

Solid state sintering of lime in presence of La_2O_3 and CeO_2

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MS received 4 July 2002

Abstract. The sintering of lime by double calcination process from natural limestone has been conducted with La_2O_3 and CeO_2 additive up to 4 wt.% in the temperature range 1500–1650°C. The results show that the additives enhanced the densification and hydration resistance of sintered lime. Densification is achieved up to 98.5% of the theoretical value with La_2O_3 and CeO_2 addition in lime. Grain growth is substantial when additives are incorporated in lime. The grain size of sintered CaO (1600°C) with 4 wt.% La_2O_3 addition is 82 µm and that for CeO_2 addition is 50 µm. The grains of sintered CaO in presence of additive are angular with pores distributed throughout the matrix. EDX analysis shows that the solid solubility of La_2O_3 and CeO_2 in CaO grain is 2.9 and 1.7 weight %, respectively. The cell dimension of CaO lattice is 4.803 Å. This value decreases with incorporation of La_2O_3 and CeO_2 . The better hydration resistance of La_2O_3 added sintered lime compared to that of CeO_2 added one, is related to the bigger grain size of the lime in former case.

Keywords. Sintered lime; cation vacancy; hydration resistance; microstructure.

1. Introduction

Lime has been considered to be the most attractive steel making refractories because it exhibits exceptional thermodynamic stability (Brezny 1976), being more stable than MgO in contact with carbon under the service condition of basic oxygen steel process (White 1972; Nadachowski 1975). This characteristic is becoming more important because of composite oxide/carbon refractories achieving increased acceptance to improve slag resistance (Wong and Bradt 1995). CaO has relatively low vapour pressure at elevated temperature (Samsonov 1973), a factor that is of primary consideration for all secondary steel making process that uses vacuum technology. However, despite these fundamental advantages, the widespread use of CaO as steel making refractory has historically been severely restricted by perceived lack of hydration resistance and the tendency to exhibit degradation by some ferruginous metallurgical slags (Carr *et al* 1968). CaO refractories that are obtained from natural limestone often contain various impurities, including SiO_2 , Al_2O_3 and Fe_2O_3 (Boynton 1980). These impurities can degrade refractoriness, slag resistance and hot strength (Carr *et al* 1968; Nadachowski 1975; Williams *et al* 1982; Shi *et al* 1984). The slag resistance as well as hydration resistance of lime can be improved by liquid state or solid state sintering with the aid of small amounts of additives (Hubble 1969; Nadachowski 1976; Shi *et al* 1984). The addition of

Fe_2O_3 , Al_2O_3 and CuO has enhanced sintering of lime through liquid phase sintering and lanthanides like La_2O_3 and CeO_2 through solid state sintering of lime (Ghoneim *et al* 1989; Ghosh *et al* 2001).

The aim of this investigation is to study the effect of La_2O_3 and CeO_2 on the solid state sintering behaviour of lime. These additives were selected on the basis of close ionic size and ionic energies compared to that of calcium (Heslop and Jones 1976). Secondly, La_2O_3 and CeO_2 are very effective in the inhibition of the discontinuous grain growth on sintering of some oxides and double oxides such as in the case of barium titanate ceramics (Bratschun 1962; Harkulich *et al* 1966).

2. Experimental

A pure variety limestone obtained from Madhya Pradesh region of India was used for this investigation. Chemical analysis of the raw limestone was done by standard wet chemical method. Carbonate derived hydroxide (FH) was produced by calcining raw limestone at 1000°C for 2 h, naturally cooling and subsequently reacting with cold distilled water. It was then kept overnight to complete the hydration and finally dried at $110 \pm 5^\circ\text{C}$ for 24 h to obtain the carbonate derived hydroxide (FH). This FH was passed through 60 mesh BS sieve, mixed with additives and 6 wt.% water as binder and uniaxially pressed at 100 MPa. Green briquettes thus produced was dried at $110 \pm 5^\circ\text{C}$ for 24 h and sintered in the temperature range 1500–1650°C with 2 h soaking at peak temperature.

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Sintering was done in an electric furnace and the heating rate was maintained at 5°C/min up to 1100°C, followed by 3°C/min up to the final sintering temperature.

