Foam Sprayed Porous Insulating Refractories

V.R. Salvini, A.P. Luz, V.C. Pandolfelli

Porous ceramics can be applied as filters for molten metals, gases or water filtration, orthopedic implants and insulating refractories. The production of these materials is mainly based on techniques involving the addition of gases, lightweight compounds and/or combustible pore forming additives to the ceramic suspensions. The present work evaluates insulating refractory compositions designed according to the *Andreasen* packing model and prepared by using a novel direct foaming procedure (applying compressed air in equipment specially developed for large-scale production of porous ceramics). Density, porosity and pore size distribution, splitting tensile strength and thermal conductivity of the foamed specimens were measured. According to the results, the prepared refractories presented a high porosity content (>69 %), low thermal conductivity (0,3–2,3 W/m·K in the range of 200 to 1200 °C) and improved splitting tensile strength (1,8–15,2 MPa). The evaluated foaming method is a feasible alternative for producing homogeneous refractory porous ceramics for thermal insulating applications. Additionally, by adjusting the composition particle size distribution, ceramic suspensions with enhanced fluidity and, consequently, fired samples with higher mechanical strength can be attained.

1 Introduction

Due to energy costs and environmental concerns, in recent years an increasing interest in the development and use of insulating refractories have been observed. These porous ceramic materials present important features such as low density and thermal conductivity, controlled permeability and high surface area, allowing their use in various industrial processes aiming to reduce heat losses and overall energy consumption. Consequently, in order to attain advanced insulating ceramics, the selection of high quality raw materials and suitable manufacturing methods are some of the main factors to be taken into account to enhance their properties and performance [1–3].

Porous materials used in gas and liquid filtering applications, for instance, should have an interconnected tridimensional structure comprised by open pores and high void fraction (between 80–95 %). In this case, the most common and widely applied production technique is the replica one, where a synthetic or natural porous polymer is coated with ceramic slurry, dried and submitted to a thermal treatment to burn out the polymer and leave a positive porous ceramic replica [4].

On the other hand, different alternative procedures can be selected for insulating refractory production, as they must present a homogenous microstructure with a high volume of small (<100 µm) and preferably closed pores, which result in lower thermal conductivity values at high temperatures [5, 6]. This aim can usually be attained by adding combustible pore forming materials (such as polymeric spheres, hydroxides, etc.) [7, 8], solid lightweight compounds (calcium hexaluminate and ceramic fibers) [9, 10], and/or hollow macrospheres (globular alumina) to the designed compositions.

The main drawback of the polymeric spheres addition is related to the pyrolysis step, which can negatively affect the mechanical strength of the final porous material, especially for larger products. Conversely, the decomposition of hydroxide compounds [i.e., $Al(OH)_3$] can generate small pores, but they can be eliminated at high temperatures by densification. Calcium hexaluminate (CA_6) and globular alumina (the latter depending on the internal pore size) are alternative compounds which present high refractoriness and low thermal conductivity at temperatures close to 1600 °C. However, the high cost of those synthetic raw materials inhibits their wide use in porous ceramic compositions.

Considering these aspects, the drawbacks of some insulating ceramics production methods are associated with their difficulties in providing products showing simultaneously low thermal conductivity at high temperatures, high mechanical strength and low cost. In this context, this work addresses the

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Tab. 1 General information of the designed ceramic compositions

Raw Materials	Compositions [mass-%]		
	Al	Al-Si-M	Al-CA_6
Reactive alumina (CL370C + CT3000SG)	83	40	20
Mullite (d <1 mm)	–	20	–
Fly ash (d <1 µm)	–	30	–
Calcium hexaluminate (SLA 8/40 + 18F + 140F)	–	–	75
Hydratable alumina (Alphabond 300)	7	5	–
Calcium aluminate cement (Secar 71)	–	5	5

evaluation of a novel direct foaming procedure, where most likely any aqueous ceramic suspension can be foamed and cast at room temperature, in a suitable length of time and without the help of any toxic additives. For this purpose, equipment developed for large-scale production of porous ceramics with higher compressive strength and porosity level was used to generate small and homogeneous air bubbles into the select aqueous suspension [11]. Physical properties (density, porosity and pore size distribution), splitting tensile strength and thermal conductivity of the attained foamed specimens were measured and their results discussed, pointing out the advantages and limits of the studied technique and the insulating refractory performance.

