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Novel cordierite foams from preceramic polymers and reactive oxide fillers

L. Fiocco [*], E. Bernardo

Dipartimento di Ingegneria Industriale, University of Padova, Italy

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ABSTRACT

Cordierite ($Mg_2Al_4Si_5O_{18}$) ceramic foams have been successfully prepared by a novel approach, consisting of the firing at 1350 °C of commercial silicone resins (Silres® MK and H62C) embedding micro-sized $Mg(OH)_2$ and Al_2O_3 powders, acting as reactive fillers. The foaming was due to a preliminary heating stage, at 300 °C, at which magnesium hydroxide decomposed, releasing water vapor in the viscous mass offered by silicone resins before their ceramic conversion. Two different strategies were employed for the mixing of components, depending on the nature of the preceramic polymer used. For a liquid polymer, the fillers were added starting from polymer solutions; for a solid polymer, the fillers were incorporated by melting in a conventional extruder. Despite significant differences in the formulations and in the mixing, the resulting ceramics are similar, in terms of remarkable phase purity, total porosity (in the order of 64%) and mechanical properties (compressive strength ≈ 2.3 MPa).

1. Introduction

Porous ceramics based on cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) are particularly appreciated in the field of catalytic converters and particulate filters for diesel engines [1–3] and, in general, for components subjected to severe thermal gradients (for a maximum temperature generally not exceeding 1250 °C) [4]. This is due to the characteristic combination of properties, such as low CTE (coefficient of thermal expansion, equal to $\sim 1.5 \cdot 10^{-6}\ K^{-1}$), good thermal stability, corrosion resistance and generally low price.

In the present work, cordierite ceramics are fabricated starting from silicone resins, filled with oxide particles. According to this approach, the fillers directly react with the product of oxidative decomposition of the resins, consisting of amorphous silica, possessing a particularly defective network and consequently prone to very favorable reaction kinetics [5]. A previous paper [6] has already been dedicated to cordierite ceramics, from silicones combined with MgO and γ-Al_2O_3, in form of nano-sized particles. Cordierite is feasible in conditions of high microstructural homogeneity and phase purity, comparable to those provided by the sol–gel route [7,8], and the distinctive possibility of shaping in the polymeric state, for preceramic polymers, can be exploited for the development of particularly strong and homogeneous foams. However, nano-sized particles and the methods for obtaining a uniform porosity remain as open issues, in the view of large scale industrial applications. In particular, toxicological effects associated with human exposure to nanoparticles are still unknown [9,10], and the formation of pores by burn-out of sacrificial polymeric beads, as proposed by Parcianello et al. [6], poses some difficulties in terms of costs and control of gaseous emissions.

The present investigation is based on a revision of the approach of silicone resins filled with oxide particles: firstly, high purity and relatively low processing temperature are maintained, despite the use of micro-sized fillers; secondly, the fabrication of highly porous components relies on the use of a “double role” filler, both reacting with polymer-derived silica to yield the desired crystalline phase and acting as foaming agent. More precisely, as observed in the development of akermanite ($2CaO \cdot MgO \cdot 2SiO_2$) porous ceramics, the double role is provided by magnesium hydroxide ($Mg(OH)_2$), decomposing, with release of water vapor, at very low temperature (300–350 °C). Since the release occurs in a silicone below the temperature of ceramic conversion (>500 °C), i.e. in a viscous mass, the developed (harmless) gas may lead to an extensive foaming, with no need for additives; the residue (MgO) is obviously incorporated in cordierite.

The commercially available silicone polymers are actually quite numerous; a protocol for the development of cordierite-based porous ceramics, based on a specific silicone, could have a limited impact. We will show, on the contrary, that the “double role” filler approach may be applied to silicone of different nature. The key

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[*] Corresponding author. Fax: +39 049 8275505.
E-mail address: laurafiocco@hotmail.com (L. Fiocco).

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constraint of the availability of a viscous mass, upon decomposition of $Mg(OH)_2$, will be fulfilled operating with different mixing strategies, operating with liquid or solid silicones.

2. Materials and methods

2.1. Preparation of ceramic foams

Two commercially available silicones, Silres MK and Silres H62C (Wacker-Chemie GmbH, Munich, Germany) were used as silica sources. MK is a solid methyl polysilsesquioxane resin with a 84 wt% SiO_2 yield after pyrolysis in air [11]. It is characterized by the presence of OH functional groups inside its chemical structure, which allow the cross-linking mechanism to occur by condensation. H62C instead is a highly viscous liquid polysiloxane resin with a 58 wt% silica yield [11], which can cross-link without the release of gaseous products, thanks to the presence of vinyl groups.

As MgO and Al_2O_3 precursors, we considered $Mg(OH)_2$ microparticles (< 10 µm, Industrie Bitossi, Vinci, Italy) and transition Al_2O_3 microparticles (Puralox UF 5/230, < 11 µm, Sasol, Brunsbüttel, Germany). The balance among the most important constituents (silicones/MgO precursor/Al_2O_3 precursor) followed the stoichiometric $MgO/Al_2O_3/SiO_2$ molar proportions of cordierite (i.e. $MgO/Al_2O_3/SiO_2 = 2/2/5$ by mol). Considering the different silica yields, the amount of polymer, with the same amount of fillers, obviously changed ($Mg(OH)_2/Al_2O_3/H62C = 0.23/0.39/1$ and $Mg(OH)_2/Al_2O_3/MK = 0.32/0.57/1$ by weight).

