Studying of PYSZ and FYSZ turbine blade coatings by small-angle neutron scattering

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Abstract. We present here results of small-angle neutron scattering (SANS) investigation of partially and fully yttria stabilized zirconia (PYSZ and FYSZ, respectively) turbine blade coatings (TBC). The samples have been prepared by electron beam physical vapour deposition method (EB-PVD) with various setup parameters. Structure parameters of porosity have been studied in-situ with high-temperature furnace. Temperature dependence of specific surface and anisotropy parameter of porosity has been obtained. Differences in character of microstructural morphology changing with in-situ thermal treatment as well as open and closed porosity ratio in PYSZ and FYSZ has been described and discussed.

1. Introduction

Turbine blade coatings (TBC) improve operational characteristics of advanced turbine blades. Engines protected with TBC blades exhibit increased their performance mainly due to the increase of gas-turbine inlet temperature [1]. Also coated blades have better corrosion resistivity and much longer lifetime. TBC produced by electron beam physical vapour deposition (EB-PVD) technique has unique columnar microstructure. These columns are mainly perpendicular to surface and thus high-temperature stability is improved during operation temperature induced cyclic altering. Conventional and most widely used material for TBC is Partially Yttria Stabilized Zirconia - PYSZ (7 wt. % \(\text{Y}_2\text{O}_3 + \text{ZrO}_2\)). It is a relatively cheap composition and allows the so-called single-source-evaporation during EB-PVD processing relying on the very similar vapour pressure values of zirconia and yttria. However, the use of PYSZ becomes problematical as the inlet temperature in future engines reaches to temperatures as high as 1400 °C causing phase instability of the standard TBC-material [2, 3]. Use of Fully Yttria Stabilised Zirconia - FYSZ (14 wt.% \(\text{Y}_2\text{O}_3 + \text{ZrO}_2\)) allows the formation of more stable cubic phase and thus extending the application to higher operation temperatures. PYSZ exhibits better thermal shock and erosion resistances than FYSZ. Despite these facts, FYSZ seems to be a promising TBC-material due to its intrinsically lower thermal conductivity and phase stability for the envisaged higher operation temperatures. In general, the porous morphology and, thus the resulting thermal flux behaviour at EB-PVD TBCs can be altered by varying the deposition parameters such as substrate temperature, rotation speed of substrate and power used for evaporation of ingots, etc. [2].
Moreover, relying on above mentioned properties, it is expected that the coating morphology and thermal conductivity value can depend on the stabilisation level of yttria in zirconia. SANS is widely used for investigation of zirconia-based ceramics [4-7]. This method provides information about bulk of studied material in contrast to e.g. electron microscopy (SEM, TEM). However, EB-PVD TBC deposits have a rather complex microstructure – wide range of sizes, high level of anisotropy and texturing of different kinds of pores, and as a consequence, the full analysis of SANS data is too complicated, it requires introduction of model with too many free parameters which are mutually independent. Nevertheless, neutron and X-ray small-angle scattering (SANS, SAXS) allows to characterize porosity in TBC materials through integral parameters of scattering function – apparent Porod constant and specific surface. One similar example of in-situ high temperature SANS measurements of plasma sprayed PYSZ TBC can be found in [9]. In present work, we show the influence of EB-PVD deposition parameters and the level of yttria stabilisation on morphology and porosity of the TBC coatings.

2. Experimental

“Von Ardenne” (Ardenne Anlagentechnik GmbH, Dresden/Germany) EB-PVD pilot equipment with max EB-power of 150 kW has been used for the preparation of the studied samples. Ingot powder has been evaporated and deposited at constant chamber pressure of about 0.8 Pa. The parameters during deposition (temperature in chamber and rotation speeds) are summarized in Table 1.

Table 1. Sample description.

| Sample name | Stabilisation level Y$_2$O$_3$, wt % | Substrate rotation speed, rpm | Substrate temperature, °C | Thermal post treatment |
|-------------|-------------------------------------|------------------------------|---------------------------|------------------------|
| PYSZ-03     | 7                                   | 3                            | 1000                      | Virgin and aged at 100 hours at 1100 °C |
| PYSZ-12     | 7                                   | 12                           | 950                       | Virgin and aged at 100 hours at 1100 °C |
| PYSZ-30     | 7                                   | 30                           | 870                       | Virgin and aged at 100 hours at 1100 °C |
| FYSZ-03     | 14                                  | 3                            | 950                       | Virgin and aged at 100 hours at 1100 °C |
| FYSZ-12     | 14                                  | 12                           | 950                       | Virgin and aged at 100 hours at 1100 °C |
| FYSZ-20     | 14                                  | 20                           | 975                       | Virgin and aged at 100 hours at 1100 °C |

Materials have deposited on FeClAl-alloy substrate without having a bond coat. After deposition TBC specimens have been removed from substrate by means of etching in an acid solution. The thickness of final samples is about 0.4 mm. Such as-deposited TBC samples were used for in-situ SANS measurements at high temperature aging in vacuum. Scanning electron microscopy pictures are summarised in figure 1.

