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Microstructures of refractory castables prepared with sol–gel additives

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Abstract

Several kinds of inorganic sol and gel materials were applied to high alumina based low and ultra low cement refractory castable compositions and these were fired at elevated temperature. A scanning electron microscope (SEM) study of the fired specimens was performed and the microstructural features were analysed in terms of the desirable properties of a refractory material, with an aim to elucidate the effect of sol gel additives on castables.

Keywords: B. Microstructure; E. Refractories; Sol–gel additives

1. Introduction

The increasing application and demand for monolithic refractory materials as a substitute for conventional bricks encourage manufacturers and researchers to explore their physical, chemical and mechanical properties at elevated temperature as well as their processing techniques [1–3]. A significant increase in the life of high-alumina based refractory castables has been possible by decreasing the cement-content, thus avoiding liquid phase formation in them at working conditions which in turn improves the corrosion resistance and creep strength. LCC, ULCC, NCC and self-flow castables have already become popular in the refractory industries [4–6]. More recently, a new group of additives prepared from sol–gel route, appeared in the refractory industries that triggered on a new prospect for castable producers. These additives comprise ultra fine particles of the same composition as the castable (e.g., silica, alumina, mullite, spinel etc.) which surround the refractory materials through a polymeric network skeleton and on heating, the reactive gel phases develop ceramic bonding and high strength through sintering [7]. These compositions have better flow properties and require no vibration to help the material move, i.e., these castables render higher flexibility during the installation. These also help in decreasing the cement contents in castables thus reducing the amount of low melting gehlenite and anorthite phases. Despite this advantage, the complete absence of high-alumina cementitious setting material may cause the formation of large flaws in the castables during the drying process because of the chance of migration of a lot of fine particles from the sol–gel additives. Apart from this, it is also well known that the green strength of castables determines the susceptibility of the refractory lining to support its own weight under the mechanical stresses developed during drying. Therefore it is a common practice to apply high alumina cement in castable to result in moderate to high prefired strength. The sol–gel additives also enable release of substantial amount of micro bubbles which may deteriorate the mechanical properties of the castable product [8] and the superior porosity also leads to a network of interconnected pores throughout the microstructure. Clearly many researchers have observed both the merits as well as demerits of the sol–gel-bond castables.

It is also well established that the properties of fired ceramic materials are determined not only by the phase constituents but also by their microstructure, i.e. the arrangement or distribution of those phases, their

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Table 1
Characteristics of different sol–gel additives applied to specific types of refractory castables

Type	Batch constituents	Sol–gel additive	Amount (%)	pH	Solid content (%)
LCC	White fused alumina, microfine alumina, high alumina cement, microsilica and sodium hexametaphosphate	Spinel gel-1	0.25–3.0	3–4	10
		Spinel gel-2	0.25–3.0	6–7	10
ULCC	White fused alumina,microfine alumina, high alumina cement, microsilica, sillimanite sand and sodium hexametaphosphate	Alumina sol	10–15	2–4	5
		Silica sol	10–15	10–12	40
		Mullite sol	10–15	3–4	6
		Spinel sol	10–15	3–4	5

relative amounts, porosity, size, shape, orientation etc. [9,10]. Therefore, to get a better interpretation of the specific application of castables prepared with sol–gel additives regarding their initial fabrication technique, raw materials utilized, phase equilibrium relation and sintering of the fired product, a complete understanding of the respective microstructures is very much essential.

The main objective of the present study is to apply different inorganic sol–gel additives for the fabrication of low and ultra low cement high-alumina based refractory castable materials and to observe micro structural features at elevated temperature, which may correlate their properties and performances.

2. Experimental

Low cement and ultra low cement type castables were prepared using white fused alumina in different grades (i.e. coarse, medium, fine) as aggregate material and micro-fine alumina, sillimanite sand, micro-silica with high alumina cement as the matrix constituents. The particle size distribution was optimised by following the packing model found in literature [11,12].

