CHARACTERIZATION OF VOID MORPHOLOGIES IN THERMALLY SPRAYED METALLIC DEPOSITS USING SCATTERING TECHNIQUES

T. Keller, W. Wagner (PSI), J. Ilavsky, A.J. Allen (NIST, Gaithersburg, USA), N. Margadant, S. Siegmann (EMPA, Thun, CH), G. Barbezat, (Sulzer Metco, Wohlen, CH), J. Pisacka, (IPP, Prague, CR), R. Enzl (Skoda Research, Plzen, CR)

The complex void microstructures of thermally sprayed deposits can be modelled by three major void subsystems: interlamellar pores, intralamellar cracks, and volumetric globular voids, each having different volume fractions, anisotropy, size and shape. This complex void morphology is expected to have a strong influence on the properties of thermally sprayed coatings. A NiCrAlY deposit was manufactured by atmospheric-plasma spray (APS), and the total specific surface area of the voids was determined by small angle neutron scattering (SANS) in the Porod regime. To characterize the void system in more detail, the technique of multiple small angle neutron scattering (MSANS) was applied. The three-component void morphology was modeled, based on empirical considerations and on the analysis of SEM micrographs of coating cross-sections. The model results suggest that for this APS metallic deposit the interlamellar pores are the dominant component of the overall void system. Only a small void volume fraction is found for the fine intralamellar crack system.

The microstructure of thermally sprayed deposits, and therefore their material properties, are to a large extent related to the internal void structure. Important parameters are the total void volume fraction and the total specific surface area of the voids. Of further interest are usually average pore size as well as the orientation of anisotropically shaped pores. Small-angle neutron scattering (SANS) techniques can provide information on the total specific surface area and, in principal, also directly on the size of voids up to about 100 nm. The complex void structure of many thermal spray deposits extends over a size regime up to a few micrometers in diameter, such that it does not allow a direct determination of the pore size by this method. Nevertheless, the total specific surface area can still be obtained in the Porod regime [1]. A method has been developed to deduce average pore size and orientational distribution by the technique of multiple small-angle neutron scattering (MSANS). The analysis employs the experimentally determined wavelength-dependent broadening of the primary neutron beam, when the neutrons undergo copious multiple scattering in the sample. Recently this method was extended to model the void structure of thermally sprayed ceramic deposits by allowing for the three distinct void subsystems [2]. In the present investigation, the MSANS technique was applied to an atmospheric plasma-sprayed metallic NiCrAlY deposit. The total specific surface area was determined previously from SANS measurements in the Porod regime [3].

The results presented here are obtained from investigations of an atmospheric plasma-sprayed (APS) metallic NiCrAlY deposit. The chemical composition of the feedstock material was 67% Ni, 22% Cr, 10% Al, 1% Y (all values in wt.%). The MSANS beam-broadening at wavelengths λ between 12 Å and 18 Å was determined for two sample orientations with respect to the neutron beam: from a cross-section sample and a free-standing deposit. The shape of the broadened neutron beam after having passed the sample was assumed to be Gaussian. The MSANS beam broadening, r_c, was expressed by the standard deviation of a Gaussian fit to the beam profile in the region of small scattering vectors. To analyze the MSANS anisotropy, the MSANS data for the cross-section sample were averaged over 15° wide sectors around the beam center, and an modelled and the model parameters fitted to the orientationally-averaged MSANS beam-broadening r_c (λ) data obtained for the two sample orientations, obeying the boundary condition of total porosity. Further modelling constraints were the total specific surface area experimentally determined from SANS and the observed MSANS anisotropy.

From the SANS analysis in the Porod regime the total specific surface area was determined to be S_{tot} = (0.766 ± 0.010) x 10^6 m^2 m^{-3}. The total volume fraction was found to be 0.081 ± 0.001. The experimentally determined orientationaly averaged MSANS beam-broadening is shown in Fig. 1 for the cross-section and free-standing deposit. Model and experimental anisotropies are displayed in the polar plot of Fig. 2. The MSANS anisotropy of the cross-section sample, determined by averaging the aspect ratios of the ellipses for all wavelengths, was found experimentally to be 1.35 ± 0.03.

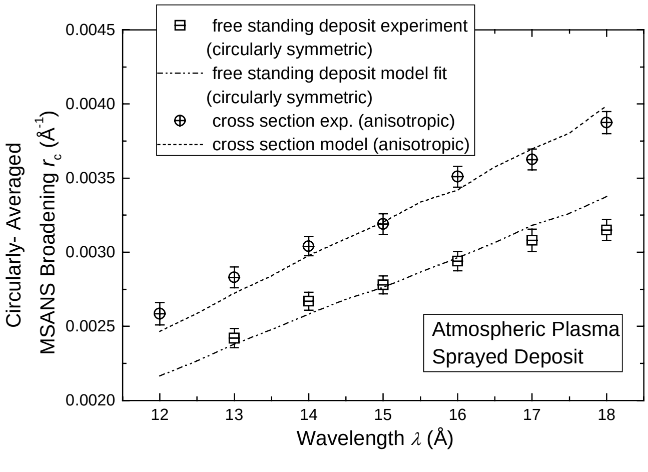

Figure 1: Beam broadening of the APS deposit. Model results and experimental data are displayed for the neutron beam parallel and perpendicular to the spray direction.

