Journal of the European Ceramic Society 36 (2016) 423–428

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Out-of-furnace oxidation of SiCN polymer-derived ceramic aerogel pyrolized at intermediate temperature (600–800 °C)

E. Zera[a],*, W. Nickel[b], S. Kaskel[b], G.D. Sorarù[a]

[a] *Dipartimento di Ingegneria Industriale, Università di Trento, Via Sommarive 9, 38123 Trento, Italy*
[b] *Department of Inorganic Chemistry, Dresden University of Technology, Bergstraße 66, D-01062 Dresden, Germany*

ARTICLE INFO

Article history:
Received 5 August 2015
Received in revised form 23 October 2015
Accepted 25 October 2015
Available online 7 November 2015

Keywords:
Polymer-derived ceramic
Polysilazane
Aerogel
Porosity
Pyrophoricity

ABSTRACT

The polymer-to-ceramic transformation of a polysilazane/divinylbenzene aerogel leading to SiCN aerogel was studied. The pre-ceramic samples were obtained by crosslinking a commercially available polysilazane with divinylbenzene in a highly diluted solution. Wet gels were supercritically dried using CO_2 to get the pre-ceramic aerogel. The weight change during pyrolysis in flowing argon was studied by thermogravimetric analysis (in-situ measurements) and by measuring the weight change on samples pyrolyzed in a tubular furnace after cooling down to room temperature (ex-situ measurements). The structural transformation was followed by infrared spectroscopy while the microstructural changes were studied by nitrogen adsorption analysis. Results point out that samples pyrolyzed at intermediate temperature, i.e., around 600–800 °C, react with the laboratory atmosphere forming Si—O bonds and Si—OH moieties. This out-of-furnace oxidation leads to an uncontrolled increase of the oxygen content of the pyrolyzed ceramics and eventually reduces the microporosity of the samples and its stability.

1. Introduction

Pyrolysis of a pre-ceramic polymers is an emerging technique that is used to produce amorphous and crystalline carbide or nitride-based ceramics. Compared to the conventional powder sintering approach, this technique has two main advantages: (i) shaping the components in the liquid state and subsequent conversion into the ceramic objects by a pyrolysis process in inert atmosphere allows the processing of components difficult to shape such as fibers, thin films or ceramic matrix composites (CMCs), (ii) the possibility to synthesize novel amorphous functional ceramics which cannot be obtained with any other process. Comprehensive reviews on Polymer Derived Ceramics, PDCs, covering the science and the application of PDCs can be found in the literature [1,2].

The PDC route has also been extensively applied to process micro-, meso- and macro-porous ceramics using a variety of methods including direct foaming [3], the use of sacrificial templates [4] or chemically bonded polymeric "spacers" [5], the HF etching of silica nanoclusters [6] and the use of porous xerogels or aerogels as starting materials [7,8]. A review of the synthesis of porous SiOC ceramics from polysiloxane has been reported by Kumar and Kim [9].

A different strategy to produce micro-meso porous ceramics from the polymer route consists in quenching the porosity, which spontaneously forms during pyrolysis in the temperature interval of 500–700 °C. This porosity is generated by the evolution of small molecules like CH_4 and H_2 and spontaneously closes-up at temperature above 700–800 °C. For this reason it is known as "transient porosity" [5,10,11]. Accordingly, many researchers tried to take advantage of the transient porosity to fabricate porous ceramics for different applications such as membranes, adsorption materials, etc. In these studies the materials often showed either a high level of oxygen or a high reactivity toward humid environment. For example, Maddoks et al. [12] investigated the production of membranes starting from polycarbosilane cross-linked with divinylbenzene and pyrolized in a temperature range between 600 and 1000 °C. They confirmed the formation of a transient microporosity at 600–700 °C due to evolution of gaseous by-products formed during the ceramization reactions. However, porosity of the samples pyrolyzed at 600 °C was found not to be stable upon hydrothermal treatment at the same temperature (600 °C), revealing a chemical instability of these pores in humid environment. Also Ciora et al. [13] faced problems to interpret the behavior of polycarbosilane based nanoporous membranes in high temperature steam environment. Bazarjani et al. [14] synthesized microporous

---

* Corresponding author.
E-mail address: Emanuele.zera@unitn.it (E. Zera).

http://dx.doi.org/10.1016/j.jeurceramsoc.2015.10.038

nanocomposites of Si—C—N—(O)/Ni with stable microporosity up to 700 °C but reported also a Ni free control sample that, after pyrolysis at 700 °C, was showing negligible SSA and more than 13%wt of oxygen without explaining the source of such a high amount of oxygen in the sample. Recently Schitco et al. [15] deeply investigated the possibility to stabilize this autogenic microporosity for the three main classes of pre-ceramic polymers, i.e., siloxane, carbosilane and silazane, by pyrolysis treatment performed in ammonia. Also in this study an unexpected high amount of oxygen was observed in SiC and SiCN samples pyrolyzed at 750 °C, however, no explanation was given for such high oxygen contamination.

We propose that, in the case of oxygen-free polymeric precursors, such as polycarbosilanes or polysilazanes, the unexpected oxygen presence in PDC samples pyrolyzed at intermediate temperatures could be due to an out-of-furnace reaction with oxygen and moisture of the air. This would explain the presence of oxygen as a post-pyrolysis effect and would clarify many experimental findings that authors in PDC field constantly face like ubiquitous presence of oxygen at low pyrolysis temperature and instability of microporosity in O_2 and/or steam environment. Accordingly, we present results of the structural and microstructural evolution of polysilazane-derived SiCN ceramics from room temperature up to 1000 °C. We have investigated the material in the form of an aerogel with high initial surface area and porosity in order to enhance potential surface reactions of the pyrolyzed material with the laboratory atmosphere and therefore facilitate their detection.

