Acta Materialia 107 (2016) 261–272

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Identification of a damage criterion of a highly porous alumina ceramic

D. Staub [a, b], S. Meille [b, *], V. Le Corre [a], L. Rouleau [a], J. Chevalier [b]

[a] IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France
[b] Université de Lyon, INSA-Lyon, MATEIS CNRS UMR5510, Villeurbanne, France

ARTICLE INFO

Article history:
Received 4 November 2015
Received in revised form
21 January 2016
Accepted 28 January 2016
Available online xxx

Keywords:
Porous ceramics
Indentation
Multiaxial damage criterion
Densification
Inverse approach
Finite element method

ABSTRACT

This paper aims at identifying the multiaxial compression behavior of highly porous ceramics used as catalyst supports. For this purpose, instrumented spherical indentation tests are performed, together with uniaxial and hydrostatic compression tests. A transition from a brittle to a damageable behavior with densification of the material is noted when increasing the triaxiality of the test. The collapse of large pores is shown as being responsible for the densification phenomenon, as confirmed by SEM and mercury intrusion porosimetry. A multiaxial damage criterion is proposed and identified thanks to a numerical finite element model.

The results described in this paper coupled with a previous work (Staub et al., *Oil and gas science and technology 2015, vol 70, n° 3, 475–86*) on the behavior of the same material under tension loading, allow for the first time to define a multiaxial criterion both in tension and in compression for highly porous ceramics. These materials are shown to present a typical behavior of dense ceramics in tension, whereas in compression, their behavior is close to that of porous rocks.

1. Introduction

Porous ceramics offer a growing interest for multifunctional applications such as construction materials (autoclaved aerated concrete, gypsum boards and nanoporous silica for insulation), biomaterials (bone substitutes), materials for energy production (single oxide fuel cells) and filtration (Diesel Particulate Filters, water treatment, liquid aluminum filtration, adsorption and catalysis). A high porous volume fraction is often targeted for such applications to ensure lightness, thermal insulation, acoustic absorption, ion exchange, filtration, cell accessibility, surface sorption and catalytic reaction [1]. On the other hand, sufficient mechanical properties are also required to withstand in use solicitations.

The present study focuses on highly porous γ-alumina used as catalyst carrier for oil refining. Current investigations concentrate on the improvement of catalytic performance, with a general trend to increase the porous volume and the specific surface area of the supports. However, this increase in porosity often induces a decrease of their mechanical properties. Yet, mechanical strength is a key parameter for catalysts supports, which are submitted to various types of mechanical loading during catalytic activation, transport and in-service life. For instance, hydro-treatment catalysts are used in large fixed bed reactors of several meters high and wide. Production processes induce cyclic fluid pressures and deformations on granular stacks. Locally, catalysts grains are submitted to multi-axial compression, bending and shearing. Therefore, a good understanding of the mechanical behavior of the supports is needed under uniaxial and multi-axial loads, in tension and in compression.

Like dense ceramics, porous ceramic materials generally exhibit a brittle fracture when subjected to tensile stresses. Brittleness indicates the absence of plastic deformation before fracture, which originates from tensile stresses concentration at the edge of an existing critical flaw [2]. Such behavior has already been observed with catalyst supports composed of mixed oxides such as transition alumina [3–6].

In contrast, under compressive stresses, a brittle to quasi-plastic transition is generally observed in porous ceramics and rocks when increasing the confinement rate [7,8]. Unlike classical plastic damage mechanisms, quasi-plastic damage appears through micro-cracking and/or densification mechanisms. Such a behavior is conveniently studied by spherical indentation [9–13]. Spherical

* Corresponding author.
E-mail address: sylvain.meille@insa-lyon.fr (S. Meille).

http://dx.doi.org/10.1016/j.actamat.2016.01.071
1359-6454/

indentation is particularly suited for the mechanical characterization of small irregularly shaped samples like catalyst supports. This technique also offers the advantage to induce theoretically an elastic contact at early stage of loading. The elasto-plastic transition of the material can thus be observed [9]. Moreover, the material volume tested during spherical indentation is larger than with sharp tips, minimizing the response sensibility to microstructure heterogeneities.

As a consequence, porous ceramics show a different mechanical behavior under tension and compression loadings. Such asymmetrical mechanical behavior is usually represented by a yield criterion sensitive to the hydrostatic pressure. The most common used criteria are Mohr-Coulomb and Drücker-Prager criteria [14–16]. However, those criteria do not account for the densification mechanism induced in porous ceramics at high pressure levels. A better representation of this phenomenon can be obtained by closing the yield surface with a "cap" for high pressures. In particular, the cap-model [17] is the association of Drücker-Prager yield surface with a closing ellipse in the meridional plane. This criterion has been successfully used by Wong et al. [18] to represent the behavior of porous sandstone in multiaxial compression.