The model assumes the total void volume fraction to be split into three distinct void subsystems, two of them consisting of oblate spheroidal elements (characterized by a radius R, aspect ratio β and probabilities g_L, g_M and g_H for

Autor: T. Keller, W. Wagner, J. Ilavsky, N. Margadant, S. Siegmann, J. Pisacka, G. Barbezat, J. Fiala and T. Pirling
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finding their short axis oriented within 0°-30°, 30°-60° and 60°-90° with respect to the spray direction). Their mean opening dimension is $<O.D.> = 4\beta<R>/3$. The third void system consists of globular pores of diameter $<2R_G>$. By non-linear least-squares fitting, the model parameters were determined [4], meeting all other constraints: the model MSANS anisotropy is 1.38, and the total specific surface area for the model is found to be 0.769×10^6 m^2 m^{-3}. The mean opening dimensions of the spheroidal pore systems together with their mean orientation distributions and the mean globular pore radius obtained by the model fit are given in Table 1. Table 2 compares the fraction of void volume with the fraction of specific surface area for each subsystem.

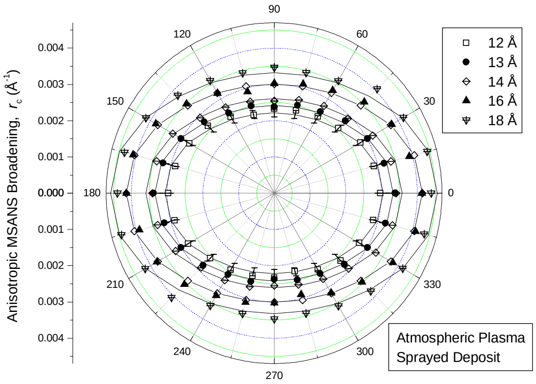

Figure 2: Anisotropic MSANS beam-broadening for the APS cross-section sample as measured and fitted by the model for different wavelengths. Standard deviations of the experimental data are indicated for $\lambda = 12$ Å.

Table 1: Modelled mean opening dimensions and orientation distributions of the void subsystems of the APS deposit.

	$<O.D.>$ (μm)	$<2R_G>$ (μm)	g_L	g_M	g_H
$\beta = 1/10$	0.097	-	0.04	0.22	0.74
$\beta = 1/5$	0.194	-	0.64	0.31	0.05
Globular pores	-	1.892	-	-	-

Table 2: Specific surface areas and volume fractions of the three void subsystems of the APS deposit, calculated from the MSANS model parameters.

	Specific surface area [10^6 m^2 m^{-3}]	Volume fraction
$\beta = 1/10$	0.127 ≅ 17 %	7 %
$\beta = 1/5$	0.563 ≅ 73 %	62 %
Globular pores	0.079 ≅ 10 %	31 %
Σ_{total}	0.769 ≅ 100 %	0.081 ≅ 100 %

The modelling of the MSANS broadening of the APS metallic NiCrAlY deposit needs three void systems to be distinguished. The different void subsystems can be described as fine intralamellar cracks (β=1/10) comprised of oblate spheroidal elements preferentially aligned perpendicular to the substrate, interlamellar pores (β=1/5), also comprised of oblate spheroidal elements mainly aligned parallel to the substrate, and globular pores. Intralamellar cracks most likely originate from a release of residual stresses built up during the spray process. The interlamellar pores are mainly located between stacked splats. The assignment of the β = 1/10 void system to intralamellar cracks and of the β = 1/5 void system to interlamellar pores is supported by their orientation distributions with preferential alignment perpendicular and parallel, respectively, to the substrate (g_L, g_M, g_H values in Table 1), as well as by the principle agreement with the analysis of SEM micrographs (Fig. 3). The relatively low volume fraction of 7 % of the intralamellar crack system can be explained by reduced residual stresses and hence less cracking in the more ductile metal matrix, compared to ceramic coatings [2].

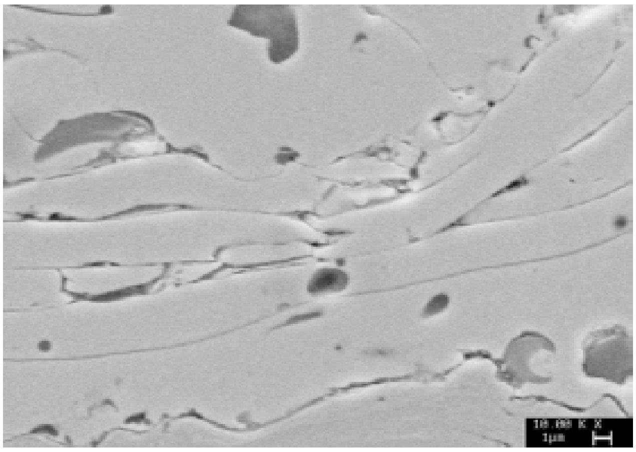

Figure 3: SEM micrograph of a polished cross-section of the APS NiCrAlY deposit. The spray direction is vertical from the top of the figure.

On the other hand, the interlamellar void system accounts for 62 % of the total porosity: This strongly suggest that, for this deposit, macroscopic anisotropic material properties (e.g. elastic modulus, electrical [5] and thermal [6] conductivity) are related to the morphology of splats and interlamellar pores.

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