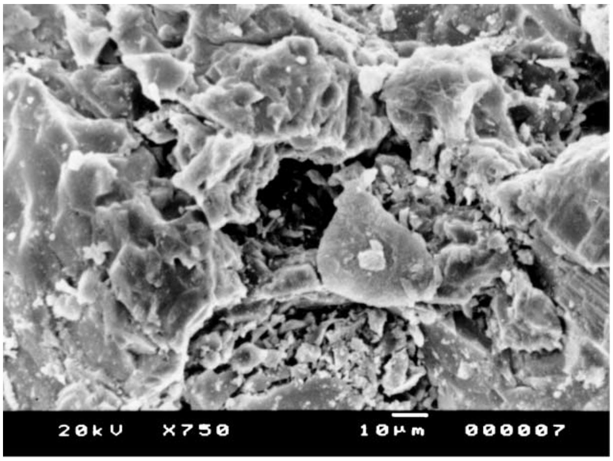


Fig. 1. SEM photographs of polished surface of LC castable prepared with spinel gel-1 additive and fired at 1500 °C.

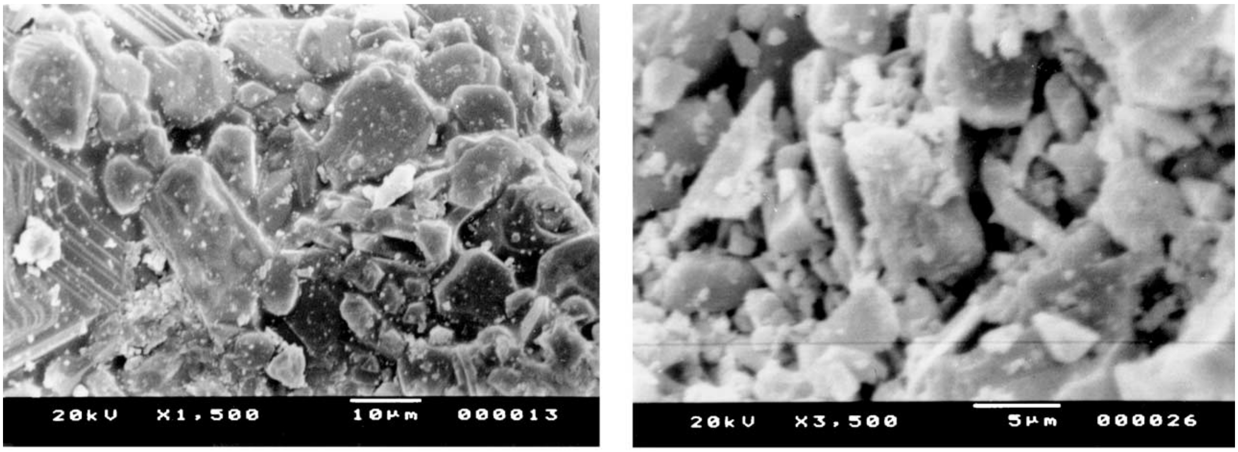
For the ULCC composition, alumina, silica, mullite and spinel sols were applied as additives. The application of silica sol is quite common in refractory castables, whereas the use of alumina, mullite and spinel sols (prepared from cheaper precursor) in high alumina based castables has been discussed by some authors [13,14]. For the LCC composition, spinel gels prepared from two different routes [14,15], were applied as additives in castables. The amount of additives, their solid content and pH values have been shown in Table 1 with the specific type of castable where these additives have been applied.

The batch materials after thorough mixing with sol–gel additives were cast by sample tapping techniques with cube (25.4 mm) and bar type (75×12.5×12.5 mm) moulds. For the ULCC composition, no water was added from outside due to the presence of 10–15% of sol; but for the LCC composition 5–6% of distilled water was added during mixing to get the desired consistency. Those specimens were cured under humid condition for 24 h followed by 24 h of air drying and oven drying at 110 °C. Finally the castable samples were fired at 900, 1200 and 1500 °C with 2 h of soaking time. To interpret the mode of interaction of sol–gel additives with castable constituents at elevated temperature the SEM study of different 1200 and 1500 °C fired samples were carried out by the instruments of Hitachi S-2300 and Jeol JSM-5200. The XRD test of some samples fired at 900 and 1500 °C were performed to substantiate the reports of SEM study.