Sintered lime was characterized in terms of bulk density, hydration resistance, microstructure and energy dispersive X-ray (EDX) analysis. Bulk density of the sintered lime was determined by liquid displacement method using Archimedes' principle in xylene medium. Lime sintered at 1650°C was crushed and - 5 + 10 BS size fraction was collected for hydration resistance test. Sinters accurately weighed near to 50 g in a petridish were subjected to hydration in a humidity chamber for 3 h. The atmosphere of the chamber was maintained at 50°C and 95% relative humidity. The percentage weight gain after hydration was the measure of hydration resistance.

Microstructure of the sintered lime was observed under optical microscope. The samples were polished and thermally etched at a temperature 50°C less than the sintering temperature followed by quick cooling up to room temperature. Grain size of the sintered lime was measured from optical photomicrographs by linear intercept method. Elemental analysis of the CaO grain was done by energy dispersive X-ray analysis. The cell dimension of the sintered lime was carried out by X-ray diffractometry.

3. Results and discussion

Chemical analysis of the limestone used as starting material in this investigation is shown in table 1. The results indicate that the limestone used in this study is purer in nature. Minor impurities like SiO₂, Al₂O₃, Fe₂O₃ and alkali content are within 2 wt.%.

The densification of lime containing 1 to 4 wt.% La₂O₃ or CeO₂ is investigated at the sintering temperatures between 1500° and 1650°C (figures 1(A) and (B)). The bulk density increases with the increase in sintering temperature, irrespective of the nature of the additive. Incorporation of 1 wt.% La₂O₃ increases the bulk density of the sintered lime from 3.04 g/cc to 3.17 g/cc at 1650°C. At 1650°C the density of sintered lime with 4 wt.% CeO₂ is slightly more (3.30 g/cc) than that containing 4 wt.% La₂O₃ (3.27 g/cc). The sintering process of lime is mainly controlled by volume diffusion mechanism, while the contribution of surface diffusion kinetics if any is very small. La₂O₃ and CeO₂ form a limited solid solution with lime (Petersen and Cutler 1968). The excess amount will coexist with the lime phase in free state. Therefore, the marginal increase in density of CeO₂ added sintered lime than La₂O₃ added sintered lime is due to the higher true

density of CeO₂ (7.12 g/cc) than La₂O₃ (6.95 g/cc), which was mostly present in undissolved state in grain boundary (Ghoneim *et al* 1989).

The mechanism of sintering of lime in presence of additives is investigated by EDX analysis and cell dimension from X-ray data. The EDX analysis reveals (table 2) that the solid solubility of La₂O₃ in lime grain (2.9 wt.%) is higher than that of CeO₂ (1.7 wt.%). The excess additives remain in the grain boundary. Due to its higher solid solubility, La₂O₃ is capable of creating more vacant sites in CaO and increases material transport at high temperature.

The lattice parameter (*a*) of CaO crystal of the lime samples containing La₂O₃ and CeO₂ and sintered at 1600°C is shown in table 2. It reveals that the calculated '*a*' value of CaO crystal of sintered lime without additive is 4.8026 Å, which is very close to the theoretical value of CaO crystal. The '*a*' values of La₂O₃ and CeO₂ added lime are 4.7658 Å and 4.7640 Å, respectively. The lattice dimension of sintered CaO is reduced in presence of

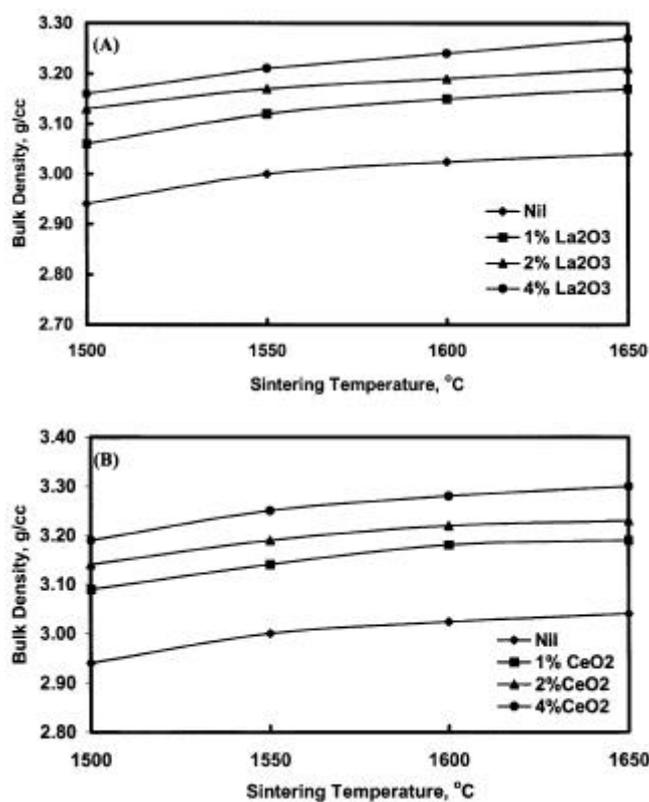
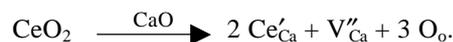


