Calcium aluminate cement as a binder to alumina-based porous ceramics

A. B. V. Emilio, M. A. Kawamura, R. Salomão

Universidade de São Paulo, Escola de Engenharia de São Carlos, SP, Brazil
e-mail: ana.emilio@usp.br

Abstract

Porous calcium hexaluminate can be applied as a thermal insulator because it combines chemical inertia, high refractoriness (melting point of 1830°C), low thermal conductivity (0.1-0,5 W·(m·K)$^{-1}$ above 1000ºC) and suitable thermomechanical properties. There are several routes for CA_6 obtaining and this work proposed the use of calcium aluminate cement (CAC) as a calcium oxide source, porogenic agent and binder, comparing different cement content and heat treatment. The physical properties of the porous structures varied with CAC content, the porosity level ranged between 17,53% up to 36,7% at 1500°C and elastic modulus from 93,35 up to 207,34 GPa at 1500°C. Therefore, such material presented all requirements to be applied as a thermal insulator.

Keywords: calcium hexaluminate, porous ceramics, CAC, casting

Introduction

Calcium hexaluminate ($CaAl_{12}O_{17}$, CA_6) is the most alumina-rich intermediate compound in the system $CaO-Al_2O_3$ and is found in nature as a mineral known as hibonite [1]–[3]. Its formation typically occurs at 1400°C by two mechanisms: solid-state diffusion, which CA_6 nucleate in the interfaces between alumina e calcium aluminate phase (CA) particles, or by the solution-precipitation reaction when CA and alumina are wet by a liquid phase [4]. The microstructure obtained is platelet-like with intra-and interparticle pores and a melting point of 1830°C, which allows the use as refractory material [5].

CA_6 porous materials can be obtained by pre-formed aggregates or *in situ* reaction combining sources of calcia (CaO) and alumina (Al_2O_3). The first type involves high costs related to energy despends in production. Therefore, *in situ* reaction is an alternative [5] at which calcined alumina is combined with calcium carbonate ($CaCO_3$), obtaining porosity due to the expansion reaction and the particle format of CA_6 and intermediate compounds [6]–[8].

The aim of this study was to use calcium aluminate cement (CAC) as porogenic agent and binder to obtaining porous ceramic. This material is widely used as a binder in dense concrete refractories, however, the use proposed in this work is poorly explored.

Experimental Procedure

The raw materials used to prepare direct cast samples were alumina (A1000 SG, Almatis, German) and calcium aluminate cement (CAC, EL 70, Elfusa, Brazil) in three proportions 10 vol%, 20 vol% and 34 vol% (stoichiometric composition).

Cast samples were prepared with 50% of solid volume and 50% distilled water. Also, it was used 0,3% solid mass of dispersant (FS20, BASF, German) to homogenization and dispersion and antifoam to avoid incorporation of air bubbles.

Alumina, additives, and water were homogenized in a flask containing alumina spheres (10:1), which was placed on a ball mill (60 rpm, 30 min). After, CAC was added to this suspension and agitated for 1 min.

Samples were cast under vibration in nonadherent polymeric cylindric molds of 15 mm diameter x 60 mm length and 20mm x 16 mm. The molds were kept in closed flasks for 24 h at 60°C to maintain humidity close to 100% during cure. Following, samples were transferred to a circulating atmosphere (Venticell, MMM Group, Germany) for 24h at 60°C, and dried at 120 ° C for more 24 h to prevent risks of explosive spalling during the first heat-up.

Three samples were destined for each thermal treatment (1100°C, 1300°C and 1500°C, 3hours hold). Following, the flexural Young's modulus (E, GPa) was measured (Sonelastic equipment (ATCP, Brazil)) using impulse excitation of vibration technique according to ASTM E 1876-01 standard ("Standard Test Method for Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio by Impulse Excitation of Vibration.

The linear thermal variation of the dried green compositions was measured during the first heating up to 1500ºC (5ºC.min^{-1} heating rate) with a contact dilatometer (DIL402C, Netzsch, Germany).

Total porosity was calculated by Eq. 1.

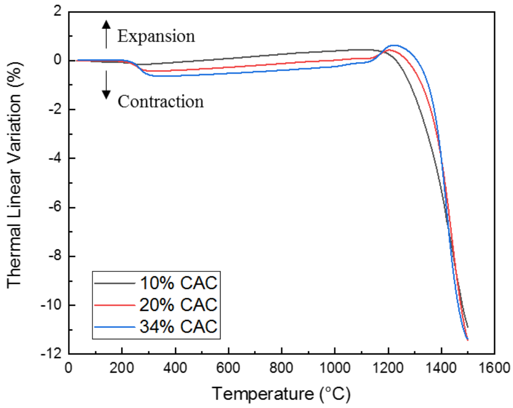
$$\mathrm{TP} = 100\% \times \left[1 - \left({}^{\mathrm{M}}/_{\mathrm{V}\rho_{\mathrm{Solid}}}\right)\right] \quad \text{Eq. 1}$$

Where M is the weight (g) of the sample, *V* is the volume, and ρ_{Solid} is the solid density (measured by Helium pycnometer method, Ultrapyc 1200e, Quantachrome Instruments, USA). Phase identification by X-ray diffraction (Rigaku ROTAFLEX Ru 200B, Japan, 20°–70° 2θ range, and 2° min^{-1} scan rate).