3. Results and discussion

3.1. Microstructure of LCC composition with spinel gel additives fired at 1500 °C

Figs. 1 and 2 show that the finest particles in the matrix occupied the space between the medium and large sized grains by forming necks and bridges due to good flow properties of sol–gel additives. Large alumina grains had flat cracks along many grain boundaries that closely approached a continuous pore-phase. Properties



(a) (b)

Fig. 2. (a) and (b) SEM photographs of polished surface of LC castable prepared with spinel gel-2 additive and fired at 1500 °C.

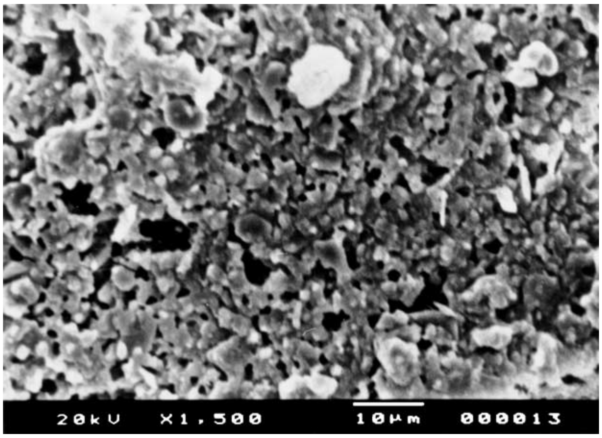


Fig. 3. SEM photograph of polished surface of ULC castable prepared with alumina sol additive and fired at 1500 °C.

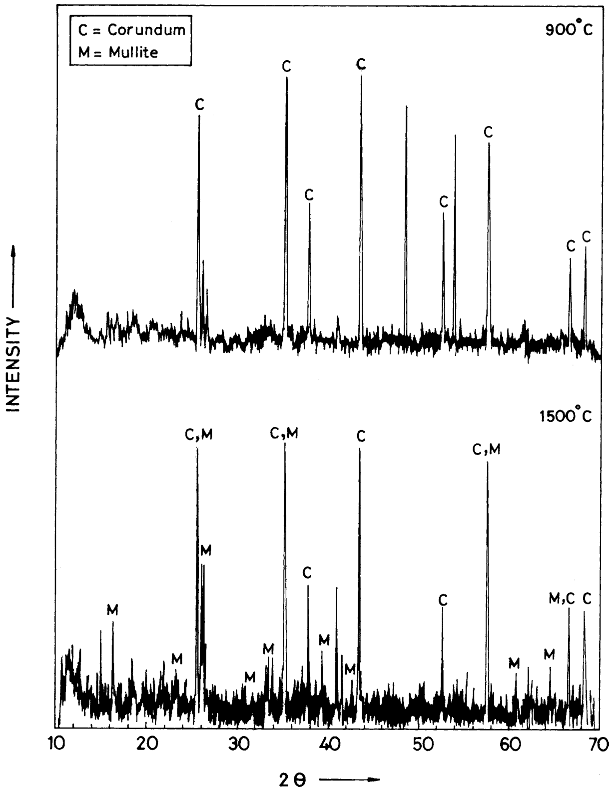


Fig. 4. XRD patterns of ULC castable prepared with alumina sol additive and fired at 900 and 1500 °C.

such as permeability could be directly affected by the open pores connected to the surface. The matrix could have various compositions in CaO–Al_2O_3 (CA), CaO–Al_2O_3–SiO_2 (CAS) and CaO–MgO–Al_2O_3–SiO_2 (CMAS) phases. Pure MgO.Al_2O_3 (MA) spinel seemed to be intensively bonded with CMAS phases. Some liquid phase sintering also took place from the reactive gels and loosening of structure found in some regions may be due to the dissolution of some part of fine Al_2O_3 grains because of the tendency of stoichiometric spinel to get saturated with excess alumina. Another third phase was also detected in the matrix with a net like morphology [Figs. 1 and 2(a)], which may consist of CaO.6Al_2O_3 (CA_6) crystals in the cluster form on the surface of fused alumina grains. In this multiphase composition, although the CA_6 phases bonded the grains and the matrix, but the difference in molar volume of CA_6 and Al_2O_3 could lead to large stresses when CA_6 forms [16] and some cracks are generated that may decrease the mechanical strength and enhance the slag penetration. The siliceous materials present in the batch may form a low melting glass (CMAS etc.) and tend to decrease the refractoriness [17]. Oppositely, the coarse fused aggregates with a spinel bonded matrix attached to a net like CA_6 structure formed an interlocking mass with pores and fissures (Fig. 1) that could prevent the extension of cracks and may contribute to spalling resistance. Another interesting feature revealed from the figure is the cracks formed [Fig. 2(b)] from the boundary stress developed may be due to the large volume change associated with the spinel formation. It is known that the spinel formation reaction is associated with a considerable volume expansion amounting around 5% or more than that [18]. This could lead to structural damage due to the uncontrolled spinel forming reaction from highly reactive amorphous spinel-gels at fairly low temperature.

