

Effect of Pyrolusite on the Densification Behaviour of Alumina-kaolin System: Towards Sintered High Alumina Refractory Aggregate

Manidip Jana, Debasis Bhattacharya, Surajit Gupta, Swapan Kumar Das

In the present study, sintered high alumina aggregates have been produced by reaction sintering of a mixture of 85 mass-% calcined alumina and 15 mass-% kaolin with (coded as HA2) or without (coded as HA1) pyrolusite mineral addition. Pyrolusite of different concentration (1–5 mass-%) was gradually added to the above mix and compact samples produced by common ceramic processing were heated for densification at various temperature. The densification studies revealed that HA2 sample achieved 93 % densification (3,53 g/cm³) at 1450 °C in presence of pyrolusite while HA1 sample achieved 88 % densification (3,33 g/cm³) at 1650 °C without pyrolusite addition. The sintered aggregates were also subjected to pore size distribution, phase and microstructural evolution. Presence of well developed corundum and mullite crystals were found in HA1 whereas HA2 contain only corundum as major phase. Pyrolusite was found to promote grain growth and dissolution of secondary phase at 1450 °C in HA2.

1 Introduction

Dense, impervious and hard sintered high alumina aggregate is one of the important raw materials for refractory application particularly for castables. Several authors developed high alumina aggregates utilizing different kinds of raw materials through synthetic route [1–4]. Sillimanite beach sand, kyanite, high purity consistent quality fly ashes are some of the newly evolved sources of alumino silicate material to produce alumina rich synthetic aggregates. Other commercially available high alumina synthetic aggregate are tabular alumina, fused alumina, sintered alumina, sintered bauxite etc. The manufacturing process, properties of such aggregates and their compatibility in refractory products are available in many published literature [5–7].

Das *et al.* [8] and few other authors [9, 10] reported an overview of refractory raw materials, production and research in Indian

context where various alumina sources are described which are used to produce synthetic aggregate. Aneziris *et al.* [11] emphasized the need of new variety of potential synthetic refractory materials for stringent application in high temperature industries. Das [12] reported the development of erosion and abrasion resistant high alumina aggregate for application in monolithic castable utilizing calcined alumina, kaolin and selective dopants. These aggregates used in a castable composition of self flow type. The author observed the presence of well developed corundum crystal as major phase with hot-MOR value of 8 MPa at 1450 °C.

In ceramic system, additives in small amount play an important role towards densification processes. A variety of di-, tri- and tetra-valent oxides such as MgO, Fe₂O₃, TiO₂ and MnO₂ etc. have been used by several authors in alumina systems for many reasons

[13–17]. Erkalfa *et al.* [13] reported that densification of pure alumina containing more than 0,5 mass-% MnO₂ is controlled by grain boundary diffusion mechanism, whereas volume diffusion mechanism is suggested in case of 0,1–0,5 mass-% of MnO₂ addition. Microhardness and strength also shows an increasing trend by MnO₂ addition. Smothers *et al.* [17] reported that some additives which increase grain growth enter into the solid solution with alumina. Some other additives forms glassy phase. Presence of this glassy phase greatly increases surface diffusion and results grain growth.

Pyrolusite, a mineral essentially consisting of oxides of manganese of varying assay concentration. It has been used as additive for densification of alumina and kaolin mixture by Das *et al.* [18] to produce wear resistant ceramic tiles. Dörre *et al.* [19] discussed that, highly sintered alumina ceramic can solve severe wear problem in textile industries due to their superior wear resistant characteristics, low coefficient of friction and micro-

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Tab. 1 Batch compositions [mass-%]

Raw Material	HA1	HA2
Calcined alumina	85	85
Kaolinitic clay	15	15
Pyrolusite	–	5 mass-% of total batch

scopically smooth surface. Hence an optimization is necessary by appropriate use of selective additive which will produce a good wetting of matrix, homogeneity and low porosity. Ray *et al.* [20] carried out an impact fatigue and indentation fracture toughness test on such type of high alumina materials. The authors found that alumina based wear resistant material showed typical fatigue behaviour under repeated impact loading, with an increase in endurance as impact energy decreases. Indentation fracture toughness increased as the square root of the crack length increase.