Foams from liquid polymer were prepared by dissolving H62C in isopropanol (15 ml for 10 g of final ceramic) and adding the fillers under magnetic stirring. Further sonication for 10 min provided a stable and homogeneous dispersion. The mixture was subsequently poured into a large glass container and dried at 60 °C overnight. After drying, the preceramic mixture was in form of a thick paste, which was manually transferred into cylindrical Al molds and thermally treated at 300 °C for 30 min. Cylindrical samples, 10 mm in diameter and 20 mm in height, were obtained by polishing the foams with abrasive paper.

Foams from solid polymer were obtained by mixing MK with Al_2O_3, $Mg(OH)_2$ microparticles and paraffin (13 wt% of the total preceramic formulation). The components were first homogenized by means of a shaker-mixer (Turbula T2F, WAB, Switzerland), then inserted in a twin-screw co-rotating extruder (Prism TSE 24 HC, 24 mm screw diameter, length/diameter ratio equal to 40:1, Thermo Prism Ltd, Stone, United Kingdom) operating at 75 °C at the die. The extrudates, which were in form of cylindrical fragments, were later subjected to secondary processing, including manual grinding, sieving to a dimension below 300 µm, pouring in Al molds and thermal treating at 300 °C for 30 min.

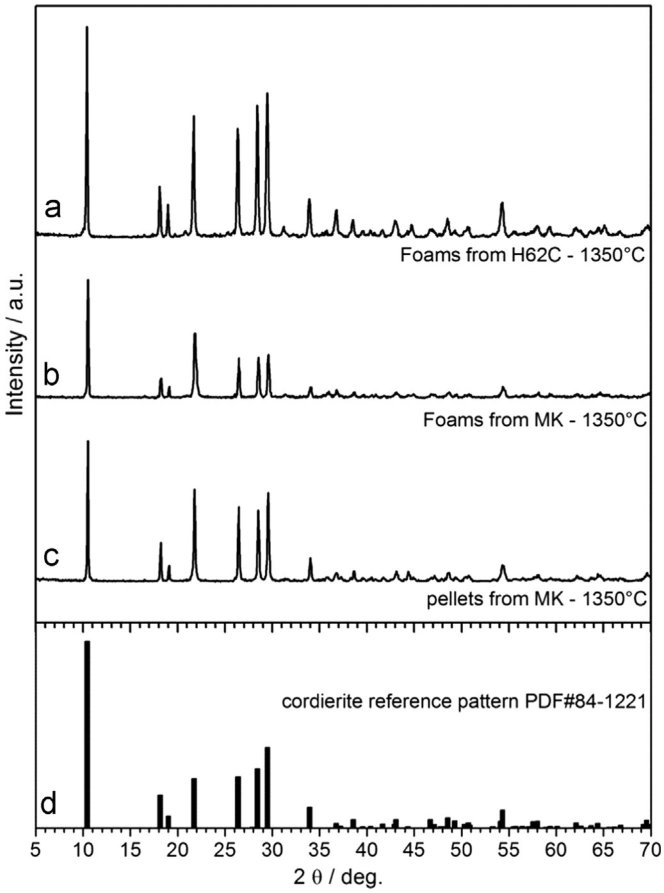

Fig. 2. Qualitative X-ray diffraction patterns of cordierite (after ceramization at 1350 °C): (a) foams from H62C; (b) foams from MK; (c) dense sample from MK; and (d) reference pattern.

All the foams obtained from both liquid and solid silicone resins have been subjected to ceramization at 1350 °C for 3 h, with a heating rate of 10°/min.

2.2. Characterization

The bulk density (ρ_b) of the foams was determined from the weight-to-volume ratio, using a caliper and a digital balance. The skeletal density (ρ_s) was measured on foams, using a He gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA). The percentage of open porosity was then calculated using the following equation:

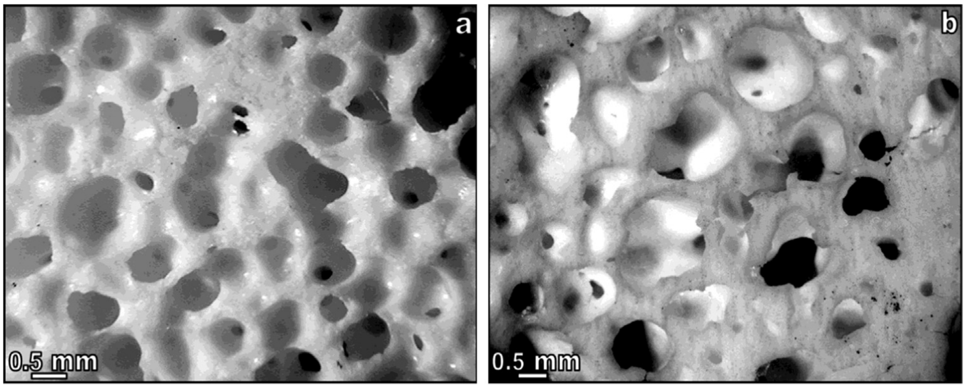

Fig. 1. Microstructural details of cordierite foams (after ceramization at 1350 °C): (a) from H62C and (b) from MK.