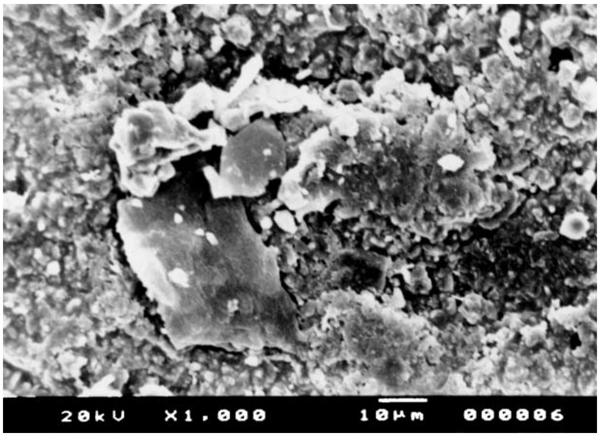
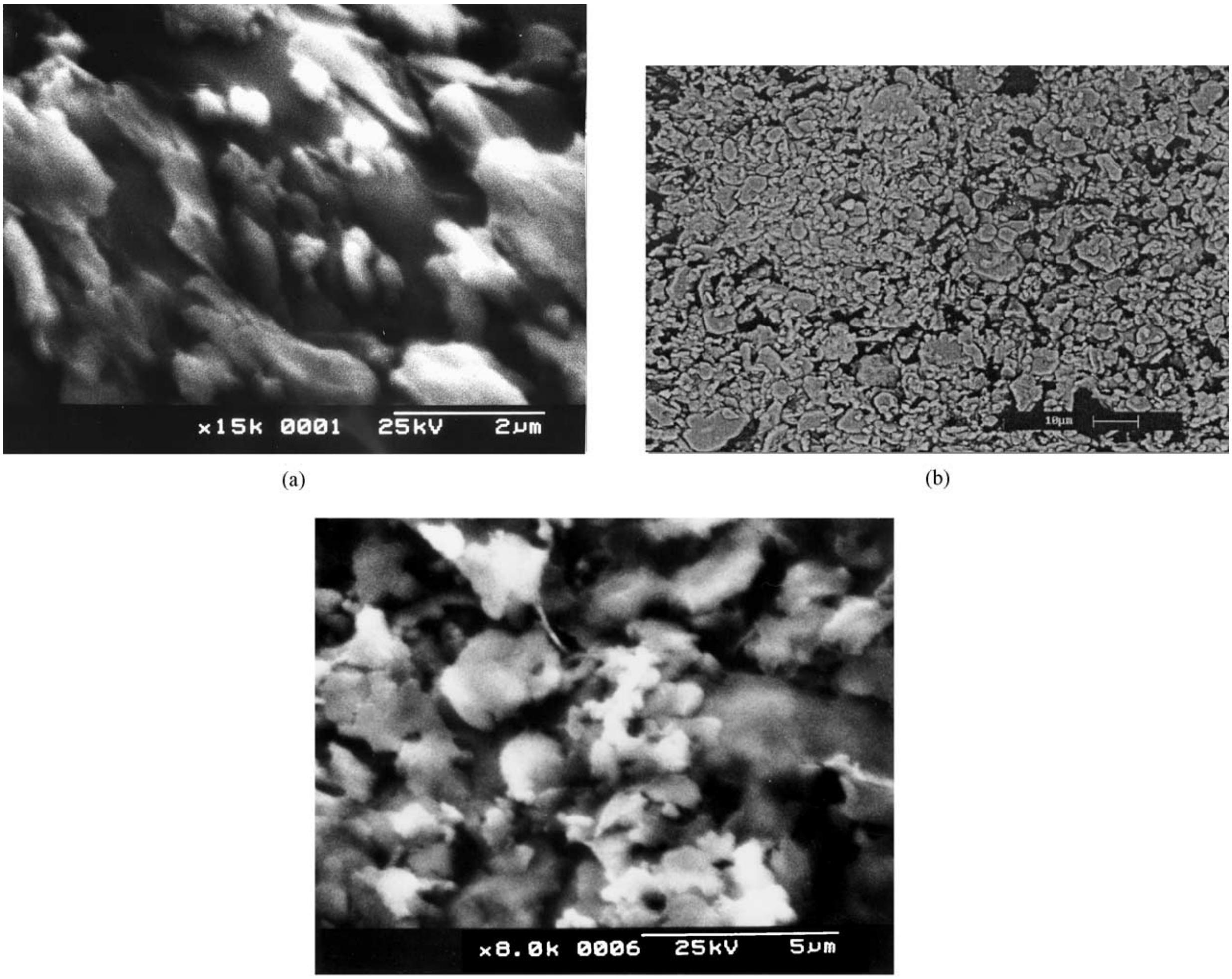


