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The effect of CuO addition on the sintering of lime

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Abstract

The sintering of lime was carried out with 1–4 wt.% CuO in the temperature range 1500–1650°C. A double calcination process was adopted in the study. The result showed that without additive the densification was 88% and with additive it maximised to 93% of the theoretical value at 1550°C with 1 wt.% CuO. The density decreased due to the presence of large closed pores with a higher percentage of CuO. Hydration resistance was measured at 50ºC in 95% relative humidity through the weight gain after 3 h. Addition of CuO up to 2 wt.% improved the hydration resistance, but it was not significantly high in comparison to that of 1 wt.% CuO. The use of a higher level of CuO in lime did not show any further improvement in hydration resistance. The CaO forms a low melting compound (2CaO.CuO) with CuO which helps liquid phase sintering of lime. When the liquid content increased in the sinterred lime grain growth takes place simultaneously along with pore growth © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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

1. Introduction

Lime refractories are derived from limestone, which contains impurities like SiO_2, Al_2O_3 and Fe_2O_3 [1]. Lime, which is basic in character, possess certain excellent properties such as high temperature melting, low vapour pressure, thermodynamic stability in the presence of carbon which is increasingly important when composite oxide/carbon refractory is concerned [2,3]. However, in spite of these primary advantageous properties, the application of lime refractory has not been popular due to its tendency to hydrate when exposed to atmosphere [4,5].

The optimum properties of lime refractory can only be developed if a high density sintered lime aggregate is used. Lime refractory with excellent slag resistance and high hot strength is also obtained when the raw materials are in “pure” form. But pure lime requires a temperature above 1800°C for high densification, which is inconvenient for most commercial purpose [6]. However, high densification can be achieved by using a two step sequential process of first calcining at 900ºC to produce “quick lime” and then hydrating the quick lime before forming and sintering [7,8]. High densification of lime is also possible through intentional incorporation of additives. Some of the sintering aids of lime are Fe_2O_3 and lanthanides like La_2O_3 and CeO_2[9].

In the present investigation, the effect of one of the transition element oxide, i.e. CuO has been studied on the densification of CaO. CuO forms a compound with CaO which melts above 1000°C [10]. Therefore, it is expected that the sintering of lime will take place by liquid phase mechanism. The effect of CuO on densification, hydration resistance and microstructure of sintered lime has been studied.

2. Experimental procedure

The raw material selected for the study was a pure variety of limestone. The material after proper washing was crushed down to a size below 1 inch. It was then processed for two step sequential firing. The limestone was initially calcined at 1000°C, hydrated and pelletised. The size of pellets was 1 inch diameter and 1 inch high and it was formed under a uniaxial pressure of 1000 kg/cm^2. The sintering of pellets was carried out from 1500 to 1650°C at an interval of 50°C with 2 h soaking in an electrical furnace operated through programmer-controller. The heating rate was maintained at 5°C/min throughout the range, except in the decomposition range of hydroxide phase (i.e. 400–600°C) the rate was slowed down to 2°C/min.

The sintered limes were evaluated by the measurement of bulk density and hydration resistance. The bulk

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density was measured by xylene displacement in vacuum using Archimedes principle. The hydration resistance test was carried out in a humidity cabinet at 50°C, 95% relative humidity for 3 h. The grains ($-16+5$ mesh BS sieve) were exposed to the above atmosphere and the weight gain was measured. The microstructural features of polished and thermally etched samples were observed under optical microscope. The grain composition was determined by energy dispersive X-ray analysis.

3. Results and discussions

The chemical analysis on dead burnt basis has been depicted in Table 1 and shows that the raw limestone is of very pure variety with low amount of impurity.

