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Characterization of the closed porosity in plasma-sprayed alumina

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The porous phase of plasma-sprayed alumina was characterized using mercury intrusion porosimetry, water immersion methods, and small-angle neutron scattering. A comparison of the results shows that the intrusion techniques did not yield a full porous phase characterization. It has been found that while the amount of closed porosity was 1.4%(± 0.5%) of the sample volume, this volume accounted for only 60% of the total internal surface area. The smallest void diameter was found to be 10 nm.

1. Introduction

Plasma-sprayed ceramic deposits exhibit a complex microstructure composed of splats, unmelted particles and various types of voids [1]. The voids, generally called porosity, may be divided into two major classes: interlamellar pores and intralamellar cracks [2, 3].

The mechanical, thermal and other properties of the deposits depend on the microstructure [4, 5]. Thus, microstructural characterization needs to be unambiguously related to the measured properties. It is appropriate to question whether the “standard” porosity measurement techniques allow useful characterization of property–microstructure relationships or if the spectrum of techniques needs to be broadened.

Intrusion porosity measurement techniques, such as Archimedes’ (water) displacement and mercury intrusion porosimetry (MIP), are used to characterize the volume of open voids within these deposits. Based on the model of tubular voids, the MIP method also yields void size. Such characterization may not, however, be dependable if the voids are connected by necks or if their shapes differ excessively from the model assumptions. Both intrusion techniques yield the residual density of the sample, which may be compared with the skeletal density, thus allowing the volume of closed voids to be calculated. Neither of the techniques yields any information on closed voids [6].

Small-angle neutron scattering (SANS) is commonly used to study voids within solids [7, 8]. SANS is not limited by the connectivity and openness of the voids; however, a model of void shape may be required. Surface scattering (often called Porod scattering), applied in this study, is an example of a technique which does not require a model and is, therefore, especially useful for studies of void systems with complex shapes.

In previous SANS studies by the authors, significant anisotropy of the void system has been measured within thermal spray deposits [9]. The different anisotropies of the intralamellar pore and interlamellar crack systems were used to characterize each system independently. The total internal surface area in alumina deposits, produced with the water-stabilized plasma spray system [10], such as used in this study, was dominated by the intralamellar cracks, which represented more than 80% of the total void surface area within the deposits. Varying ratios of surface areas in these systems were found in the alumina and yttria-stabilized zirconia deposits manufactured with a gas-stabilized plasma spray system [11].

In this paper, we compare the results of the SANS surface measurements with the results of intrusion techniques and draw conclusions about the surface characteristics of closed voids within these deposits.

2. Experimental procedure

A 1.4 mm thick plasma-sprayed alumina deposit was produced by the water-stabilized plasma spray process (system PAL160[†], Institute of Plasma Physics, Czech Academy of Sciences, Prague, Czech Republic). This spray process results in generally the same type of deposits as produced by the standard atmospheric (gas-stabilized) plasma spray process [10, 12] at significantly higher spray rates. The deposit was sprayed on a mild steel substrate (20 mm wide, 100 mm long, and 2 mm thick) covered with a layer of salt (KCl). The salt

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[†] Information on commercial products is given for completeness and should not be considered as an endorsement by NIST.

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layer was dissolved in water after spraying so that a free-standing deposit would be obtained.

A mercury intrusion porosimeter Autoscan 33[†] (Quantachrome, FL) with filling apparatus as well as an Archimedes (water displacement) method described elsewhere [13], were used for porosity volume and (for MIP) pore-size measurements. The SANS studies were performed on the 8 m SANS Instrument at the Cold Neutron Research Facility, National Institute of Standards and Technology (NIST), Gaithersburg, MD.

2.1. Small-angle neutron scattering

The SANS studies focused on measurements of Porod scattering [14] to determine the surface characteristics of the voids. This technique yields quantitative information on surface area of interfaces within the deposits.