Fig. 5. SEM photograph of polished surface of ULC castable prepared with silica sol additive and fired at 1500 °C.

3.2. *Microstructure of ULCC composition with alumina and silica sol additives fired at 1500 °C*

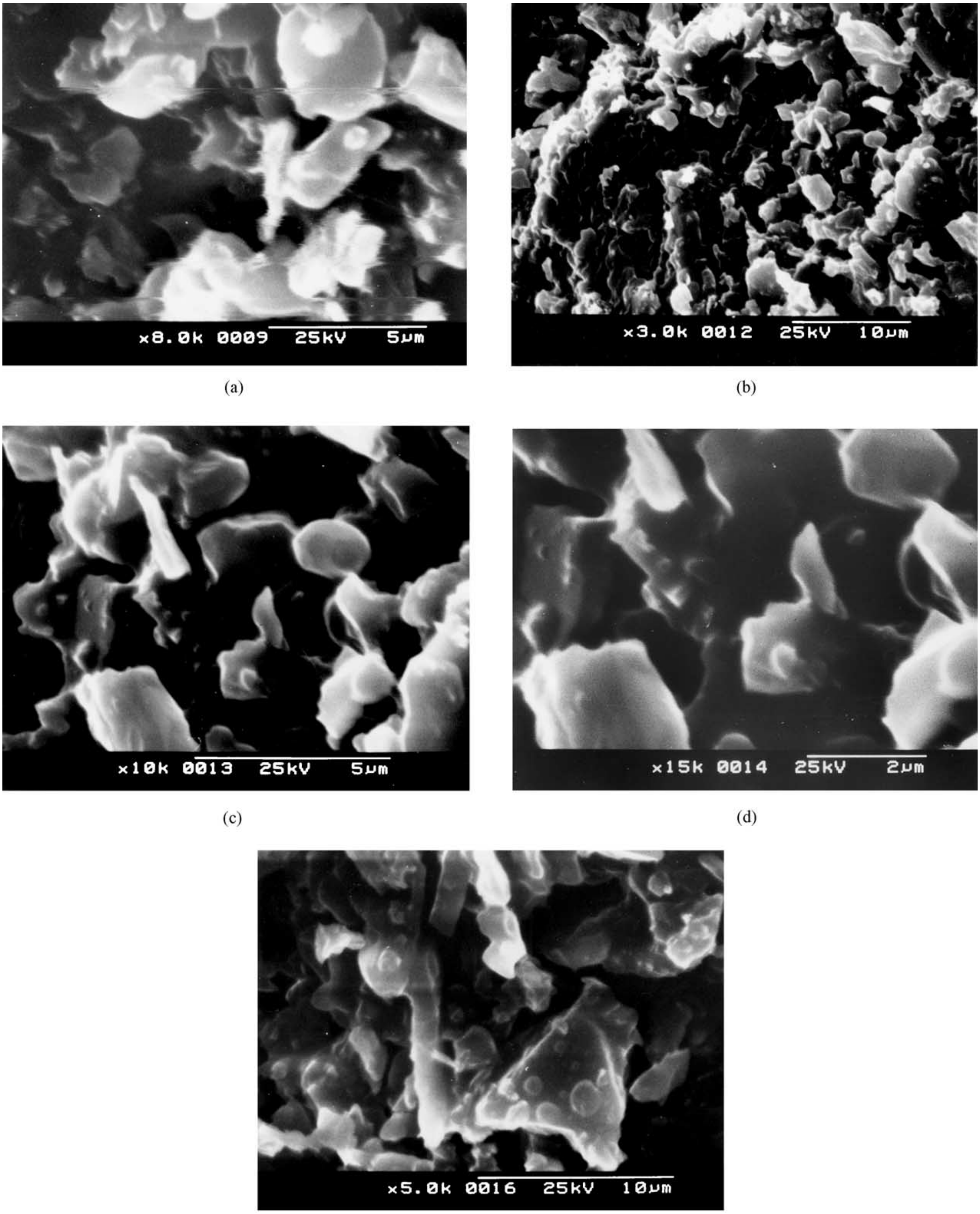
Fig. 3 shows a densely packed microstructure of alumina sol-bonded castable with an abundance of corundum grains of comparable size, rounded or subrounded, homogeneously embedded in the matrix; some acicular mullite crystals too are distributed in various regions that gave a clear indication of good hot strength. The interlocking nature with very few cracks may give rise to better thermo-mechanical properties. Fig. 4 showing the XRD patterns of alumina sol-bonded ULCC fired at 900 and 1500 °C, makes it evident that low temperature mullitization took place beyond



