In situ SANS study of pore microstructure in YSZ thermal barrier coatings

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Abstract

Air plasma sprayed yttria stabilised zirconia (YSZ) thermal barrier coatings (TBCs) were investigated by means of SANS. The measurements were performed in situ at different temperatures up to 1200 °C and ex situ after annealing at 1200 °C up to 100 h. Scattering curves were described by three populations of pores. The parameters of nanometric and medium-sized (20 nm) pores were determined. Specimens produced under different spray parameters showed qualitatively similar behaviour of nanometric and medium-sized pores during thermal exposure at elevated temperatures. The population of nanopores increased strongly at about 800 °C. The evolution of volume and size of nanopores and medium-size pores at 1200 °C indicated their sintering. The elimination of these pores coincides with the increase of Young’s modulus.

1. Introduction

Ceramic thermal barrier coatings (TBCs) [1] allow for an increase of temperature in the combustion chamber of turbines employing Ni-base superalloys by more than 100 °C and – at the same time – protect the surface against highly corrosive environment. Air plasma-sprayed (APS) coatings generally contain a large number of cracks and pores which strongly affect their thermal and mechanical properties [2,3]. The porosity is in fact desired because it lowers the thermal conductivity and enhances strain tolerance during thermal cycling. Nevertheless, the pore size in a good TBC should remain small. Even though TBC – and particularly their porosity – are widely investigated, a lot of questions remain open. TBCs have engineering reliability problems which can restrict their utilisation [4,5]. The use of TBCs is also restricted by the fact that no reliable life time prediction exists. In the background of these problems is the incomplete understanding of the link between macroscopic properties, microstructural parameters and processing of the coatings.

In Fig. 1, the scanning electron microscopy (SEM) of a fracture surface of an APS TBC is displayed. It shows the typical microcracks between spray lamellae and also the larger pores. In addition, some small intra-lamellar pores can be seen. These type of defects (closed porosity) are difficult to analyse via standard methods like BET surface analysis or mercury porosimetry as the pores are not connected to the surface.

It has been proved in the past that small-angle neutron scattering (SANS) can deliver important information on microstructure of porous ceramic materials, particularly those prepared by plasma spraying and suitable for thermal barrier coatings [6–8]. Contrary to most standard techniques, SANS can provide size of closed pores even on the nanometer scale [9,10] and enables in situ studies at high temperatures [11].
The combined in situ and ex situ characterisation of porosity in APS deposits of YSZ by SANS technique is presented.

2. Experimental

2.1. SANS

Small-angle neutron scattering [12] is caused by fluctuations of scattering length density \( q(r) \) on a size scale 1 nm – 5 \( \mu \)m in the studied material connected with compositional and/or structural inhomogeneities (in our case pores). The fluctuations of scattering length density result in the scattering contrast
\[
D_q(r) = \frac{q(r)}{\bar{q}} = \frac{q(r)}{C_0/C_2}
\]
being the coordinate in the real space, \( \bar{q} \) is the average scattering length density of the sample.

The scattering contrast gives rise to the coherent elastic scattering of neutrons to small magnitudes of the scattering vector \( Q = |Q| = 4\pi \sin \theta /\lambda \). \( Q = k - k_0 \); \( k, k_0 \) being the wavevectors of the incident and scattered neutron, respectively, \( |k| = |k_0| = 2\pi/\lambda; 20 \) is the full scattering angle, \( \lambda \) is the incident neutron wavelength).

2.2. Samples

For SANS measurement, three sets of YSZ samples (92 wt% ZrO\(_2\), 8 wt% Y\(_2\)O\(_3\)) were prepared. The sets (denoted 47, 48 and 49 – see Table 1) differ by spray parameters and thus also by porosity [13]. Coatings were prepared in a Sulzer Metco APS facility with a TRIPLEX I gun which uses He and Ar as process gases. While coating 47 shows a porosity level of 12–13% (measured by mercury porosimetry), coating 48 reveals a higher porosity level (16–18%). The spraying conditions used for coating 49 lead to a rather dense coating (11–12%) with the formation of segmentation cracks parallel to the spray direction.

The layers were sprayed on steels substrates, which were removed by hydrochloric acid. The free-standing layers were then heat treated at 1200 °C in air for different times: 0, 1, 10 and 100 h in order to follow the time-dependent evolution of porosity at operational conditions. An additional as-sprayed sample was used for in situ experiment.