The identification of such behavior laws is possible thanks to a finite element analysis of the indentation test. Material parameters are determined by minimizing the error between the numerical force–displacement curve and the experimental behavior. Unlike pyramidal indentation, a unique solution to the optimization problem can theoretically be obtained with spherical indentation [19,20]. This method has been successfully used to identify the elasto-plastic behavior of heterogeneous materials such as argillite [21], human femoral cartilage [22,23] and plaster with a porous volume up to 60% [13].

In order to balance the lack of knowledge concerning the mechanical behavior of catalyst supports under compressive stresses, the objective of this study was to give an insight of the damage mechanisms involved. In particular, three types of tests with various confinement rates were performed to characterize the brittle/quasi-plastic transition: uniaxial and hydrostatic compression tests, and spherical indentation. Furthermore, this study aimed at identifying a damage criterion accounting for potential densification of the material, by coupling spherical indentation data and a numerical analysis of the test, and solving an optimization problem.

2. Materials and methods

2.1. Materials – catalysts samples

The samples were cylindrical extrudates made of highly porous γ-alumina, processed by IFPEN (Solaize, France) with the aim of mimicking industrial production of the material. They were typically prepared by shaping of boehmite [24] from precipitation of aluminum salts, washing with deionized water and drying. Boehmite powder was kneaded by acid solution (peptization) then with basic solution (neutralization). Subsequently, the paste was extruded through a die with a unique cylindrical hole, then dried and calcined. The sample final diameter was 1.5 mm and its final length varied from 3 to 6 mm.

As presented on Fig. 1, the material exhibited a bimodal porosity with mesopores (between 2 and 50 nm) and macropores (larger than 50 nm) following the IUPAC classification [25]. Its physical properties are presented in Table 1, as determined by mercury intrusion porosimetry and nitrogen physisorption (BET specific surface area).

For compression and indentation tests, the surfaces of the samples were hand-polished with diamond papers down to 1 μm particle size. Moreover, for indentation tests, polished samples were pasted vertically on a steel plot with a thin layer of glue. Surface roughness (R_a) was measured with a profilometer and was about 80 nm.

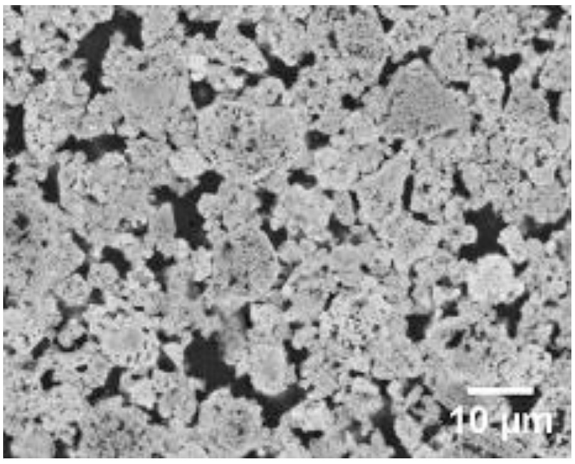

Fig. 1. SEM observation (Backscattered Electron Imaging mode) of a polished section of a γ-alumina sample.

2.2. Observation of sample structure

Observations of the fracture surfaces of the samples were carried out with a SEM Supra 40 (Zeiss, Germany). Samples were glued on the sample holder with conductive double sided carbon adhesive tape and their sides were covered with conductive carbon paint. To avoid charge effects, a 2 nm thick layer of Pt/Pd-metal was deposited on the surface of the samples.

2.3. Uniaxial compression test

The uniaxial compressive strength was measured with an Bose ElectroForce® 3200 test instrument (Prairie Valley, USA) with a 220 N load cell. Compressive tests were performed on previously polished cylindrical supports (diameter 1.5 mm, height 3 mm), at a crosshead speed of 0.2 μm/s. As presented in Fig. 2, an hemisphere of 3 mm of diameter was placed between the sample and the upper compressive platen, in order to compensate the lack of parallelism of the sample's faces and obtain an homogeneous load distribution in the sample's section. Platens and hemisphere were lubricated with a Teflon-based spray to reduce contact friction. For each test, a load/unload cycle was performed between 1 N and 10 N before loading the sample until fracture. 14 samples were tested.

2.4. Hydrostatic compression test (non-intrusive mercury porosimetry)

Hydrostatic loading was performed in the hyperbaric chamber of a mercury porosimeter (AutoPore IV 9500, Micromeritics, Norcross, USA) in order to determine the pressure corresponding to the initiation of samples damage. A single 5 mm long support was sealed under primary vacuum in an impermeable polymeric membrane, and placed in the 15 cc cell of the porosimeter. An increasing hydrostatic pressure was applied to the sample, up to 100 MPa, by increasing mercury volume in the cell. Three samples were tested. To calibrate the test and obtain the real volumetric variation of the sample, preliminary tests were performed on an empty polymeric membrane sealed under vacuum. Thus, a hydrostatic pressure versus volume variation curve was obtained. After the test, the induced volume variation was measured by comparing