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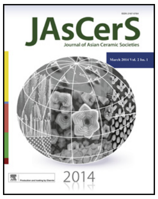

Implementation of industrial waste ferrochrome slag in conventional and low cement castables: Effect of microsilica addition

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ABSTRACT

Ferrochrome slag is a waste material obtained from the manufacturing of high carbon ferrochromium alloy. This slag is formed as a liquid at 1700 °C and its main components are SiO_2, Al_2O_3 and MgO. Additionally it consists of chrome, ferrous/ferric oxides and CaO. Present work outlines a novel approach in formulating castables with this industrial waste.

Samples with decreasing cement content 15–05 wt.% were formulated in combination of both slag and calcined bauxite as matrix components. Effects of varying 0–10 wt.% microsilica as a micro-fine additive in these castables were investigated in this work. Pore filling properties of microsilica improved apparent porosity and bulk density. Phase analysis through X-ray diffraction techniques demonstrates successful formation of spinel and mullite crystalline phases. Mechanical behavior was evaluated through cold crushing strength and residual cold crushing strength after five consecutive water quenching cycles. Scanning electron microscopy measurements were carried out in order to better understand the packing density and reaction mechanisms of fired castables. Slag containing castables portrays good thermal properties such as thermal shock resistance, permanent linear change and pyrometric cone equivalent.

1. Introduction

Bauxite based castables with conventional and low cement castables have drawn great attention in non-recovery coke oven batteries, coal-fired power boilers, industry furnaces and iron industries [1] for many years. Addition of micro silica in these castables, improves the refractory properties, gives reduction in water demand, and increases packing density [2–5]. Debilitation of deposits of ore and non-ore minerals increases ecological problems and the costs for mineral raw materials. It can be minimized by secondary resources, composite processing of raw material and development of low waste for such castables. The use of secondary resources makes it possible to solve the problems of natural raw materials and reduces costs involving their extraction, processing and reduces industrial discharges into the atmosphere [6].

In the production of refractories, there is an option of metallurgical industry wastes to be utilized. Slags formed in production of high carbon ferrochrome are usually dumped. Utilization of dumped ferrochrome slag in refractory castables reduces the cost of product and is friendly to the atmosphere. This material is being used for road construction, brick manufacturing and has recently been tried in cement industry and as a base layer material in road pavements due to its excellent technical properties [7–11]. Global ferrochrome production is totaled around 8.9 million tons in the year 2011. The world's major ferrochrome producers are South Africa 42%, China 23%, Kazakhstan 13%, and India 10% [12]. Almost all ferrochrome is produced in submerged electric arc furnaces [13,14]. The slag production is 1.1–1.6/t of Ferrochromium alloy depending on feed materials [14].

Ferrochromium is a master alloy of iron and chromium. In high carbon ferrochromium, metallic Cr content is 60–65% with varying amounts of Fe and C. Ferrochromium is produced pyrometallurgically by carbothermic reduction of chromite ore ($FeO{\cdot}Cr_2O_3$). The main raw material in the production of ferrochrome is chromite, which is basically chrome and iron oxides containing mineral. Chromite is used as lumpy ores, which must be generally agglomerated to make them usable to charge for the furnace. Fines in the smelting furnace cause unbalanced operation and thus decrease productivity. Different types of carbon are used to reduce metal

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oxides in the furnace. The most important of them is metallurgical coke. Quartzite, bauxite, dolomite, corundum, lime and olivine are used as fluxing materials [15] to get the right composition of slag. A careful quality control of raw materials ensures maximum output and uniform quality in the smelting process. The main components of the slag are SiO_2, MgO, and Al_2O_3. The slag also includes Cr and Fe oxides and calcium oxide. Common phases in the slag are glass, spinels (Al_2O_3–MgO) and forsterite (MgO–SiO_2) [16–18] and small amount of CaO.

Aim of this work was to prepare conventional castable and low cement castables by utilizing this waste ferrochrome slag, calcined bauxite and microsilica. They were characterized by X-ray diffraction (XRD) for structural changes and evolution of new phases. Refractory properties such as PCE (pyrometric cone equivalent), PLC (permanent linear changes) and TSR (thermal shock resistance) were investigated to have a better understanding in order to design refractory castables with enhanced properties. Use of secondary resources makes it possible to solve problems of materials availability; it reduces cost for their extraction, processing and their industrial discharge in the atmosphere thereby providing an economical and financial environment to country. Possible applications of present work include non-recovery coke ovens, boilers and reheating furnaces.