The objective of this present investigation was to study the effect of pyrolusite addition on the densification, phase and microstructural evolution in a mixture of 85 mass-% Al₂O₃ and 15 mass-% kaolin with an ultimate aim of producing a high alumina sintered aggregate.

2 Experimental

The major raw materials calcined alumina and kaolin were used in this study. Pyrolusite (70 mass-% assay content) was selected as additive to promote densification. To optimize the maximum percentage of pyrolusite addition, an initial experiment was conducted by varying the concentration in the level

of 1, 3 and 5 mass-%. From this experiment it was observed that without pyrolusite the sintering temperature was 1650 °C, with 3 mass-% pyrolusite the sintering temperature was 1575 °C and 5 mass-% containing sample resulted highly densified, fully sintered sample. Based on the initial findings, it was finally decided to conduct the experiment with two main composition as per the batch provided in Tab. 1.

The usual ceramic processing of wet milling and powdering was followed to obtain ready powder for compaction. Samples of 25 mm × 25 mm × 8 mm were fabricated in a hydraulic press at 500 kg/cm² pressure. The dried samples were heated in the different temperature range for the two aggregates separately based on their predetermined PCE values. For HA1 samples the heating temperatures were fixed in the range of 1550–1650 °C, whereas for HA2 samples the heating temperatures range were fixed in the range of 1350–1450 °C. The heating rate was maintained 5 °C/min up to 1000 °C, then 2 °C/min up to 1250 °C and 1–0,5 °C/min up to the final temperature. The soaking was done for 2 h at the peak temperature. The fired samples were subjected for detailed characterization with respect to their densification [linear shrink-

age (LS), bulk density (BD), apparent porosity (AP)], pore size distribution, phase and microstructural properties. Standard technique was followed for the determination of LS, BD and AP on the bulk sample. The sintered samples of both the compositions were crushed into small samples of approximately 4 mm sizes and subjected to pore size distribution studies. Pore size distribution experiment was done *in Quantachrome* PoreMaster 60 by the mercury penetration method. The X-ray diffraction method was used to determine the phases present in the fired aggregate. The aggregates HA1 and HA2 were finely grounded and passed through 100 mesh sieve and the small iron particles were removed by a magnet. The X-ray diffraction patterns of the samples were recorded in X'pert Pro MPD diffractometer (*PANalytical*) using X'celerator operating at 40 kV and 30 mA uses CuK_α radiation. The XRD data were recorded in step-scan mode with step size 0,05° (2θ) and step time 70 s from 10° to 80 degree. The fining of the particle size was done to expose more number of atoms to the incoming x-rays so that a sufficient intensity could be obtained after diffraction. The X-ray analysis data was compared with the standard JCPDS data file to identify the phases. The quantitative estimation was done using Rietveld refinement. Known amount of pure standard calcium fluoride was used as standard reference material with the fine powder of HA2 to calculate the mass percentage of crystalline and vitreous phases in the sample using *Rietveld* analysis.

The surface morphology and elemental analysis of the fired aggregate has been observed in *JEOL JSM5800* and *ZEISS EVO 60* scanning electron microscope with *Oxford EDX* analyzer. Both the Microscope works with tungsten filament acceleration potential was used 20 kV. The sintered aggregates (1650 °C heated HA1 and 1450 °C heated HA2) were polished well with diamond paste. Both the samples were non-conducting; to make it conductive a thin gold coating was done. Then the microstructure was observed.

