Microstructural Development in Calcium Hexaluminate with and without Fe_2O_3 Doping at Different Forming Method

Manidip Jana, Swapan Kumar Das

Calcium hexaluminate (CA_6) was synthesized from a mixture of anhydrous $Ca(OH)_2$ and $Al(OH)_3$ with or without Fe_2O_3 doping at a predetermined temperature of 1550 °C. Two different forming methods (uniaxial and isostatic pressing) were adopted to fabricate samples. Uniaxially pressed sample without Fe_2O_3 results higher porosity (17,14 %) with the formation of hexagonal platelet CA_6 grains while isostatic pressed sample with lower porosity (8,22 %) resulted more equiaxed CA_6 grains. Low concentration of Fe_2O_3 (5 %) did not formed CAF_2, which is the only stable phase in $CaO–Al_2O_3–Fe_2O_3$ system. However it was observed that 5 % Fe_2O_3 addition enhances the grain growth which is beneficial for refractory application.

1 Introduction

Alumina and alumina based composite aggregate plays a leading role in the refractory manufacturing industries due to its various applications in ferrous and non-ferrous, glass and cement manufacturing units [1,2]. Calcium aluminate exists in various form such as CA, CA_2, C_3A, $C_{12}A_7$ and CA_6 (C = CaO, A = Al_2O_3). CA is considered to be hydraulically optimum high alumina cement used in refractory castable as binder. CA_2 recently gained its importance as high temperature cementing material but its hydraulic activity is poor which can be enhanced by $C_{12}A_7$ addition [3]. Among these calcium aluminates, calcium hexaluminate (CA_6) is the most alumina rich intermediate compound in the $CaO–Al_2O_3$ binary equilibrium phase diagram and high thermally stable material up to the peritectic point (~1875 °C) [4]. It has some unique properties which makes it highly useful in refractory world. Low solubility in iron containing slag, high stability in reducing atmospheres, high chemical resistance in alkaline environment and low wettability by molten metal and slag and thermal expansion coefficient similar to corundum are some of them [5]. Theoretical density of CA_6 is 3,79 g/cm^3 and crystallizes in hexagonal system. Magnetoplumbite structure composed of alternative spinel blocks and conduction layer. Spinel blocks containing of Al^{3+} and O^{2-} ions, have the same rigid structure as spinel. Large cations such as Ca^{2+} are usually located in the spacious conduction layer, which has a mirror symmetry plane [6–9]. Recently, these magnetoplumbite crystal structure has been receiving very much attention because of their diverse application in various field especially in luminescent and laser host materials [10, 11], containers of radioactive waste [12], high temperature combustion catalyst hosts [13] etc. Asmi and Low [14] studied the mechanical behavior of Ca-hexaluminate/alumina composite with graded microstructure. They found that graded composites exhibits lower hardness in graded region than non-graded region because of the presence of relatively soft CA_6. Thus it also shows improved fracture toughness by crack deflection or crack-bridging by CA_6 platelets than the non-graded region. CA_6 has also used as a reinforcing material in alumina composite because of its chemical compatibility and coefficient of thermal expansion. Also the elongated grains act as bridging sites in the wake of a crack, thus improved the mechanical properties of the system [15] *Costa* and *Ribeiro et al.* [16] synthesized a new structure for ceramic pigments, based on hibonite doped with Ni. SnO_2 act as a buffer to ensure the charge neutrality of the hibonite lattice.

$CaO–Al_2O_3–Fe_2O_3$ ternary phase diagram exhibit the presence of stable phase CAF_2 in the lower temperature region and CA_6 forms extensive range of solid solution and also forms a large primary crystallization field. It signifies that this compound has low solubility in the iron oxide containing slag, thus it becomes a potentially suitable refractory material in iron and steel industries [17–20]. CA_6 and CF_6 forms a solid solution compound which is a subject of interest due to their specific magnetic and electronic properties [21, 22].

In this paper a study was carried out to observe the effect of the forming methods and Fe_2O_3 dopants on the densification behaviour, phase and microstructure evolution.