The density of the Y\(_2\)O\(_3\) stabilised tetragonal zirconia was calculated from the lattice parameters reported in the neutron-diffraction study [14] and taking into account slightly different ZrO\(_2\)/Y\(_2\)O\(_3\) ratio of our material than that one in the paper. Using this density (6.07 g/cm\(^3\)) and the known composition of the sprayed material, the scattering contrast of pores was determined to be \( D_q = 5.55 \times 10^{10} \) cm\(^{-2}\). It should be noted that the scattering contrast is not very sensitive to the ZrO\(_2\)/Y\(_2\)O\(_3\) ratio within the range up to 15% Y\(_2\)O\(_3\). With the knowledge of the scattering contrast between pores and YSZ basic material, absolute values of volume fraction of some size-distribution regions can be calculated.

2.3. Experimental facility

The SANS experiment was performed at V4 SANS facility of BENSIC (HMI, Berlin) [15,16] equipped with 2D position sensitive detector (PSD). The wavelengths \( \lambda = 6 \) and 19.4 Å and sample-to-detector distances 16, 4 and 1 m were used, covering thus the range of momentum transfers \( Q \) from 0.008 to 2.5 nm\(^{-1}\). The bottom limit of the measured \( Q \)-range is restricted by a resolution of the facility \( \Delta Q = 0.0008 \) Å\(^{-1}\) for measurement with \( \lambda = 19.4 \) Å. However, it has to be noted that the measurement performed at 19.4 Å (smallest \( Q \)-values) is expected to be strongly influenced by multiple scattering.

Table 1

<table>
<thead>
<tr>
<th>Set</th>
<th>Sample</th>
<th>Exposure time at 1200 °C (h)</th>
<th>Porosity level (%)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>47A</td>
<td>As sprayed</td>
<td>12–13</td>
<td>0.298</td>
</tr>
<tr>
<td></td>
<td>47B</td>
<td>1</td>
<td></td>
<td>0.295</td>
</tr>
<tr>
<td></td>
<td>47C</td>
<td>10</td>
<td></td>
<td>0.291</td>
</tr>
<tr>
<td></td>
<td>47D</td>
<td>100</td>
<td></td>
<td>0.303</td>
</tr>
<tr>
<td></td>
<td>2F</td>
<td>In situ</td>
<td></td>
<td>0.294</td>
</tr>
<tr>
<td>48</td>
<td>48A</td>
<td>As sprayed</td>
<td>16–18</td>
<td>0.282</td>
</tr>
<tr>
<td></td>
<td>48B</td>
<td>1</td>
<td></td>
<td>0.283</td>
</tr>
<tr>
<td></td>
<td>48C</td>
<td>10</td>
<td></td>
<td>0.280</td>
</tr>
<tr>
<td></td>
<td>48D</td>
<td>100</td>
<td></td>
<td>0.286</td>
</tr>
<tr>
<td>49</td>
<td>49A</td>
<td>As sprayed</td>
<td>11–12</td>
<td>0.307</td>
</tr>
<tr>
<td></td>
<td>49B</td>
<td>1</td>
<td></td>
<td>0.307</td>
</tr>
<tr>
<td></td>
<td>49C</td>
<td>10</td>
<td></td>
<td>0.305</td>
</tr>
<tr>
<td></td>
<td>49D</td>
<td>100</td>
<td></td>
<td>0.306</td>
</tr>
</tbody>
</table>

Fig. 1. Scanning electron microscope photo of a fracture surface of an APS TBC (set 47). Examples of microcracks (A) and large pores (B) are marked. Medium-size intralamellar pores and nanopores cannot be resolved here.
due to the large scattering contrast, the relatively dense system and the large wavelength. Therefore, the conclusions in this Q-region can only be qualitative.

For the high temperature neutron-scattering experiment, the ILL-type furnace [17] was used.

3. Ex situ results

3.1. Evolution during heat treatment

At first, the SANS measurement of ex situ treated samples was performed. The layers were aligned perpendicular to the beam, i.e. the neutron beam was parallel to the spray direction. As expected, the scattering was isotropic. The resulting scattering curves of all layers for the set 48 (i.e. samples 48 A, B, C, D) are displayed in Fig. 2. The changes of the scattering curves for other sets with the thermal exposure are qualitatively very similar to those visible in Fig. 2 for the set 48. There is clearly visible evolution of the cross-section with treatment time at large Q-values. Less visible, but noticeable on a logarithmic scale is the difference between curves in the medium Q-range (0.05–0.5 nm⁻¹).