3 Results and discussion

3.1 Analysis of raw materials

The properties of the major raw materials are provided in Tab 2. It may be seen that

Tab. 2 Properties of the raw materials

Property	Calcined Alumina	Kaolin
Chemical constituents [mass-%]		
Al ₂ O ₃	98,95	28,50
SiO ₂	–	64,92
Fe ₂ O ₃	0,10	0,95
TiO ₂	–	1,40
CaO	0,32	0,70
MgO	0,21	0,65
Na ₂ O	0,37	0,47
K ₂ O	0,02	1,80
L.o.I.	0,95	7,25
Average particle size (d ₅₀) [μm]	6–8	15–16
α-Al ₂ O ₃ content [%]	>95	–
Residue over 325 mesh [%]	<1,5	<1,5
Dry MOR [N/mm ²]	–	5,00
Shrinkage at 1200 °C [%]	–	7,00
Fired MOR [N/mm ²] at 1200 °C	–	35,0

calcined alumina is of high purity with low soda content. The kaolin is siliceous and contain 1,8 mass-% K_2O . The oxide compositions of both the compositions are given in Tab. 3. It may be seen that HA1 contain around 88 mass-% alumina compare to 85 mass-% in HA2. No significant variation in other chemical constituents is seen in both the composition except HA2 contain 3,5 mass-% MnO_2 due to addition of pyrolusite. In both the compositions the alkali level is below 0,7 mass-%. The presence of 1,8 mass-% K_2O in kaolin is not affecting the overall composition. Hence it is very interesting to study the effect of MnO_2 on the densification behavior and other related properties of HA2.

Tab. 3 Oxide composition of the batches

Constituent [mass-%]	HA1	HA2
Al_2O_3	88,09	85,11
SiO_2	9,24	8,93
Fe_2O_3	0,13	0,13
TiO_2	0,21	0,20
CaO	0,28	0,27
MgO	0,18	0,17
Na_2O	0,28	0,27
K_2O	0,19	0,17
MnO_2	Nil	3,40
L.o.I.	1,40	1,35

3.2 Densification study

The variations in [%] linear shrinkage of HA1 and HA2 samples are shown in Fig. 1 (a) and (b) respectively. It may be observed that shrinkage increases with increase in tem-

perature which normally happens in such type of ceramic composition. The interesting phenomenon may be worth to note here that HA1 shows steady increase in shrinkage during the initial stages of sintering up to 1600 °C followed by sudden increase at 1650 °C. In case of HA2 a sharp increase in

shrinkage at all temperature is observed due to presence of MnO_2 which enhanced sintering.

The variation in bulk density and apparent porosity of HA1 and HA2 with heating temperature is illustrated in Fig. 2 (a) and (b) respectively. It is revealed from this figure that

