



CHARACTERIZATION OF ANISOTROPIC, THERMALLY SPRAYED MICROSTRUCTURES USING SMALL-ANGLE NEUTRON SCATTERING

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ABSTRACT

Increasing industrial importance of thermally sprayed deposits accelerates the need for reliable and sufficiently complex microstructure characterization techniques. Practice has shown that industry standard techniques—image analysis of cross sections and intrusion porosimetry—do not yield enough detailed picture to be able to distinguish properties controlling mechanisms. Anisotropic Porod scattering technique of Small Angle Neutron Scattering (SANS) has been shown to be a useful tool for characterization of complex anisotropic microstructures. This technique is able to distinguish major void systems in the thermally sprayed deposits if they sufficiently differ in anisotropy.

Series of results obtained on thermally sprayed metallic deposits from NiCrAlY feedstock are reviewed. Microstructure characterization obtained using SANS is compared with the results of image analysis, intrusion porosimetry. It will be shown how by combination of the standard techniques and SANS novel microstructure understanding can be obtained and how this can be used to optimize deposits microstructure for different applications. Suggestions how this technique can be used in other materials will be presented.

KEYWORDS

Small-Angle Neutron Scattering, SANS, Thermal Spray, NiCrAlY, microstructure, porosity, Atmospheric Plasma Spraying, APS, Flame Spraying, FS, Vacuum Plasma Spraying, Water Stabilized Plasma Spraying, WSP.

INTRODUCTION

Improved spray control tools allow reproducible manufacturing of deposits for different applications. Therefore, generally, design of application-specific thermally sprayed deposits is possible. This design is, however, complicated by the need to fulfil several requirements at the same time, for example the need for good wear and corrosion resistance. Designing

deposits with suitable properties requires a general understanding of the coating processes, i.e. spraying techniques and their parameters, of the microstructure, and also of the relationships between microstructure and deposits performance and properties. This brings about the need for better microstructure characterization tools. The techniques using neutron scattering can often provide unique information since the penetration depth of neutrons compared to x-rays is high.

The present work reports results from measurements of the voids specific surface areas obtained by Small-Angle Neutron Scattering (SANS) in NiCrAlY coatings and compares them with results of standard porosity characterization techniques.

EXPERIMENTAL

1. Feedstock Material, Spray Techniques and Parameters

Nickel based alloy NiCrAlY (67% Ni, 22% Cr, 10% Al, 1% Y) was used as feedstock material. Commercially available powders were used with size ranges suitable for the different spraying techniques.

Various thermal spray techniques were used to manufacture the deposits – atmospheric plasma spraying (APS), vacuum-plasma spraying (VPS), flame spraying (FS), and water stabilized plasma spraying (WSP). Each technique deposits feedstock particles with different combination of speeds and temperatures resulting in a different microstructure. All spraying techniques applied within this project were used to manufacture not only the “standard” microstructures, but the widest possible range of microstructures reasonably attainable by each of the different techniques. Details on the spray parameters applied are described in [1].

2. Small-Angle Neutron Scattering

Small-Angle Neutron Scattering can provide information on the total area of homogeneous interfaces in a two component system in the so called “Porod Regime” [2], where the scattering cross section, i.e. the absolute intensity $I(Q)$, decreases with the fourth power of the scattering vector Q or of its modulus, the momentum transfer Q , respectively. The latter is defined in the usual way as $Q = (4\pi/\lambda) \sin \theta$, where θ is half the angle between the direction of incident and scattered neutrons, and λ the neutron wavelength. If L is the smallest dimension of the scatterers, a necessary condition for the validity of the Porod Regime is $QL > 3$. For thermally sprayed coatings, the relevant interfaces are the surfaces between the pore system and the matrix and, if present, between the matrix and secondary phases, like oxides. The voids and the metallic matrix have a different scattering length density, ρ , which causes some of the neutrons to be scattered at the interfaces.

The measurements were performed at the SANS instrument at the neutron spallation source SINQ at Paul-Scherrer-Institute (PSI) in Villigen/Switzerland. Cold neutrons of a wavelength of 0.5 nm were used. A detailed description of the instrument can be found elsewhere [3,4,5].