In the SANS experiment, a neutron beam passes through the sample and interacts with the interfaces within the sample. The interfaces are characterized by their scattering length density, ρ, which is a material characteristic. The Porod scattering occurs at high $\boldsymbol{Q}(\boldsymbol{Q} = 4\pi\sin\theta/\lambda$ is the scattering vector, 2θ is the full scattering angle and λ is the neutron wavelength [14]), where the scattered intensity, I, is proportional to the scattering contrast, $\Delta\rho^2 = (\rho_1 - \rho_2)^2$, between the materials (1 and 2) on both sides of the interface, to the interfacial surface area, S, and to Q as

$$I(\boldsymbol{Q}) = 2\pi|\Delta\rho|^2 S\boldsymbol{Q}^{-4} \quad (1)$$

The relationship between the intensity of the Porod scattering and the surface area for anisotropic scattering systems is discussed below and elsewhere [2]. Information about the smallest scatterer sizes within the sample can also be deduced from the minimum magnitude of the scattering vector, $\boldsymbol{Q}$, for which the Porod ($\boldsymbol{Q}^{-4}$) dependence holds.

Interfaces between materials with the same ρ (i.e. $\Delta\rho = 0$) are invisible for SANS, independent of the interfacial chemistry and crystal structure. This fact is used in the commonly employed technique of contrast matching [15], in which part of the void fraction within the sample is filled by a masking fluid with the same ρ as the skeletal material. This causes the scattering from the filled voids to diminish. This technique often takes advantage of the different scattering length densities, ρ, for (light) water (H_2O) and heavy water (D_2O). These are -0.558×10^{10} cm^{-2} for H_2O and 6.341×10^{10} cm^{-2} for D_2O [16] at room temperature. H_2O and D_2O are mixed together so the ρ of the mixture equals that of the solid material [15].

Samples containing more than one type of scattering interface may create a problem for data evaluation. The intensities scattered from different interfaces are added, each being proportional to the surface area of its interface according to Equation 1. This may complicate the evaluation of the contrast matching experiment, because an interface with a large difference in $\Delta\rho^2$ dominates the result. For example, the air–alumina interface ($\Delta\rho = 5.3 \times 10^{10}$ cm^{-2}) dominates the scattering by about 28 to 1 compared to the heavy water–alumina interface with $\Delta\rho \approx 1 \times 10^{10}$ cm^{-2}. To avoid this problem, multiple scattering was used to find the contrast match point in this experiment.

In the case of multiple scattering, the neutrons passing through the sample with a high volume of large scatterers are copiously scattered, which results in the broadening of the beam. This broadening is observed at small Q and is most dominant for long wavelengths. This broadening can be quantified as a variation in the width, r_c, of the Gaussian profile of the neutron beam intensity versus $\boldsymbol{Q}$. The r_c may be related to the volume of scatterers as well as to the $\Delta\rho$ of the materials [17]. The r_c dependence on the $\Delta\rho$ is complex but weaker than quadratic as is the dependence of Porod scattering intensity on the $\Delta\rho$. This, together with the fact that larger voids (which are more likely to scatter copiously) are more likely to be open, made the multiple scattering measurements more sensitive as a measure of quality of contrast match than the usually applied Porod scattering measurements.

3. Results

Mixtures of H_2O and D_2O (referred to as "masking fluids") were prepared with scattering length densities around the calculated scattering length density of plasma-sprayed grey alumina. After soaking samples for 48 h (the same as for Archimedes' porosity measurements), the multiple scattering experiment was carried out with a neutron wavelength of 1.8 nm The minimum r_c (the contrast match) was found for a mixture with mass fraction of 15% water and 85% heavy water, Fig. 1. The ρ for this mixture is 5.3×10^{10} cm^2, in agreement with the value calculated for grey alumina.