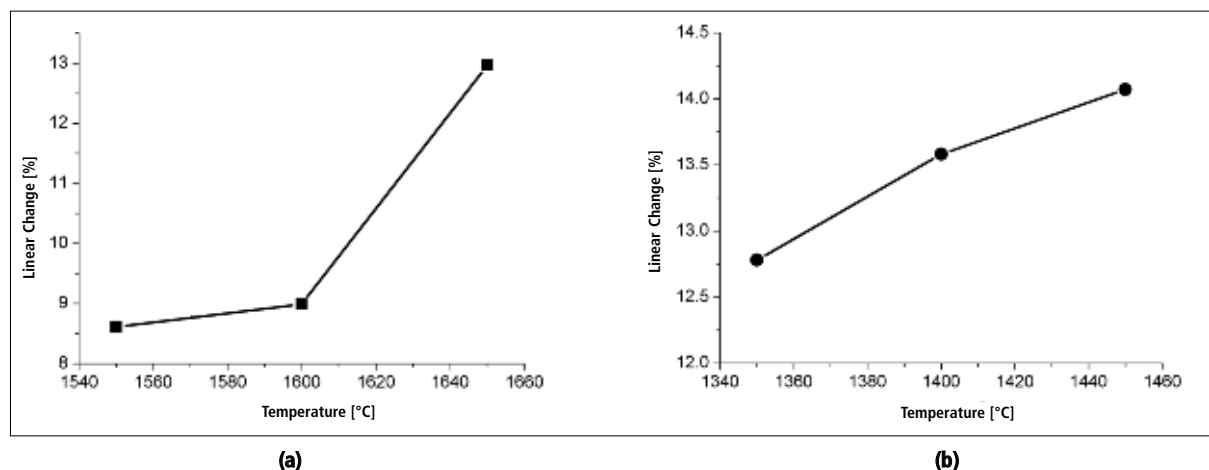


Fig. 1a–b Variation of linear shrinkage in [%] in relation to the heating temperature of (a) HA, and (b) HA2 specimens

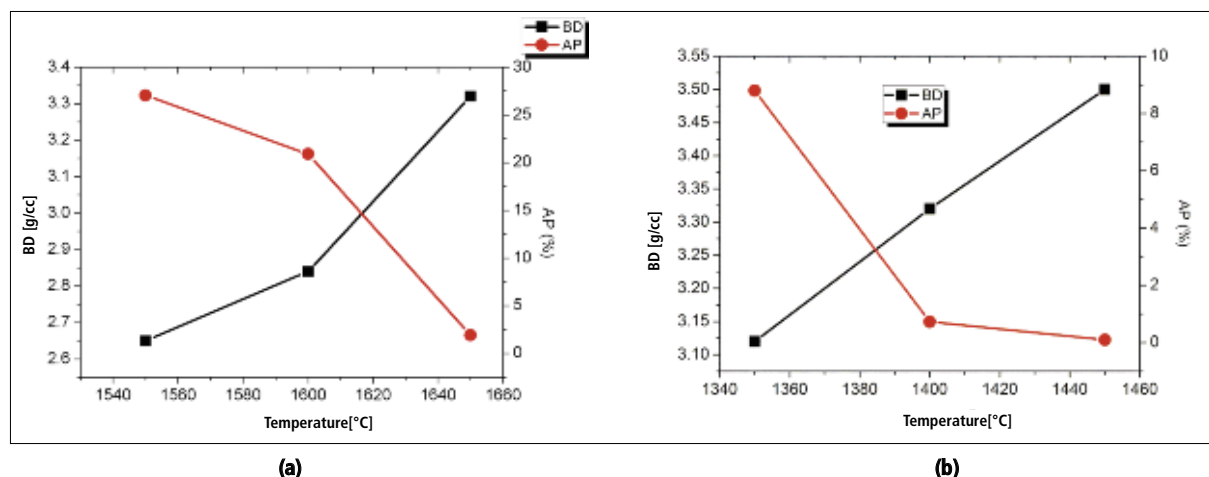


Fig. 2a–b Variation of bulk density and apparent porosity with respect to the heating temperature (a) HA1, and (b) HA2 specimens