2. Materials and experimental procedure

2.1. Raw materials

Calcined bauxite (Shiva minerals Pvt. Ltd., Rourkela) and Ferrochrome (byproduct of TATA Ferroalloy, India) were used as aggregates, details of which are included in Table 1. High alumina cement CA-270 (Almatis, India) is introduced as a hydraulic binder and microsilica (Shiva Minerals Pvt. Ltd., Rourkela) as additives. Fig. 1 shows how ferrochrome slag is used in different particle fractions. The specific gravity of this slag is 2.57 g/cm^3. Aggregate percentage was kept constant 85 wt.% throughout the study. Microsilica content with respect to high alumina cement (HAC) was varied from 0 to 10 wt.%. The batch composition of the castables is listed in Table 2.

Table 1
Particle size and chemical composition of the raw materials.

	FC-Slag	Calcined bauxite	HAC	Silica fume
Particle size	0–5 mm	0–5 mm		−0.15 μm
Al_2O_3 (wt.%)	22.21	85	72	1.36
SiO_2 (wt.%)	27.14	8	–	93.89
Fe_2O_3 (wt.%)	4.01	3	–	1.06
CaO (wt.%)	5.13	–	28	0.61
MgO (wt.%)	24.88	–	–	1.68
TiO_2 (wt.%)	–	4	–	–
Cr_2O_3 (wt.%)	12.57	–	–	–

Table 2
Batch composition of ferrochrome slag based castables.

Sample code	FC slag (wt.%)	Calcined bauxite (wt.%)	HAC (wt.%)	Fume silica (wt.%)
S0	50	35	15	00
S5	50	35	10	05
S7.5	50	35	7.5	7.5
S10	50	35	05	10

FC, ferrochrome slag; HAC, high alumina cement.

2.2. Preparation of castables

Conventional and low cement refractory castables are generally prepared using approximately 15–10 and 3–5 wt.% HAC respectively. The ferrochrome slag and calcined bauxite were used in castable formulation in the present study with small additions of microsilica. The formulation in Table 2 shows the detailed composition with their specific names. In the first step for castable formulation, ferrochrome slag was oven dried, crushed, and ground for grading into three groups: coarse (6 −2 mm), medium (1–0.5 mm) and fine (<0.5 mm). The jar and grinding media were of titanium-coated stainless steel material. At one time 250 g of ferrochrome slag material was taken in the jar and ground in