The dependence of densification on sintering temperature is presented in Fig. 1. It is observed that for all the samples with and without CuO when the temperature is raised from 1500 to 1650°C, the density has increased. The density of the sample without any additive is 2.94 g/cm^3 (88%) at 1500°C which increases to 3.05 g/cm^3 (92%) at the same temperature with 1 wt.% CuO. The copper oxide reacts and generates liquid above 1050°C. The liquid at high temperature facilitates sintering by liquid phase mechanism. The sintering is achieved with the reduction of solid–liquid dihedral angle, which increases the wettability and thus the liquid drags the grain towards each other. The effect of CuO is maximum at 1 wt.% level. Density increased upto 93% of theoretical at 1550°C. The density deteriorates marginally with 4 wt.% CuO when it comes down to 91%. The excess amount of liquid hinders the evolution of gaseous products from the grains. This resulted in closed porosity and lowering of density.

Table 1
Chemical composition of raw limestone (dead burnt basis, wt.%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
0.8	0.4	0.2	98.0	0.5

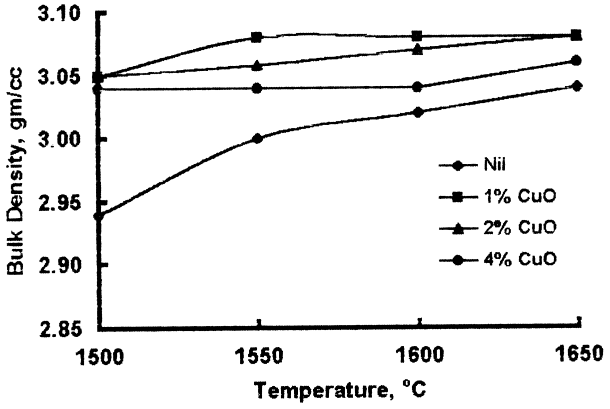

Fig. 1. The bulk density of lime sintered with and without CuO addition at different temperatures.

The microstructure of sintered lime fired at 1600°C are shown from Figs. 2–4. The sintered lime aggregate without additive (Fig. 2) has a density of 88% with a small grain size of 35 μm. The addition of CuO enhances the grain growth substantially and the grain size ranged between 80 to 100 μm (Figs. 3 and 4). However, with 4 wt.% CuO (Fig. 4) pore growth occurs simultaneously along with grain growth. The sintering is enhanced by the formation of liquid phase and as the additive increases, the wettability increases which helps solution-precipitation process to occur resulting in grain growth.

Discontinuous grain growth is a common phenomena in the sintering of pure oxide systems, which leads to non-uniform microstructure. Suitable additives,when dispersed in the matrix pin down the grain boundaries and act as grain growth inhibitors. In the present study the open porosity is below 1% on an average, but closed pores were observed both in the intergranular as well as intragranular position. A large amount of liquid hindered the removal of gaseous phases, leading to higher porosity.

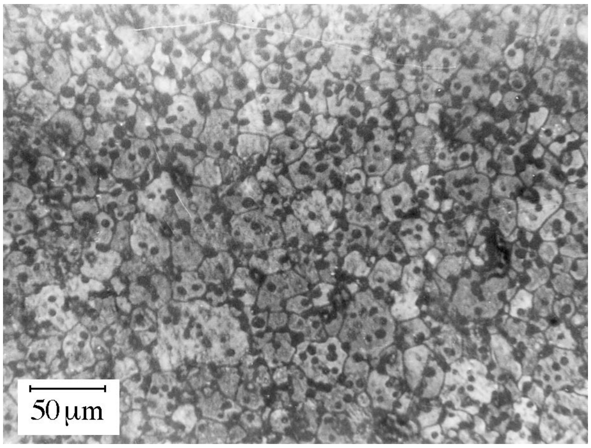

Fig. 2. Photomicrograph of lime sintered at 1600°C without additive.