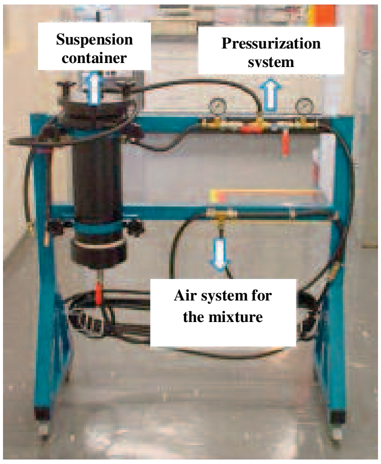

Fig. 1 Foaming equipment developed by Salvini et al. [11]

2 Experimental

Calcined aluminas (CL370C and CT3000SG), hydratable alumina (Alphabond 300) and lightweight aggregates of calcium hexaluminate ($CaO{\cdot}6Al_2O_3$ or CA_6, SLA 92) by *Almatis*, as well as mullite (Mulcoa #70, *Treibacher/BR*), calcium aluminate cement (Secar 71, *Kerneos*/FR) and silico-aluminate microspheres (fly-ash, d <1 µm) were the main raw materials used in this work.

The development of improved insulating refractories was based on optimizing the ceramic suspensions packing and dispersion. All evaluated compositions (Tab. 1) were designed according to the Andreasen packing model (q = 0,37). Moreover, the use of different raw materials (as proposed in the Al-Si-M composition) was analyzed in order to confirm the versatility of the selected direct foaming procedure for the production of thermal insulating refractories.

As the compositions contained raw materials with distinct densities, citric acid (0,31 mg·m^{-2}, *Sigma*) and surfactants were used to properly disperse and provide a homogeneous mixture. Firstly, aqueous ceramic suspensions of each composition containing 50 vol-% of solid plus dispersant and surfactants were prepared. In parallel, the foam was separately produced by mixing and stirring the foaming additive, cellulose and water. After mixing the aqueous foam with the ceramic suspension, the attained mixture was poured into the developed equipment container (Fig. 1) and compressed air (pressure ~7,8 atm) was used to pump the suspension through a rubber pipe to generate small and homogeneous air bubbles [11].

The prepared ceramic foams were cast into cylindrical (50 mm × 50 mm) and prismatic (230 mm × 110 mm × 600 mm) moulds. The sample curing step was carried out at 25 °C or 40 °C (in the presence of moisture), depending on the binder additive used. After demolding, they were dried at 110 °C for another 24 h and sintered in air, according to the temperatures presented in Tab. 2. As the Al and Al-CA_6 compositions were developed to be applied in steel foundry processes, such samples were thermally treated at higher firing temperature (1500 °C). On the other hand, insulating sleeve materials (as for Al-Si-M composition) are commonly placed in service without a previous thermal treatment. Nevertheless, in this work the Al-Si-M samples were pre-fired at 1100 °C in order to attain a suitable mechanical strength level, which is related to the chemical transformations of the calcium aluminate cement (binder source).

The physical properties of the porous ceramics were analyzed based on the density, relative density, total porosity and pore size distribution. The relative density ($\rho_{relative}$) and total porosity (P_t) were calculated as follows:

$$\rho_{relative} = \frac{\rho_v}{\rho_{real}} \qquad (1)$$

$$P_t = (1 - \rho_{relative})\,x100 \qquad (2)$$

where, ρ_v is the volumetric density (g·cm^{-3}) and ρ_{real} is the real density (g·cm^{-3}) of the ceramic composition after being sintered, crushed and evaluated in the AccuPyc 1330 (*Micromeritics*) equipment. Apparent porosity of cylindrical samples (50 mm × 50 mm) was measured by the *Archimedes* method using kerosene as the immersion liquid. In addition, the closed porosity values were calculated based on the total and apparent porosity values. The pore size distribution of the sintered porous specimens was determined by mercury intrusion porosimetry (Porosizer 9320, Micromeritics).

