Sintering behaviour and hydration resistance of reactive dolomite

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Abstract

Sintering of raw dolomite and hydroxides derived from dolomite was carried out in the temperature range 1350–1650 °C. The hydroxide derived from dolomite was developed through pre-calcination of dolomite followed by its hydration. For hydroxide development, after precalcination one sample was air-quenched and the other powder was furnace cooled before hydration. The air quenched samples showed better densification than that of the furnace cooling process at the same temperature. Fe_2O_3 addition enhances sintering by liquid formation at higher temperature. The grain size of doloma with Fe_2O_3 addition is bigger than that without additive. Hydration resistance was related to densification and grain size of sintered dolomite.

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1. Introduction

Dolomite is a basic refractory material with the ideal composition $[MgCa(CO_3)_2]$. Doloma $(MgO \cdot CaO)$ produced from dolomite consists of a phase mixture of lime and periclase. They have extremely high melting point with a eutectic temperature of 2370 °C. Varying amounts of impurities including SiO_2, Al_2O_3 and Fe_2O_3 are present in dolomite [1,2]. The amounts and types of these impurities may have a large effect on the extent of densification. Dolomite was traditionally used as fettling material for the hearth of furnaces (Bessemer converter) [3]. Hydration of dolomite refractory is a major problem due to the presence of CaO phase. To minimize this problem, at earlier times stabilized doloma was produced with the reaction of dolomite with silica or iron oxide materials [4]. Sintering allows the formation of phases, like dicalcium ferrite, tetracalcium aluminoferrite, which stabilize the microstructure against hydration.

After the introduction of basic oxygen furnace (BOF) more attention was drawn to develop better quality highly dense and corrosion resistant doloma. The development of highly dense well shrunk particles is essential not only to resist hydration but also to hinder the slag penetration into the material [5,6]. Originally in BOF, pitch/tar bonded dolomite/magnesite refractories were being used [7]. With the development of MgO–C refractory, the BOF converters are lined only with this refractory. Today world wide Argon oxygen decarburisation (AOD) process is standard route for the production of stainless steel with EAF–AOD route being the most common one [8,9]. Here the primary process involves preblowing of oxygen to oxidize the carbon of steel followed by inert gas blowing to revert oxidized component like Ni, Mo into the bath. The conditions of AOD converters are temperature above 1700 °C, turbulence of liquid metal and gas and corrosion of slag having basicity 1.5–2.0. Dolomite is a thermodynamically stable material in the steelmaking environment. By virtue of its chemical nature, dolomite does not get affected by reducing conditions generated during stainless steel manufacturing process.

Ghosh et al. reveal [10] that when the starting material is in the submicron range (0.5 μm) dolomite may be densified by single firing technique at 1650 °C. The crystal size of CaO and MgO in doloma is controlled by the temperature and impurity content [11]. Increasing these impurities would increase the crystallite size. Wong and Bradt [12] observed that when dolomite in original carbonate form is sintered, a classical interpenetrating cluster microstructure occurs. During the

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sintering of dolomite, it was observed that the CaO grains adhered to each other grow faster than MgO grains and as a result bigger CaO grains are formed [13].

Baldo and Bradt [14] experimented in details the growth of individual CaO and MgO in dolomite. They explained that the activation energy for grain growth of CaO is 333 kJ/mol, which is similar to that being reported for Ca^{2+} diffusion in CaO. Since CaO is the continuous matrix in doloma, the result appeared reasonable. But the same for MgO is 437 kJ/mol is due to the discontinuity of MgO phase in dolomite and the Mg^{2+} must diffuse through CaO.

The reactivity of oxide derived from hydroxide decomposition at 550 °C is much greater than that formed by the decomposition of original carbonate at 1000 °C. It is thus seemed reasonable to consider that the MgO and CaO produced at lower temperatures from its precursors should be better suited for sintering [15].

In this work the sintering behaviour of dolomite was studied in relation to their reactivity and the microstructure and hydration resistance of doloma were evaluated.

2. Experimental procedure

2.1. Preparation and characterisation of precursors

The starting material used in this investigation was a natural dolomite obtained from Jabalpur, India. Raw dolomite was crushed to get −300 BS mesh size. Chemical composition of dolomite was determined by standard wet chemical method. Two hydroxide precursors were made by precalcination followed by hydration in two different ways. In the first case dolomite was calcined at 1000 °C for 2 h, allowed to cool inside the furnace, taken out from the furnace at room temperature and poured water into it. This hydroxide was designated as "F". In the second case the sample after calcination was taken out of the furnace at high temperature and quenched directly in flowing air followed by hydration. This sample was designated as "A".