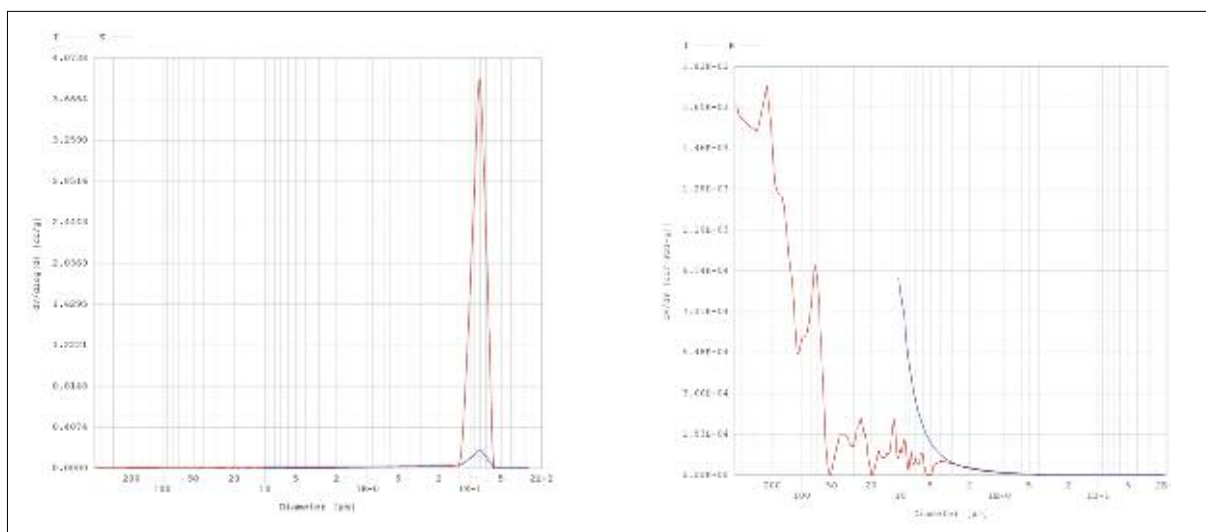


Fig. 3a–b Pore size distribution of (a) HA1 specimen sintered at 1650 °C and (b) HA2 specimen sintered at 1450 °C

HA2 sintered at lower temperature (1450 °C) than HA1 (1650 °C). The increase in sintering rate of HA2 is attributed towards the presence of 3,40 mass-% MnO₂. Manganese in pyrolusite exists in complex series of oxides and hydroxides due to its variable valency. As a result, valency change of manganese leads to defect structure. Manganese with different valency states created vacancy substituting the Al cation and promoted sintering at lower temperature in HA2 sample. This phenomenon is also observed by *Erkakalfa et al.* [13]. From the above figure

it may also be noted that the HA2 sample achieved 93 % densification (3,53 g/cm³) at 1450 °C in presence of pyrolusite while HA1 sample achieved 88 % densification (3,33 g/cm³) at 1650 °C without pyrolusite addition.

This enhanced densification of HA2 at lower temperature may be attributed towards increased surface diffusion in presence of glassy phase. The formation of glassy phase in HA2 sample was confirmed by XRD studies and discussed in later section. HA1 sample possesses around 2 % apparent porosity

which may be beneficial towards its application as refractory aggregate.

3.3 Pore size distribution study

The pore size distribution of 1650 °C heated HA1 and 1450 °C heated HA2 are illustrated in Fig. 3 (a) and (b) respectively. It may be seen that smaller size and homogeneous pore distribution is obtained in HA1 sample which is advantageous for refractory aggregate. Similar observation was made by *Yan et al.* [21].

The nature of pore size distribution in HA1 is of mono-peak mode and the pores are distributed within 0,06–1,0 μm range. The pore size distribution curve of HA2 is quite different from HA1. Due to the presence of additive in HA2 composition, the matrix is wetted by glassy phase with almost nil porosity and accordingly the curve is broadened.

3.4 Phase analysis

Fig. 4 shows the XRD pattern of both sintered aggregates of HA1 and HA2. From the figure it may be observed that HA1 contain corundum and mullite as major phases. Presence of calcined alumina in higher percentage resulted corundum as major crystalline phase and clay on heating formed mullite and some silica. Silica further reacted with free alumina and form mullite. The quantitative estimation of corundum and mullite in HA1 is provided in Tab. 4.

It is also observed from XRD pattern that HA2 contains only corundum as major crystalline phase. Mullite is appeared to be dissolved in

