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Densification and properties of lime with V_2O_5 additions

A. Ghosh [a,*], T.K. Bhattacharya [b], S. Maiti [b], B. Mukherjee [a],
H.S. Tripathi [a], S.K. Das [a]

[a] *Refractories Division, Central Glass and Ceramic Research Institute, Kolkata 700032, India*
[b] *College of Ceramic Technology, 73 A.C. Banerjee Lane, Kolkata 700010, India*

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Abstract

Sintering of lime was carried out in the presence of V_2O_5 by a single firing process. A pure limestone was crushed, mixed with 1, 2 and 4 wt.% V_2O_5, pelletised and fired between 1550 and 1650 °C. The sintered lime was evaluated by bulk density, apparent porosity, microstructure, hydration resistance and hot modulus of rupture (HMOR) at 1300 °C. Incorporation of V_2O_5 forms liquid phase with lime at elevated temperature and influences the densification process by liquid phase sintering. As a result bulk density of sinters improved and they become more hydration resistant due to the larger grain size of the lime phase. The hot strength increased up to a certain temperature followed by deterioration because of the pressure of higher amount of liquid phase.

Keywords: A. Sintering; B. Microstructure; Hydration resistance; Lime

1. Introduction

Lime is often considered for use as a refractory material due to its numerous high temperature superior properties and world wide availability [1,2]. CaO has exceptional thermodynamic stability [3], being more stable than magnesia (MgO) in the presence of carbon [4]. This is becoming important because composite oxide/carbon refractories are getting more acceptances to industries due to its improved slag resistance. CaO has also low vapour pressure at high temperature, which is of primary consideration for steel making process using vacuum technology [5]. The only detrimental property, of lime is its hydration susceptibility in atmospheric moisture. This can be minimized by sintering the lime to a large extent and increasing the grain size [6,7]. Densification of lime can be improved by suitable processing of starting materials such as particle size reduction, incorporation of proper additives, increasing the firing temperature etc. There are different additives which promotes the sintering of lime. Fe_2O_3, Al_2O_3 and CuO [8] improve the sintering of lime through liquid phase formation, while lanthanides like La_2O_3 and CeO_2 [9] enhances solid state sintering of lime. In the present investigation sintered lime is developed from limestone in the presence of V_2O_5 additive. An attempt is made to correlate the densification of lime with microstructural features, hydration resistance and hot modulus of rupture of sintered products.

2. Experimental procedure

The starting material used was limestone of Madhya Pradesh region in India. Its appearance was whitish in colour and in the lump form of assorted size. Initially it was crushed into 3/4 to 1-in. size, properly washed and dried. The dried limestone was ground and passed through 300 mesh (BS) sieve. Batches were prepared by mixing the powdered limestone with 1, 2 and 4 wt.% V_2O_5 in a pot mill for 2 h. Subsequently the batch was mixed with 5 vol.% poly-vinyl alcohol solution as binder and uniaxially pressed at 100 MPa. The pellets were dried at 110 °C for 24 h. Finally the samples were fired at a temperature of 1550 and 1650 °C in an electrically operated programme controlled muffle furnace with 2 h soaking at peak temperature.

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* Corresponding author. Tel.: +91-33-4838084; fax: +91-33-24730957.
E-mail address: arup@cgcri.res.in (A. Ghosh).

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Chemical analysis of raw material was carried out by wet chemical method. The reactivity of the powdered limestone was measured by specific surface area of the just decomposed oxides (calcining the powder at 1000 °C). Phase analysis was done in an X-ray diffractometer using nickel filtered Cu Kα radiation at a scanning speed of 2° per min.

Sintered lime was characterized in terms of bulk density (BD), apparent porosity (AP), hot modulus of rupture (HMOR), hydration resistance and microstructure. BD and AP of the sintered lime were determined by a liquid displacement method using Archimedes' principle in xylene medium. True density of sintered powders was measured in a pycnometer bottle using xylene as liquid medium. From the ratio of bulk density and true density, relative density of the sintered material was determined. Hot modulus of rupture was measured at 1300 °C by three point bending method using samples having dimension of 0.5 cm × 0.5 cm × 5 cm.