2.2. Sintering

The dolomite (DS) carbonate (−300 BS mesh) was mixed with 5 wt.% PVA solution and hydroxide powders ('A' and 'F') were mixed with 5 wt.% water as binder and all of the samples were uniaxially pressed into briquettes at a pressure of 140 MPa. Briquettes after drying at 110 ± 5 °C for 24 h were fired between 1350 °C and 1650 °C at an interval of 100 °C with 2 h holding time at peak temperature. Firing was done in a programmer controlled electric furnace and the heating rates were maintained at 5 °C/min up to 1000 °C followed by 3 °C/min up to the maximum temperature.

2.3. Characterisation of doloma

The doloma was characterised in terms of bulk density, apparent porosity, hydration resistance and microstructural development. Bulk density and apparent porosity were measured by standard liquid displacement method in xylene using Archimedes' principle. For hydration resistance measurement, doloma was crushed and ground to pass through 5 mesh BS sieve. Accurately weighed 50 g of −5 + 10 BS mesh doloma was taken in a glass petridish and subjected to hydration at 50 °C and 95% relative humidity in a steam humidity cabinet for 3 h. After the experiment the percentage weight gain was measured. Microstructural characterisation was done by scanning electron microscopy. Thermally etched sintered and polished samples were used with gold coating.

3. Results and discussion

The chemical composition of natural dolomite selected for the study is shown in Table 1. Result indicates the dolomite is relatively pure with an impurity content of around 2 wt.%.

3.1. Densification

The sintering behaviour of raw dolomite and hydroxides derived from dolomite was carried out by dilatometric study (Fig. 1). It shows that the carbonate sample (DS) has poor sintering characteristics. The shrinkage starts from 1000 °C and the rate is slow up to 1200 °C. For hydroxide samples the shrinkage starts from 600 °C after hydroxide decomposition and significant shrinkage occurs up to 1100 °C. The shrinkage of the sample 'A' is higher compared to the 'F' sample. The surface area of oxides derived from carbonate (DS) and hydroxides (F and A) is shown in Table 2. It shows that oxide obtained from the original carbonate decomposition at 1000 °C has lower surface area (1 m²/g). Whereas the oxide derived from hydroxides (F and A) at 600 °C show much higher surface area (25–30 m²/g), which helps in the sintering process. These early borned oxides from hydroxides undergoes plastic flow [16] and show significant sinterability at lower temperature. Therefore, the shrinkage due to sintering of 'F' and 'A' are much higher compared to that of DS.

The densification of raw dolomite (DS) and hydroxides derived from dolomite (F and A) is shown in Fig. 2. It is seen that the bulk density of DS is much lower compared to F and A. The bulk density of all the samples increase with the increase in sintering temperature up to 1450 °C. It is reported that the sintering rate of hydroxide at 870 °C is equivalent to that of carbonate at 1400 °C [15]. Moreover, the water vapour evolves from hydroxides enhances the sintering by lowering the dihedral angle between oxide grains and pores [17].

Table 1
Chemical composition of raw dolomite.

Chemical constituents	Wt.%
SiO_2	1.70
Al_2O_3	0.13
Fe_2O_3	0.27
Na_2O	0.72
CaO	59.07
MgO	38.11
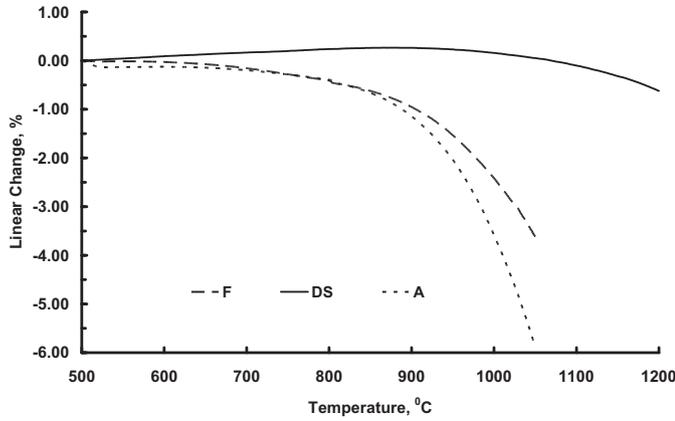
Fig. 1. Dilatometric study of samples from carbonate (DS) and hydroxides (A and F).

Fig. 2. Bulk density of doloma from carbonate (DS) and hydroxides (A and F) with sintering temperature.