Results and Discussion

From the thermal linear variation analysis (Fig.1) it is possible to observe that at 300°C occurred a dimensional reduction due to hydrates decomposition and the greater the CAC amount used, the more intense the shrinkage. At 1200°C, samples presented an expansion due to aluminate formation, which has a smaller density than alumina. Following, occurred a shrinkage due to the sintering process.

Figure 1- Thermal Linear Variation of the green samples



Due to the expansive formation of hydrates at 1200°C, with the increase of CAC concentration, occurred an increase of expansive reactions, and consequently, the porosity level was greater in samples with more cement in the composition (Fig. 2). Therefore, the most porous samples had the smallest elastic modulus.

Comparing the results of X-ray diffraction (Fig.3) both compositions of 20% CAC and 34% CAC sintered to 1500°C/3h presented calcium hexaluminate and alumina. The peaks of calcium hexaluminate are more intense, and the alumina ones are less intense in the 34% CAC than in the 20% CAC sample. The sample with greater CAC concentration should present just calcium hexaluminate because it was stoichiometric composition, however, there was alumina in the sample, indicating that the reaction was not completed.

Figure 2- Total porosity and Elastic Modulus of samples at 1100°C, 1300°C and 1500°C

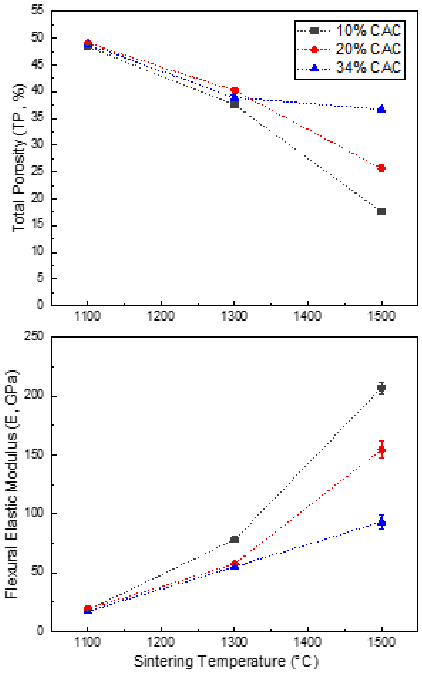
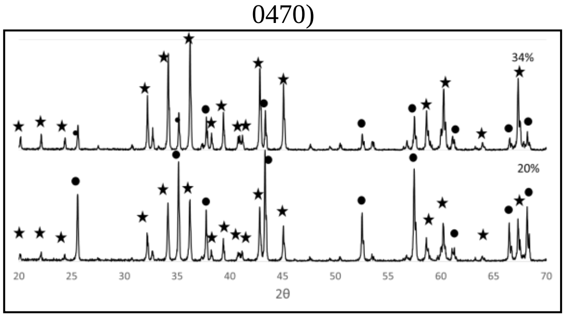


Figure 3- XRD pattern for samples sintered to 1500°C Symbols: ● = α- Al_2O_3 (JCPDS files, 46-1212), ★= CA_6 (JCPDS files, 38-0470)



Conclusions

Calcium aluminate cement can be used as a binder and source of calcium to hexaluminate formation, presenting good results of the amount of CAC used determines the porosity levels and mechanical properties.

Acknowledgments

FAPESP (2010/19274-5), CNPq, CAPES and Almatis (Brazil, Germany and USA).

References

[1] D. Holtstam, "Iron in hibonite: a spectroscopic study," *Phys. Chem. Miner.*, vol. 23, no. 7, Oct. 1996.

[2] C. Domínguez, J. Chevalier, R. Torrecillas, L. Gremillard, and G. Fantozzi, "Thermomechanical properties and fracture mechanisms of calcium hexaluminate," *J. Eur. Ceram. Soc.*, vol. 21, no. 7, pp. 907–917, Jul. 2001.

[3] E. Y. Sako, M. A. L. Braulio, E. Zinngrebe, and V. C. Pandolfelli, "In-Depth Microstructural Evolution Analyses of Cement-Bonded Spinel Refractory Castables: Novel Insights Regarding Spinel and CA6 Formation," *J. Am. Ceram. Soc.*, vol. 95, no. 5, pp. 1732–1740, May 2012.

[4] L. An, H. M. Chan, and K. K. Soni, "Control of calcium hexaluminate grain morphology in in-situ toughened ceramic composites," *J. Mater. Sci.*, vol. 31, no. 12, pp. 3223–3229, 1996.

[5] J. Sakihama and R. Salomão, "Microstructure Development in Porous Calcium Hexaluminate and Application as a High-Temperature Thermal Insulator: A Critical Review," *InterCeram*, vol. 68, no. 1, pp. 66–71, 2019.

[6] C. Domínguez, J. Chevalier, R. Torrecillas, and G. Fantozzi, "Microstructure development in calcium hexaluminate," *J. Eur. Ceram. Soc.*, 2001.

[7] T. Nagaoka, T. Tsugoshi, Y. Hotta, M. Yasuoka, and K. Watari, "Forming and sintering of porous calcium-hexaaluminate ceramics with hydraulic alumina," *J. Mater. Sci.*, vol. 41, no. 22, pp. 7401–7405, Nov. 2006.

[8] I. R. de Oliveira, V. M. C. Leite, and R. Salomão, "Production of porous ceramic materialusing different sources of alumina and calcia," *Matéria (Rio Janeiro)*, vol. 20, no. 3, pp. 739–746, Sep. 2015.