SANS samples were prepared by cutting cross sections of 1.9 mm in thickness, and subsequent grinding to obtain flat surfaces. The sample cross section was masked by a Cadmium slit such that only the coating was illuminated edge-on and scattering from the substrate was avoided. An electromagnet allowed to apply a horizontally oriented magnetic field to the sample to avoid magnetic refraction effects. The magnetic field at the sample position was about 1 Tesla such that magnetic saturation was almost achieved. Still, to identify and separate possible (anisotropic) magnetic scattering contributions the samples were measured in two positions, i.e. aligned horizontally and vertically with respect to the magnetic field. The data were calibrated by the incoherent scattering of a water sample to account for the different detector pixel efficiency and to scale the data to absolute values.

The data were averaged in sectors around the beam center in steps of 10° , the width of each sector being 15° , to compute the absolute intensity as a function of momentum transfer Q for different directions of the scattering vector \vec{Q} . By fitting a Q^{-4} power law to the Porod Regime for each sector the apparent Porod constant in this direction is obtained. Assuming isotropic scattering around the axis of symmetry perpendicular to the surface plane (which was experimentally verified for selected coatings), the apparent Porod constant is known for all (3-dimensional) directions. Then the total specific surface area S_{total} can be obtained from the 2-dimensional data by averaging the contributions for all 3 dimensions. This orientational average then relates to S_{total} as follows [2]:

$$\left\langle \frac{d\Sigma(\vec{Q})}{d\Omega} \right\rangle_{\text{ORIENTATION}} = \frac{2\pi|\Delta\rho|^2 S_{\text{TOTAL}}}{Q^4} \quad (1)$$

$|\Delta\rho|^2$ is the neutron scattering length contrast between the pores and the matrix.

3. Porosimetry

The density of the samples was used to evaluate the porosity using estimates of the oxide content and bulk densities of the materials present in the samples. Layer removal method was used to measure the sample density. For details see [1]. For the calculation of the porosity a three-phase model was assumed: a metallic phase, an oxide phase and pores. The metallic phase density was assumed to be equal to the powder density, which was measured by helium pycnometry. The amount of oxygen was determined by means of hot gas extraction. The samples were heated up to approx. 2500°C and the oxygen was measured as CO_2 by infrared detection, the nitrogen content was quantified by conductivity measurement of the extracted N_2 . The oxides were assumed to be mainly chromium oxide (as confirmed by the Auger measurements) with a density of $5,21 \text{ g/cm}^3$ [6]. The pores were assigned density of zero. The porosity was calculated based on these powder, oxide and pore densities, the overall density and the oxide weight percentage. The oxides, with lower density than the bulk material, would significantly reduce the apparent porosity of the coating.

4. Metallography and Microscopy

Samples were cut by abrasive saw and mounted in cross section in a methyl metacrylate base resin. Samples were metallographically prepared; first ground with SiC papers, then diamond polished and finished with colloidal silica. Samples were observed by means of optical microscopy. For details see [1].

RESULTS

1. Small-Angle Neutron Scattering

Figure 1 shows the scattering cross section from a NiCrAlY deposit as a function of Q measured for two sectors, parallel and perpendicular to the coating surface. Different heights of the two fitted lines, both representing a Q^{-4} behaviour, indicate different Porod constants for these two directions (at high Q the background of incoherent scattering dominates into which the Porod scattering merges). Since the value of the Porod constants obtained for each of these sectors does not by itself reflect the surface area of the scatterers in that particular direction, it often is called apparent Porod constant. The total specific surface area of the scatterers in the sample can be obtained from the apparent Porod constants by averaging over all directions, c.f. equation (1), provided that these are known. Furthermore, the anisotropy of the microstructure can be related to the angular dependence of the apparent Porod constant, even though the relationship is not simple. From the apparent Porod constant an apparent surface area in a specified direction can be defined.