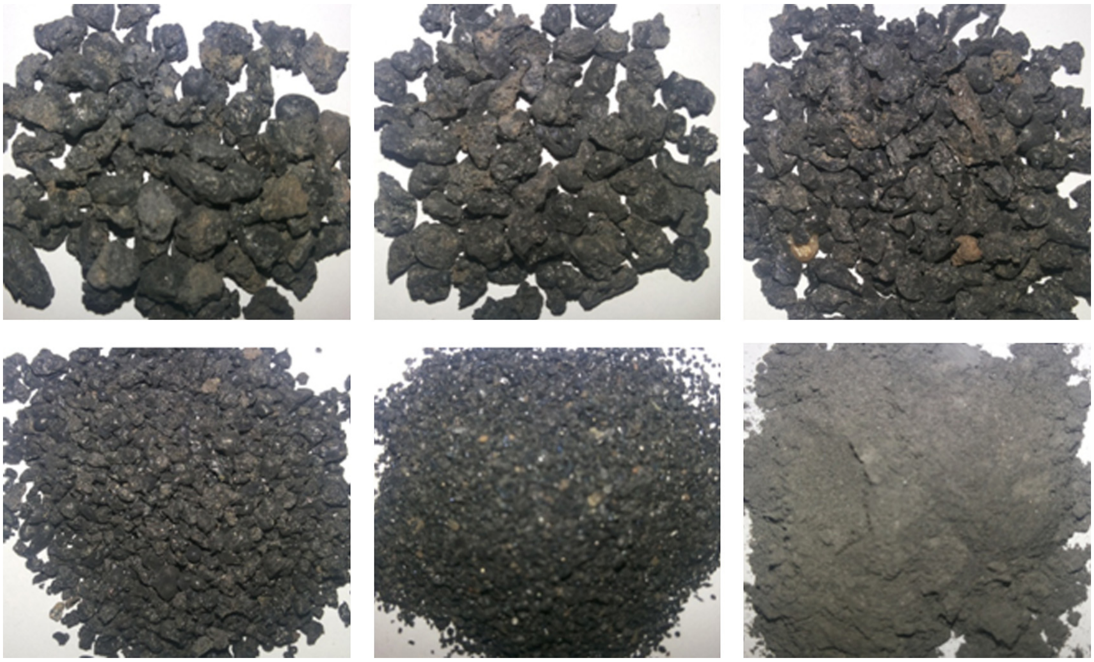

Fig. 1. Pictorial representation of the ferrochrome slag used graded in different particle sizes.

a high energy ball mill for 30 min at 400 rpm. Similarly, it was processed to complete the grinding of complete material. The ground material was then kept in various selected sieves and set up on the motorized vibro-sieving equipment for grading. Same technique was used for grinding and grading calcined bauxite material. The particle size distribution has an important role in the properties of refractory castable. Incorrect particle size distribution may cause militancy or the excess water requirement by the castables. The particle size distribution of the fine fraction is generally a representation of the flow characteristics. The trials of aggregate proportions were taken in a 1000 cm^3 flask filled up to 250 cm^3 and vibrated for 30 s and the packing density calculations were carried out for each trial. Aggregate having highest packing density was chosen for further analysis. The materials were dry mixed in a plastic container for 10 min by spatula and then were taken for sample preparation. Generally, conventional and LCCs require less than 12 and 5 wt.% of water respectively to achieve the desired rheology; therefore, water was added in two steps. The casting was done by adding first two-thirds proportion of water at a time. Then, one-third of water was added slowly to get a homogenous mixing. The wet mixing was performed for up to 5–6 min to achieve proper flow. Immediately after wet mixing, the castable mix was filled into a cubic mold (50 mm) made of hard steel. The mold was placed on the vibrating table filled with the wet mixed castable and the mixes were vibrated for 10 min, showing better compactness. For each composition, several samples were prepared for laboratory testing. The samples were cured in a moisture-saturated environment (95% RH) in a humidity chamber at room temperature for different time periods. For firing the samples, they were first oven dried at 110 °C for 24 h. The test samples were fired at 1100 and 1300 °C with dwelling time of 3 h, using electric furnace at a heating rate of 5 °C/min. Furnace was equipped with SiC heating element and a programmer PID528, manufactured by Selectron Process Controls Pvt Ltd,. India. The programmer has the temperature control accuracy of ±1 °C.

2.3. *Characterizations of prepared castable*

Apparent porosity and bulk density of sintered castables were investigated according to ASTM C20-00 [19]. Cold crushing strength (CCS) is the capacity of a material to withstand axially directed pushing forces. Cubic test specimens of 50 mm size were prepared and the value of maximum uniaxial load (in N) was noted when the sample block failed completely. Finally CCS value was calculated using the method stated in ASTM C133-97 [20].

Thermal shock resistance (TSR) determines the strength loss or reduction in continuity or both of the castables subjected to thermal cycling. TSR of the castables was determined on the basis of ASTM C1171-05 standard that measures strength loss after cycling samples from 1000 °C to room temperature for five times [21].

ASTM C113-02 Test method reveals the determination of permanent linear change (PLC) of refractories when heated under prescribed conditions. For each test, castable samples were prepared in stainless steel molds in the rectangular shape of size 25 mm × 25 mm × 150 mm. A reference mark was made on each specimen by using ceramic paint to indicate the exact position where the measurements were made. Length of marked line was measured before firing and after firing to perform this experiment [22].

Pyrometric cone equivalent (PCE) is common method of ascertaining the fusion point by equating the bending characteristics of the sample with those of a series of standard pyrometric cones that all run in the same furnace. This test method measures the PCE of specimen by comparison of test cones with standard pyrometric cones (Segar cones). For PCE measurements all the castable samples were crushed using mortar pestle followed by grinding in a planetary mill (400 rpm) and passing it through a 65 mesh (Tyler standard series) according to ASTM C24-09. Dextrin (as a binder to create plasticity) and water were added into the fine material and molded in a cone shape. Both the test cone samples and standard pyrometric cones were mounted with certain angle (82°) and heated at a 10 °C/min [23].

