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ScienceDirect

Ceramics International 41 (2015) 10725–10729

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Mechanical characterization of micro- and nano-porous alumina

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Received 25 March 2015; received in revised form 28 April 2015; accepted 3 May 2015
Available online 13 May 2015

Abstract

Advanced membrane concepts are based on thin layers that require a mechanically robust porous substrate material. Aiming at the use in pre-combustion systems, alumina substrate with different pore sizes were characterized with respect to their mechanical properties. Elastic moduli and fracture stresses were assessed using ring-on-ring bending tests. Furthermore, elastic moduli were compared to data obtained from indentation tests. Although porosity of the micro- and nano-porous materials were equal, elastic moduli and fracture stress values revealed significant differences, indicating that based on mechanical considerations the nano-porous material is far superior, although initial permeation test indicate difficulties in using it as porous substrate. Elastic moduli showed good agreement with a model based on the load-bearing contact area. Microstructural investigations supported that the higher strength of the nano-porous material is a result of a larger contact area between grains.

Keywords: B. Porosity; C. Mechanical properties; E. Membrane; Ceramics; Pore size

1. Introduction

Energy production with fossil power coal-fired plants contributes strongly to the global CO_2 emissions. The detrimental effect of CO_2 onto the environment led recently to significant interest in CO_2 reduction concepts. Main concepts are: (1) post-combustion, (2) oxyfuel combustion, (3) pre-combustion, which are discussed in detail in [1].

In the pre-combustion concept, the carbon content is removed from the fuel before it is burned [2]. First, it is converted into a synthesis gas that primarily consists of CO and H_2. Then the CO reacts with steam in a shift reactor to produce CO_2. The CO_2 is thereafter separated and the remaining H_2-rich gas is combusted in a gas turbine, which results in water as exhaust gas. Advantages are that multiple fuels might be used and that the power plant can also be used for the production of hydrogen and chemicals. A disadvantage in comparison with the other concepts is that it can only be implemented into new power plants [1]. Membrane units are an alternative to solvent absorption columns [3]. The membrane needs to withstand operating temperatures in the range of 200–350 °C, pressures in excess of 20 bar and reactive gaseous components of the shifted gas, i.e. CO, CO_2, H_2, H_2O, H_2S. Furthermore the membranes must combine a high H_2 permeability with a sufficient H_2/CO_2 selectivity [4].

With respect to application relevant membrane designs, the most efficient solution to obtain high permeation rates appears to be a thin membrane layer with a typical thickness < 100 μm supported by a porous substrate [5,6], in the case of pre-combustion for H_2/CO_2 separation microporous membrane layers based on SiO_2 and ZrO_2 variants appear to be promising [4]. The porous substrate provides mechanical stability of the entire membrane structure [5]. Considering that the structural integrity has to be warranted, knowledge of the deformation and fracture behavior are of great importance for proposed porous substrate materials, requiring a characterization of elastic modulus and fracture strength [7,8]. The elastic modulus links applied strains to induced stresses, whereas the strength gives the stress limit that the material can sustain in terms of a discrete failure probability [9]. Hence, the present study focuses mainly on these two aspects.

The porous ceramic substrate should have both high permeability and high mechanical strength. Whereas the permeation increases with increasing porosity, the strength decrease with increasing porosity [10], requiring optimization with respect to necessary porosity and microstructure. Although a large number

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http://dx.doi.org/10.1016/j.ceramint.2015.05.007
0272-8842/

of studies exist on the effect of porosity on the strength of ceramic materials [11,12], a study that compares micro- and nano-porous materials for a particular porosity appears to be absent.

In the current work fracture strength and elastic modulus of micro- and nano-porous materials are characterized using ring-on-ring bending tests. Furthermore, elastic moduli were compared to data obtained from indentation tests. Microstructural studies aid the interpretation of the data.

2. Experimental

A modified slip casting process was used for the manufacturing of nano-porous substrates. First, a slurry was prepared adding α-Al_2O_3 powder (AKP30, Sumitomo, Japan) with a mean particle size of 0.32 μm to a 0.02 M HNO_3 solution. The slurry was treated for 15 min by an ultrasonic device (Sonifier 450, Branson, USA) for homogenization and crushing of agglomerates. Then the liquid was removed by a polymeric membrane (support-800-0.8 μm, diameter 47 mm, Pall, USA) of a suction filter device. The filtration process was supported by a vacuum pump on the permeate side. The filtering cake was dried for 10 h in the suction filter without further evacuation on the permeate side. Afterwards, the α-Al_2O_3 discs were sintered for 1 h at 1100 °C in air (heating and cooling ramp 2 K/min). The final geometry of the nano-porous substrates (diameter 39 mm, thickness 2.4 mm) was obtained by grinding and lapping. For further improvement of the surface quality, the surface was polished using diamond pastes with 6 μm and 3 μm particles, respectively. Finally, the samples were cleaned by ultrasonic treatment in ethanol and subsequently dried.