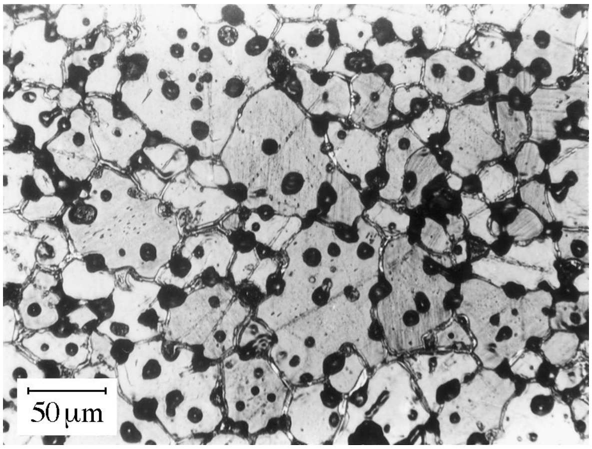

Fig. 3. Photomicrograph of 1 wt.% CuO added lime sintered at 1600°C.

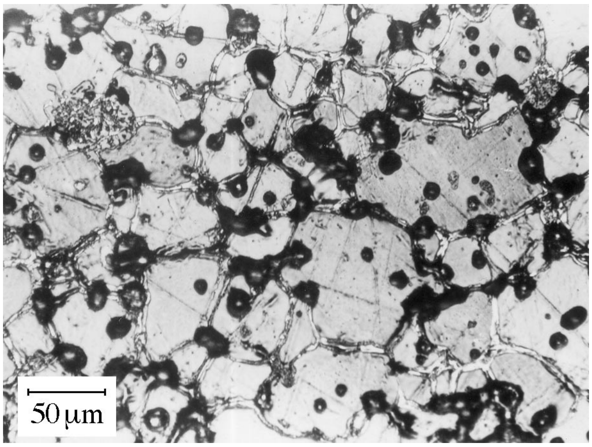

Fig. 4. Photomicrograph of 4 wt.% CuO added lime sintered at 1600°C.

The EDX analysis shows the composition of phases at different point (Table 2). It reveals that within the lime grain there is no other element except 100% CaO. It also confirms that the additive does not form solid solution with lime. The CuO is present at the grain boundary as a separate phase. Grain boundary phase compound is 2CaO.CuO. The composition suggests the absence of another compound CaO.2CuO, which is reported elsewhere [11]. The compound 2CaO.CuO present in the grain boundary (Fig. 5) forms a thin film over the grain. It melts incongruently at 1085°C to form lime and liquid at this peritectic temperature [10]. Thus, at high temperature it activates sintering through the liquid stage process.

Table 2
Composition of phases in sintered lime

Area	CaO (wt.%)	CuO (wt.%)
Grain	100	–
Phase in grain boundary	57.8	40.2

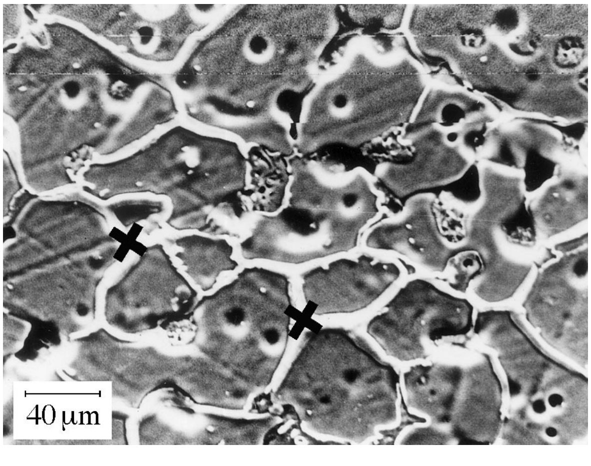

Fig. 5. SEM photomicrograph of sintered lime showing formation of compound 2CaO.CuO at the grain boundary (marked '**x**').