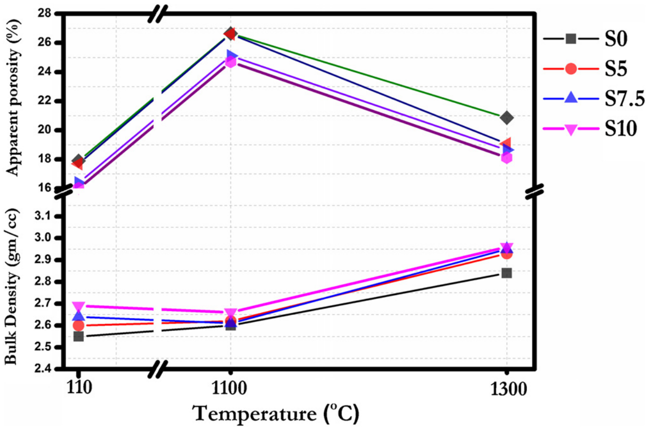

Fig. 2. Bulk density and apparent porosity of ferrochrome slag based castables as a function of temperature.

Samples were analyzed by XRD for the investigation of phases present. X-ray diffraction patterns were observed using a portable XRD machine (Rigaku, Japan) using Ni filtered Cu K_α radiation operating at 30 mA and 40 kV. Phase identification analysis was carried out by comparing the respective powder XRD patterns with the standard database stated by JCPDS (PDF-2 database 2003).

Sintered castables were polished using emery papers of grade 1/0, 2/0, 3/0, and 4/0 (Sia, Switzerland) followed by polishing on a velvet cloth using diamond paste of grade 1/4-OS-475 (HIFIN). Then these were etched thermally at 1200 °C. Micrographs were recorded with the help of a Scanning Electron Microscope (INSPECT 50 FEI).

3. Results and discussion

3.1. *Bulk density (BD) and apparent porosity (AP)*

BD and AP were determined at different temperatures (110 °C, 1100 °C and 1300 °C). Fig. 2 shows that in castables S5, S7.5 and S10 there is significant increment in the densification accompanied by valuable decrement in the porosity at highest sintering temperature (1300 °C). In the temperature range 110 °C to 1100 °C there is an abrupt drop in bulk density which could be correlated to evaporation of chemically combined hydraulic phases. At this temperature no ceramic bonding occurred. However for 1300 °C the bulk density and apparent porosity improved, this behavior may be attributed to ceramic bonds being formed [24]. At 1300 °C reactions between alumina, slag, silica and cement form a liquidus phase filling the interspaces among the constituents of castables. Fine particle size distribution of the microsilica mixture also helped in improvement of packing density of the castables. This finally leads to a much denser structure as when compared to castables sintered at lower temperature.

3.2. *Cold crushing strength (CCS)*

CCS of all the castables as a function of temperature is shown in Fig. 3. It can be observed that at 110 °C castable S0

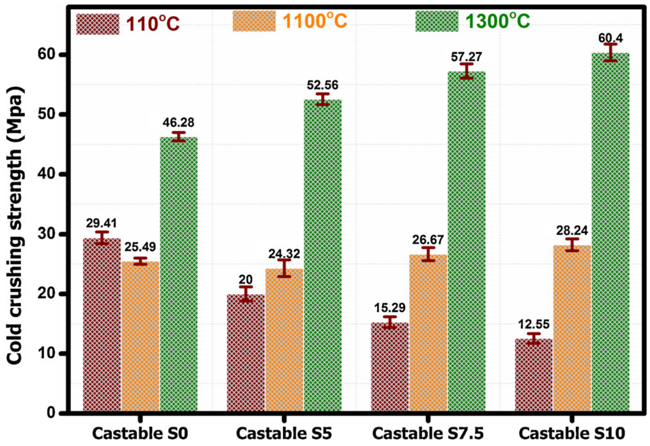

Fig. 3. CCS of different ferrochrome based castable samples fired at different firing temperatures.

