Journal of the European Ceramic Society 35 (2015) 3917–3926

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

High temperature behavior of monodisperse porosity in alumina films

Robert M. Pasquarelli*, Jefferson J. do Rosário, Lars Rath, Gerold A. Schneider, Rolf Janssen*

Institute of Advanced Ceramics, Hamburg University of Technology (TUHH), 21073 Hamburg, Germany

ARTICLE INFO

Article history:
Received 13 May 2015
Accepted 3 June 2015
Available online 10 July 2015

Keywords:
Alumina
Porous materials
Pore/porosity
Sintering

ABSTRACT

Understanding the sintering behavior of tailored porosity in thin-film ceramics is essential for applications in photonics, thermal coatings, catalysis, and electrodes. Alumina films exhibiting a random distribution of templated pores with monodisperse size were produced by spin coating from suspensions of alumina powder and polystyrene microspheres. The microstructural evolution, grain size, pore size, and their respective distributions were determined as a function of the initial volume fraction of templated pores, sintering temperature, and time. The behavior between grains and pores at the surface and in the bulk was evaluated and compared to other disordered and ordered porous alumina systems. Above a pore fraction threshold of ~9 vol%, increasing pore fractions retarded grain growth, with smaller grains observed between close pores. While the average bulk pore size did not change with sintering temperature, time, or pore fraction, it did produce a broader pore size distribution with different pore geometries.

1. Introduction

While ceramic materials with tailored porosity have been widely studied for decades, structures with different length scales and for new applications are constantly being developed. Films with ordered and disordered arrangements of pores have attracted interest for thermal barrier coatings (TBCs) by reducing thermal conductivity [1] and by taking advantage of photonic properties [2,3]. The pore periodicity of inverse opals is well-known to affect the propagation of electromagnetic radiation in optical films [2] and has also been utilized for electrochemical applications [4]. Additionally, disordered structures have been considered for random lasing and resonance-dependent Anderson localization [5,6], as well as for omnidirectional reflectors, TBCs [7], and structural coloration [8,9] due to their strong scattering of light.

Their performance requires control over pore structure, size, and spatial distribution. Well-defined and tailored porosity is typically achieved by replica techniques, using sacrificial templates, or direct foaming methods [10,11]. These processes can generate pores much larger than the average particles size and any intrinsic porosity and allow for the preparation of materials with disordered, monomodal porosity and even materials with ordered (periodic), monomodal porosity. The latter are referred to as three-dimensionally ordered macroporous (3DOM) materials, or as inverse opals, and are typically prepared by the infiltration of self-assembled polymer sphere templates. Core–shell, macroporous structures prepared by heterocoagulation have also been demonstrated [12]. For emerging optical and thermal radiation applications, the pore sizes should be on the wavelength scale of the radiation, with pores diameters between 200 nm to 3 μm being of interest for visible–infrared applications. In this work, we will consider an initial pore size of ~750 nm as a representative size in this range.

While intrinsic pores typically are eliminated during the early stages of sintering, larger and templated pores in the films can remain stable, shrink, or grow. For functional applications, thermal stability is necessary during processing and under operating conditions, and such changes in the specified pore structure can be detrimental to performance [13]. There are various theories about the behavior of large pores under sintering conditions. Early theories extended to sintering by Kingery and Francois, based on the Mullins–Neumann N-6 rule, state that a pore intersected by grain boundaries will exhibit a surface curvature that depends on the number of coordinating grains and the dihedral angle [14]. Later work by Kellett and Lange instead argued for an equilibrium size at a given grain and a transition from convex to concave pore geometries proportional to grain growth [15]. Simulations by Pan et al. demonstrated that pores with irregular grains or distortions in symmetry always shrink regardless of coordination number and

* Corresponding authors.
E-mail addresses: robert.pasquarelli@tuhh.de (R.M. Pasquarelli), janssen@tuhh.de (R. Janssen).

http://dx.doi.org/10.1016/j.jeurceramsoc.2015.06.003
0955-2219/

that there is always a thermodynamic driving force to eliminate the pores [16,17]. Conversely, Slamovich and Lange showed that it is the number of diffusion paths and their characteristic diffusion distance (kinetics), not the coordination number (thermodynamics), that controls the behavior of large pores [18,19]. A clear, widely accepted consensus about pore stability has yet to be reached.

Additionally, the roles of different pore arrangements and pore size distributions in films are not fully understood. Detailed modelling and experimental work by Zhao and Harmer has studied the grain growth and evolution of random, large, templated pores (1–8 μm) in bulk alumina compacts [20–22]. The preparation and thermal stability of 3DOM alumina and yttria-stabilized zirconia have been investigated by Sokolov et al. [23] and Lashtabeg et al. [24,25], respectively, using pore sizes (450–1000 nm) in the range of optical interest. Sokolov et al. noted that structural degradation accompanied grain growth and that mass transport occurred from the struts to the nodes in such periodic structures [23]. Further understanding is still required about the behavior of individual pores and the consequences of bring pores into closer proximity with increasing pore fractions in ordered and disordered structures. In addition, such insights are valuable in the field of porous ceramics in the general sense, with a broad range of applications in catalytic supports [26,27], absorption and filtration [26], electrodes in fuel cells and batteries [4,28].

In this work, we seek to study pore behavior and grain growth in thin-films under sintering conditions. Alumina films exhibiting a random distribution of templated pores with monodisperse size were produced by spin coating from suspensions of alumina powder and polystyrene microspheres. The microstructural evolution, grain size, pore size, and their respective distributions were determined as a function of the initial volume fraction of templated pores, sintering temperature, and time. The behavior between grains and pores at the surface and in the bulk was also evaluated. Lastly, the sintering behavior of the films was compared to and placed in context of understanding other disordered and 3DOM porous alumina systems.

2. Experimental

2.1. Preparation of suspensions and films with disordered porosity

A stock alumina suspension containing 50 vol% of 100 nm alumina powder (Taimei Chemicals Co.) and 1 wt% by solids content of the dispersant Dolapix CE 64 (Zschimmer & Schwarz GmbH) was prepared in deionized water by attritor milling at 500 rpm for 30 min in an alumina vessel using zirconia milling media. An aqueous suspension of monodisperse polystyrene (PS) spherical particles (Microparticles GmbH, coefficient of variation ≤3%) with a diameter of 756 nm were concentrated from 10 w/v% as-received to 40 w/v% by centrifugation at 5000 rpm for 60 min. The coating suspensions were prepared by mixing the stock suspensions in a ball mill with zirconia milling spheres to produce final suspensions with 3, 6, 9, 15, and 30 vol% of PS by solids content. Single-crystal sapphire substrates (CrysTec GmbH, double-side polished, random orientation, 25 × 20 × 0.53 mm) and quartz substrates (Ted Pella Inc., 76 × 25 × 1 mm) were rinsed with deionized water and plasma cleaned (Polaron PT7160) under 0.5 mbar oxygen at 100 W for 20 min. Alumina films exhibiting a random distribution of templated pores were produced by spin coating (SPS Spin 150) 500 μl of the coating suspension onto the substrates at 1000 rpm for 60 s, followed by subsequent burnout of the PS particles in a muffle oven at 600 °C for 2 h. The average film thickness was determined by weight to be 7 ± 2 μm, depending upon the amount of PS suspension, and thus water, in the coating suspensions.

2.2. Film treatment and processing

Films at each PS content were annealed at 1200, 1400, and 1450 °C in a tube furnace under air atmosphere with 5 °C min^{-1} heating and 10 °C min^{-1} cooling rates. Annealing times were 2, 6, 12, and 24 h. Different approaches were used to reveal the internal structure of the films. Vertical cross-sections were cut with a Brilliant 220 diamond circular blade saw at 3000 rpm, a feed rate of 2 mm s^{-1}, and a depth feed steps of 50 μm per cycle. Ion milling (Gatan Model 600 DuoMill) was performed for 2 h under Argon using a single top gun set to 6° from the horizontal and operated at a gun voltage of 5 kV and gun current of 0.5 mA. Milling depths of about 900–1100 nm in the focal point of the ion beam and up to 600 nm depth at 5 mm distance from the center were achieved. Steeper angles of 12° and milling times of 3 h completely milled through the film down to the substrate. Grain boundaries were rendered visible following ion milling *via* chemical etching by immersing in boiling, concentrated phosphoric acid for 3–10 min and then rinsing with ethanol [29–31].

2.3. Characterization

The resulting surface and internal bulk microstructures were investigated by scanning electron microscopy (SEM, Zeiss Supra 55 VP). Grain size measurements were performed using the linear intercept method with a minimum of at least 250 grains measured per sample. Pore size analysis was performed using a custom automated routine in MATLAB with an average of 450 pores measured per sample. The program matched brightness and contrasts levels and converted the micrographs into binary images using a threshold filter. Templated pores were distinguished from cracks and intrinsic porosity by scanning open and closed disk elements of selected sizes across the image. Partially merged pores and pores at edges were eliminated. The final reported pore diameter is the equivalent diameter of a circle with an area equal to that measured for the porous features identified by the image analysis program.

3. Results and discussion

3.1. Microstructural assessment of films

Alumina films exhibiting a random distribution of templated pores with monodisperse size were produced from suspensions of alumina powder and PS microspheres, as described in the experimental section. The SEM images in Fig. 1 show an alumina film at various stages of processing. After spin coating, it was observed that all of PS microspheres at the surface were around the same depth, as seen in Fig. 1a. Given that the film thickness was on average an order of magnitude larger than the PS diameter (7 versus 0.756 μm), the effect cannot be the result of the PS microspheres simply resting on the substrate. Instead, it was attribute to either surface tension of the suspension or drying effects during the coating process.

Fig. 1b shows an alumina film after burnout of the template PS microspheres at 600 °C for 2 h. Two types of porosity were observable. The first type was the PS templated pores (601 ± 22 nm); the second type was the much smaller intrinsic porosity (30 ± 20 nm) that is inherent to the packing of the alumina powder. Throughout the remainder of the manuscript, the volume fraction of pores for a given sample shall refer to the fraction of PS to alumina in the suspension and, thus, refer only to the initial volume fraction of templated pores. The initial microstructure yielded large pores at the film surface and a grain size of 99 ± 33 nm, which resulted in a coordination number of 15–20 grains around a pore, when viewed in plane. The measured surface pore diameter was approximately 20% less than the starting PS microspheres (756 nm). This lower