SANS measurements of studied FYSZ TBC samples in matching liquid have been conducted in HZB at V4, and partially at PAXY in LLB (Saclay) instruments. Mixture of D$_2$O (89 wt%) and H$_2$O (11 wt%) was used for “shadowing” of open pores since it has the same scattering length density (SLD=5.55*10$^{10}$ cm$^{-2}$) value. Measurements of PYSZ samples have been carried out at V4 instrument (HZB) with neutron wavelength of $\lambda$=6.05 Å and sample-detector (SD) distances of 1 m and 4 m. FYSZ TBC material was measured at PAXY (LLB) with neutron wavelength of $\lambda$=4.8 Å and sample-detector (SD) distances of 0.6 m and 5 m.
Figure 1. Scanning electron microscopy (SEM) images of PYSZ (A: PYSZ-03, B: PYSZ-12, C: PYSZ-30) and FYSZ (E: FYSZ-03, F: FYSZ-12, G: FYSZ-20) as-coated samples, growth direction is normal to image plane.

Experimental SANS data have been corrected for the instrument and sample holder and buffer background and calibrated by water scattering.

3. Results and discussion

3.1. In-situ high temperature SANS

Porosity structure of the studied coatings consists of three pore types – intercolumnar gaps sized about 0.5-2 µm, voids between feather-arms (100-500 nm) and intra-porous arrays (5-300 nm) [5]. Although SANS Q-range covers only nano-sized porosity i.e. about 1-50 nm for both presented here SANS measurements, specific surface of whole porosity is reachable in measured high Q in so-called Porod regime [9]. Thus, a simple model of ellipsoids of rotation with preferred orientation has been chosen in order to follow change of anisotropy induced by in-situ temperature treatment. We have used SASProfit program for fitting of 2D scattering patterns [10]. This software allows carrying out fitting of 2D SANS data simultaneously for sample-to-detector distances 1 m and 4 m. Neutron beam has been monochromatized by means of velocity selector at wavelength 6.05 Å with Δλ/λ = 10 %.

Irreversible decreasing of porosity anisotropy in given specimen during heat treatment can be observed in example of two-dimensional SANS diffraction pictures of in-situ measured in high temperature furnace (HTF-2) of as-coated PYSZ-12 sample (see in figure 2).

It should be mentioned that specimens were exposed by heat treatment in evacuated environment (at about 10⁻³ bar), however, usual heat aging procedure assume to be conducted at ambient air pressure. We expect that environmental pressure difference can just slightly influence sintering process and, thus, porosity structure of the end-point coatings.
In situ SANS pattern of PYSZ-12 sample measured before high-T treatment at room temperature (A), during treatment at 1100 °C (B) and after treatment at room temperature (C).

Fitted aspect ratio ($r/R_0$) values for PYSZ and FYSZ samples are shown in figure 3. Obtained values of aspect ratio are highly dependent on sample orientation with respect to incident neutron beam because of high anisotropy of inter columnar pores. For both samples groups fitted $r/R_0$ values behave similarly with temperature. These anisotropy parameters keep constant quantity at the beginning of heating, then smoothly decrease and stay unchanged during cooling from maximum reached (1100 °C) down to room temperature. However, observed decrease of the $r/R_0$ ratio (see figure 3) starts at lower temperature in FYSZ (800 °C) than in PYSZ (900 °C) coatings. But, on the other hand, fitted specific surface values dependence on temperature is different for PYSZ and FYSZ materials. Porosity specific surface in partially yttria stabilised coatings slowly decreases or stays constant at the first stage of heating (up to $T \sim 700$ °C) and then decreases. In case of FYSZ, material specific surface significantly increases for temperatures up to $T \sim 600$ °C and then decreases ($700$ °C < $T \leq 1100$ °C). Finally, the measured specific surfaces in all samples slightly increase after cooling, it could be ascribed to thermal shrinkage and as consequence changing of scattering contrast, identical results have been described for $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{SrZrO}_3$ in [11].