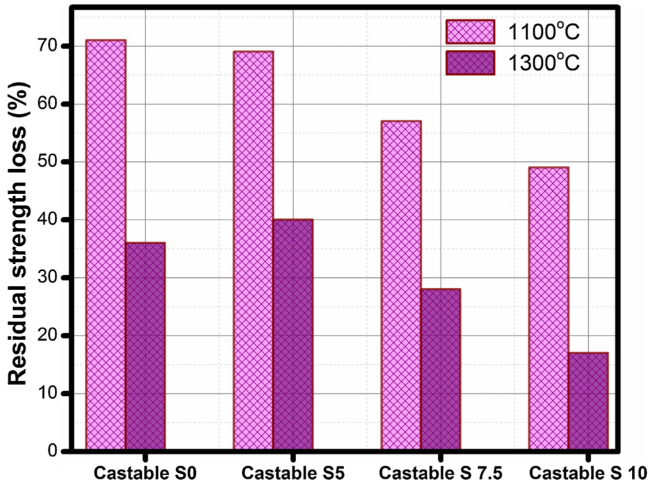

Fig. 4. Strength loss of ferrochrome based castable samples fired at 1100 °C and 1300 °C.

containing 15 wt.% cement and no microsilica depicts the highest strength which is attributed to the higher amount of the cement hydrated phases CAH_{10} ($CaO \cdot Al_2O_3 \cdot 10H_2O$) and monoclinic AH_3 ($Al_2O_3 \cdot 3H_2O$). Possible reaction propagation is mentioned below:

$$CaO \cdot Al_2O_3 + 10H_2O \rightarrow CaO \cdot Al_2O_3 \cdot 10H_2O\,(\text{hexagonal}) \qquad (1)$$

$$2CaO \cdot Al_2O_3 + 11H_2O \rightarrow 2CaO \cdot Al_2O_3 \cdot 8H_2O\,(\text{hexagonal}) + Al_2O_3 \cdot 3H_2O \qquad (2)$$

$$3CaO \cdot Al_2O_3 + 12H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O\,(\text{cubic}) + 2Al_2O_3 \cdot 3H_2O \qquad (3)$$

These phases play the essential role of hydraulic bonding. Decreasing the cement content up to 10 wt.% adversely affects the strength in castable S5. Ferrochrome slag is a non-plastic material and absence of cement binder causes deficiency in hydrated phase formation which could be considered a major cause of strength degradation. Even the presence of microsilica and increased compactness owing to it could not make up for this deficiency. Decrease of the cement content down to 7.5 wt.% and 5 wt.% (castable S7.5 and S10) further leads to strength deterioration. This is due to low amount of cement available for good bonding. At 1100 °C all the castables have similar low strength due to the breakdown of the hydraulic bond while no ceramic reactions could take place. Castables S7.5 and S10 show highest CCS values at 1300 °C while containing the least amount of cement. This phenomenon is certainly related to high temperature reaction bonding, liquid phase sintering and the formation of acicular mullite phase which strengthens the structure at high temperature. The higher CCS value of S10 castable compared with other castables is due to the highest amount interlocking crystals of mullite phase.

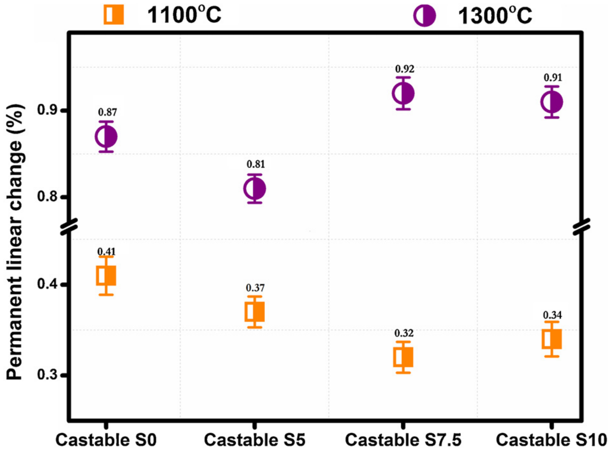

Fig. 5. Permanent linear change of ferrochrome based castable samples fired at 1100 °C and 1300 °C.

