Doctoral Thesis

Pore morphology in thermally sprayed nickel-based deposits and the influence on deposit properties

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Pore morphology in thermally sprayed nickel-based deposits and the influence on deposit properties

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presented by

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2003
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Symbols and abbreviations

\( a \)  
Lattice parameter

\( b \)  
Total neutron scattering length of a nucleus

\( C_S \)  
Attenuation factor

\( d \)  
Particle diameter of the feedstock powder

\( d_{hl} \)  
Crystal lattice spacing depending on the Miller indices \( h, k, l \)

\( E \)  
Energy of neutron;
Macroscopic in-plane Young’s modulus of deposits

\( E_S \)  
Young’s modulus of substrate

\( f(\theta) \)  
Scattering amplitude

\( FWHM \)  
Full width at half maximum (e.g. of a gaussian profile)

\( h_D \)  
Deposit thickness

\( H_S \)  
Substrate thickness

\( I(\mathbf{Q}) \)  
Scattering intensity

\( I_{S,ij} \)  
Normalized count rate of the sample in pixel \( i, j \)

\( I_{S-EB,ij} \)  
Normalized count rate of the sample background in pixel \( i, j \)

\( I_{H_2O,ij} \)  
Normalized count rate of the water in pixel \( i, j \)

\( I_{H_2O-EB,ij} \)  
Normalized count rate of the water background in pixel \( i, j \)

\( I_{Cd,ij} \)  
Normalized count rate of the Cd background in pixel \( i, j \)

\( J_i \)  
Bessel function of order \( i \)

\( \mathbf{k}_0; \mathbf{k} \)  
Wavevectors of the incident (0) and scattered waves

\( K(\beta, \mathcal{X}) \)  
Orientational factor for a spheroid with the spheroid axis \( \beta R_0 \)
at an angle \( \eta \) relative to \( \bar{Q} \), \( \mathcal{X} = \cos \eta \). \( R_0 \) is the large radius
and \( \beta \) the aspect ratio between the small and the large radius

\( l \)  
Scattering mean free path

\( L \)  
Smallest dimension of a scattering particle

\( L_{X\text{-ray}} \)  
Mean volume weighted column length of grains

\( m \)  
Mass (of neutron)

\( m_{\text{m, Dep}}; m_{\text{m, NiCrAlY}} \)  
Mass of deposit and NiCrAlY feedstock

\( m_{\text{m, Oxide}} \)  
Mass of oxide
SYMBOLS AND ABBREVIATIONS

\[ n = N/\Phi \]  Number density of \( N \) scatterers in volume \( \Phi \)

\( N \)  Number of nuclei

\( N/V \)  Average nuclear density in volume \( V \)

\( N_p \)  Number of particles (\( P \))

\( N_p (R, R_0) \)  Particle size distribution around mean particle radius \( R_0 \)

\( N_{Pr} \)  Size distribution of precipitates

\( o \)  Oxide content

\( \langle \text{O.D.}\rangle_{C,P} \)  Mean opening dimension of the spheroids \( C \) and \( P \)

\( p_{l,m,h} \)  Probabilities over random to find the short axis of the model spheroid in an angular range \( 0-30^\circ \) (l), \( 30-60^\circ \) (m) or \( 60-90^\circ \) (h) with respect to the surface

\( P \)  Porod constant

\( \tilde{P} \)  Apparent Porod constant

\( P_l (\cos(\theta)) \)  Legendre polynomial

\( q(\zeta) \)  Real space function relating the single scattering cross-section to \( W(\vec{Q}|\tau) \)

\( \vec{Q} \)  Scattering vector with modulus \( Q = |\vec{Q}| \)

\( \vec{r} \)  Position vector with moduli \( r = |\vec{r}| \)

\( 1/r \)  Inverse radius of bending

\( r_c (\lambda) \)  Curvature of beam profile at \( \vec{Q} = 0 \)

\( r_1 \)  Length of Porod constant projection of the crack pore system parallel to spray direction

\( r_2 \)  Length of Porod constant projection of the interlamellar pore system parallel to spray direction

\( R \)  Radius of sphere

\( R_0 \)  Volume weighted mean pore radius

\( R_{0C,P} \)  Large radii of spheroidal pores \( C \) and \( P \)