The hydroxide sample (A) obtained through air-quenched process shows better densification at 1450 °C. The oxides generated from 'A' have higher surface area than that of oxide generated from furnace cooled sample 'F'. The air-quenched sample 'A' experiences thermal shock at the time of removing out from the furnace after calcination, which generate defects in the oxide lattice. This will facilitate the transport of matter by accelerating the diffusion rate of the grain [18]. The decomposed oxide when furnace cooled 'F' was relatively coarser, which shows lower surface area and results in lower densification.

Additives play an important role on the sintering of a product. Fe_2O_3 is an important additive on the densifiation of dolomite. In the double stage process air-quenched samples show better results. So the effect of Fe_2O_3 on the densification study was carried out with sample 'A' (Fig. 3). It is observed that for sample without additive the bulk density increases from 3.05 g/cc to 3.25 g/cc with the increase of sintering temperature from 1350 °C to 1650 °C. When Fe_2O_3 (2 wt.%) is added the density reached a maximum of 3.35 g/cc at 1450 °C. Fe_2O_3 reacts with the oxides and form di-calcium ferrite $(2CaO \cdot Fe_2O_3)$, which melts at 1436 °C and thereby favours liquid phase sintering [19]. While Fe-ions diffuse into periclase grains and forms solid solution, they change the crystal structure and increase the inner crystal energy by developing thin inclusions. This provides the growth of periclase (MgO) grain and facilitates the sintering by increasing the recyrstallisation ability [2]. The bulk density deteriorates to 3.20 g/cc with the increase in sintering temperature to 1650 °C. As the sintering temperature increases the secondary phase formation is more, which reduces the bulk density of doloma at higher temperature.

Table 2
Characteristics of oxides derived from carbonate (DS) and hydroxide samples (A and F).

Properties	Oxides derived from		
	DS	A	F
Specific surface area, m^2/g	1	30	25
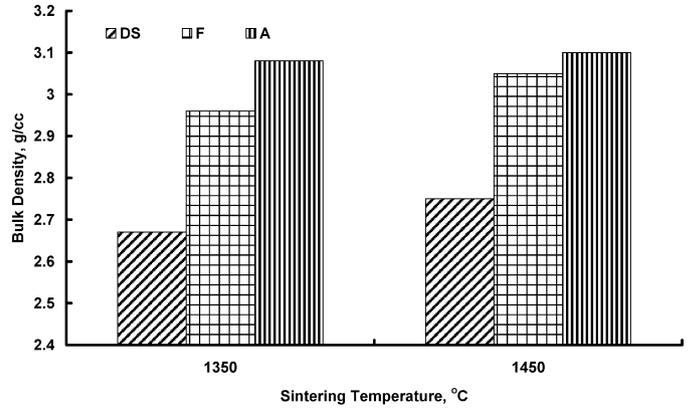
3.2. Microstructure

The scanning electron photomicrographs of doloma obtained from sample 'A' with and without Fe_2O_3 sintered at 1650 °C is shown in Fig. 4a and b. The sample without additive shows that rounded grains is formed. The grain to grain contact are present, at the same time presence of pores (black) is also visible. The grain size varies between 1 and 2 μm. In contrast the photomicrograph of Fe_2O_3 added doloma (Fig. 4b) shows much compact microstructure and bigger grain size. The CaO grains are relatively brighter and bigger in size compared to MgO grains. The average grains size of CaO phase is 10 μm, whereas that of MgO phase is 5 μm. In doloma as the CaO phase is continuous, the activation energy is less compared to MgO phase, resulting in bigger size of CaO grains. Moreover, the presence of Fe_2O_3 enhances further grain growth of doloma due to liquid phase sintering.

3.3. Hydration resistance

The weight gain due to hydration of sintered dolomite with respect to time and temperature is plotted in Fig. 5. It shows that
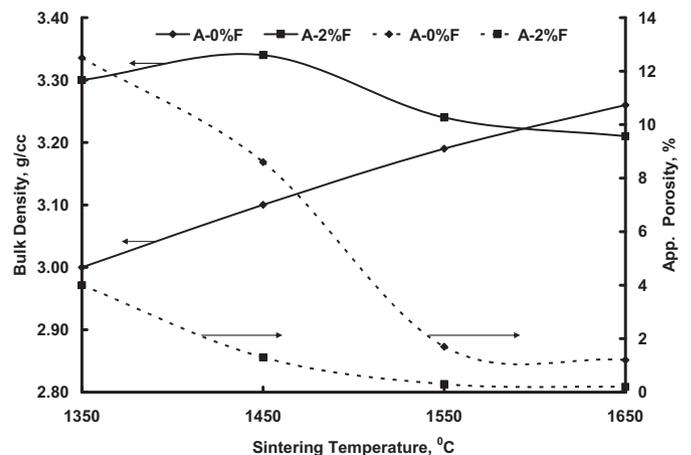