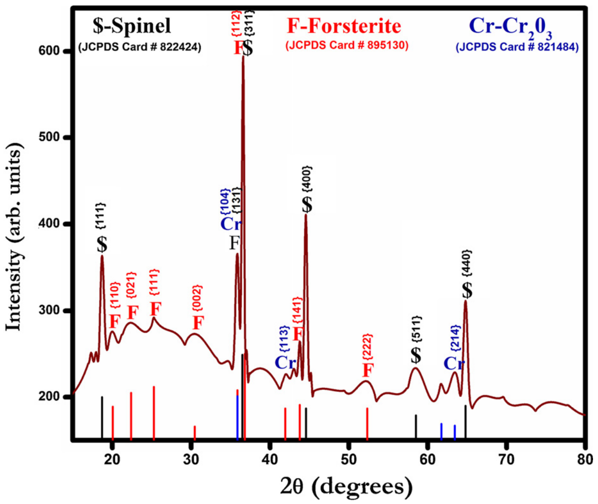

Fig. 6. X-ray diffraction pattern of ferrochrome slag used.

3.3. Thermal shock resistance (TSR)

Thermal shock resistance properties enlighten pre-firing conditions since strength loss behavior can be highly dependent on the firing temperature. Thermal shock resistance properties are determined on castables heated to a predetermined temperature (T), and quenched in water (T_{water}). After water cooling, the residual cold crushing strength (CCS_r) is measured and compared to the original

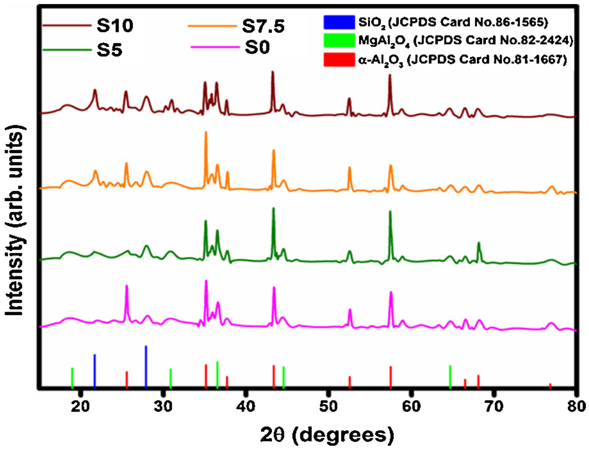

Fig. 7. X-ray diffraction pattern of ferrochrome slag based castables fired at 1100 °C.

strength (CCS_0). A percentage residual strength loss was calculated as:

$$TSR = \frac{CCS_0 - CCS_r}{CCS_0} \times 100 \qquad (4)$$

Fig. 4 shows the strength loss of the fired castables (1100 °C and 1300 °C). Better thermal shock resistance is obtained for the castables S7.5 and S10 fired at 1300 °C. Strength loss for S7.5 and S10 castables are 20% and 13%, respectively. This is dedicated to absence of free silica and good distribution of the mullite phase from the in situ reaction of microsilica and alumina. The poor spalling resistance of castables sintered at 1100 °C is due to the absence of mullite and ceramic bonds.

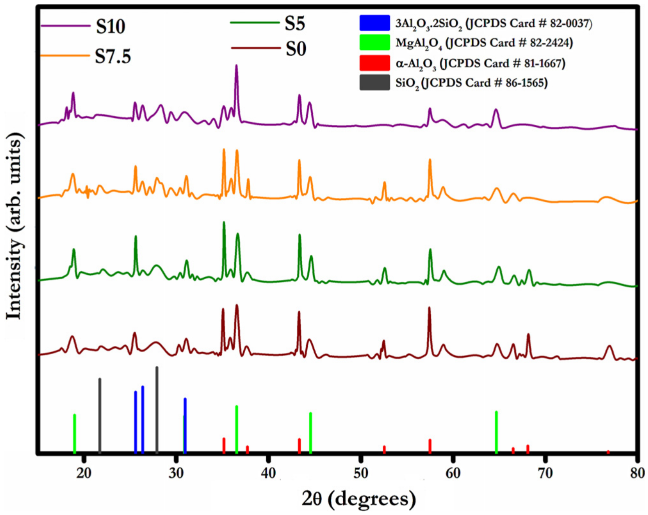

Fig. 8. X-ray diffraction pattern of ferrochrome slag based castables fired at 1300 °C.