The modulus of rupture of the porous ceramics was evaluated by splitting tensile strength tests (ASTM C496-90 – samples' size: 50 mm × 50 mm) in MTS equipment (*MTS Systems,* Model 810, USA) under a

Tab. 2 Curing and firing conditions used in the processing step of the porous ceramics

Compositions	Curing Stage	Firing Temperature
Al	25 °C for 24 h	1500 °C for 5 h
Al-Si-M	40 °C (relative humidity ~80 %) for 24 h	1100 °C for 1 h
Al-CA_6	40 °C (relative humidity ~80 %) for 24 h	1500 °C for 3 h

strain rate of 0,5 mm/min. The prepared shaped brick samples (230 mm × 110 mm × 600 mm) have also their thermal conductivity measurements carried out in the 200–1200 °C temperature range, using the hot wire method (TCT 426 *Netzsch)*.

3 Results and discussion

In general, the thermal conductivity of insulating refractories is a useful parameter that guides the application of such materials, as well as the fuel consumption rate and the design of units of industrial plants. Based on the evaluation of the samples' physical properties (mainly total porosity, pore size distribution and density), it is possible to infer the porous ceramics performance at a high temperature, considering that the presence of a high amount of closed pores should lead to lower thermal conductivity levels.

As shown in Tab. 3, the novel processing method (using compressed air to generate and scatter homogeneously the air bubbles in the aqueous suspension) resulted in materials with very low relative density (0,21–0,31) and high porosity level (>69 %) as required for thermal insulators. It must be pointed out that the attained volumetric density (ρ_v) is not only dependent on the ceramic composition, but also on the particle size of raw materials used. Thus, some differences in the performance of the designed porous ceramics were expected.

It is also known that, at high temperatures, the thermal conductivity is mainly related to the radiation power or photons energy (*P*, Eq. 3).

$$P = \in \cdot \sigma \cdot A \cdot T^4 \qquad (3)$$

where, $\in$ is the emissivity factor, σ is the Stefan-Boltzman constant [W·m^{-2}·K^{-4}], A is the radiating surface area [m^2] and T is the temperature [K]. Moreover, the higher the pore size in the samples, the higher the radiation power effect will be. Therefore, a high amount of small and spherical pores homogeneously scattered in the refractory microstructure (as the ones presented in Fig. 2 a) are desired for insulating purposes.

The pore size distribution of the sintered samples is shown in Fig. 2 b. It can be observed that the evaluated ceramics comprise small pores (80 % lower than 20 µm) and the differences among the attained curves can be related to the materials chemical composition and the chosen sintering conditions.

Tab. 3 Physical properties of the sintered foamed ceramics

Compositions	Density, ρ_v [g·cm^{-3}]	Relative Density, $P_{relative}$	Total Porosity, P_t [%]	Closed Porosity, ρ_{closed} [%]
Al	1,15 ± 0,02	0,30 ± 0,01	71,2 ± 0,7	4,9 ± 0,3
Al-Si-M	0,68 ± 0,01	0,21 ± 0,01	78,9 ± 0,1	5,1 ± 0,2
Al-CA_6	1,13 ± 0,01	0,31 ± 0,01	69,5 ± 0,1	26,9 ± 0,3

Fig. 3 presents the thermal conductivity (K) behavior of the prepared samples and some data from commercial insulating refractory materials [13]. In order to analyze these results two aspects must be taken into account: the samples composition and their microstructure.

High alumina (99 mass-%) dense refractories usually present high thermal conductivity (K ~ 5,8 W/m·K) at temperatures close to 200 °C [6], however this value can be extensively reduced with pore addition in the material microstructure. This concept was applied to the development of globular alumina (hollow alumina spheres) bricks. Nevertheless, as presented in Fig. 3, the large size of the used globular alumina spheres (1–5 mm) does not act efficiently reducing the thermal conductivity of such material. A low cost alternative consists of applying the direct foaming technique for the production of high-alumina porous ceramics. Based on the evaluated foaming procedure proposed in this work, the fired Al samples showed micropores in their structure (D_{50} = 50 µm, Fig. 2) and, consequently, thermal conductivity of 0,7 W/m·K could be attained at 1200 °C.