3.2. Test of anisotropy

Plasma spraying usually leads to macroscopically anisotropic microstructure of large pores, so-called “microcracks”, between splats. In order to determine a degree of anisotropy of the porous structure, samples were also tilted by approximately 50° from the orientation perpendicular to the beam. 2D data measured at all four investigated Q-ranges are displayed in Fig. 3 for the sample 47B. It was found that the scattering curves are again isotropic and identical with those measured without the tilt. This means that the pores observed by SANS can be described as an isotropic system. It does not mean that no preferential orientation of some pore population exists, but these pores (e.g. those between splats) are either too large to be observed in the investigated Q-range or they do not contribute to the observed scattering due to their large anisotropy (e.g. disk-like pores parallel to the layer surface would cause scattering practically only in case the surface of the layer is oriented parallel to the beam).

The scattering from observable pores can thus be treated as isotropic (i.e. without azimuthal dependence of the intensity on 2D PSD) and the model used for its evaluation can assume an isotropic distribution of pores.

3.3. As-sprayed samples

The scattering curves for the as-sprayed (i.e. non-treated) layers of all the sets 47, 48 and 49 together with the fits to the corresponding data are displayed in Fig. 4. It can be seen that 47A and 49A do not differ significantly (except the large Q-range discussed later in Section 3.4) while the scattering curve of the sample 48A can be clearly distinguished from 47A and 49A in the whole measured Q-range. The curves 47A and 49A are shifted with respect to 48A by a constant value on the logarithmic scale in the medium Q-range (0.05–0.6 nm⁻¹). The significant difference is only in the low Q-range (below 0.05 nm⁻¹). As the scattering from the medium and small pores is superimposed on the scattering from the larger ones (radius >100 nm), this indicates that a significant difference in the porosity between 48A and the other samples exists only for large pores (while medium and small pores exhibit no significant difference). It cannot be, however, easily evaluated quantitatively as the low Q-region is strongly affected by multiple scattering. It can only be qualitatively estimated that the large-pore size is larger for the set 48 as for the other two sets.

3.4. Scattering at large-Q

In the large-Q region, all three as-sprayed scattering curves (Fig. 4) exhibit nearly constant and relatively large scattering cross sections. Such high scattering is not observed for the heat treated samples (see Fig. 2). There can be in principle three explanations of such behaviour of non-treated samples:

(a) This part of the scattering curves is influenced by increased incoherent background (e.g. from hydrogen containing matter in the pores or on the surface absorbed during the preparation of the layer – most probably hydrochloric acid).

(b) There is a huge number of the subnanometric pores present in the original sample.

(c) A combination of (a) and (b).

The explanation (b) is unlikely as the simulations shows extremely large fraction volume of pores (occupation around 20%) in that case. The opposite extreme,
i.e. the large-$Q$ scattering caused by incoherent scattering only, is unlikely as well because of the extrapolated tendency from 100, 10 and 1 h exposure which all contain a certain amount of very small pores. Thus, the hypothesis (c) seems to be the most probable one. However, in order to clarify this behaviour, the evolution between 0 and 1 h exposure was investigated by in situ experiment described in the later sections.

4. Evaluation of ex situ measurement

Three populations of pores are necessary to describe the data for the as sprayed and thermally exposed material (see the fits in Figs. 2 and 3): large cracks and pores, medium-size pores (10–30 nm) and nanometric pores (1–10 nm). All the samples contain large pores and cracks (radius >100 nm) which produce the main contribution to the scattered intensity. The scattering from other (smaller) inhomogeneities is superimposed on it.

The evaluation was performed using the program SASFIT [18]. It is a non-linear least square fitting routine which uses analytical shape of size distribution and fixed shape of the particles (i.e. relatively low number of fitting parameters) to model and to fit SANS data. For the presented data evaluation, the modelled medium-size pores and nanopores were approximated by spheres as no prefered direction is expected on this size scale inside the splats. The individual size distributions were assumed to be of log-normal shape.

The use of a particular shape of size distributions generally constrains the result with respect to free-form methods; on the other hand it is not necessary to stabilize artificially the result of the fit. Moreover, the information content of the measured scattering curves is here influenced by the fact that the medium-size- and nanopore scattering is superimposed on the intense scattering from large pores and microcracks. Therefore, detailed (i.e. free-form) shape of the size distribution cannot be revealed and its approximation by log-normal distribution satisfactorily describes the data. Each fitted distribution (the medium-size pores as well as nanopores) was thus modelled by three parameters: the number of pores, the size in maximum of the distribution and the width of the distribution. To improve the convergence, some of these parameters were temporarily fixed during the fit; the final fit, however, included all of them. The resulting size distributions (number weighted)
were afterwards recalculated to the volume weighted ones which were used for determination of mean pore radius and of volume fraction. Further details of the evaluation applicable in particular cases are included later in the text at proper places.

