spinels to resist the slag penetration inside the castable.

4. Conclusions

From the present study it may be concluded that

1. The spinel additive from the sol–gel route contained more fine particles and showed better performance in castable than coprecipitated spi-

nel additive, although both of them are energetically favorable to produce the desired spinel phases at lower temperature but with significant volume expansion.

2. The coprecipitated and the sol–gel derived additives prepared from chemical routes with cheaper precursors generate a substantial amount of micro bubbles which enhanced the porosity of castable and affected its slag corrosion resistance.
3. Microsilica content in a spinel bonded high alumina castable must be reduced to a very low level to eliminate the detrimental glassy phases.
4. The spalling resistance of castable can be improved by in situ spinel bond addition due to the pores that can prevent crack growth.

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