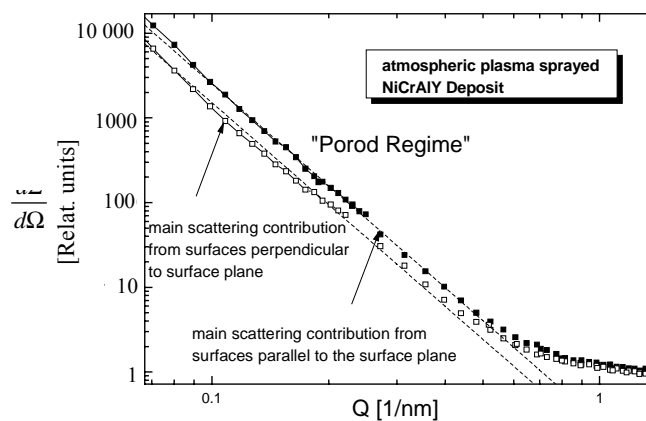


Fig. 1. Example of the scattering intensity of an atmospheric plasma sprayed NiCrAlY coating as a function of the momentum transfer Q . Two sectors, one parallel to the coating plane and the other perpendicular, are shown to stress the anisotropy in the Q^{-4} “Porod regime” (in this graph, region of linear dependence).

Figure 2 shows examples of the anisotropic apparent Porod surface area distributions for the NiCrAlY coatings obtained by fitting a Q^{-4} law to the intensity $I(Q)$ in each sector around the central beam. The results obtained by the same evaluation procedure, with the neutron beam passing *perpendicular* to the deposit top surface showed *no* anisotropy, proving that the in-plane microstructure of the investigated coatings was isotropic [7].

Measurements of samples mounted horizontally as well as vertically (parallel or perpendicular to the magnetic field direction) showed the same anisotropy in both positions, giving evidence that possible magnetic scattering contributions are negligible and do not require corrections to be applied. The low oxide content of the NiCrAlY deposits, determined to be less than 1%, ensures that only a negligible Porod scattering contributes from oxide-metal and oxide-pore interfaces. The calculated total specific surface areas of the NiCrAlY deposits for the investigated spraying techniques and spraying parameters are collected in Table 1 and visualized in Figure 3.