The Porod scattering was carried out with the neutron beam perpendicular to the deposit surface. In this orientation, the scattering vector $\boldsymbol{Q}$ is nearly parallel to the substrate plane. The results are dominated by the surfaces perpendicular to $\boldsymbol{Q}$, which in this

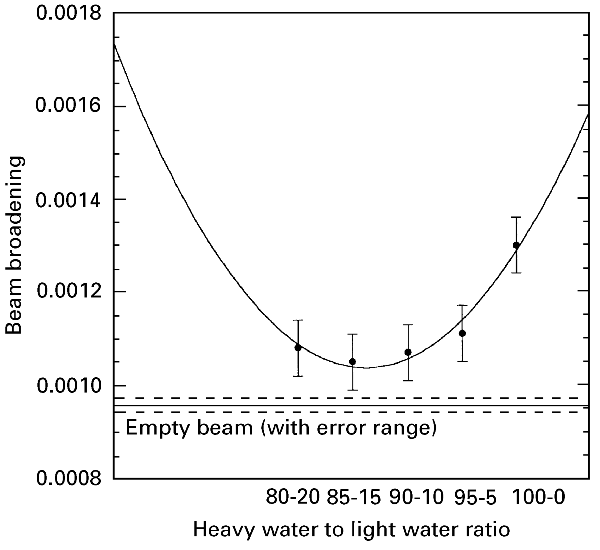

Figure 1 Dependence of beam broadening, r_c, on masking mixture composition.

orientation are surfaces perpendicular to the substrate plane. While for samples with an isotropic distribution of the void surfaces measurement with any $\boldsymbol{Q}$ orientation yields the total surface area, the anisotropy of the voids causes complications. To obtain the true value of the surface areas within the anisotropic material, a three-dimensional analysis is necessary. Therefore, a result in any one orientation represents only an apparent (Porod) surface area. These apparent surface areas, even though weighted by the orientation, may be used for comparison of samples if measured for all samples in the same sample–beam orientation.

As mentioned above, the three-dimensional analysis [2] showed that for these alumina deposits the true surface area is dominated by surfaces of intralamellar cracks (by more than 80%). These cracks are mostly perpendicular to the substrate plane and, therefore, the apparent surface areas measured in the current sample–beam orientation ($\boldsymbol{Q}$ parallel to the substrate plane) are dominated by the intralamellar crack surfaces.

The apparent surface area measured on the dry sample was 2.62 (0.03)* $\times 10^6$ $\mathrm{m^2\,m^{-3}}$, assuming only one scattering interface (alumina–air) within the deposit. The sample soaked with the contrast match fluid, i.e. where the open voids were filled with the H_2O–D_2O mixture having the same ρ as alumina, had an apparent surface area of 1.68 (0.08) $\times 10^6$ $\mathrm{m^2\,m^{-3}}$. This value was calculated assuming that the residual surfaces were composed of unfilled voids (i.e. alumina–air interface). This measurement revealed the surprising fact that 64 (5)% of the original apparent void surface area belongs to the voids not filled by the masking mixture under these conditions.

Another surface-characterized sample was soaked in 100% D_2O, which has a higher scattering length density than alumina. In this case, the scattering from the sample consisted of two additive parts, i.e. scattering from the interfaces of unfilled voids (air–alumina interface) and scattering from the voids filled with heavy water (D_2O–alumina interface). Such data cannot be simply solved (i.e. the two surface areas separated). Therefore, because the scattered intensity from the heavy water–alumina interface is negligible against the scattering from the air–alumina interface (see above argument on differences in $\Delta\rho^2$), the results were at first treated as if only one interface (air–alumina) were present. This treatment should give a higher result and the difference in the surface areas of the sample filled with the masking mixture having the same ρ as alumina and this sample could be later related to the D_2O–alumina interface surface. These apparent surface areas were, however, equal within experimental error.

The above experiment demonstrated the insensitivity of the contrast-match technique to small variations in the masking solution chemistry and the technical difficulties of applying the Porod scattering for contrast-match evaluation. As a generalization, this method may be extended to other small variations of scattering contrast within the sample caused by differences in chemistry or density, which would also have negligible effect on the results of these experiments.