3.4. Permanent linear change (PLC) and pyrometric cone equivalent (PCE)

This test method reports the determination of the permanent linear change of refractories when heated under prescribed conditions. The ferrochrome slag based bauxite castables is supported by their volume stability, i.e. limited permanent linear change (PLC) when fired at 1100 °C and 1300 °C. Fig. 5 shows that all the castables have less than 1% contraction after firing at 1100 °C/3 h and 1300 °C/3 h.

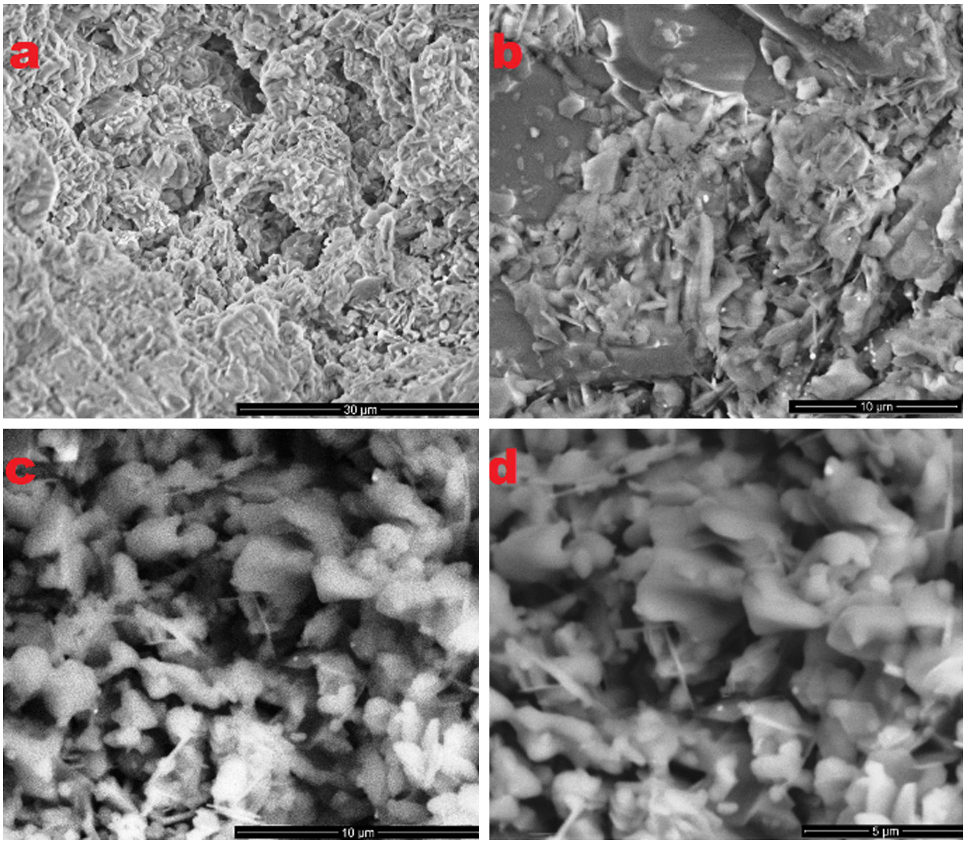

Fig. 9. SEM micrographs of castable S7.5 fired at 1300 °C for 3 h.

