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Silicon nitride foams from emulsions

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ABSTRACT

Si_3N_4 foams with open cells were developed by emulsification of an aqueous powder suspension containing an alkane phase (70 vol% of octane or decane), using a surfactant as emulsion stabilizer. 5 wt% of Y_2O_3 and 5 wt% of MgO were used as sintering additives, and the samples were pressureless sintered at 1600 °C in N_2. Ceramic foams, mainly based on α-Si_3N_4, with total porosity ranging from ~70 to ~77 vol%, average cell size of ~31 μm for octane and ~55 μm for decane, and compression strength ranging from ~5 to ~20 MPa were produced.

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1. Introduction

High performance ceramics, with cellular structure and containing more than 60 vol% of interconnected porosity, find application particularly where the transport of fluids is required, e.g. molten metal and gas filtration at high temperature, gas-burner media, catalyst support, pollutant removal from gaseous or liquid streams [1–6]. Among non-oxide ceramics, Si_3N_4 is one of the most widely used structural ceramic materials because of its outstanding properties, such as high strength and Young's modulus, fracture toughness, hardness, wear resistance, refractoriness, corrosion and oxidation resistance [7–9], low density, expansion coefficient, reasonably high thermal conductivity and good resistance to thermal shock [7,10,11]. However, the high cost of production (generally requiring pressure sintering) is a significant problem limiting the use of Si_3N_4-based ceramics to specialized, high value applications. Concerning porous Si_3N_4, various methods of processing, such as partial sintering [12,13] and reaction sintering [14,15], sacrificial templating using starch consolidation [16], direct foaming [17], gelcasting [18] and preceramic polymers [19] have been used to obtain components to be used in various applications. In particular, porous Si_3N_4 is good a candidate for Diesel Particulate Filters [20,21], membrane/catalysts supports, and reactor beds [22].

Recently, emulsions have been used as efficient intermediates in the production of porous materials via direct foaming processes [2,23,24–26]. They consist of two immiscible fluids, one being dispersed in the other, in the presence of surface active agents [27], and are thermodynamically unstable because of their large oil–water interfacial area and thus high overall free energy. Therefore surface active agents (e.g. surfactants or proteins) are used to reduce the free energy of the system [28]. The objective of the present work was the development of porous Si_3N_4 ceramics employing an emulsion approach that would lead to foams with highly interconnected pores by conventional pressureless sintering.

2. Experimental

Si_3N_4 powder from Yantai Tomley (China)— purity > 90%, oxygen content 7.4 ± 0.08 wt%, average particle size 1.95 μm, BET 9.6 m²/g, containing above 91.5% α-Si_3N_4 phase, was used. The equilibrium pH_{iep} 8.2 ± 0.01 of the powder was measured after 24 h aging in water, following the procedure reported in Ref. [29]. High purity Y_2O_3 (d_{50}=50 nm, Inframat (USA)) and MgO (d_{50}=4.6 μm, Bitossi (Italy)) were used as sintering additives (5 wt% for both additives)[30]. The powder mixture was wet-milled in ethanol for 4 h at 300 rpm using planetary mill and silicon nitride cylinders, dried, sieved through a 300 μm screen and then treated in air at 600 °C for 2 h to improve the aqueous dispersibility [31,32]. Polyacrylic acid (PAA 1 wt% based on the powder content, Sigma-Aldrich, Italy) was used as a dispersing agent. Polysorbate (0.22 vol% with respect to the suspension volume, Tween 80, VWR BHD Prolabo, UK), was used as a nonionic surfactant. Water-based Si_3N_4 slurries with 35 vol% of solids and containing PAA were prepared by ball milling for 2 h at 200 rpm. Afterwards, the emulsification process took place at room temperature by addition of the alkane phase (70 vol% of octane or decane, Sigma-Aldrich, Italy), and the mixture was stirred at 700 rpm for 3 min. The emulsions were poured in a Teflon mold and dried under ambient conditions for 24 h. Sintering was conducted in two steps: first the samples were pre-calcinated in

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vacuum at 800 °C (2 h, 0.85 °C/min heating rate), to decompose the organic phase; secondly, the samples were heated to 1600 °C (3 h, 2 °C/min heating rate) under 99.99% N_2[30].

The crystalline phases were determined on powdered samples by X-ray diffractometry (Philips PW 1710; CuKα, 40 kV, 40 mA, 0.05°, 2 s). The microstructure of the Si_3N_4 based foams was investigated by scanning electron microscopy (FEI Quanta 200, FEI Italia, Milan, Italy). Cell size and cell windows sizes were measured by the linear intercept method (ASTM E112-12), using an image analysis program (Axio Vision LE). The average values were obtained considering stereological relations (ASTM D3576-98).

The bulk density and the total porosity were calculated from the weight-to-volume ratio of the samples, while the open porosity and true density were measured using a mercury porosimeter (Pascal 140/440 Porosimeter 2000, Germany).
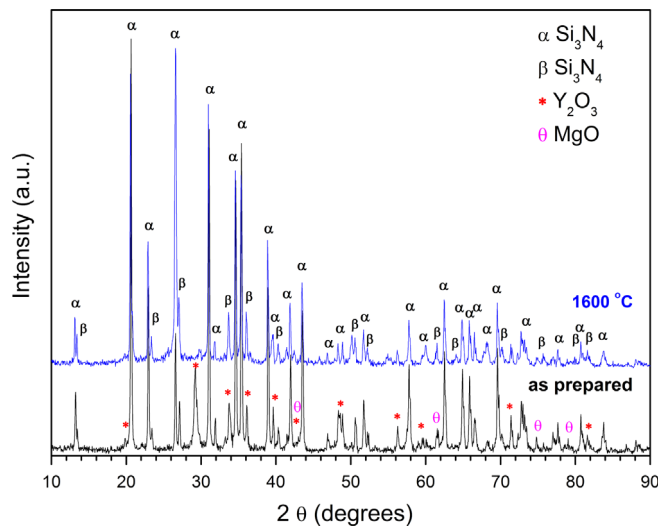

Fig. 1. XRD patterns for un-sintered and sintered Si_3N_4 foams.