\( R_{0G} \)  Radius of a globular pore

\( R; R_V \)  Mean and volume weighted mean radius of precipitates

\( s \)  Width of size distribution of precipitates

\( s_{\text{in-plane}} \)  Average macroscopic in-plane stress in deposit

\( P_s \)  Scattering probability

\( S \)  Equivalent Eshelby polarization factor

\( S_T \)  Total specific surface area

\( S(\vec{Q}) \)  Form factor of a single particle

\( S_{C,P,G} \)  Specific surface area in the pore sub-systems \( C, P \) and \( G \)
**SYMBOLS AND ABBREVIATIONS**

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$T_S$</td>
<td>Transmission of the sample</td>
</tr>
<tr>
<td>$T_{S,EB}$</td>
<td>Transmission of the sample background</td>
</tr>
<tr>
<td>$T_{H_2O}$</td>
<td>Transmission of the water</td>
</tr>
<tr>
<td>$T_{H_2O-EB}$</td>
<td>Transmission of the water background (cuvette)</td>
</tr>
<tr>
<td>$v_{\text{in-plane}}; v_{\text{through-thick}}$</td>
<td>Aspect ratio of the sound velocity</td>
</tr>
<tr>
<td>$v_{\text{ar}} = v_{\text{in-plane}}/v_{\text{through-thick}}$</td>
<td>In-plane and through-thickness sound velocity</td>
</tr>
<tr>
<td>$V(x)$</td>
<td>Scattering potential</td>
</tr>
<tr>
<td>$V_P$</td>
<td>Volume of one particle (P)</td>
</tr>
<tr>
<td>$W(Q</td>
<td>\tau)$</td>
</tr>
<tr>
<td>$\vec{x}$</td>
<td>Sample coordinates, $z$ denoting the direction parallel to the incident beam, $x$ and $y$ are the transversal components</td>
</tr>
<tr>
<td>$\bar{z}$</td>
<td>Mean number of scattering events</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Angle between spray direction and $\vec{Q}$</td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>Average total bend of an incident particle after $\bar{z}$ impacts</td>
</tr>
<tr>
<td>$\beta_{C,P}$</td>
<td>Aspect ratio of crack and interlamellar spheroids $C$ and $P$</td>
</tr>
<tr>
<td>$\delta(2\theta_{hkl})$</td>
<td>Integral breadth of the Bragg reflection $hkl$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Strain; angle between the $z$ axis and projections of the neutron flight path in the $yz$ plane</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Impact parameter</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Angle with $\lambda = \cos \eta$</td>
</tr>
<tr>
<td>$\eta_1$</td>
<td>Aspect ratio of Porod constant projection of crack pore system</td>
</tr>
<tr>
<td>$\eta_2$</td>
<td>Aspect ratio of Porod constant projection of interlamellar pore system</td>
</tr>
<tr>
<td>$2\theta$</td>
<td>Scattering angle</td>
</tr>
<tr>
<td>$2\theta_{hkl}$</td>
<td>Peak position of the Bragg reflection $hkl$</td>
</tr>
<tr>
<td>$\kappa_{\text{in-plane}}; \kappa_{\text{through-thick}}$</td>
<td>In-plane and through-thickness thermal conductivity</td>
</tr>
<tr>
<td>$\kappa_{ar} = \kappa_{\text{in-plane}}/\kappa_{\text{through-thick}}$</td>
<td>Aspect ratio of the thermal conductivity</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of neutrons or X-rays</td>
</tr>
<tr>
<td>$\mu = \delta + 1$</td>
<td>Index of refraction</td>
</tr>
<tr>
<td>$\nu_0, \nu$</td>
<td>(Mean) phase shift parameter</td>
</tr>
<tr>
<td>$\nu_l$</td>
<td>Phase shift of $l$th partial wave</td>
</tr>
<tr>
<td>$\nu_S$</td>
<td>Poisson’s ratio of substrate</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Dimensionless integration parameter</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$\rho_n(\vec{r})$</td>