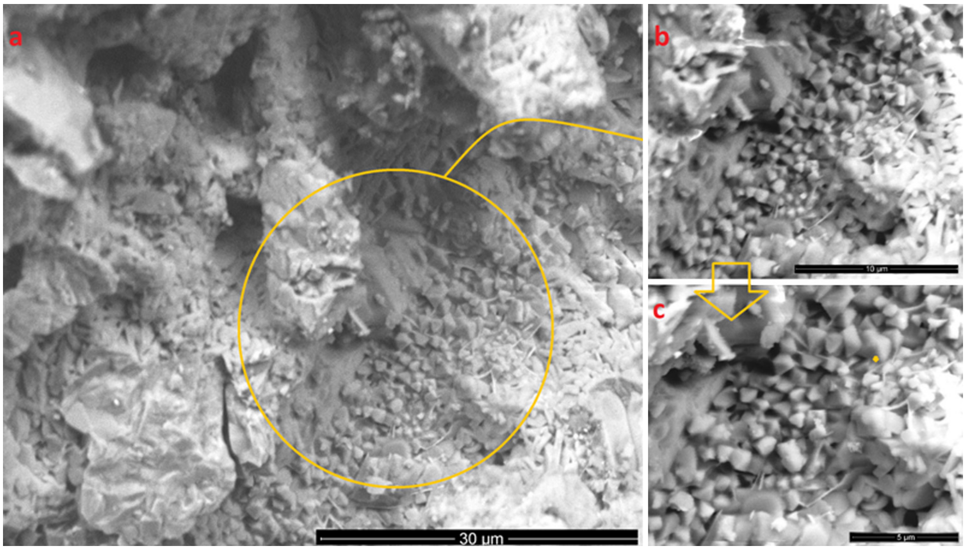

Fig. 10. SEM micrographs of castable S10 fired at 1300 °C for 3 h.

A percentage permanent linear change can be calculated as:

$$\%PLC = \frac{initial\ length - final\ length}{initial\ length} \times 100 \qquad (5)$$

Pyrometric cone equivalent test method measures the refractoriness of the materials with the comparison of standard Pyrometric cones. PCE value of all castables is equivalent to Segar cone 31 which resemble to a softening temperature equivalent of 1750 °C.

3.5. *Evolution of phases in castables at different firing temperatures*

Fig. 6 shows the XRD pattern of ferrochrome slag. Diffraction peaks are matched with JCPDS file no. 89-5130 and 82-2424 which correspond to presence of forsterite and spinel phases in the slag. Small amount of trigonal chromium has been observed in the slag and its corresponding intensity peaks have been verified by JCPDS file no. 82-1484. The XRD of castable samples heat-treated at 1100 °C and 1300 °C are shown in Figs. 7 and 8. At 1100 °C the major crystalline phase is α-Al_2O_3 in addition to small amount of spinel phase in castable S0. Similarly, α-Al_2O_3 and spinel both phases are present in addition to SiO_2 phase in castables S5, S7.5 and S10. Free silica phase was found to increase with increasing microsilica content in an order as follows: castable S5 < S 7.5 < S10. At 1300 °C it was found that the major crystalline phase was α-Al_2O_3, spinel and some amount of mullite. Added microsilica and silica present in bauxite as impurities react with fine alumina to form mullite. The presence of different impurities in bauxite also helps in the densification process and the formation of mullite. Mullite phase increases with a simultaneous reduction in the amounts of alumina and silica owing to high temperature reactions.

3.6. *Microstructure*

The microstructural evolution of castables fired at 1300 °C was observed using the scanning electron microscope of representative regions of cut specimens. Figs. 9 and 10 demonstrate photomicrographs of S7.5 and S10 castables respectively after sintering at 1300 °C. Results of BD-AP, thermal shock and CCS may be explained by drawing analogy to their respective microstructures. Fig. 9 shows castable S7.5 containing alumina, some glassy phases and needle shaped mullite structure. Presence of different impurities in bauxite and addition of microsilica helps the formation of mullite. Fig. 10 shows dense packed microstructure with an abundant of corundum grains homogenously embedded in the matrix. Some needle shaped mullite crystals are also distributed from place to place. Formation of mullite is greater in the castable S10 than that of S7.5 which corresponds to high amount of silica addition in S10. The presence of mullite creates an interlocking structure in the castables. This in situ reaction bonding is responsible for increase in density, thermal shock and CCS of the castables [25–27]. Spinel phase present in a uniform matrix is in conformance to the XRD pattern of the ferrochrome slag used.

4. Conclusion

Conventional and low cement castables prepared from ferrochrome slag, calcined bauxite, high alumina cement and microsilica exhibit good physico-mechanical and refractory properties. The superior mechanical strength of S10 castable is predicted due to high amount of in situ acicular mullite formation. Less than 1% dimensional variation in all prepared castables owes to usage of already heat treated byproduct (ferrochrome slag). Sample S10 containing castable shows superior spalling resistance than the rest other three castables prepared. Ferrochrome slag had been successfully implemented by us as conventional castables (25 wt.% slag + 75 wt.% Al_2O_3) for non-recovery coke oven door at VISA Steel Ltd. This door completed 90 cycles successfully without any repair. Using approximately 50% ferrochrome slag as an aggregate in conventional castables saved around the 40% production cost per ton.

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