Hydration resistance of sintered lime was measured on the size fraction of $-5+10$ BS mesh. Sinters accurately weighed near to 50 g in a Petri-dish 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 samples was characterized by optical microscopy using reflected light. The samples were polished and thermally etched at a temperature 50 °C less than the sintering temperature followed by rapid cooling to room temperature. The grain size of the sintered lime was measured from optical photomicrographs using the linear intercept method.

3. Results and discussion

The physico-chemical analysis of the raw material is shown in Table 1. It is a pure variety of limestone with CaO content of 98% on dead burnt basis. The differential thermal analysis (DTA) shows a sharp endothermic peak at 914 °C which is the characteristic peak of lime stone decomposition [10]. XRD analysis (Table 1) reveals that limestone is the major phase with no minor phase is visible.

Table 1
Physico-chemical properties of the starting materials

Chemical analysis	Limestone
SiO_2	0.8
Al_2O_3	0.4
Fe_2O_3	0.2
TiO_2	–
CaO	98.0
MgO	0.5
Physical properties	
Sp. surface area (m^2/g) (calcining at 1000 °C)	1.8
Phase analysis by X-ray	Limestone
DTA (endothermicpeak, °C)	914

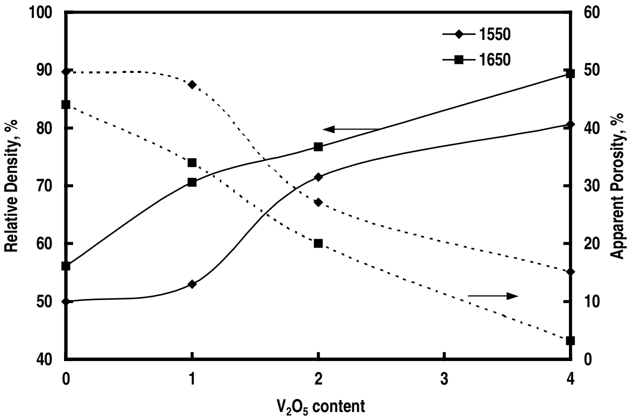

Fig. 1. Physical properties of sintered lime fired in the presence of V_2O_5.

The specific surface area of the ground limestone (−300 BS mesh) is below the limit of instrument. When the limestone is just decomposed the oxide has a surface area of 1.8 m^2/g. The reduction in particle size of just decomposed oxide will be the driving force for sintering of lime at elevated temperature.

3.1. Densification

The relative density and apparent porosity of sintered lime with and without V_2O_5 additive is presented in Fig. 1. It is seen that the relative density is only 50% when the lime without additive is fired at 1550 °C. Densification has significantly improved up to 80% with the increase of V_2O_5 up to 4 wt.%. Elevating the firing temperature to 1650 °C has further enhanced the densification from 57 to 90% for sintered lime without and with V_2O_5 addition respectively. The additive V_2O_5 helps the sintering of lime by the formation of liquid phase and facilitates the mass transfer through it. Fig. 1 also shows that with the improvement in relative density of lime the corresponding apparent porosity of the compacts reduces as the sintering proceeds.

3.2. Microstructure

The optical photomicrographs of sintered lime fired at 1650 °C are shown in Figs. 2–5. The microstructure of sintered lime without additive is not visible. However, when the polished samples are thermally etched the grains are prominent (Fig. 2). The grains size is only 8 μm and pores are present in the intergranular and intragranular position. The sintered lime with 1 wt.% V_2O_5 addition (Fig. 3) shows that the grain size has increased to 17 μm. However, the pore phase is widely distributed throughout the matrix. The microstructure of sintered lime with 4 wt.% V_2O_5 (Figs. 4 and 5) shows that the grain growth takes place substantially in the presence of additive. The average grain size is 40 μm. The pores are present only in the intergranular position. The intragranular pore which was observed in previous samples

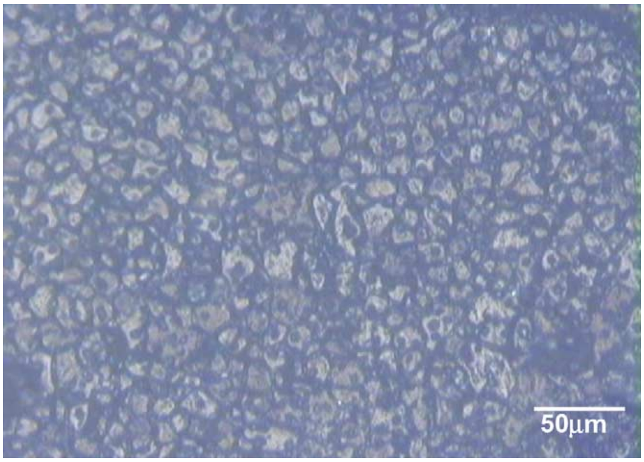

Fig. 2. Optical photomicrograph of lime sintered at 1650 °C without additive.