As an example of the fit output, Fig. 5 displays the size distributions obtained for the samples from the set 48. The distribution of nanopores for as-sprayed sample in the figure is obtained according to the results of the in situ measurement (see Section 5).

4.1. Large pores

An interpretation of changes of morphology for large pores and cracks is difficult due to the limited $Q$-range and due to the multiple scattering (see the grey area on the left side of the cross-section graphs – Figs. 2 and 4). Nevertheless, these large pores seem to be stable and there is no visible change of the scattering curve in the $Q$-range below 0.05 nm$^{-1}$ for individual samples at different heat-treatments. This means that neither the volume fraction nor the specific surface had significantly changed during the treatment. It is known from other experiments that the porosity changes during the annealing at 1200 °C [19]. However, these changes are rather small (in the percent range), and hence difficult to detect by SANS for the given size range ($>100$ nm).

Therefore, this part of the size distribution will not be further discussed here and it will be assumed that the scattering from smaller pores is superimposed on the nearly constant (exposure independent) scattering from large pores (radius $>100$ nm).

4.2. Medium-size pores and nanopores

The resulting dependencies of the volume fraction and the mean size (volume weighted) of the medium and nanometric pores are displayed in Figs. 6 and 7. For the nanometric pores (Fig. 7), no result for as sprayed sample is displayed as this is strongly influenced by incoherent scattering from adsorbed hydrogen (see discussion to Fig. 4 in the previous Section 3).

5. In situ results

As already mentioned, the discrepancy in the large $Q$-region initialized the in situ measurement at elevated temperatures to clarify the origin of the high constant scattering level. The opportunity was also used to reveal detailed evolution of nanometric porosity at the beginning of the thermal exposure (0–1 h). Therefore, the stepwise thermal history profile was selected. The temperature was increased step by step (by 100 °C) and the scattering curves were recorded at the temporary stops (duration approximately 1 h) in the increase.

5.1. Incoherent scattering from adsorbed hydrogen

The selected full scattering curves are displayed in Fig. 8 and the zoomed large-$Q$ region can be seen in
Fig. 9. The selected scattering curves from in situ measurement – zoomed large-$Q$ range.

Fig. 8. The selected full scattering curves from in situ measurement. The inset shows the treatment of temperature-dependent diffuse scattering which is superimposed on the incoherent scattering.

5.2. Diffuse scattering and its treatment

The inset in Fig. 8 shows how the temperature-dependent diffuse scattering in the large-$Q$ region was taken into account for the in situ SANS measurement. The scattering curves with no incoherent-scattering from hydrogen and with the smallest influence of nanometric-pore scattering on the constant-background evaluation were fitted with a free constant (i.e. $Q$-independent) background. In fact, such background is composed of incoherent part (not caused by hydrogen but by other elements in the sample and thus temperature independent) and of diffuse part (temperature dependent). The result is plotted in the inset of Fig. 8. For the final fit of all the in situ scattering curves, the constant background level for each temperature was fixed on the value resulting from the polynomial fit displayed in the inset. This background was also subtracted from the measured and fitted curves in Figs. 8 and 9 in order to pronounce the discussed effects.

5.3. Creation of nanopores

The fact that there is only a very low amount of nanopores at 400 °C (and thus also in as-sprayed material) and, on the other hand, there is certainly relatively large volume fraction of them after 1 h exposure at 1200 °C (see the results of the ex situ measurement – Fig. 7) leads to the conclusion that those pores are created between 400 and 1200 °C. Therefore, the in situ experiment was continued step-by-step up to 1200 °C.

It can be seen in Fig. 9 that the scattering cross section starts to increase strongly at the largest $Q$-values when holding at 800 °C.

During the exposure at 1200 °C, the scattering curve at large $Q$-values changes: the scattering is lowered and its center of weight is shifted towards smaller $Q$-values. The cooling from 1200 °C after 1 h exposure brings change of the scattering curve only due to the slightly longer exposure at 1200 °C (by 10 min) with respect to the last measurement at high temperature. The tendency in the scattering-curve shape evolution is the same there as during the whole treatment at 1200 °C.

6. Discussion

The evaluation of the in situ SANS data was again carried out using the SASFIT program and resulted in the dependencies of the volume fraction and the mean size which are displayed in Figs. 10 and 11 for nanopores and medium-size pores, respectively.