Porod scattering can be used to establish the minimum size of the scatterers present in the sample from the minimum $\boldsymbol{Q}$ for which the surface scattering dominates the measured intensities. The presence of scatterers with sizes smaller than $2\pi/\boldsymbol{Q}$ would cause a difference from $\boldsymbol{Q}^{-4}$ dependence of intensity. The beginning of the Porod plateau [18] was found for $\boldsymbol{Q} \approx 0.3\ \mathrm{nm^{-1}}$, which is equivalent to scatterers of about 20 nm. The real Porod plateau may actually extend to even smaller $\boldsymbol{Q}$s (i.e. larger scatterer sizes) and may be masked by the multiple scattering. The reliably observed Porod plateau indicates that there should be no significant amount of scatterers smaller than 20 nm. This finding was confirmed by MIP analysis of these samples, which showed that there were no voids within the microstructure with diameters smaller than about 10 nm.

The MIP porosity of these samples was 7.4 (0.5)%. The residual density (sometimes called "skeletal density") was 3.63 (0.03 $\times 10^4$ $\mathrm{kg\,m^{-3}}$, close to the expected skeletal density (3.65 $\times 10^4$ $\mathrm{kg\,m^{-3}}$ for plasma- sprayed gamma-alumina [19]) suggesting that the amount of closed porosity is small (about 0.5%).

Archimedes' (weighing) measurements showed an open porosity of 6.8 (0.5)% and a residual density of 3.60 (0.03) $\times 10^4$ $\mathrm{kg\,m^{-3}}$. These give the amount of closed porosity in these measurements as 1.4 (0.5)%.

Both techniques result in the total porosity (open and closed together) of about 8%. The exact value depends on the skeletal density, which was not measured in this study.

4. Discussion

The closed porosity measured by the Archimedes method (1.4 (0.5)%) contained more than 60% of the apparent surface area of the dry sample. Keep in mind that in this experimental setup the apparent surface areas are dominated by the cracks within the deposits. Even so, this measurement indicates that the part of the void network which was not filled with the masking mixture has a large surface area.

It has been independently shown by both MIP and SANS, that there is no significant volume of voids with dimensions below about 10 nm. These findings indicate that the closed porosity, less than 1.4 (0.5)%, may contain a large part of the surface area, while the open porosity (about 6.8 (0.5)%) may represent only a small fraction of the apparent surface area. The open porosity should, therefore, be mostly large voids because they have a small surface-to-volume ratio. Consequently, the closed voids are mostly small voids with a large surface-to-volume ratio. However, both the Porod scattering and MIP yield a limit to the minimum size of the voids within the deposits to about 10 nm. This implies that these voids are macroscopic within the microstructure and that they may have

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*Errors (given in parentheses) are standard uncertainties obtained by statistical analysis of measurements and calculations or from statistical analysis of results of multiple measurements of similar samples.

sizes comparable with other structural constituents within these deposits. It should be noted that in these experiments, the maximum size of the closed voids is not measured.

While it is widely recognized that the properties of plasma-sprayed deposits depend on porosity [4, 5], there is little discussion of if and how specific properties of the deposits depend on the void shapes, sizes, surfaces, and orientation. This study has shown that frequently used intrusion techniques yield incomplete void characterization, which may be inadequate for an understanding of some properties. For example, recent experiments of the authors show that dielectric impedance is related to the complex structure of the deposits. Preliminary results indicate a close relationship of the impedance and the void surfaces (area and anisotropy), whereas there seems to be no direct relationship with the porosity volume.

The intrusion techniques, however, are still important and cannot be currently replaced. Other techniques reflecting the void shapes and anisotropies may, in some cases, be necessary for a better understanding of the microstructure–properties relationships.

5. Conclusion

The results suggest that most of the porosity (void) volume within plasma-sprayed ceramic deposits are concentrated within open and large pores containing a relatively small fraction of the total surface area. A large part of the surfaces (more than 60% of the total surface area) within the deposits is found to be in the closed voids (closed to water intrusion). The size of the voids within the deposits is found to be more than 10 nm. This work suggests that intrusion techniques (Archimedes and to some degree MIP) may not be able fully to characterize the void structure. Properties of the deposits which may be related to void characteristics other than volume, i.e. to the surface area, width, density, etc. may limit the usefulness of the intrusion techniques and may require additional measurements such as SANS.

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