



## Sliding wear of CaZrO<sub>3</sub>–MgO composites against ZrO<sub>2</sub> and steel



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### ABSTRACT

The wear behaviour of a fine grained and dense CaZrO<sub>3</sub>–MgO composite is presented. Un-lubricated Pin-on-disc tests at room temperature have been performed using 10 N as normal force and 0.10–0.15 ms<sup>-1</sup> as sliding rate and ZrO<sub>2</sub> and steel counterparts. The coefficient of friction versus the sliding distance and the specific wear, together with a complete microstructural analysis of the worn surfaces by field emission scanning electron microscopy is reported. The composite presents a wear resistance similar to other ceramics under ceramic/ceramic sliding contact and improved wear resistance in contact with steel.

Initial wear is dominated by abrasion independently of the chemical nature of the counterpart. The second stage wear depends on the characteristics of the third body formed. Zirconia leads to a brittle particulate third body with little protective capability. Steel forms a strongly bonded and plastic cermet third body that protects the material limiting the level of further wear.

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### 1. Introduction

Calcium zirconate (CaZrO<sub>3</sub>) is a ceramic oxide of the perovskite family that presents several properties of interest as structural as well as functional material. [1–4] It is known as a ceramic material for high temperature applications due to its high melting point (~2365 °C) and excellent corrosion resistance against alkali, earth alkali oxides, and basic slags, in particular against KOH and mixtures of NaVO<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> environments. At low oxygen pressure CaZrO<sub>3</sub> is an oxygen ion conductor, whereas at high oxygen pressure it is a mixed ion and electronic conductor. Due to their high chemical stability and good ionic conductivity at elevated temperatures, CaZrO<sub>3</sub> materials are used in devices to monitor oxygen, hydrogen and water, such as oxygen sensors for steel melts and for solid oxide galvanic cells. CaZrO<sub>3</sub> has also considerable interest for fuel cells, filler, resonator for microwave telecommunication and temperature compensating materials of capacitance multilayer ceramic capacitors or dielectric applications because it displays a high dielectric permittivity, around 30, low dissipation factor, with

a temperature coefficient of capacitance of 40 ppm °C<sup>-1</sup> and a good behaviour under electrical field versus temperature.

CaZrO<sub>3</sub> based materials are also alternative refractories for casting titanium and its alloys, because they have the advantage of being inert to hydration while showing similar performance in use as CaO [5,6].

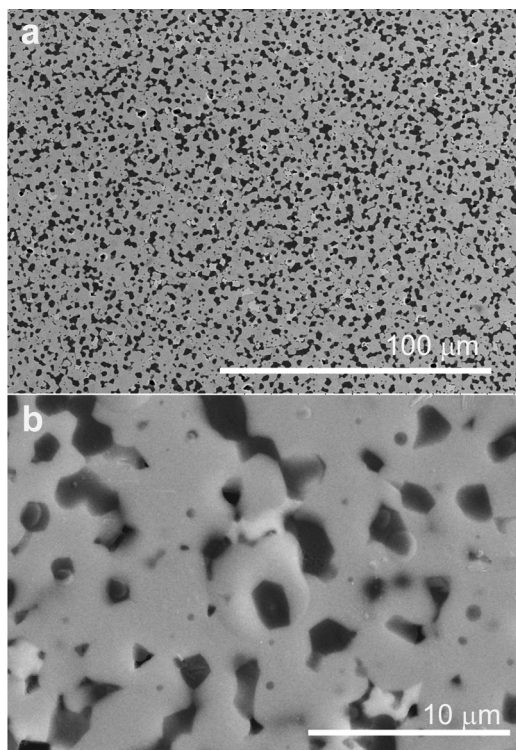
MgO–CaZrO<sub>3</sub> composites have been suggested as chrome free refractories to replace not only magnesia – chromite, but also magnesia over saturated spinel refractories. First temperature for liquid formation in pure MgO–CaZrO<sub>3</sub> is 2060 °C and CaZrO<sub>3</sub> is compatible with the main phases of Portland cement clinker in the solid state (C<sub>2</sub>S:Ca<sub>2</sub>SiO<sub>4</sub>, C<sub>4</sub>AF:Ca<sub>4</sub>Al<sub>2</sub>Fe<sub>2</sub>O<sub>10</sub> and C<sub>3</sub>S:Ca<sub>3</sub>SiO<sub>5</sub>). Therefore, CaZrO<sub>3</sub> as a second phase of MgO refractories would improve their resistance against clinker phase melting and alkali attack. Moreover, CaZrO<sub>3</sub> increases the resistance of MgO to hydration and thermal shock [7–11].

In addition, due to the similarities between the thermal expansion and thermal conductivity of CaZrO<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>-fully stabilised ZrO<sub>2</sub> (YFSZ), CaZrO<sub>3</sub> has been proposed as potential candidate for thermal and environmental barrier coatings (TBC, EBC). [12,13].

Due to the above described characteristics, CaZrO<sub>3</sub> – based materials can be considered as a good alternative to YFSZ for structural applications [14].

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**Fig. 1.** Main microstructural features of the  $\text{CaZrO}_3$ -MgO studied composite, DBZ. The black areas with shiny borders are pores. Major phase (gray) is  $\text{CaZrO}_3$  (EDX analysis, wt.%:  $\approx 31$ – $33$  CaO and  $\approx 67$ – $69$   $\text{ZrO}_2$ ) and the clearest particles are  $c\text{-ZrO}_2$  (EDX analysis, wt.%:  $2$ – $4$  MgO,  $8$ – $10$  CaO and  $85$ – $89$   $\text{ZrO}_2$ ). The second phase (black) is MgO.