The addition of mullite, CA_6 and SiO_2 to the other prepared compositions (Al-Si-M and Al-CA_6) helped to keep their lower thermal conductivity levels in the temperature range of 200–1000 °C, resulting in a similar performance as the SLA 92 castable (Almatis) and ceramic fiber module commercial products [13]. However, an additional densification (due to the presence of low refractoriness phases) followed by the increase of the K values was observed for Al-Si-M samples above 1000 °C (Fig. 3). This effect was induced by the lower thermal stability and expressive reduction of the small pores content (diameter <1 µm) during the samples' firing step, as can be seen in Fig. 4 a. On the other hand, the changes in the pore size dis-

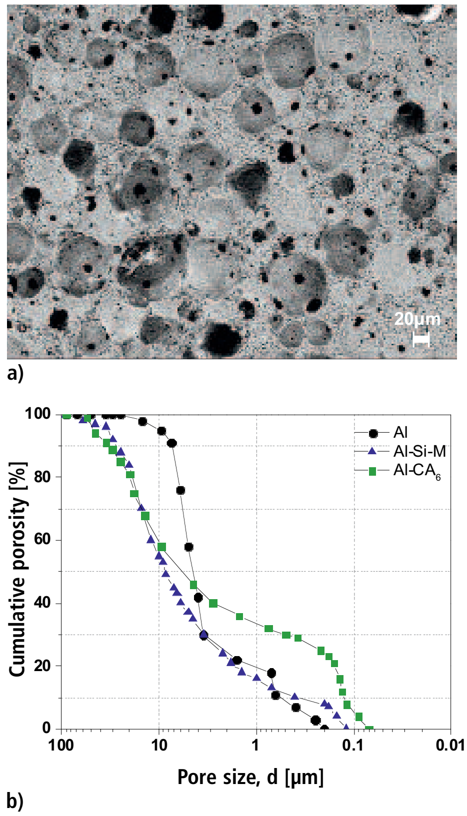

Fig. 2 a) Cross section area of the Al sample sintered at 1500 °C/5 h, and (b) pore size distribution of the porous ceramics after firing at 1100 °C/1 h (Al-Si-M), 1500 °C/3 h (Al-CA_6) and 1500 °C/5 h (Al)

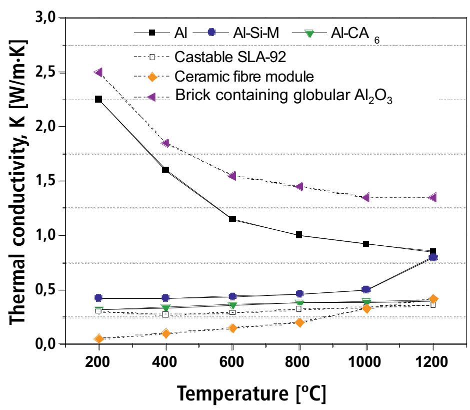

Fig. 3 Thermal conductivity of the sintered foamed ceramics (Al, Al-Si-M and Al-CA_6) and commercial insulating materials (some results were adapted from reference [13])