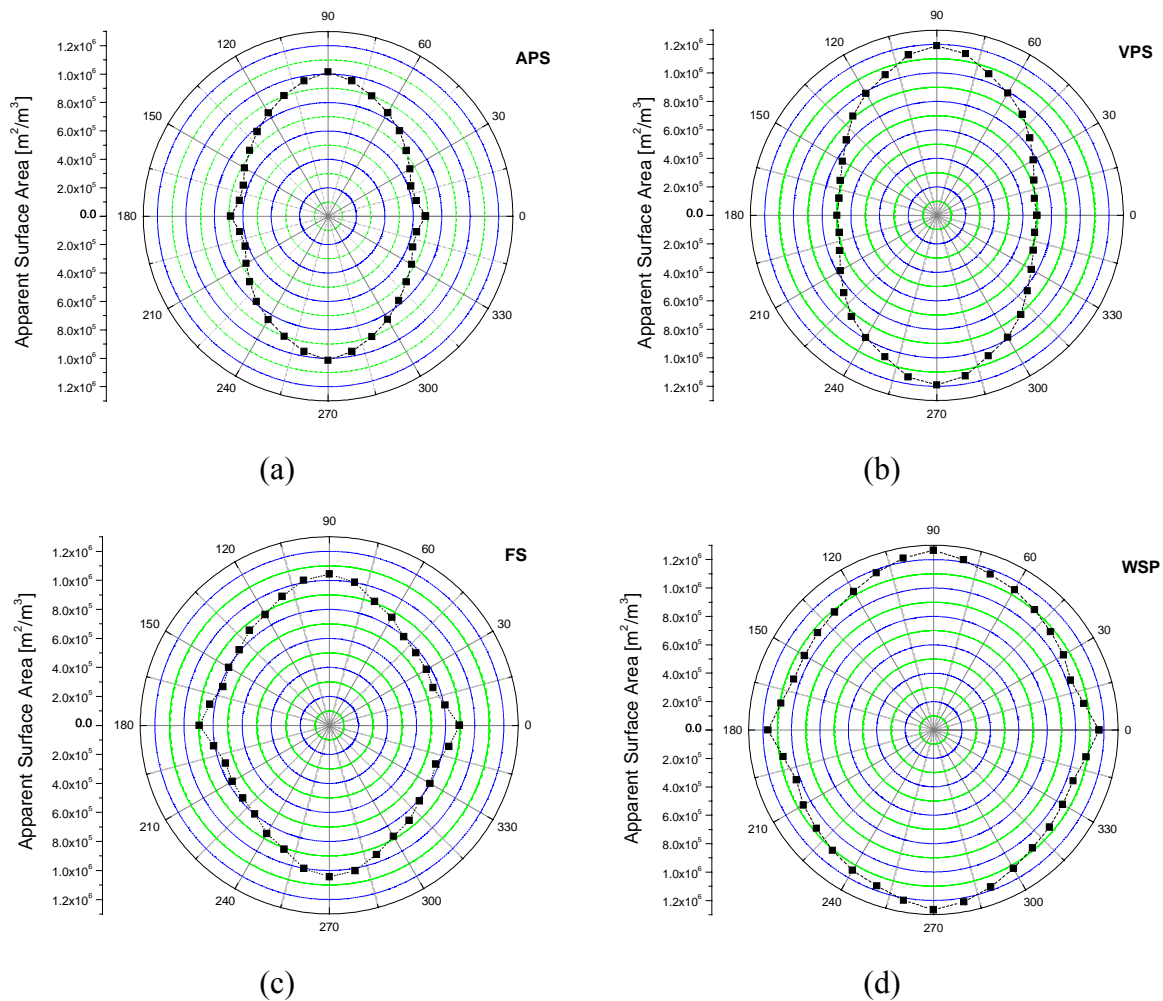


Fig. 2. Anisotropic apparent surface area as a function of the azimuthal angle around the incident beam of a NiCrAlY coating, deduced from scattering curves as shown in Fig. 1 by fitting the Q^{-4} -power law to each sector: (a) – APS, (b) – VPS, (c) – FS, (d) – WSP

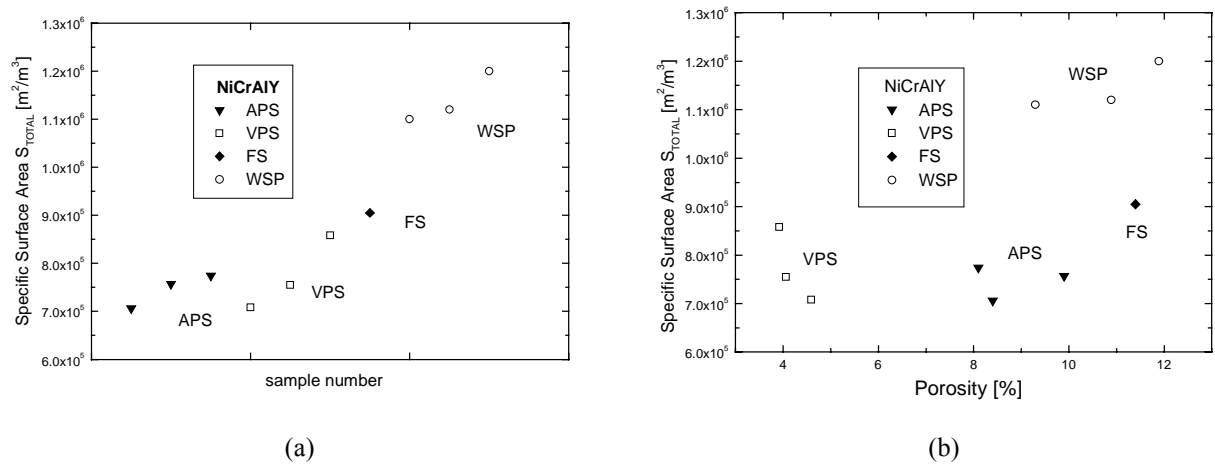


Fig. 3. Total specific surface areas of the NiCrAlY coatings (a), and relationship between the porosity volume fraction and its specific surface area (b), obtained for the different spraying techniques.

2. Microscopy

Figures 4 and 5 present examples of the cross sections of the NiCrAlY. All the images have the same magnification factor to render the structure more comparable. All micrographs show coatings in the as sprayed state without any additional treatment.