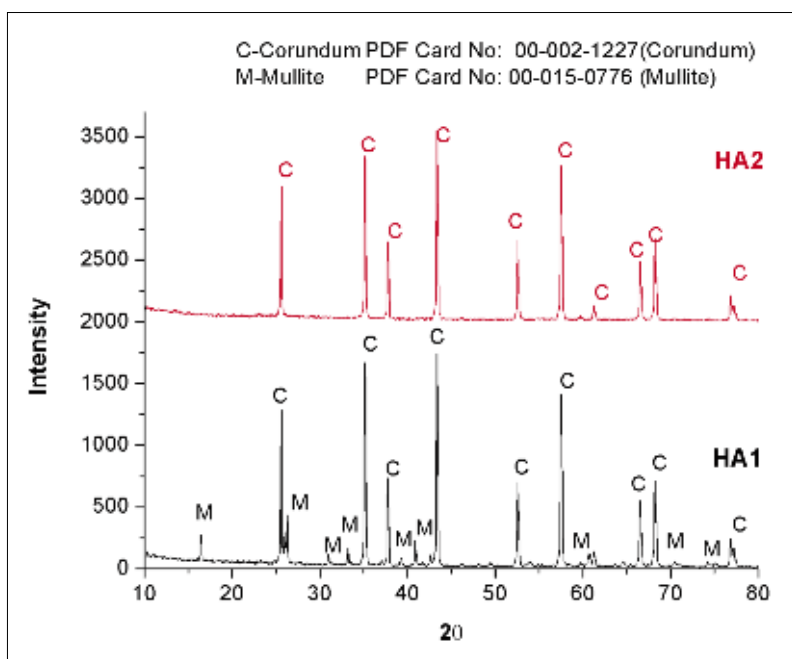


Fig. 4 XRD pattern of sintered HA1 and HA2 specimens

the glassy phases formed in the presence of pyrolusite. The draining of second phase in MnO₂ containing sample was also observed by other authors [13]. The quantitative estimation of this sample confirms 85 mass-% corundum as major crystalline phase and 15 mass-% glassy phases (Tab. 4). The fitted curve matched well for both the samples with the raw data and the reliability parameters in Rietveld analysis. It is interesting to study the effect of this glassy phase on the thermo-mechanical properties when it is used in refractory products by replacing synthetic high alumina aggregate. Since the glassy phase in HA2 enriched with silica and alumina, it is expected to be highly viscous which may not deteriorate the thermo-mechanical properties significantly. The effect of such HA1 and HA2 aggregate in refractory castable product is our next course of study.

3.5 Morphological and elemental analysis

The SEM micro-photograph along with EDS analysis of HA1 and HA2 are given in Fig. 5 (a) and (b) respectively. A well developed corundum and mullite crystals are seen in HA1 sample. The presence of needle shaped mullite crystal gives the interlocking

Tab. 4 Quantitative estimation (Rietveld analysis) of different phases in HA1 and HA2 samples [mass-%]

Phase	HA1	HA2
Corundum	80,20	85,0
Mullite	19,80	–
Glassy phase	–	15,0

property which enhances the strength of aggregate. This type of compact microstructure is also observed in some commercially available in high alumina sintered aggregate. The EDS analysis confirms the presence of O, Al and Si as major element, which are responsible for corundum and mullite phase.

Fig. 5 (b) shows corundum crystals with enhanced grain size in HA2 sample. MnO₂ present in this composition produced a glassy phase which increase surface diffusion and resulted grain growth. Similar effect of MnO₂ was observed by *Smothers et al.* [17] in case of pure alumina system. It is necessary to mention here that irrespective of different magnification of the SEM photographs of HA1 and HA2, the grain size of HA2 appears larger, although HA1 was sintered at higher temperature (1650 °C). Clusters of corundum crystals are seen in the matrix. The EDS analysis confirms the presence of Al and O as

major elements which support the formation of corundum phase. Some other elements Si and Mn are also found which might have present in the glassy phase.