2 Experimental

Pure anhydrous aluminum, calcium hydroxide and iron oxide (Merck) were used as raw materials for synthesizing CA_6. Raw materials were taken in a proper weight ratio based on the stoichiometric composition $CaO{\cdot}6Al_2O_3$. Two separate batches were prepared with and without Fe_2O_3 addition and mixed homogeneously in Eirich mixer. After mixing, ~5 mass-% of water was added and again mixed homogeneously. The amount of water was perfectly determined by "ball in hand" test method. Two

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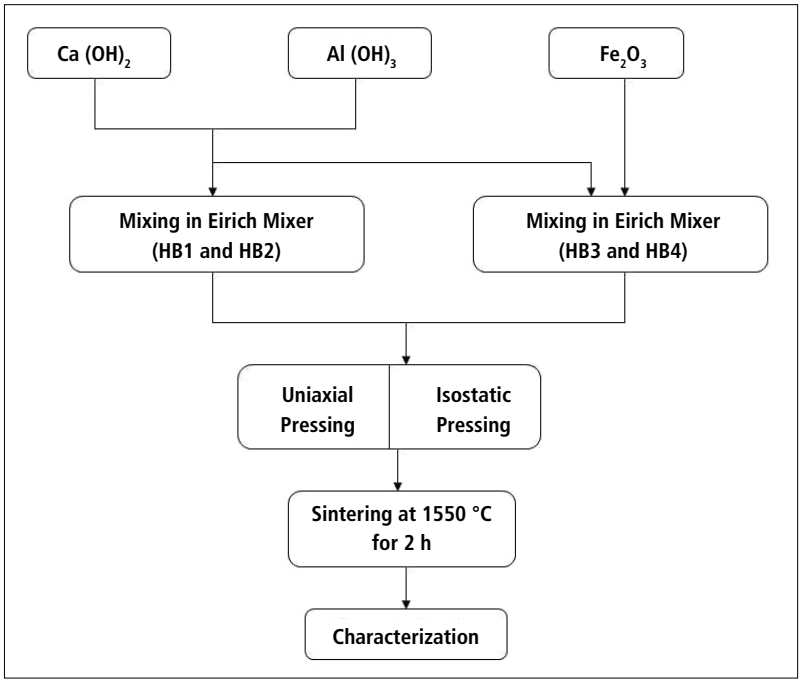

Fig. 1 Experimental flow sheet diagram followed in this study

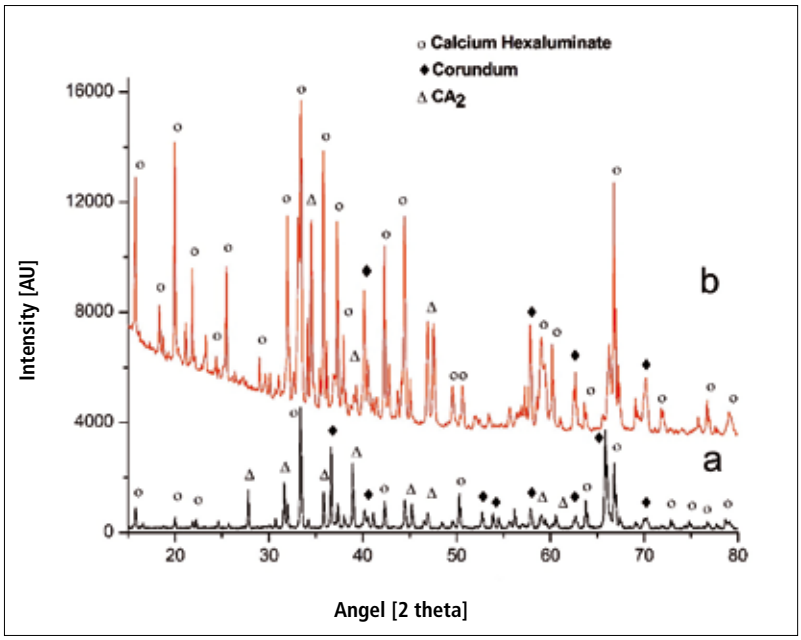

Fig. 2 XRD pattern of Isostatically pressed (a) HB2 (without Fe_2O_3) and (b) HB4 (with Fe_2O_3) fired at 1550 °C for 2 h