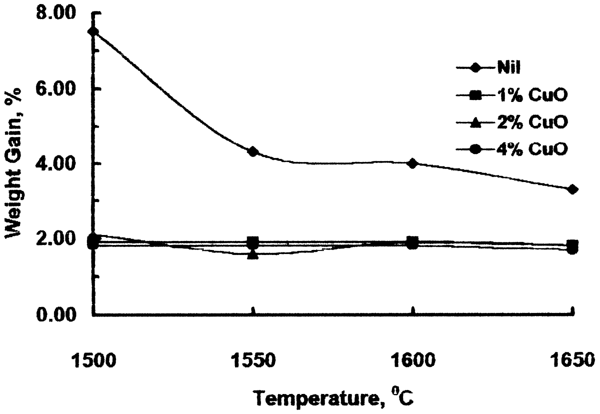

Fig. 6. Percentage weight gain on hydration of lime sintered at different temperatures.

The results of hydration susceptibility is produced in Fig. 6. It shows that weight gain due to hydration is reduced from 7.5 to 3.3% when the sintering temperature of lime without CuO is raised from 1500 to 1650°C. Weight gain is reduced further to 2% (increased hydration resistance) when lime is sintered with CuO. Although 2 wt.% CuO has shown maximum hydration resistance, the result is not significantly high in comparison to that of 1 wt.% CuO. In 4 wt.% CuO, though grain growth occurs the hydration resistance lowers slightly. This is due to the growth of pores which help moisture penetration and react with the grain. The higher CuO percentage in the sintered lime doesn't reduce the open porosity at high temperature. It may be concluded that the addition of 1 wt.% CuO is optimum for achieving high densification and hydration resistance of the sintered lime.

4. Conclusion

1. The incorporation of CuO in lime improves the densification of sinter up to 93% of theoretical density at a relatively low temperature of 1550°C.
2. The sintering occurs through liquid phase mechanism with the formation of compound 2CaO.CuO.
3. The higher amount of liquid helps in grain growth as well as pore growth. The optimum level of CuO is 1 wt.% for achieving high densification and hydration resistance.

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References

[1] R.S. Boynton, Chemistry and Technology of Lime and Limestone, John Wiley and Sons, New York, 1980, pp. 18–21.

[2] B. Brezny, Equilibrium partial pressure of Mg, Si, Ca and CO in carbon containing doloma refractories, J. Am. Ceram. Soc. 59 (1976) 529–530.

[3] F. Nadachowski, Lime refractories, Interceram. 24 (1975) 42–45.

[4] K. Carr, J.L. Evans, L.A. Leonard, H.M. Richardson, Study of oxygen convertor linings I, Trans. Brit. Ceram. Soc. 64 (1968) 473–491.

[5] K. Carr, J.L. Evans, L.A. Leonard, H.M. Richardson, Study of oxygen convertor linings II, Trans., Brit. Ceram. Soc. 64 (1968) 493–519.

[6] L.L. Wong, R.C. Bradt, Lime refractories with limestone and synthetic calcium hydroxide additions, J. Am. Ceram. Soc. 78 (1995) 1611–1616.

[7] M.A. Hepworth, J. Rutherford, Fabrication of high density calcium oxide ceramics, Am. Ceram. Soc. Bull. 43 (1964) 42–45.

[8] W.J. Schlitt, G.W. Healy, Preparation of lime specimen with closely controlled properties, Am. Ceram. Soc. Bull. 49 (1970) 212–215.

[9] N.M. Ghoneim, M.A. Mandour, M.A. Serry, Sintering of lime doped with La_2O_3 and CeO_2, Ceram. Int. 15 (1989) 357–362.

[10] C. Tsang, J.K. Meen, D. Eithon, Phase equilibria of the calcium oxide–copper oxide system in oxygen at 1 atm, J. Am. Ceram. Soc. 78 (1995) 1863–1868.

[11] A.M. Yankin, Y.V. Golikov, V.F. Balakirev, Phase equilibria in the Ca–Cu–O system under variable temperatures and oxygen pressures, Ceram. Int. 22 (1996) 83–85.