The mechanical behavior of the Si_3N_4 based foams was determined by uniaxial compression using a universal testing machine (Instron 1121, Instron Danvers, MA; ASTM C133-94; 1.0 mm/min cross-head speed). Five to ten specimens of $10 \times 10 \times 10$ mm^3 size, cut from larger 50×12 mm^3 disks, were tested for each sample.

3. Results and discussion

The X-ray diffraction patterns of the as prepared and sintered Si_3N_4 foams are shown in Fig. 1. The main phase was α-Si_3N_4 in both samples, and a slight increase in the β-phase was observed after sintering, from 8.2% for the as received powders to 19.5% in the sintered foams, as estimated based on the ratio of the intensities of the [210] peak for both phases (located at 35.3 2θ for the alpha phase and at 36.1 2θ for the beta phase) [33]. The latter can be explained by the α to β phase transformation that starts to occur at around 1600 °C, in the presence of a liquid Y_2O_3–MgO-containing phase through a solution–reprecipitation mechanism [34]. The peaks relative to the sintering aids disappeared almost completely after heating, because of their incorporation into an amorphous intergranular phase enhancing the homogeneous distribution of liquid phase at the grain boundary [35–37]].

The morphology of the Si_3N_4 foams emulsified with different alkanes is shown in Fig. 2. The microstructures of these surfactant stabilized foams show the presence of highly interconnected pores (open cells) because the thin liquid films among the bubbles rupture during drying and when adjacent oil bubbles come into contact; in contrast to particle stabilized Si_3N_4 based foams which possess closed pores [38–40], the displacement of powder from the interface is thermodynamically unfavorable, as explained in Ref. [2]. A weak degree of packing can be observed among the particles in the un-sintered foams, due to absence of a binding agent and the fact that no pressure was applied to consolidate the green body, and in the sintered foams due to a limited degree of sintering. Octane and decane un-sintered foams had different average cell sizes (36 ± 1.4 µm and 58.3 ± 2.3 µm, respectively).
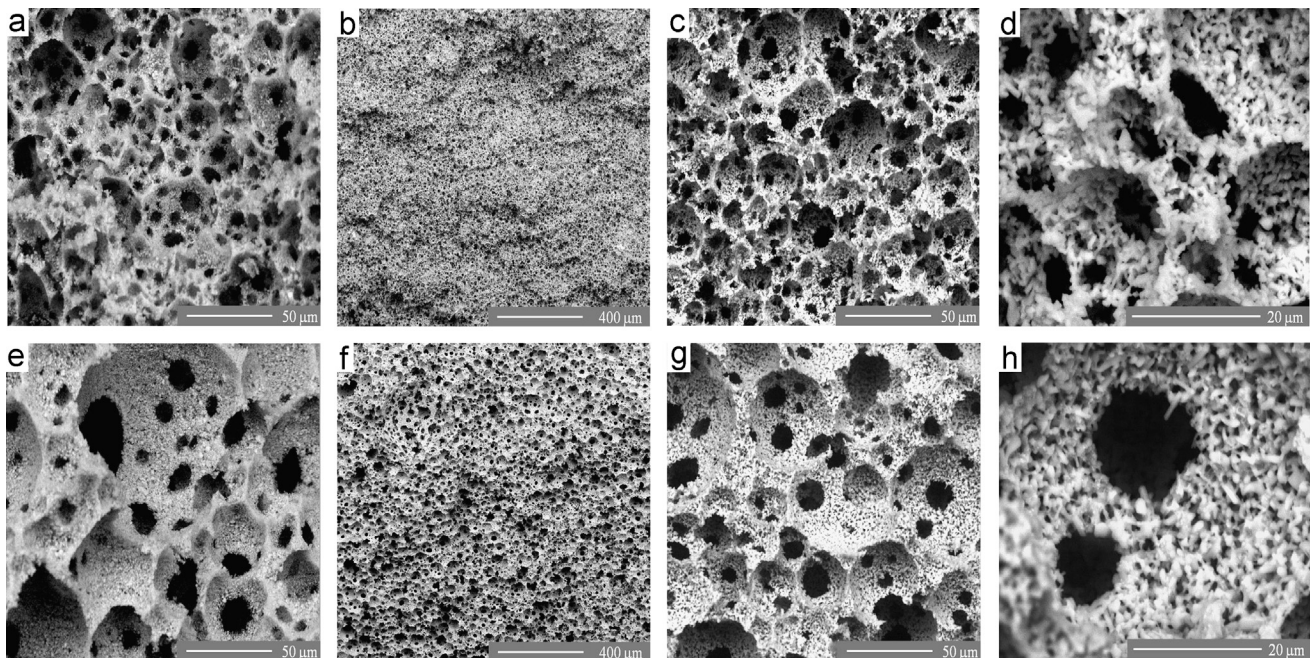

Fig. 2. SEM images of the fracture surface of Si_3N_4 foams: a) octane (un-sintered); b) octane (sintered, general view); c) octane (sintered, higher magnification); d) octane (sintered, detail of cell walls and struts); e) decane (un-sintered); f) decane (sintered, general view); g) decane (sintered, higher magnification); h) decane (sintered, detail of cell walls and struts).