![Figure 2](image1.png)

![Figure 3](image2.png)

**Figure 2.** In situ SANS pattern of PYSZ-12 sample measured before high-T treatment at room temperature (A), during treatment at 1100 °C (B) and after treatment at room temperature (C).

**Figure 3.** Changing of fitted porosity aspect ratios during thermal treatment in PYSZ (a) and FYSZ (b).
As was mentioned above, the method of EB-PVD causes that most of pores in as-deposited material are highly anisotropic [12] thus, 3D analysis should be performed in order to obtain proper surface area values. Moreover, size range distributions of pores are rather wide, mutually overlapping and thus porosity model requires too many free parameters, which could give faulty results. Therefore, radially averaged apparent Porod constant [13] was used for qualitative characterization of total (i.e. open and closed) and closed porosity in PYSZ and FYZS samples. Apparent Porod constants were obtained from radial averaged SANS data measured for virgin (as-deposited) and thermally aged (100 hours at 1100 °C in air) PYSZ and FYSZ coatings. The rotation speed has strong influence on porous morphology in EB-PVD TBCs [3] and thus on different thermal resistivity properties. The open and closed porosity at the EB-PVD TBCs can be differentiated by employing comparable SANS analysis in scattering length density (SLD) matching liquid. Figure 6 shows obtained apparent Porod constants from the SANS data of heat-treated EB-PVD FYSZ coatings deposited with different rotation speeds (filled symbols in figure 6). Addition of matching liquid (D$_2$O/H$_2$O in 89/11 mass %) during SANS measurement results in SANS curves with lower intensity (open symbols in figure 6) due to “shadowing” of open porosity. Higher incoherent background level caused by hydrogen presented in light water.

Figure 4. Fitted specific surface parameters from in-situ SANS during thermal treatment in partially-(a) and fully-(b) yittria stabilized zirconia coatings.

3.2. SANS with SLD matching liquid

Figure 5. SANS scattering of FYSZ TBC samples measured in air (a) and in matching liquid (b).
Dependences of these apparent Porod constants values on rotation speed during deposition for FYSZ are shown in figure 6. High-Q region of SANS data (Q>0.5 nm\(^{-1}\)) were used for fitting with the help of SASFit program [10]. Incoherent background was included in scattering procedure for data measured in D\(_2\)O/H\(_2\)O.

In all studied specimens significant reduction of specific surfaces was detected after sintering (see figure 6). It was obviously caused by smoothing of porosity surface due to thermal aging, as was observed by SEM earlier [5]. In PYSZ (so-called feather-arms) growth of secondary columns was found to relate with the vapour flux and the rotation axis in respect of the vapour incident angle (VIA). The rotation of the substrates produces a “sunrise-sunset” vapour incidence pattern, that determines the deposition rate over a differential area as a function of time. Thus, the interplay between neighbouring column tips and VIA of the incoming particles enhances the dominance of the shadowing effect over the surface diffusion. This shadowing phenomenon enhances the formation of secondary columns [14]. The data obtained on the EB-PVD PYSZ TBCs by employing the same experimental method display an increasing trend of the open porosity population with the rotation speed [12]. However, the highest rotation speed employed during the deposition of EB-PVD FYSZ results in the formation of the lowest total porosity population. This opposite tendency may be related to the difference in the preferred column growth direction in cubic and tetragonal phases. Obviously, scattering from closed pores should be reduced more significantly with thermal aging then it was measured. This could be attributed with converting of open feather-arms to close porosity.

4. Conclusions

Deposition parameter induced changes of porous morphology in PYSZ and FYZS coatings has been measured and demonstrated by in-situ high temperature SANS experiments and SANS measurements with shadowing of open pores utilizing matching liquid immersion technique. FYSZ coating samples exhibited lower anisotropy of bulk porosity in comparison to PYSZ. Moreover, the reduction of average pore aspect ratios starts occurring at lower temperature in FYSZ (~800 °C) than in PYSZ (~900 °C). As the apparent specific surface area increases in FYSZ at the first stage of thermal treatment, does not change in PYSZ. Specific surface area value is highest in PYSZ coatings grown using the fastest substrate rotation speed, whereas, this is the lowest in FYSZ, which could be ascribed
to multiple growth direction of material with tetragonal phase as often encountered in PYSZ and cubic – which is the overwhelming phase at FYSZ.

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