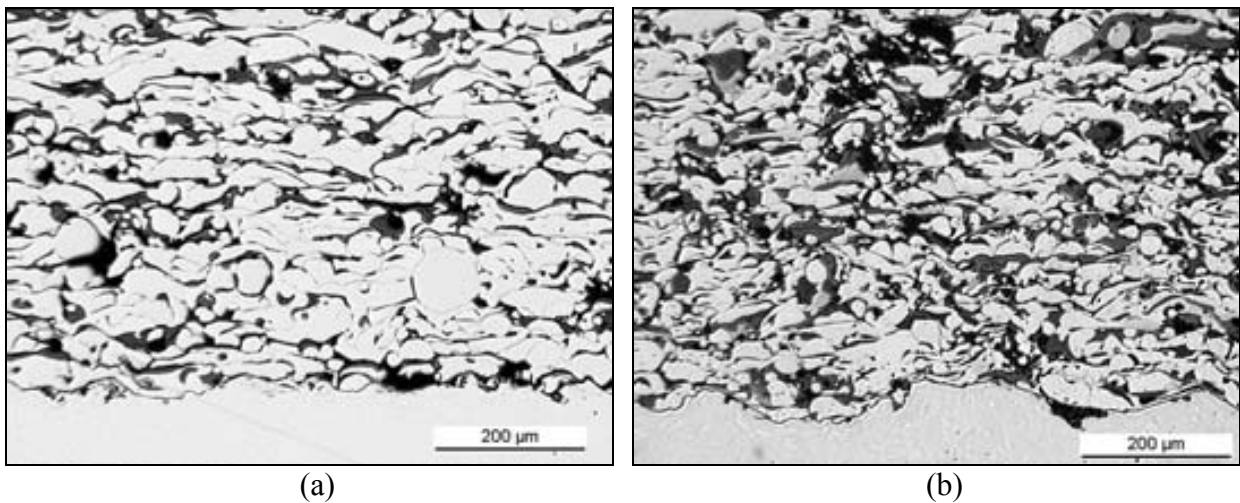


Fig. 4. NiCrAlY coating, (a) – flame sprayed, (b) – WSP.

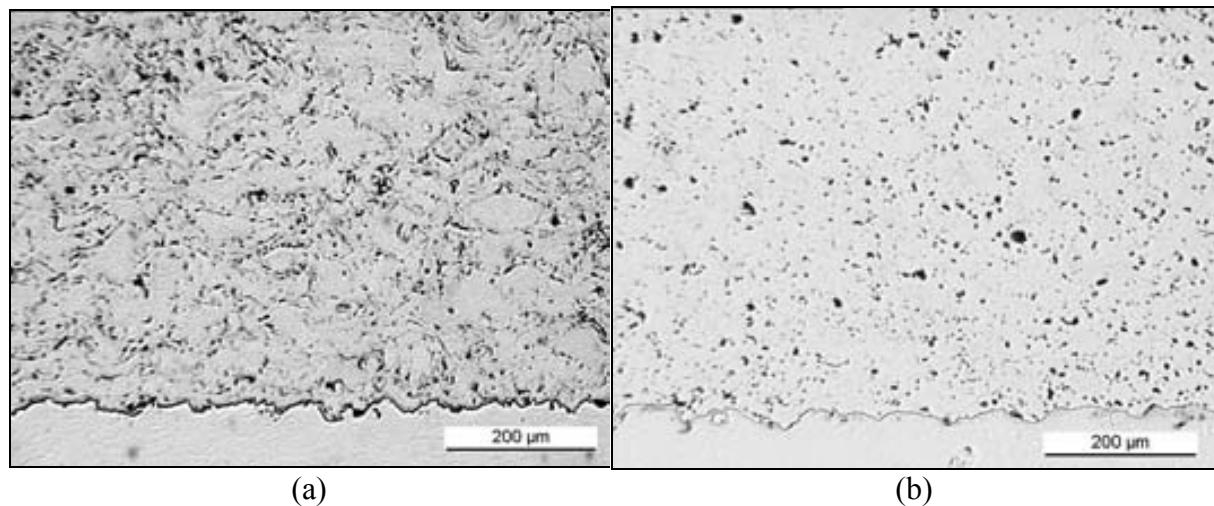


Fig. 5. NiCrAlY coating, (a) – APS, (b) – VPS.

3. Porosity

Table 1 presents the values of the density, the calculated porosity, and the specific surface areas calculated from SANS results of the NiCrAlY coatings. The exact oxygen content of the NiCrAlY deposits is under investigation at this time, but preliminary results show, that it is low (below 1wt%) for all measured samples.