Tab. 1 Variation in apparent porosity and bulk density of the 1550 °C heated sample in relation to process variation

Sample	Process Description	Apparent Porosity [%]	Bulk Density [g/cm³]	Densification [%]
HB1	without additive, uniaxially pressed	17,14	2,61	69
HB2	without additive isostatically pressed	8,22	2,72	72
HB3	with additive, uniaxially pressed	8,82	2,92	77
HB4	with additive, isostatically pressed	7,85	2,82	74

different forming methods (uniaxial and isostatic pressing) were adopted to fabricate sample from different batches. Uniaxial pressing was done at 500 kg/cm^2 using hydraulic press and Isostatic pressing was done at a pressure of 1950 kg/cm^2. Callender and Barren [7] reported that substitution of Al^{3+} by Fe^{3+} in the stoichiometric composition of CA_6 results lower temperature of sintering (~1550 °C). With this finding, the present green compact samples were dried and heated at this specific temperature of 1550 °C with a 2 h soaking in an electrically heated furnace for densification. The heating rate was carefully maintained 5 °C/min up to 1000 °C and then 6 °C/min up to the maximum temperature. The major steps of the experimental process have been schematically expressed in the following Fig. 1. The samples obtained are coded as HB1 (uniaxial) and HB2 (isostatic) for the batches without Fe_2O_3 dopants and HB3 (uniaxial) and HB4 (isostatic) for the batches with Fe_2O_3 addition.

The sintered samples were characterized with respect to its bulk density and apparent porosity by known standard technique. The developed phases were identified by X-ray diffraction study. The diffraction pattern of the samples were recorded in X'pert Pro MPD diffractometer (PANalytical) using X'celerator operating at 40 kV and 30 mA uses Ni filtered CuK_α radiation. The XRD data were recorded in step-scan mode with step size 0,01671° (2θ) from 10° to 80°. The surface morphology of the fired specimens was observed in VEGA TESCAN scanning electron microscope. The microscope works with tungsten filament and acceleration potential used was 30 kV. The fracture surface of the heated samples was gold coated for SEM study.

3 Results and discussion

The following reaction scheme is suggested for the stepwise formation of CA_6:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

$$Ca(OH)_2 \rightarrow CaO + H_2O$$

$$CaO + Al_2O_3 \rightarrow CaO{\cdot}Al_2O_3\ (CA)$$

$$CaO{\cdot}Al_2O_3 + Al_2O_3 \rightarrow CaO{\cdot}2Al_2O_3\ (CA_2)$$

$$CaO{\cdot}2Al_2O_3 + 4Al_2O_3 \rightarrow CaO{\cdot}6Al_2O_3\ (CA_6)$$

The variation in sintered density and apparent porosity with respect to process variation at a specific heating temperature of 1550 °C is shown in Tab. 1. The result shows that there is significant reduction in apparent porosity with iron oxide additive particularly for uniaxially pressed sample, whereas the effect is not that significant for isostatically pressed sample. This may be due to maximum green density achieved in isostatically pressed sample. Dominguez and Torrecillas [17] also pointed out that the addition of Fe_2O_3 enhances sintering of CA_6 at this specific temperature. Also addition of Fe_2O_3 increases percentage densification from 69 – 77 % in case of uniaxially pressed sample and very marginally for 72 – 74 % in case of isostatically pressed sample.

As a typical example, the XRD patterns of the isostatically pressed sintered specimens are shown in Fig. 1. It is seen from the XRD diagram that HB4 (with additive) sample shows large number of CA_6 formed at 1550 °C due to better sintering compared to sintered HB2 (without additive) sample. At the level of 5 % Fe_2O_3, no formation of CAF_2 (the only ternary phase in the CaO–Al_2O_3–Fe_2O_3 phases diagram) was noticed at 1550 °C. Other authors [18, 19] reported most remarkable effect of iron oxide addition towards formation of CA_6 along with CAF_2 in the temperature range of 1200 – 1400 °C. Stable CAF_2 phase formation was observed by Dominguez and Torrecillas [17] at 1550 °C when the concentration of Fe_2O_3 was increased to 20 %.