<td>Locally averaged neutron scattering length density</td>
</tr>
<tr>
<td>$\rho_{n,P}(\vec{r})$</td>
<td>$\rho_n(\vec{r})$ of a particle (P)</td>
</tr>
<tr>
<td>$\rho_{n,M}(\vec{r})$</td>
<td>$\rho_n(\vec{r})$ of the matrix (M)</td>
</tr>
<tr>
<td>$\rho_{P}(\vec{r})$</td>
<td>$\rho_n(\vec{r})$ of a precipitate</td>
</tr>
<tr>
<td>$</td>
<td>\Delta \rho_n(\vec{r})</td>
</tr>
<tr>
<td>$\rho_m$</td>
<td>Mass density</td>
</tr>
<tr>
<td>$\rho_m, \text{Dep}$, $\rho_m, \text{NiCrAlY}$</td>
<td>Mass density of deposit, NiCrAlY feedstock</td>
</tr>
<tr>
<td>$\rho_m, \text{Oxide}$</td>
<td>Mass density of oxide</td>
</tr>
<tr>
<td>$\sigma_{\text{el}, \text{O, P}}$</td>
<td>Electrical conductivity of oxide phases or pores</td>
</tr>
<tr>
<td>$\sigma_{\text{el}, \text{M}}$</td>
<td>Electrical conductivity of the NiCrAlY matrix</td>
</tr>
<tr>
<td>$\sigma_{\text{el, EFF}}$</td>
<td>Experimental in-plane effective electrical conductivity of deposits</td>
</tr>
<tr>
<td>$\sigma(Q', \nu)$</td>
<td>Microscopic single scattering cross-section</td>
</tr>
<tr>
<td>$\Sigma(Q', \nu)$</td>
<td>Macroscopic single scattering cross-section</td>
</tr>
<tr>
<td>$\Sigma_T(\nu)$</td>
<td>Total macroscopic single scattering cross-section</td>
</tr>
<tr>
<td>$\Sigma_{\text{geo}}$</td>
<td>Total macroscopic cross-section of refraction</td>
</tr>
<tr>
<td>$\Sigma_{\text{C,P,G}}$</td>
<td>Total macroscopic single scattering cross-section of interlamellar pores, cracks and globular pores</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Sample thickness parallel to the incident beam</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Angle between the $z$ axis and projections of the neutron flight path in the $xz$ plane</td>
</tr>
<tr>
<td>$\phi_{\text{Porod}}$</td>
<td>Total Porod aspect ratio</td>
</tr>
<tr>
<td>$\phi_{\text{MSANS}}$</td>
<td>Aspect ratio of MSANS profile</td>
</tr>
<tr>
<td>$\Phi_{\text{NiCrAlY}}$</td>
<td>Volume of NiCrAlY matrix</td>
</tr>
<tr>
<td>$\Phi_{\text{Oxide}}$</td>
<td>Volume of oxide phase</td>
</tr>
<tr>
<td>$\Phi_{\text{Pr}}$</td>
<td>Total volume of precipitates</td>
</tr>
<tr>
<td>$\Phi_{\text{C,P,G}}$</td>
<td>Pore volume fractions in the pore sub-systems c, p and g</td>
</tr>
<tr>
<td>$\Phi_T = n V_P$</td>
<td>Total pore volume of $N$ particles of volume $V_P$</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Standard deviation of fit</td>
</tr>
<tr>
<td>$\Psi_0(\vec{x}), \Psi(\vec{x})$</td>
<td>Wave function of incident (0) and scattered neutron</td>
</tr>
<tr>
<td>$\omega_0, \omega$</td>
<td>Width of beam profile before and after passage of sample</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Solid angle element</td>
</tr>
<tr>
<td>$\mathcal{X}$</td>
<td>$\mathcal{X} = \cos \eta$</td>
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Summary

The present work focuses on a comprehensive microstructure characterization of thermally sprayed NiCrAlY deposits with a chemical composition 67 wt.% Ni, 22 wt.% Cr, 10 wt.% Al, 1 wt.% Y in order to understand the influence of the pore morphology on macroscopic deposit properties. Vacuum-, atmospheric-, and water-stabilized plasma spraying, flame spraying and wire-arc spraying are applied to generate large variations in the pore morphology to establish spray-technique independent microstructure-property relations.