(a) (b) (c)

Fig. 6. (a)–(c) SEM photographs of fractured surface of ULC castable prepared with mullite sol additive and fired at 1200 °C.

900 °C by the reaction between microsilica present in the batch and alumina sol additive, which develops prominently in due course of firing at 1500 °C. But for silica sol-bonded castable, Fig. 5 shows a non-uniform heterogeneous matrix where bonding is disjointed at several places with locally agglomerated particles and fractured platelets. High solid content of silica sol may lead to early mullitization (by reacting with microfine



(a) (b) (c) (d) (e)

Fig. 7. (a)–(e) SEM photographs of fractured surface of ULC castable prepared with spinel sol additive and fired at 1200 °C.

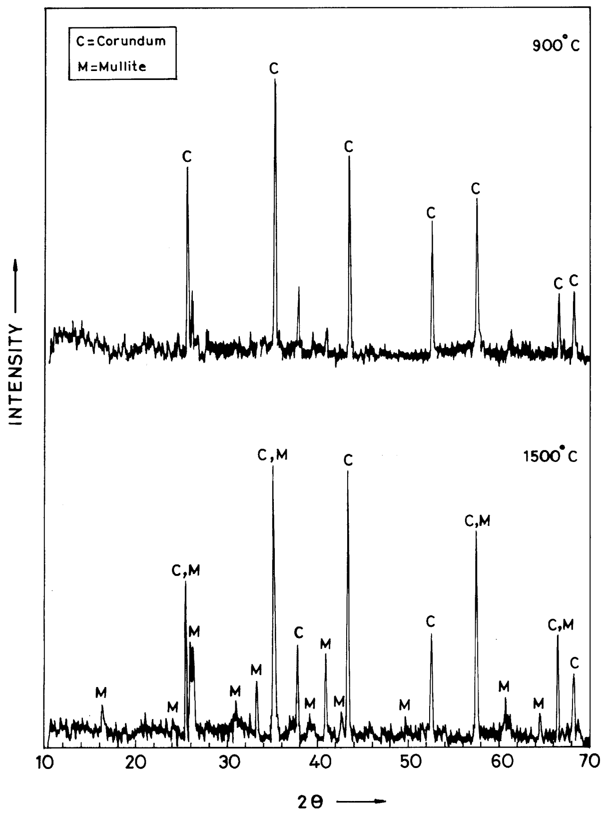


Fig. 8. XRD patterns of ULC castable prepared with mullite sol additive and fired at 900 and 1500 °C.