For comparison, commercial α-Al_2O_3 substrates were characterized in this study, which were delivered by the project partner Atech innovations GmbH (Gladbeck, Germany). Manufacturing of these substrates was based on extrusion of coarse, edged α-Al_2O_3 powders using confidential parameters.

Elastic modulus and fracture stresses were determined using bi-axial ring-on-ring bending test following ASTM C1499. The central displacement of the specimen was recorded with a sensor that contacted the lower surface of the sample (tensile surface). The loading rate was 100 N/min in all tests. All investigated samples fractured at a displacement value much smaller than half of the specimen thickness, which is a prerequisite for the linear elastic stress–strain analysis (ASTM C1499-05). The mechanical properties were determined from the fracture stresses and load–displacement data obtained in ring-on-ring bending test (specimens thickness 1 mm, inner support ring 7 mm, outer loading ring 15 mm). Details of the ring-on-ring fracture tests along with the equations used for evaluation can be found in [13,14]. Characteristic strength σ_0 and Weibull modulus m were derived using a maximum likelihood method as outlined in ASTM C1239-07.

For comparison the elastic modulus was also assessed using Vickers hardness impression tests, which were introduced into polished cross-sections using a micro-indentation device (Helmut Fischer KG, Germany, maximum load 1 N), and a nano-indentation device (CSM, Switzerland, maximum load 500 mN) as outlined in [15–18].

Microstructural investigations of as-received and tested materials were performed by light (LM, CSM instruments) and scanning electron microscopy (SEM, Zeiss Supra 50) on cross-sections prepared by grinding with abrasive papers followed by polishing to mirror finish. Porosity and pore size distributions were evaluated using a mercury porosity analyzer (Pascal 440). The grain contact area was derived from the mean contact area and the mean particle size. It was calculated from the measured lengths in the cross-sectional micrographs. The narrowest width of each junction position was measured and then added resulting in a mean contact area and then divided by the mean particle size.

3. Results

Mercury porosimetry revealed for the substrate materials produced from Atech and IEK-1 powder almost identical porosities of 42.0% and 43.5%, respectively. However, as can be seen in Fig. 1, the pore size distributions differed strongly. The pore size of Atech powder based substrates was about 2–5 μm and the pore size of the IEK-1 based substrates about 30–40 nm, i.e. the former material was micro- and the later nano-porous.

The difference in pore sizes was also verified by microstructural analysis. Polished cross-sections and fracture surfaces of both materials in Fig. 2 clearly verify the large pore-size difference. Furthermore, the Atech powder based substrates showed coarse grains with an average grain size of 50 μm, whereas the IEK-1 powder based substrates had fine grains with an average grain size of 300 nm.

The ring-on-ring tests along with the statistical evaluation yielded characteristic strengths of 42 ± 1 MPa for the Atech powder based substrates and a much higher value of 157 ± 11 MPa for the IEK-1 powder based material; the Weibull moduli were 7 ± 1 and 3 ± 1 (see Table 2), respectively. Furthermore, the ring-on-ring bending test load–displacement curves yielded elastic moduli of 48 ± 10 GPa for the Atech and 102 ± 13 GPa for the IEK-1 powder based specimens (see Table 2), i.e. again significantly higher values for the nano-porous material.

For a comparison nano-indentation tests have been carried out with loads of 5 mN and 10 mN. Obviously indentation testing yields only the local property of the material [19], which for very low loads should correspond to the literature

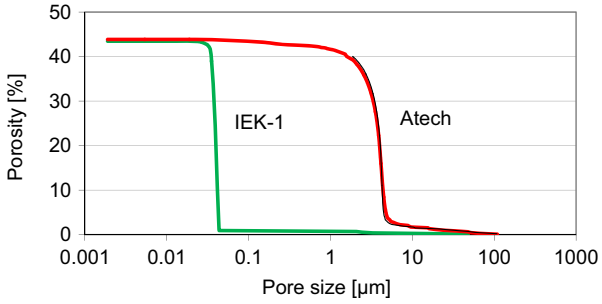

Fig. 1. Pore size distributions of IEK-1 substrate and Atech substrate.