Table 1. Density, porosity and specific surface area of NiCrAlY coatings. Specific surface areas obtained from the Q^{-4} region by averaging the Porod constants. The estimated error for the results is about 5%.

Process	Parameter	Density [g/cm ³]	Porosity [%]	Specific Surface Area S_{total} [m ² /m ³]	
FS	a	6.4	11.4	0.91×10^6	
	VPS	a	6.88	3.9	0.86×10^6
		b	6.89	4.6	0.71×10^6
APS	c	6.91	4.1	0.76×10^6	
	a	6.63	8.1	0.77×10^6	
	b	6.49	9.9	0.76×10^6	
WSP	c	6.62	8.4	0.71×10^6	
	a	6.37	11.9	1.20×10^6	
	b	6.45	10.9	1.12×10^6	
	c	6.57	9.3	1.11×10^6	

DISCUSSION

The total specific surface areas of the NiCrAlY deposits displayed in Figure 3 show differences between the spraying techniques within a factor of two. The scatter of total surface areas for each of the spraying techniques is due to the variation of microstructures created by varying the spray parameters. This scatter is less than the difference between the spraying

techniques. This indicates that the specific surface area is a characteristic of the spraying technique rather than of the spray parameters applied for one technique. The relationship between the porosity volume fraction and the specific surface area (Figure 3b) shows the same principal trend. The clustering of the points of each spraying technique indicates a “typical” microstructure, even though the spray parameters were varied with the intention to produce a wide range of microstructures for each spraying technique. This can be explained when each of the spray techniques produces different, but “typical” pore sizes and shapes.

Insight into the pore sizes can be obtained from the Figure 3b. While for example VPS and APS deposits have quite the same surface area, the APS porosity volume is about twice as high compared to the VPS deposits. A smaller porosity volume at almost the same specific surface area could be explained by a smaller pore size with the same or similar pore microstructure. This is confirmed by the optical micrographs of these deposits as shown in Figure 5, indicating (on average) smaller pores in the VPS deposits. The WSP deposits have about the same porosity as the FS coating, but a higher specific surface area. However, a similar comparison as for the APS and VPS coatings is more difficult since the micrographs of the WSP and FS deposits show quite a different microstructure.

Special attention should be drawn to the anisotropy present in these coatings. The APS and VPS NiCrAlY coatings show similarly pronounced apparent surface area anisotropy (Figure 2), whereas the FS and WSP coatings are more isotropic (Figure 4). The APS and VPS apparent surface area anisotropy can well be described by a single ellipsoid, which indicates that one void system in the microstructure is dominant. The apparent surface area anisotropy of the FS coating (Figure 4a) seems to consist of two ellipsoids perpendicular to each other, suggesting that two significantly scattering void systems with the main orientations perpendicular to each other are present in the microstructure. Similarly, the WSP apparent surface area anisotropy (Figure 4b) also seems to be better described by two ellipsoids, even though due to lower overall anisotropy it is more difficult to reliably separate them.

The orientation of the ellipsoids indicates that one dominating void system in all the deposits is that of interlamellar pores oriented mostly parallel to the substrate. The weight of the other system, most likely cracks, which are dominantly found in ceramic deposits and mostly oriented perpendicular to the substrate, is less relevant in the metallic NiCrAlY deposits.

It should further be noted that by the nature of the surface characterization of the voids by their surface area, large globular pores with small surface area, possibly present in the microstructure, have almost no weight. These can better be characterized by the so-called multiple small-angle neutron scattering method (MSANS), which is currently planned to be applied to these deposits.

CONCLUSION

Small-Angle Neutron Scattering can be a useful tool for characterization of the microstructure of thermally sprayed deposits. The total specific surface area as well as the anisotropy of the apparent surface area, are found to be different for the different spraying techniques. At the same time the porosity volume varies significantly for different spraying techniques. These

results, in combination, allow a more detailed characterization of the voids microstructure in these materials.

The presented results show wide variability of the microstructures which can be obtained by various thermal spray techniques.

The presented technique of Porod scattering is, of course, not limited to the thermally sprayed deposits. One of the areas, in which similar approach is being considered at this time are fatigue stress cracks. These cracks exhibit similar anisotropy and therefore similar measurement should be possible. Other areas are at this time being sought, because studies of anisotropic materials are important part of materials science of today as well as of tomorrow.

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