(a) Low magnification SEM micrograph (BSE COMPO image).

(b) High magnification FE-SEM micrograph. Small amounts of glass (dark gray) are observed together with the MgO particles dispersed in the  $\text{CaZrO}_3$  matrix.

$\text{CaZrO}_3$  is very rare in nature due to its high crystallization temperature and the high affinity of Zr with Si, resulting in the formation of  $\text{ZrSiO}_4$  instead of  $\text{CaZrO}_3$ .

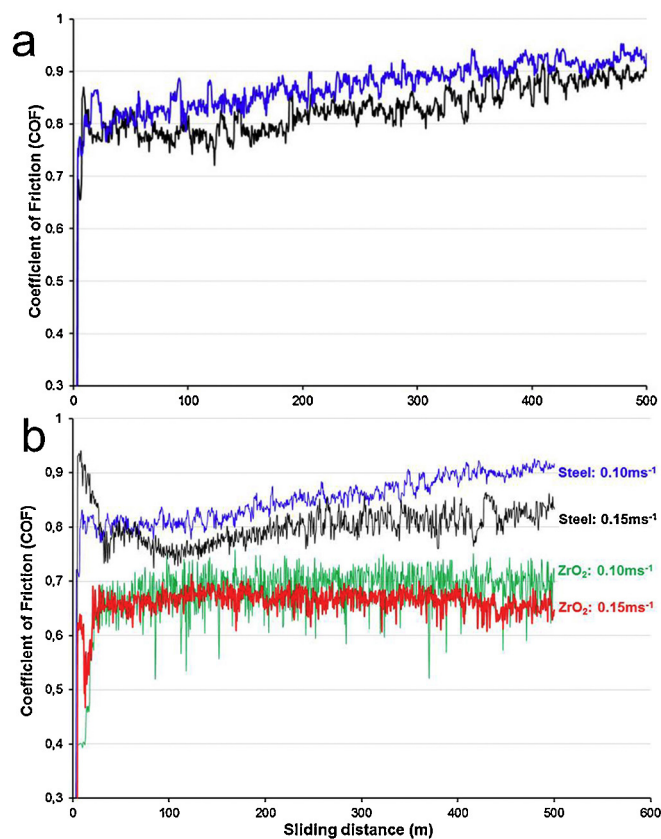
There are several methods to synthesize  $\text{CaZrO}_3$ , being the most used one the solid state reaction of equimolar CaO-ZrO<sub>2</sub> mixtures. The use of natural limestone or dolomite, with consistent chemical composition, mixed with ZrO<sub>2</sub> is an attractive alternative way for the low cost production of structural refractory materials.

shows the specific wear values. Differences between values for different tests under nominally equal experimental conditions were inside the variability limits of those obtained for one wear track. The volume loss for tests performed using ZrO<sub>2</sub> balls was significantly larger than for those performed with steel. There were no significant differences between values for different sliding rates.

The balls used as counterparts also lost some volume after testing, especially in the case of the ZrO<sub>2</sub> ones which presented elliptical wear scars as shown in Fig. 4

Particularly, composite materials  $\text{CaZrO}_3$ -MgO have been investigated as refractories for steel and cement industry [7–10,15].

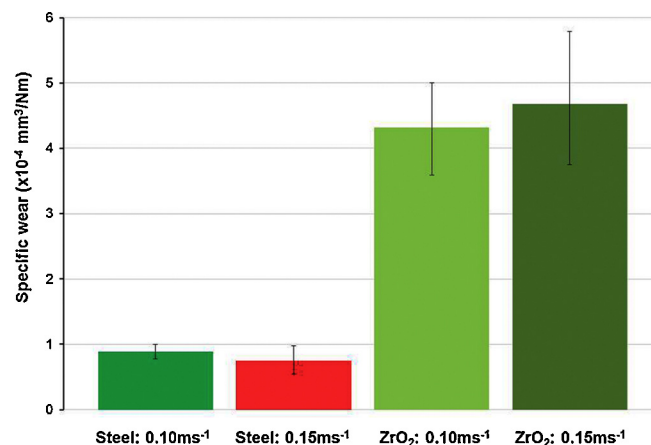
In a previous work [14] it was demonstrated that fine grained and dense  $\text{CaZrO}_3$ -MgO based materials with potential uses in advanced structural applications can be fabricated from natural dolomites if the nature and amount of impurities is carefully controlled. In particular, the phase composition – mainly the presence and amount of  $c\text{-ZrO}_2$  and glass as secondary phases- and the grain size of the sintered materials are highly dependent on impurities in the natural dolomites used. Higher glass content and larger microstructure were responsible for lower hardness and strength of the lowest purity material. Moreover, depending on the nature of the minor impurities, the silica liquids formed in these materials



**Fig. 2.** Evolution of the coefficient of friction with the sliding distance.

(a) Values for two nominally identical tests.

(b) Average values for the four experimental conditions used.



**Fig. 3.** Specific wear for the indicated experimental conditions.

might present low viscosity at low temperature ( $\approx 1400$  °C) which would restrain their use in structural applications of responsibility.

All of the above mentioned actual and potential applications of  $\text{CaZrO}_3$ -MgO based composites require the materials to be resistant to wear. Consequently, the study of their surface damage mechanisms when interacting with other surfaces is required.

This study is focused to understanding the sliding wear behaviour of  $\text{CaZrO}_3$ -MgO composites. From the previously developed materials, the one fabricated with the purest raw materials was chosen for this investigation. It is well known that the mechanical and chemical interactions of the contact surfaces remarkably

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