Figure 1. Densification of lime in presence of (A) La₂O₃ and (B) CeO₂.

Table 1. Chemical analysis of raw limestone.

Constituent	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	LOI
Weight %	1.48	0.20	0.11	54.56	Trace	0.11	0.33	42.88

additives. The lattice contraction is more when Ce^{+4} substitutes Ca^{+2} as the ionic size of Ce^{+4} (0.92 Å) is less than La^{+3} (1.06 Å). The defect reaction of vacancy formation by incorporating the additives can be expressed as follows



The lowering of 'a' value of CaO and defect reaction suggests that cation vacancy is formed when La_2O_3 or CeO_2 is incorporated in lime which enhances the material transport and favours the densification process.

The optical photomicrographs of lime sintered at 1600°C are shown in figures 2A–C. It reveals that the grain size of sintered lime without additive (figure 2A) is low (avg. size 30 µm). Grain growth occurs substantially when the above additives are incorporated in CaO. Grain to grain binding is higher for La_2O_3 added sintered lime and the grains meet at almost 120°, indicating stable microstructure. The average grain size of sintered lime with La_2O_3 additive is 82 µm and the same with CeO_2 additive is 50 µm. The pores are present in all the three samples. However, it is mainly intragranular and lesser in amount for La_2O_3 added sintered lime. It shows that the grain growth of sintered lime in presence of La_2O_3 is higher compared to others. Therefore, La_2O_3 can be considered to be a superior additive than CeO_2 on the sintering and microstructure development of lime.

The hydration weight gain of sintered lime containing 1 to 4 wt.% La_2O_3 and CeO_2 as a function of sintering temperature is shown in figures 3A and B. It shows that with the increase in sintering temperature the % weight gain decreases. 1 wt.% La_2O_3 addition decreases wt. gain from 3.30% to 2.60% but for CeO_2 addition it is 3%. The higher hydration resistance (lesser wt gain) of sintered lime by La_2O_3 addition is due to the development of large grain size. The rate and degree of hydration of sintered CaO depends on the rate of chemisorption of water on the grain boundary surface (Gropyanov and Novikov 1923). The more the grain size the lesser will be the grain boundary surface area, hence the diffusion of water will be minimized.

Table 2. Lattice parameter of CaO crystal and solid solubility of additive in lime grain developed at 1600°C.

Sintered samples	Lattice parameter (Å)	Solubility of additive in lime grain
FH	4.803	Nil
La_2O_3 (4 wt.%)	4.766	2.90 wt.% La_2O_3
CeO_2 (4 wt.%)	4.764	1.70 wt.% CeO_2

4. Conclusions

Solid state sintering of lime by double calcinations process enhances in the presence of La_2O_3 and CeO_2 additive. Both the additives form solid solution with CaO thereby form cation vacancy and promotes the densification process. Up to 98.5% of theoretical density