2. Experimental

2.1. Aerogel synthesis and pyrolysis

Polysilazane aerogels, with a nominal porosity of 70 vol%, were produced according to a general procedure developed in our laboratory [16] and applied by Nguyen et al. [17] to the SiCN system. Briefly, 3.06 g of PSZ-20 (Kion defense technology), 1.86 of divinylbenzene (DVB, Sigma–Aldrich, mixture of isomer 80%), 9.18 g of cyclohexane (Alfa Aesar, HPLC grade) are mixed together in a PTFE liner of a Parr Digestion Vessel (Parr Instrument) and stirred for 5 min with a magnetic stirrer. Then, in order to promote the hydrosilylation reaction between the Si—H bonds of the polysilazane and the vinyl groups of the DVB [18], 11 µL of Karstedt's catalyst solution (2%Pt, in xylene, Sigma–Aldrich) were added and the solution was stirred for additional 15 min. All these operations were performed under a gentle Argon flow to avoid contamination with the laboratory atmosphere. After sealing, the pressure reactor was put in an oven at 150 °C for 20 h. The obtained gels were demoulded as cylindrical monoliths and washed with an amount of clean cyclohexane equal to 5 times the volume of the gels once a day for three days, in order to remove catalyst and eventually unreacted reagents. After the last washing step, the gels were charged in a home-built supercritical drier. The gels were kept soaked with liquid in a glass boat and the cyclohexane was exchanged with liquid CO_2 (approximately same volume of liquid CO_2 and cyclohexane) twice a day for five days. The fifth day the drier was brought to 45 °C and the pressure rose up to 100 bar. After 1 h the supercritical CO_2 was evacuated paying attention of keeping a depressurization rate lower than 1 bar/min. Care was taken to avoid prolonged contact with lab atmosphere and accordingly the samples were put in polyethylene tubes with screw cap sealed with Parafilm(TM) and stored in a desiccators until used for the characterization tests or pyrolysis.

Pyrolysis of the polysilazane/DVB aerogels were performed at various temperature in an alumina tubular furnace (Lindbergh blue) under 100 mL/min argon flow, taking care of purging the furnace before starting the treatment for at least 20 h due to the large inner volume of the alumina tube (9 L). The furnace was allowed to cool down to room temperature – keeping the Ar flow – before opening it to retrieve the aerogel samples.

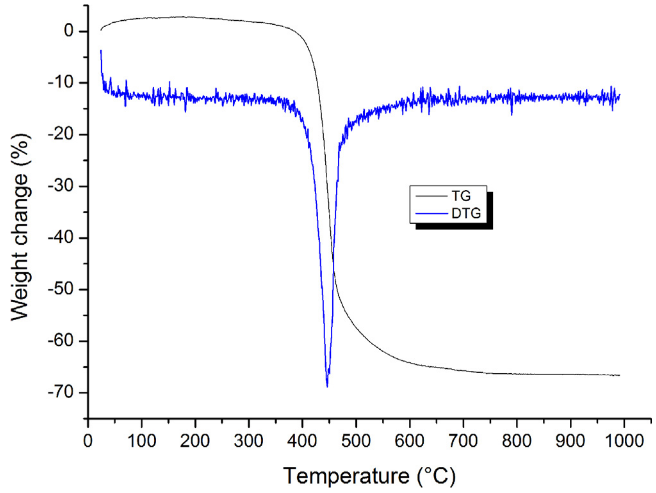

Fig. 1. TGA and its derivative, DTG, recorded on the polysilazane/DVB aerogel in flowing argon showing the polymer-to-ceramic transformation.

2.2. Samples characterization

The weight loss during pyrolysis was measured in situ by means of thermogravimetric analysis (TGA) and ex-situ measuring the weight of the samples pyrolyzed in the tubular furnace before and after pyrolysis. Thermogravimetric analysis was performed on a thermobalance (Netzsch STA 409) evacuating and refilling the whole instrument with pure Argon 3 times before the analysis. Approximately 30 mg of aerogels were used for the measurement with a heating rate of 10 °C/min up to a maximum temperature of 1000 °C, under an Argon flow (100 mL/min). The linear shrinkage was evaluated measuring 5 times the dimensions of regularly cut samples with a caliper before and after the pyrolysis treatment.

The structural evolution associated with the polymer-to-ceramic transformation was studied by means of Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. DRIFT spectra were recorded using a VERTEX 70/70 v FT-IR spectrometer (Bruker) on 1 mg of sample diluted with 300 mg of dry KBr, 128 scan with a resolution of 1 cm^{-1}.

The microstructural changes and the porosity evolution during pyrolysis were studied by N_2 adsorption analysis. The nitrogen physisorption tests were performed on a Quadrasorb SI Surface Area Analyzer (Quantachrome Instruments) and the isotherms were analyzed with AsiQwin 3.01 software. SSA values were calculated by multipoint BET method in pressure range P/P_0 0.05–0.2. The micro- and small mesopore size distribution was evaluated by the slit/cylindrical QSDFT kernel of AsiQwin software assuming nitrogen on carbon at 77 K. The BJH kernel on desorption branch was also used for the analysis of pores in the meso-and small macropores range.

3. Results and discussion

3.1. TGA analysis and weight losses measured for the samples pyrolyzed in the tubular furnace

The thermogravimetric curve measured on the aerogel sample is reported in Fig. 1. TGA curve shows, beside a slight weight increase below 50 °C due to a buoyancy effect, a major weight loss step centered at 450 °C, followed by a tail at higher temperature which ends