4 Conclusion

The reaction sintering of 85 mass-% alumina and 15 mass-% kaolin mix at 1650 °C produced a crystalline structure consisting of corundum and mullite. Addition of ~3,5 mass-% of MnO₂ in the form of pyrolusite reduced the sintering temperature to a level of 1450 °C due to formation of glassy phase which increased the surface diffusion and promoted the growth of only corundum crystal. Also it was observed that MnO₂ promoted the sintering and densified the product at a faster rate than samples without pyrolusite. Presence of 1–0,06 μm pore size in mono peak mode of sample HA1 may offer better thermomechanical properties than

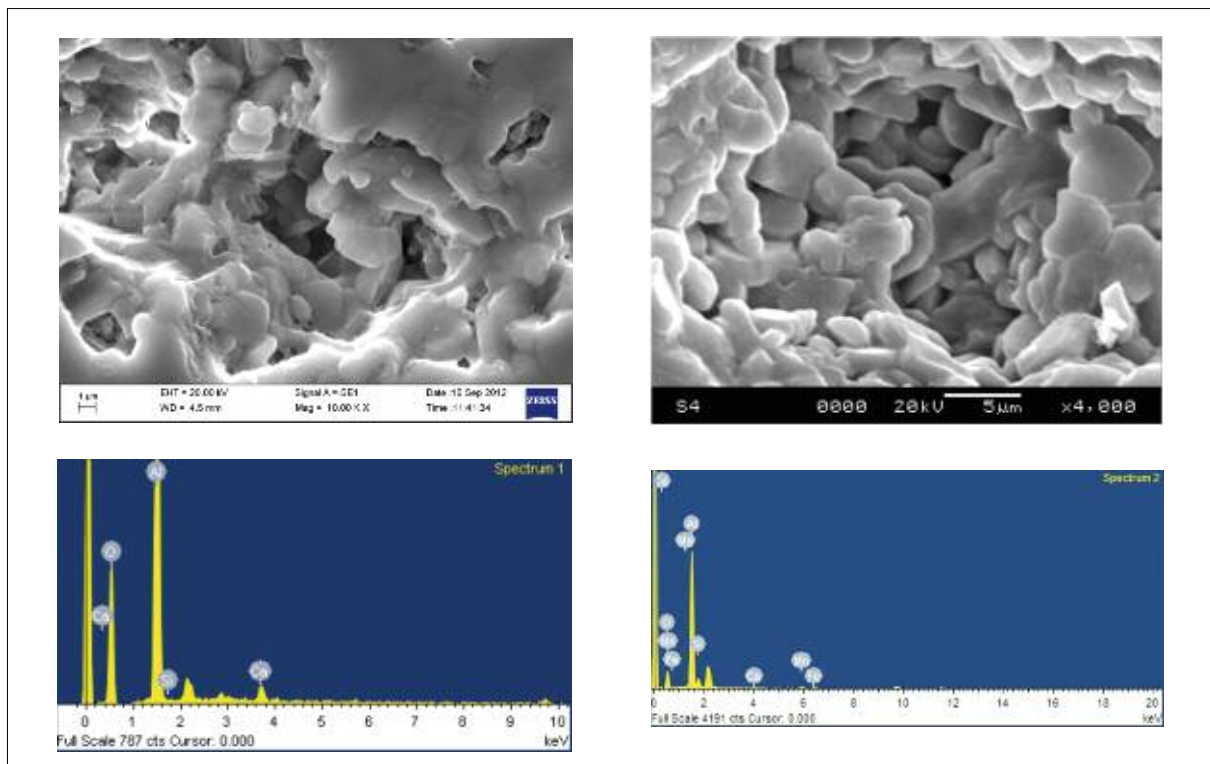


Fig. 5a–b SEM photo along with EDS spectrum of (a) HA1 and (b) HA2 specimens



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HA2 which has almost nil porosity due to wetting of matrix by glassy phase. However it will be interesting to study the effect of such aggregates on the thermo-mechanical properties by incorporating them in refractory castable composition. The authors of this paper will report the results of this study in future communication.

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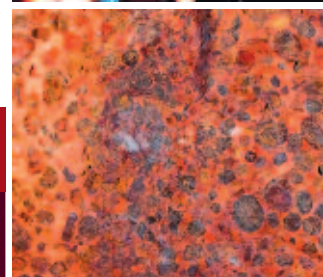
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