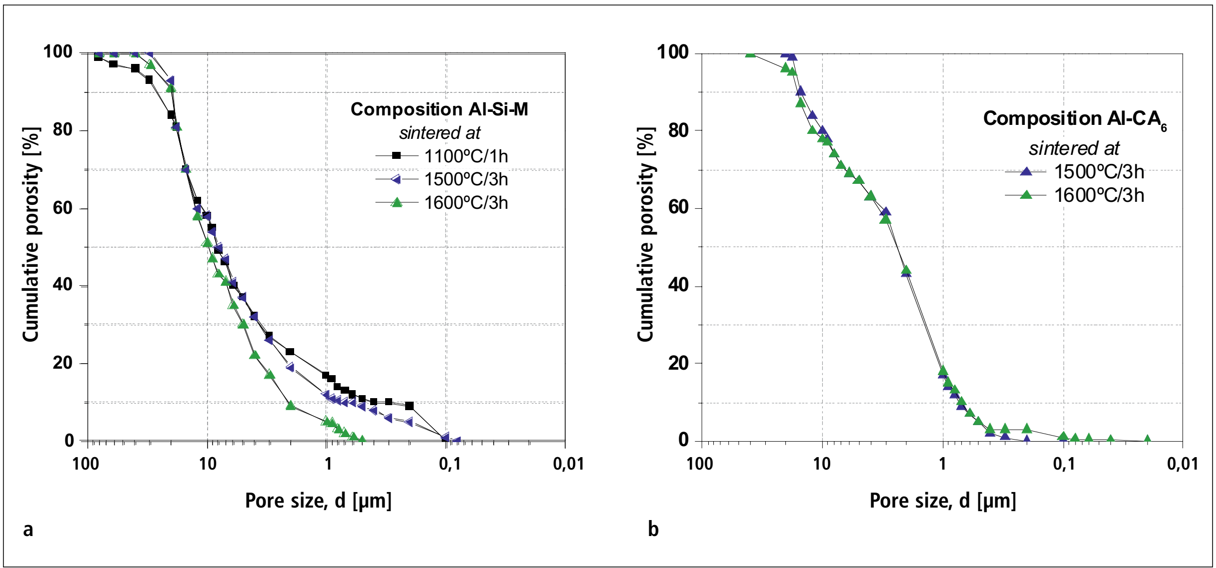

Fig. 4 **Thermal treatment effect on the pore size distribution of (a) Al-Si-M and (b) Al-CA_6 foamed ceramics**

tribution of the Al-CA_6 samples were not significant even at 1600 °C (Fig. 4 b). Most likely, this behavior is a consequence of two independent factors: high refractoriness of CA_6 grains and the improved particles packing of the designed composition.

Besides the thermal stability, insulating materials should also present suitable mechanical properties to withstand the stress faced during service. Therefore, the splitting strength and apparent porosity of the sintered foamed samples is shown in Fig. 5.

Considering the apparent porosity level of the fired samples, the attained mechanical strength values are significantly high when compared to the data from the literature [12, 13]: 0,3 to 1,7 MPa (uniaxial compression tests) for bulk density ranging from 0,5 to 1 g·cm^{-3}. Moreover, the splitting tensile values are equivalent to 1/5 of those on cold crushing strength experiments [14]. Therefore, it is expected that the designed refractories should present much higher results when evaluated under an uniaxial compression technique. The higher apparent porosity and lower density of Al-Si-M samples led to a poorer mechanical performance.

Nevertheless, the use of compressed air and the equipment developed for producing homogeneous porous ceramics coupled with a suitable particles packing, allowed the production of improved insulating materials with different chemical compositions based on an aqueous ceramic suspension with no toxic additives.

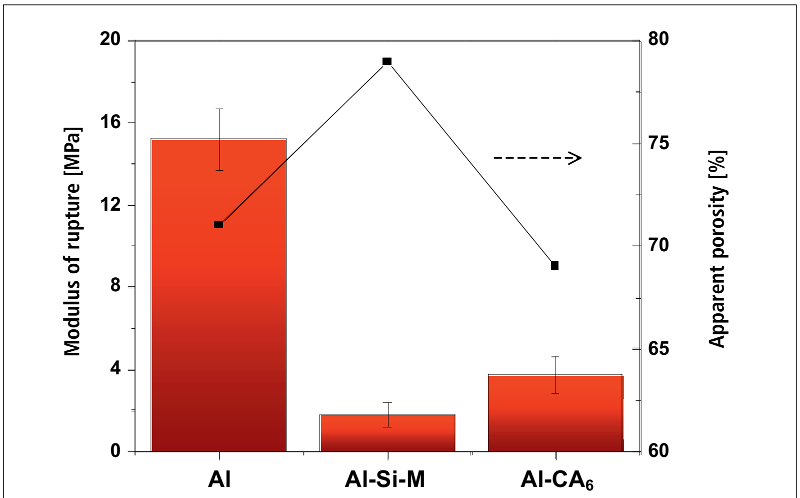

Fig. 5 **Splitting tensile resistance and apparent porosity of the porous ceramics after sintering (firing temperatures: Al = 1500 °C/5 h, Al-Si-M = 1100 °C/1h, and Al-CA_6 = 1500 °C/3 h)**

4 Conclusions

The proposed method evaluated in this work (based on the optimization of the suspensions particle packing, the use of non toxic additives and equipment especially developed for producing highly porous ceramics) allowed the production of insulating refractories presenting high porosity (>69 %), improved splitting tensile mechanical strength (1,8–15,2 MPa for bulk density ranging from 0,7 to 1,2 g·cm^{-3}) and low thermal conductivity (0,3–2,3 W/m·K from 200–1200 °C). Therefore, the evaluated direct foaming process is an efficient and feasible method for producing refractory porous ceramics for thermal insulating applications. A suitable particle size distribution of the compositions also enhanced the ceramic suspension fluidity and, consequently, fired samples with higher mechanical strength and thus lower shrinkage can be attained.

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