Fig. 3 (a–d) show the microstructure of HB1, HB2, HB3 and HB4 respectively. Fig. 3a confirms the formation of well-crystallized hexagonal platelet CA_6 grains. Due to presence of higher porosity in this sample (~17 %), CA_6 grains get sufficient free space to develop in their preferential grown direction which results in hexagonal platelet structure. Fig. 3b sample was iso-statically pressed, thus the sintered microstructure shows equiaxed grains as the particles were so compacted that grains were unable to grow along their preferential growth direction.

A similar phenomenon of variation in grain morphology was also observed by Dominguez, et al. [15]. Presence of Fe_2O_3 additives shows a great effect on microstructure development. From the photomicrographs in Fig. 3c–d, it may be observed that Fe_2O_3 additive enhances grain growth significantly with maintaining the morphology as obtained in uniaxially pressed sample. Grain growth is very important for refractory application to resist corrosion.

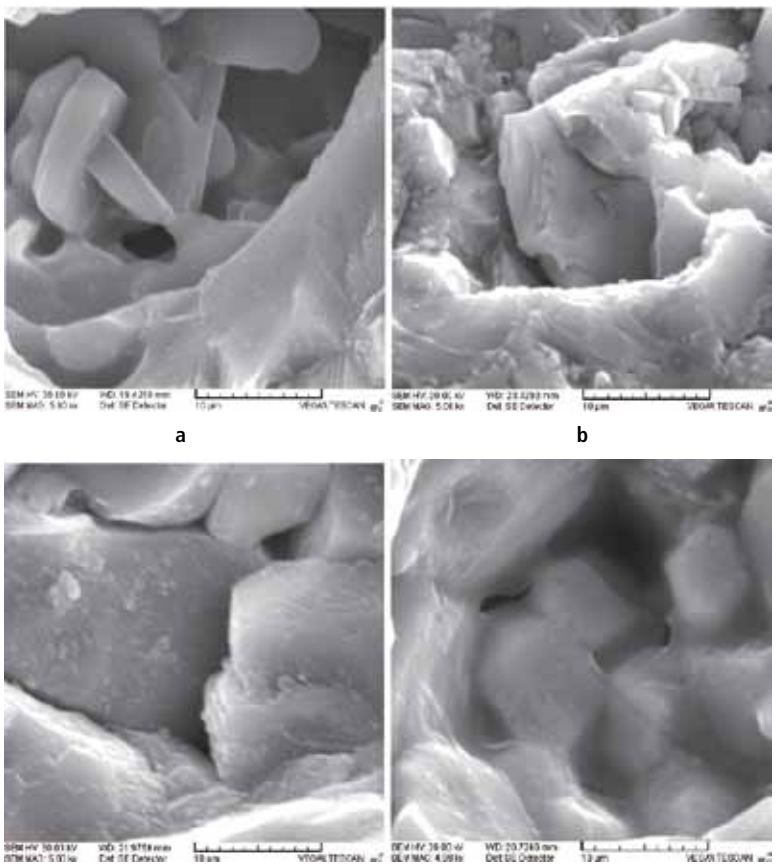

Fig. 3 a–d SEM photomicrographs of sintered samples HB1 (a), HB2 (b), HB3 (c) and HB4 (d) respectively

4 Conclusion

From the present investigation, it is observed that 5 % Fe_2O_3 addition enhances sintering of stoichiometric CA_6 mixture particularly for uniaxially pressed sample. Distinct change in microstructure was also seen between Uniaxial and isostatically sintered sample. The uniaxially pressed sintered sample without Fe_2O_3 addition shows formation of hexagonal CA_6 platelet grains due to higher porosity (availability of significant free space), while the isostatically pressed sample with lower porosity (8,22 %) shows equiaxed CA_6 grains for its compact structure. It was interesting to note that 5 % Fe_2O_3 addition enhances grain growth which is highly beneficial for refractory application particularly to corrosion resistant.

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