As the deposition takes place drop-by-drop, on the microscopic level most thermally sprayed deposits contain pores that originate from incomplete filling (globular pores), insufficient contact and bonding to subsequently deposited layers (interlamellar pores) but also as a result of relaxation of residual stresses (fine-scale crack-type pores).

From small-angle neutron scattering (SANS) data in the Porod-regime the total specific surface area of all pores may be determined. A multiple-small-angle neutron scattering (MSANS) analysis further allows the interlamellar, fine-scale crack-type and globular pores to be quantified. From modelling of the pore morphology, mean pore sizes, pore orientations and the pore shape are obtained and the total pore volume fraction and the total specific surface area assigned to the different pore-types. The results of SANS and MSANS evaluations agree qualitatively with those of scanning-electron- (SEM) and optical microscopy imaging, but represent statistically relevant values of a sample volume of a few tens mm$^3$ and comprise length scales from a few nanometers up to micrometers.

The MSANS analysis shows that for the majority of the investigated deposits the interlamellar pore system generates the largest fraction of the total specific surface area. The influence on macroscopic deposit properties is for example reflected in the reduction of sound velocity and thermal conductivity with increasing interlamellar pore volume. A comparably smaller fraction of the total pore volume is found in fine-scale crack-type pores that may be decisive for certain deposit properties. The reduction of the average residual stress parallel to the deposit plane with an increasing surface area in the crack-type pores suggests a mechanism of stress relaxation by crack initiation.
1. SUMMARY

Small-angle neutron scattering of the vacuum-plasma sprayed deposits suggests that nanometer-sized precipitates are present. The phase analysis by X-ray diffraction shows that in these deposits, a crystalline $\alpha$-Cr phase can be identified. The Bragg reflections indicate a particle size similar to that obtained from SANS. Therefore it is concluded that the SANS scattering originates from a nano-crystalline $\alpha$-Cr phase. From transmission-electron microscopy these precipitates are found to be located within the NiCrAlY matrix.

A decreasing lattice parameter of the $\gamma$-NiCrAlY matrix with increasing oxide content is observed for all microstructures generated by the spray techniques. This is caused by the partial oxidation of the most oxygen-affine elements like aluminum during the whole process of deposition and subsequent cooling. From energy-dispersive X-ray spectroscopy the oxides $\text{Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$, located at the boundaries of solidified droplets (splits), are identified. Certain deposit properties like the electrical conductivity are strongly influenced by the oxide content. At a low oxide content as in the vacuum-plasma sprayed deposits, a reduction of the electrical conductivity is related to an increasing total specific pore surface area. Complex processes like abrasive or particle-erosive wear are differently influenced by the total specific surface area. The dependence on the latter indicates for the erosive wear a material removal as complete splats or single parts of splats in contrast to the abrasive wear with a more continuous material removal and no significant breakouts.

The ratio between the sound velocity parallel and perpendicular to the deposit plane increases with increasing Porod anisotropy, which is a measure of the distribution of surface area in the deposits. On the other hand, the ratio between the thermal conductivity parallel and perpendicular to the deposit plane increases with increasing anisotropy of the MSANS scattering, which on a larger length scale reflects the size and orientation of anisotropic pores. This agreement between anisotropies of the microstructure and of macroscopic properties shows the significance of the microstructural SANS and MSANS analysis. The combination of SANS and MSANS besides conventional techniques like SEM and X-ray diffraction allows the microstructure to be quantitatively described and therefore in many cases the property-determining microstructural parameters to be identified and finally the spraying process to be optimized.
Zusammenfassung


Bedingt durch den tropfenweisen Auftrag enthalten die meisten thermischen Spritzschichten auf mikroskopischer Skala Poren, die vor allem durch unvollständiges Auffüllen von Hohlräumen (kugelförmige Poren), durch nicht optimalen Kontakt bzw. mangelnde Haftung zur unterliegenden Schicht (interlamellare Poren), aber auch als Folge des Abbaus von Eigenspannungen (feine rissartige Poren) entstehen.