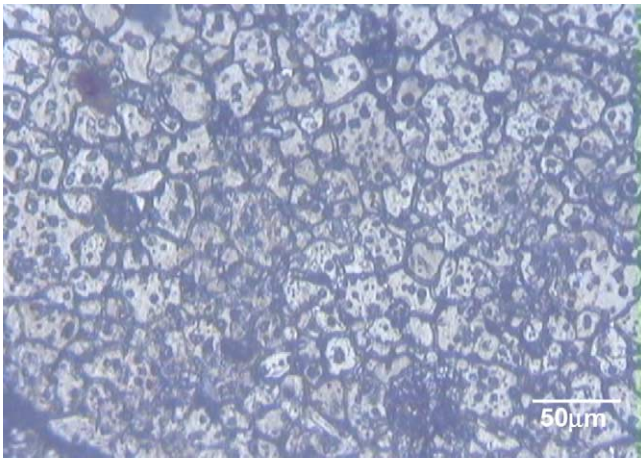

Fig. 3. Optical photomicrograph of lime sintered at 1650 °C with 1 wt.% V_2O_5.

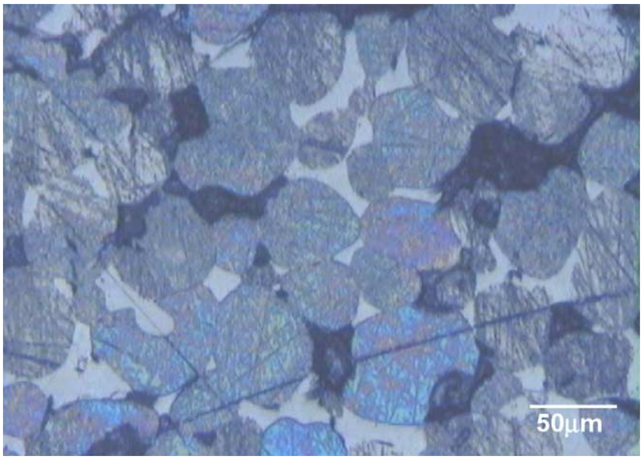

Fig. 4. Optical photomicrograph of lime sintered at 1650 °C with 4 wt.% V_2O_5.

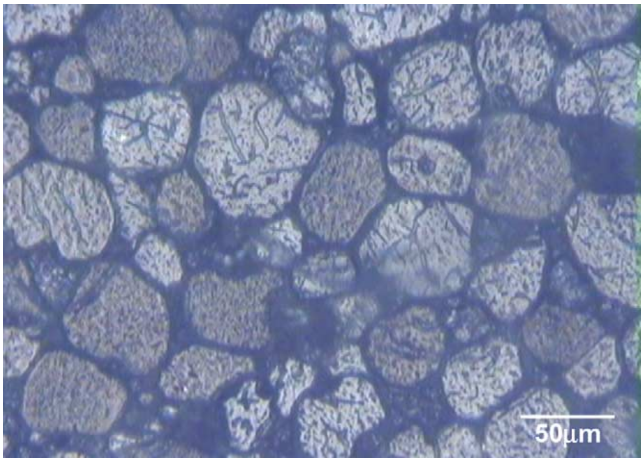

Fig. 5. Optical photomicrograph of lime sintered at 1650 °C with 4 wt.% V_2O_5 after thermal etching.

has been eliminated. Fig. 4 shows that the pores are present in some locations particularly in between the grains. The glassy phase (whitish) is uniformly distributed in between the grains. CaO reacts with V_2O_5 at elevated temperature and form 3CaO. V_2O_5 [11], which is the source of glassy phase in the microstructure. The presence of V_2O_5 in lime forms liquid above 1380 °C at the grain boundary and promotes sintering. Increasing additive content helps to generate more liquid phase in between grains. Therefore, wettability of grain increases and results in grain growth through solution and precipitation process [8]. The amount of glassy phase increases with increasing the additive concentration. It is clearly visible from Figs. 3 and 4 that glassy phase increases by increasing V_2O_5 from 1 to 4 wt.%. The polished sample after thermal etching is shown in Fig. 5. The grain boundaries are more prominent and the glassy phase is not visible.