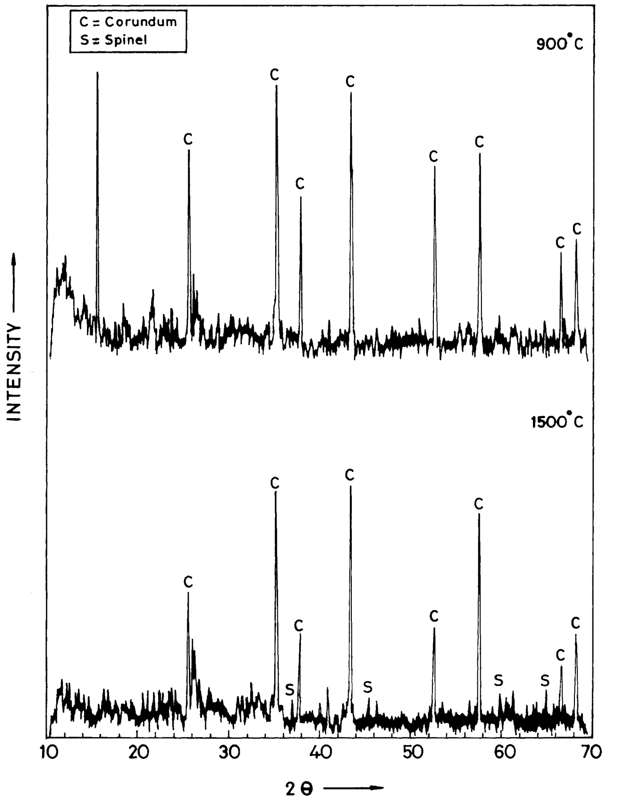


Fig. 9. XRD patterns of ULC castable prepared with spinel sol additive and fired at 900 and 1500 °C.

alumina) and large abnormal grain growth occurs sporadically due to pore grain boundary break away that may deteriorate the mechanical properties. In addition to this, the expansion of amorphous silica may cause some stressed regions and render friability of the texture.

3.3. Microstructure of ULCC composition with mullite and spinel-sol additives fired at 1200 °C

Fig. 6(a)–(c) for mullite bonded castables showed the acicular mullite crystals dispersed from place to place, by reinforcing the matrix and confirmed the high strength and load bearing capacity of the material. A compact microstructure with relatively lower porosity [14] and larger particles held together by bond forming lenses are also prominent, which may result in improved corrosion resistance. But for spinel bonded castable, Fig. 7(a)–(e) showed that the pores are trapped inside the grains, because the high chloride concentration [14] and micro bubble formation may lead to swelling. The excessive volume expansion of spinel bond causes some highly stressed regions with some continuous fissures generated in some regions. This can affect the corrosion resistance and mechanical strength of castables. Early spinel formation gave rise to large sized grains and the habit of growth of grains is columnar, spheroidal, prismatic, cubic and their orientations also vary widely with regard to the matrix. This also could affect densification and hamper the mechanical properties. The XRD reports at 1500 °C for mullite and spinel sol-bonded ULC castable from Figs. 8 and 9, corroborate the generation of mullite or spinel phases form the respective sols, while the predominant corundum phases appear due to the presence of alumina aggregates in the batch composition of castables. It is also clear from these figures that although at 900 °C those mullite and spinel phases do not appear but it has already been reported earlier that they are quite prominent at 1200 °C [14], because it is a special feature of sol–gel materials to mature at well below the conventional firing temperature.

4. Conclusions

Sol–gel materials render good installation flexibility and homogeneous distribution of fine particles in refractory castables along with the evolution of desirable phases at relatively low temperature. But in a lot of cases their microstructures are associated with pore formation, crack generation due to volume mismatch and excessive grain growth. Therefore poor corrosion resistance, strength and other thermo-mechanical properties may cause some limitation towards their practical applications. However these additions can be energetically favorable and in some cases those castables show good spalling resistance.

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