Die MSANS-Analyse ergibt, dass die Porenmorphologie in den NiCrAlY-Schichten von interlamellaren Poren dominiert wird. In makroskopischen Schichteigenschaften zeigt sich dies beispielsweise in der Schallgeschwindigkeit und der thermischen Leitfähigkeit, die hauptsächlich mit zunehmendem interlamellaren Porenvolumen abnehmen. Ein vergleichsweise kleiner
Anteil des gesamten Porenvolumens findet sich in feinen rissartigen Poren, die für einige Materialeigenschaften entscheidend sein können. Die Abnahme der mittleren Eigenspannung parallel zur Schichtebene mit zunehmender spezifischer Oberfläche in dem feinen rissartigen Porensystem legt einen Mechanismus der Spannungsrelaxation über Rissbildung nahe.


3

Introduction

The demand for development of new high performance materials is steadily growing. An important aspect of materials are their surfaces, and therefore one objective of research and development is tuning and optimization of surface properties to special applications as well as protection against destructive environments. Thermal spraying is nowadays a widely applied processing technology to deposit functional coatings with desired properties on base materials [ML01]. The considerable coating thickness achievable and the easy handling enables and facilitates applications. Major advantages are achieved by the possibility to melt and therefore to apply almost all materials. For different applications, a large variety of deposition techniques combined with new feedstock materials have been developed. The choice of deposition technique, parameter setting and starting materials strongly influence the microstructure and therefore the performance of the coatings [Paw95]. Best performance and most suitable properties for a given application can in principle be achieved by a microstructural optimization. However, insufficient knowledge of the influence of the microstructure on properties often leads to an optimization only achieved by a “trial and error” method, i.e. by using different parameter sets during deposition and then testing the resulting properties. Current interest is focused on reducing this time-consuming work by the development of a fundamental understanding of the correlations between microstructure and materials properties on one hand and the spray parameters and techniques on the other hand.

A major microstructural feature of thermally sprayed deposits is their pore morphology with pore volume fractions from a few up to several tens of percent. Pores are therefore expected to strongly influence the materials properties. Molten, semi-molten or even solid feedstock droplets impinging on the substrate or deposit surface partly dissociate by their impact energy and rapidly solidify as flat splats and form the final pore morphology. The number of pores and their size, shape and orientation is influenced by the difference in kinetic and thermal energies of the different spray techniques, but also to some extent by specific spray parameter settings and the feedstock properties. The pores can often be separated into different pore species, since different mechanisms form specific pores during the deposition and subsequent cooling. Frequently, the size distribution is bimodal with coarse pores in the range of a few micrometers and fine-scale pores with mean opening dimensions of 0.1 µm.
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The coarse pores, in the following called globular pores, are associated with the incomplete filling of interstices between previously deposited particles [McP89]. Further, two fine-scale pore systems are distinguished in thermally sprayed deposits; interlamellar pores and intralamellar pores. Interlamellar pores emerging between successive splats are attributed to incomplete contact between lamellae [McP81]. They are mainly oriented with their short opening dimension parallel to the spray direction. The second fine-scale pore system originates from the buildup of residual stresses during deposition, cooling and shrinkage. Stress relaxation may induce the formation of fine-scale crack-type pores within single splats, the intralamellar pores. They are mainly oriented with their short opening dimension perpendicular to the spray direction [KMP+].

For the optimization and development of new deposits with desired properties, experimental studies as well as simulations and modelling attempts on various specific aspects of the thermal spray deposition have been reported in the literature. However, many studies are limited to the description of the influence of only a few spray parameters like the spray distance and the substrate temperature during the deposition process, or a certain desired property. Often, a microstructure discussion is absent in the interpretation of the presented properties. For different deposit materials and spray techniques, Nuutinen et al. [NVAM01] showed the influence of the feedstock particle size and the flame temperature on the coating density and the oxide content. By optical image analysis, Koeschlig and Lallement [KL01] determined the porosity and the crack distribution, direction and density to relate the microstructure of oxide coatings to spraying parameters and coating properties.

The elasticity characteristics of plasma sprayed coatings have been discussed by Dekhtyar et al. [DKBA96] and Ilavsky et al. [WI97, WI98], and the influence of the Young’s modulus and Poisson’s ratio on mechanical properties of alumina ceramics has been addressed by Asmani et al. [AKLO01]. