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Quantification of void network architectures of suspension plasma-sprayed (SPS) yttria-stabilized zirconia (YSZ) coatings using Ultra-small-angle X-ray scattering (USAXS)

Antoine Bacciochini[a], Jan Ilavsky[b,*], Ghislain Montavon[a,**], Alain Denoirjean[a], Fadhel Ben-ettouil[a], Stéphane Valette[a], Pierre Fauchais[a], Karine Wittmann-teneze[c]

[a] SPCTS, UMR CNRS no. 6638, Faculté des Sciences et Techniques, Université de Limoges, 123 avenue Albert Thomas, 87060 Limoges Cedex, France
[b] Advanced Photon Source, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, USA
[c] Commissariat à l'Energie Atomique (French Atomic Agency), Centre du Ripault BP 16, 37000 Monts Cedex, France

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ABSTRACT

Suspension plasma spraying (SPS) is able to process a stabilized suspension of nanometer-sized feedstock particles to form thin (from 20 to 100 μm) coatings with unique microstructures. The void (pore) network structure of these ceramic coatings is challenging to characterize and quantify using commonly used techniques due to small sizes involved. Nevertheless, the discrimination of these pores in terms of their size and shape distribution, anisotropy, specific surface area, etc., is critical for the understanding of processing, microstructure, and properties relationships. We will show that one of suitable combinations of techniques providing sufficient detail is ultra-small-angle X-ray scattering (USAXS) and helium pycnometry, combined with scanning electron microscopy (SEM).

Yttria-partially stabilized zirconia (YSZ) coatings were manufactured by plasma processing of suspension of particles with average diameter of ~50 nm. Several sets of spray parameters (plasma gas mixture, spray distance, electric arc intensity, etc.) were used to generate plasma jets with different mass enthalpies and coefficients of thermal transfer and different heat fluxes transferred to the substrate. Free-standing coatings were studied as-sprayed and annealed at 800 and 1100 °C for 10 and 100 h (non-constrained sintering). Results indicate that the SPS coatings exhibit nanosized pore microstructure: average void size was about the same size scale as the feedstock size; *i.e.*, nanometer sizes with multimodal void size distribution. About 80% of the pores (by number) exhibited characteristic dimensions smaller than 30 nm. Total void content of as-sprayed SPS coatings varies between 13% and 20%. Most of the voids were found to be opened with only between one-tenth to one-third of voids volume being inaccessible by intrusion (not connected to either surface). During annealing, even at temperatures as low than 800 °C, the microstructure transformed: while the total void content did not change significantly, the void size distribution evolved toward larger sizes.

This unique void system, together with the nanometer scale of the particulate matrix itself, gave these coatings very low apparent thermal conductivity (in the order of 0.1 W m^{-1} K^{-1}), as rarefaction effect and phonon scattering mechanisms are very likely emphasized.

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1. Introduction

1.1. Finely structured (sub-micrometric scale) thermal barrier coatings

Plasma-sprayed yttria (8 wt.%) partially stabilized zirconia (YSZ) coatings are by far the most widely implemented thermal insulating barrier coatings (TBCs) in applications (aircraft engines, land-based power generation gas turbines, etc.) [1]. A conventional thermal insulation system is usually composed of four primary parts: (i) the ceramic top-coat; *i.e.*, the ceramic TBC, which is commonly manufactured using air plasma spray process; (ii) the

* Corresponding author.
Tel.: +1 630 252 0866; fax: +1 630 252 0862.
** Corresponding author. Current address: LERMPS – EA3316, Université de Technologie de Belfort-Montbéliard, site de Sévenans, 90010 Belfort Cedex, France. Tel.: +33 0 384 583 161.
E-mail addresses: ilavsky@aps.anl.gov (J. Ilavsky), ghislain.montavon@utbm.fr (G. Montavon).

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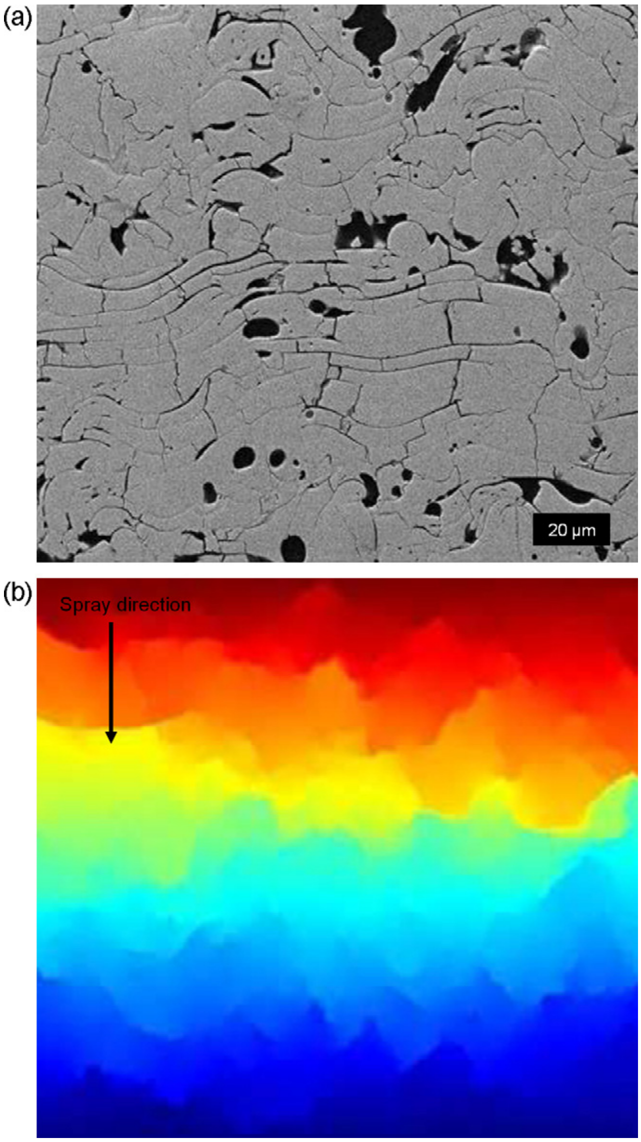

Fig. 1. (a) Typical architecture of an air plasma spray 8Y-PSZ TBC. (b) Computed 2D temperature gradient within coating depicted in (a) [6].

substrate materials, most commonly a superalloy or a refractory steel; (iii) an aluminum containing bond-coat (BC) located between the metallic substrate and the ceramic TBC; (iv) a thermally grown oxide (TGO), predominantly α-alumina [2], that growths between the ceramic TBC and the BC. The ceramic TBC behaves as the thermal insulator, the BC provides oxidation protection and behaves as a compliance layer and the metallic substrate sustains the structural loads. The TGO is an oxidation reaction product growing during the use (it keeps growing with time at high temperature) of the system and plays a relevant role in the BC/TBC adhesion and failure mechanism [3].

Applying such a system on top of components located in the hot zone of the turbine (*e.g.*, walls of combustion chambers, turbine diffusers, etc.) permits, with an adequate cooling at the back side of the component, to decrease its operating temperature by about 200 °C, allowing an increase in their life duration and/or an increase in the operating temperature (required for higher thermodynamic efficiency) [4].

The thermal insulation properties of the ceramic TBC (Fig. 1a) rely on the intrinsic low thermal diffusivity of the ceramic material as well as on the thermal resistance provided by voids embedded in

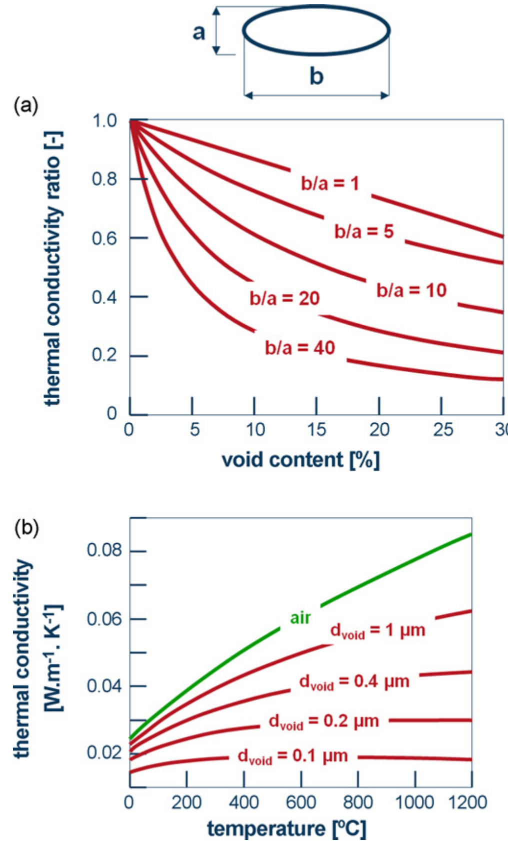

Fig. 2. (a) Evolution of coating apparent thermal conductivity *vs.* void content for various void aspect ratios following [9]. (b) Void equivalent thermal conductivity *vs.* temperature for various void diameter following [10] depicting the effect of rarefaction in the decrease in apparent thermal conductivity.

the microstructure [5]. For an example of the 2D computed thermal gradient within TBC, see Fig. 1b [6]. The voids result from stacking defects and stress relaxation within the TBC ceramic during coating manufacturing and subsequent cooling and spray parameters are optimized with respect to their content, size, shape, spatial repartition, etc. Also, the void network is used to tailor the apparent mechanical properties of the coatings (*i.e.*, apparent Young modulus, apparent coefficient of thermal expansion, etc.) in order to sustain thermomechanical loads during coating service [7].

As noted above, the void content, void size, and void shape play an important role in reducing the apparent thermal conductivity of a ceramic TBC [8]. As demonstrated first by Hasselman [9] by a 2D analytical model, the ceramic TBC layer apparent thermal conductivity varies as a function of the void content and the void shape factor. As depicted in Eq. (1), the higher the void content and the more elongated the void (longest axis oriented perpendicular to the heat flux), the lower the coating apparent thermal conductivity, Fig. 2a:

$$\frac{\kappa_{\text{coating}}}{\kappa_{\text{bulk}}} = \frac{1}{1 + (2/\pi) \times VC \times (b/a)} \quad (1)$$

where κ_{coating} is apparent thermal conductivity of the coating [$\text{W m}^{-1}\,\text{K}^{-1}$]; κ_{bulk} thermal conductivity of bulk material [$\text{W m}^{-1}\,\text{K}^{-1}$]; VC the void content [%] and (b/a) the void aspect ratio.

The void size also plays also an important role in the induced thermal resistance. Indeed, the smaller the void size, the lower the thermal conductivity of the gas entrapped in the void and so the higher the thermal resistance provided by the void. This is due to an evolution of the flow nature of the gas in the void. This nature depends upon the characteristic dimensionless Knud-