Fig. 3. Bulk density and apparent porosity of doloma obtained from hydroxide 'A' at different sintering temperatures with and without Fe_2O_3.
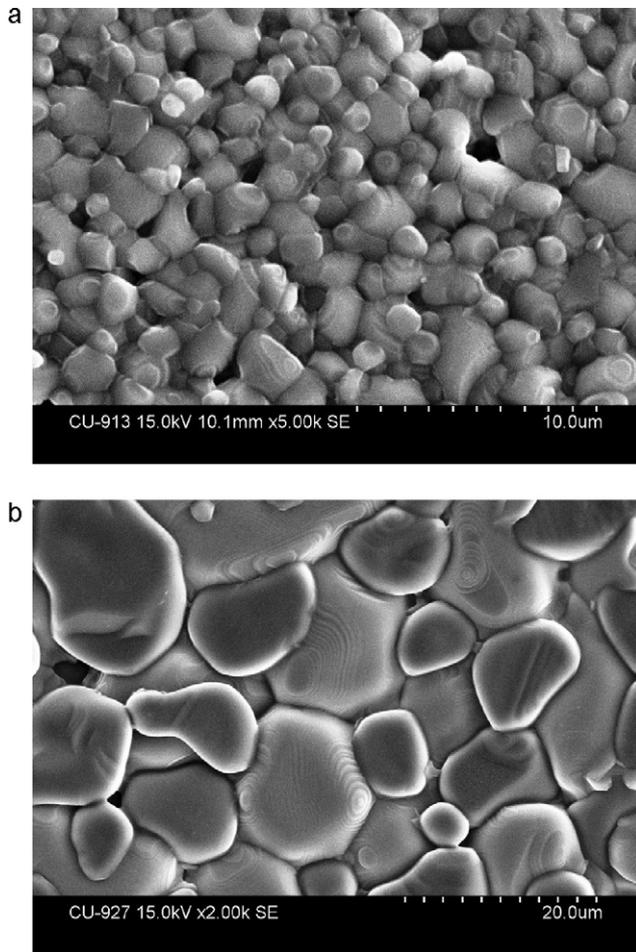
Fig. 4. SEM photomicrographs of doloma obtained from hydroxide 'A' at 1650 °C. (a) without additive (b) with 2 wt.% Fe_2O_3.

for all the temperatures the weight gain increases with the duration of the test. The sample with out additive (A–0F) sintered at low temperature, shows significant weight gain at low temperature due to lesser bulk density of doloma. However, as the densification of doloma with Fe_2O_3 (A–2F) at low temperature is highest, it becomes immune towards hydration.
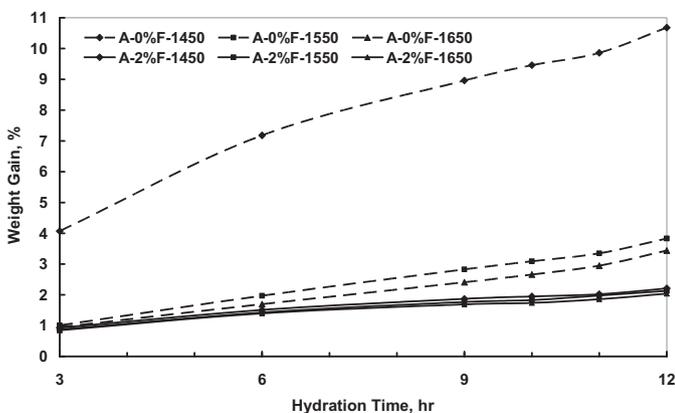

Fig. 5. Weight gain of doloma with respect to sintering temperature and hydration time.

It reveals from the study that with higher grain size lower will be the grain boundary surface area, so diffusion of water will be minimized and ultimately hydration resistance will improve.

4. Conclusions

Dolomite converted to its hydroxide shows better densification than that from its original carbonate form. For two stage calcination process the oxides derived from its hydroxide at 600 °C has smaller particle size, which is responsible for the better densification. The hydroxide sample obtained by air quenching show superior densification compared to furnace cooled sample. Air quenched sample experiences thermal shock, which creates small particle with defective structure and improves the bulk density of doloma. Fe_2O_3 addition significantly enhances grain growth of both CaO and MgO phases of doloma. With the increase in grain size, the hydration resistance of this highly dense doloma increases.

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