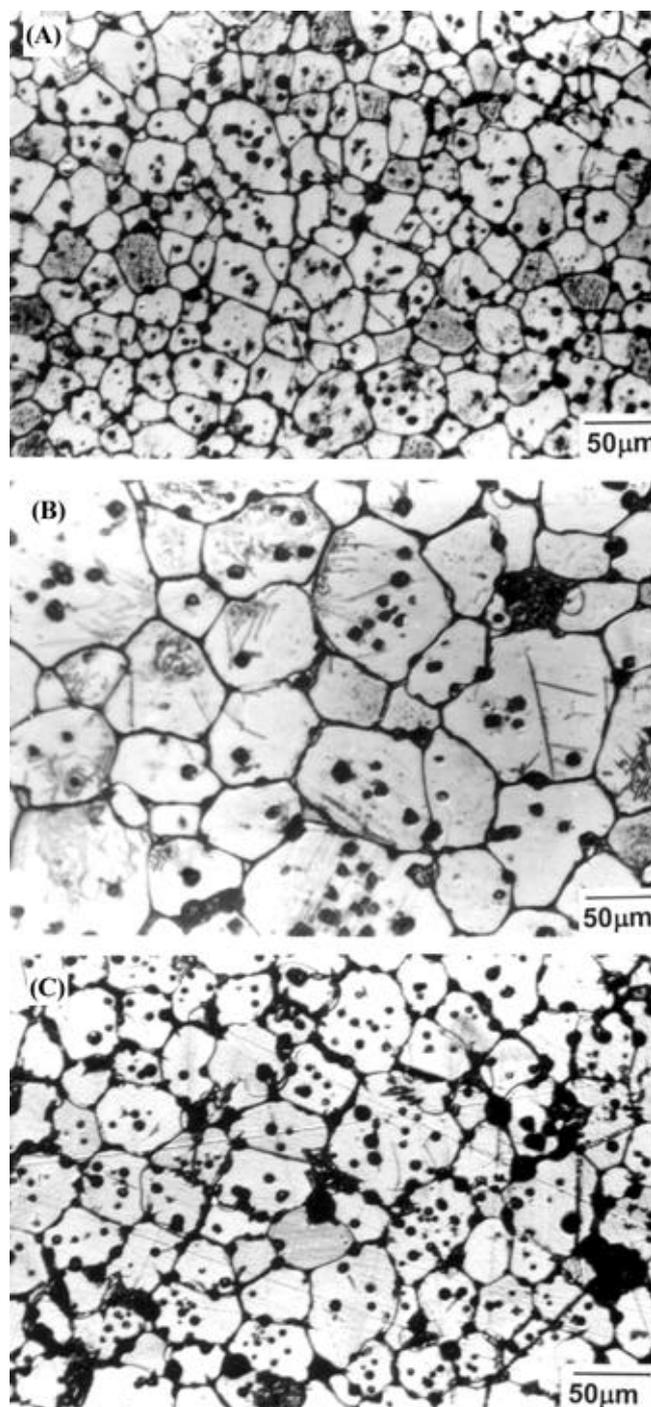


Figure 2. Optical photomicrographs of lime sintered at 1600°C (A) without additive, (B) with 2 wt.% La_2O_3 and (C) with 2 wt.% CeO_2 .

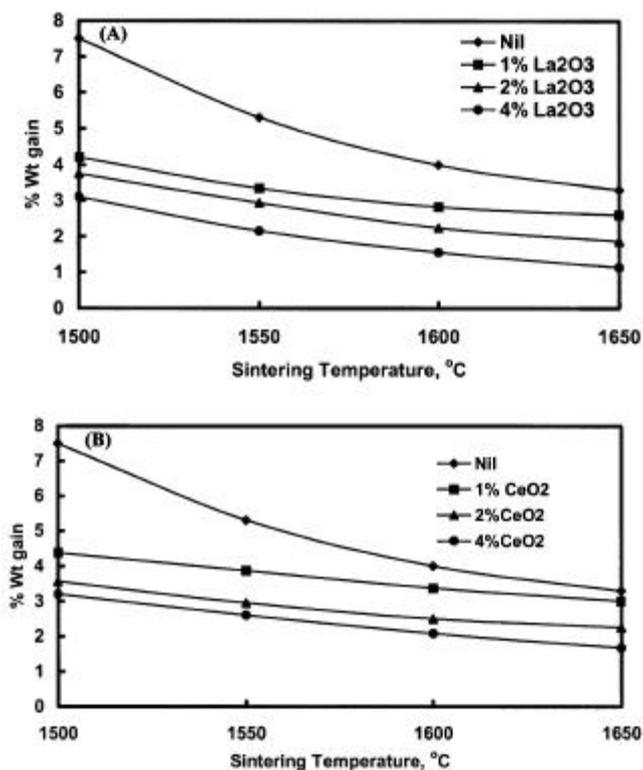


Figure 3. Hydration resistance of sintered lime in presence of (A) La₂O₃ and (B) CeO₂.

is achieved at a sintering temperature of 1650°C. It was found that both the additives reduce the cell dimension of CaO crystal. The higher hydration resistance of sintered lime with La₂O₃ addition than CeO₂ is attri-

buted to the bigger grain size development (82 μm) than the latter.

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