3.3. Hydration resistance

The hydration susceptibility of sintered lime grains is illustrated in Fig. 6. The weight gain reduces with the increase in V_2O_5 concentration in lime for both the sintering temperatures. The weight gain is 18 and 4% when the samples were sintered without additive and with 4 wt.% V_2O_5, respectively. V_2O_5 addition improves densification which reduces the moisture to penetrate through the pores. Moreover, with the grain growth the grain surface area reduces and it becomes more stable towards hydration reaction. Increase of firing temperature further reduces the weight gain due to more grain growth and lower grain porosity. The degree of hydration is related to the chemisorption of water in grain boundary surface [12]. Hence, the grain surface area reduces along with grain growth, which is ultimately responsible for improving hydration resistance.

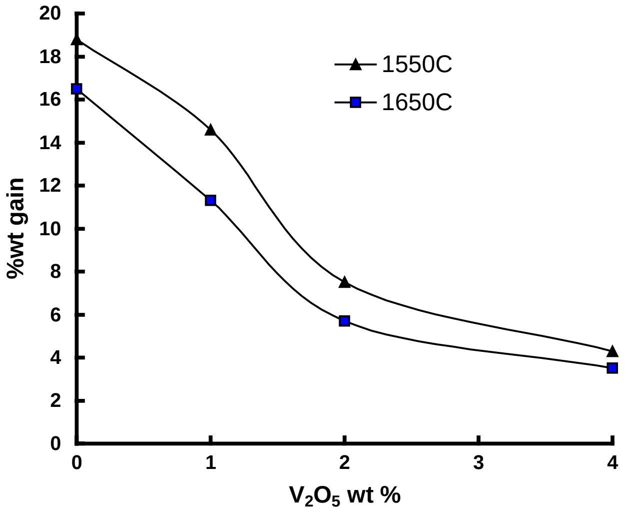

Fig. 6. Percentage weight gain on hydration of lime sintered at different temperatures.

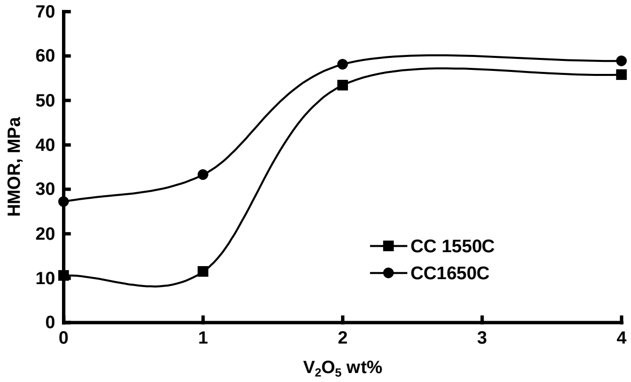

Fig. 7. Hot modulus of rupture of sintered lime at 1300 °C.

3.4. *Hot modulus of rupture*

The thermo-mechanical property of the sintered lime fired at 1550 and 1650 °C is presented in Fig. 7. There is a significant improvement in hot modulus of rupture with additive incorporation up to 2 wt.%. The cause of this improvement is related to the increase in densification and lowering of porosity. However, above 2 wt.% V_2O_5 HMOR value decreases slightly inspite of increased densification. The maximum value of HMOR is 60 MPa when the sintered lime is fired at 1650 °C. The amount of glassy phase rises with the higher additive concentration which deteriorates the HMOR. The hot strength of sample fired at 1650 °C is always better than that of 1550 °C due to superior densification.

4. Conclusion

1. Densification of lime improves from 57 to 90% of relative density by incorporation of V_2O_5 at 1650 °C.
2. V_2O_5 forms liquid phase with lime at elevated temperature and promotes the densification through liquid phase sintering.
3. Sintered lime in the presence of additive has lower porosity and higher grain size upto 40 μm.
4. The hydration resistance and hot modulus of rupture improves with the increase in V_2O_5 concentration. However, the addition of V_2O_5 above 2 wt.% slightly deteriorates the HMOR value due to excessive liquid formation.

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