6.1. Nanopores

Fig. 10 clearly shows that a new (not present in the original as-sprayed sample) population of pores of nanometre size is created at the temperature of 800 °C.

Between 800 and 1200 °C, this population remains practically unchanged. During holding at 1200 °C, the size of the nanopores increases and their volume fraction decreases. This trend is identical for both in situ and ex situ measurements which fit very well together.
The development of nanopores might be related to the darkening of the coatings in the as-sprayed condition [20]. This darkening can be explained by the partial reduction of Zr$^{4+}$ to Zr$^{3+}$ during spraying under reducing conditions at high temperatures [21]. The reduction will lead to the formation of oxygen vacancies within the as-sprayed coatings. During annealing, these vacancies become mobile and form clusters and pores. These nanopores can be then observed by SANS. Simultaneously, Zr$^{3+}$ ions are oxidised to Zr$^{4+}$ to keep the balance of charge within the lattice. During long term annealing at 1200 °C, conventional sintering starts and leads to the reduction of the volume fraction of these pores.

The hypothesis of nanopore formation by agglomeration of vacancies was strongly supported by an additional SANS test. After the first thermal cycle was finished, a subsequent 800 °C in situ exposure was applied for as-sprayed layer No.47. The full thermal history was thus RT – 800–1200 °C – cooling to RT – 800 °C – RT; RT denotes room temperature. It was found that the nanopores are not created on the second exposure at 800 °C. They are created in the first cycle only, which fully corresponds with the above described vacancy-based creation of nanopores.

### 6.2. Medium-size pores

As can be seen from Fig. 11, the in situ heat treatment had practically no influence on the medium-size pores up to temperature of 1200 °C is reached. At this temperature, their volume fraction starts to decrease. The initial increase of the mean size of the pores at 1200 °C (first hour of the exposure) together with the volume decrease indicates that smaller pores from its size distribution vanish faster than the larger ones.

At longer exposures, the population of medium-size pores practically disappears (their volume fraction is only 10% of the original amount after 100 h). That means that medium-size pores either vanish after longer thermal exposure at 1200 °C and/or join the large pores and cracks (and thus disappear because of their low volume fraction with respect to the volume of large pores and cracks). As a consequence, the scattering from them becomes nearly undistinguishable from the asymptotic scattering intensity of the large pores and from the scattering of the growing nanopores. The resulting mean size is thus determined with large error and possibly also contaminated by parasitic scattering from other inhomogeneities.

Fig. 12 displays the sum of the obtained volume fraction of nanopores and medium-size pores. Its evolution at 1200 °C is a sign of sintering. It is interesting to note that a fast increase of Young’s modulus within the first hours of annealing at 1200 °C was observed in a separate experiments carried out with these layers [22]. The similarity in the time scale of pore sintering and of Young’s modulus increase indicates that the sintering of

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**Fig. 10.** Volume fraction and mean radius (volume weighted) for nanopores, both in situ and ex situ measurements.

**Fig. 11.** Volume fraction and mean radius (volume weighted) for medium-size pores, both in situ and ex situ measurements.

**Fig. 12.** Summed volume fraction of nanopores and medium-size pores.
intra-splat pores plays a significant role in the stiffening of the coatings. The effect can lead to a stiffening of individual spray lamellae. In combination with the sintering of the microcracks, it leads to the overall increase of Young’s modulus.

7. Conclusions

In agreement with observations by SEM and mercury intrusion porosimetry, the SANS measurement has shown that the investigated layer 48 differs from the layers 47 and 49 in the porosity of large pores (due to the different spraying parameters).

The thermal exposure at 1200 °C up to 100 h has practically no influence on observable large (>100 nm) pores and cracks in the investigated TBC layers. On the other hand, it influences significantly medium-size pores and nanopores. The evolution of porosity is qualitatively the same during annealing in all three types of layer.

The as-sprayed material of all the sets contains medium-size pores (10–30 nm) which gradually vanish during heat treatment. The observed dependencies of volume and size of medium-size pores indicate their sintering.

The in situ measurement at high temperatures revealed that there is only less than 0.01% volume fraction of nanopores in the original as-sprayed material. A population of nanometer-sized pores (volume fraction around 0.1%) is, however, created at about 800 °C. Between 800 and 1200 °C, this population remains practically unchanged. During 1-h holding at 1200 °C, the size of nanopores increases and their volume fraction decreases. The measurement of the specimens annealed for longer time ex situ at 1200 °C clearly confirmed this trend.

The experiment demonstrated the suitability of SANS for TBC-microstructure characterisation at simulated operational conditions.

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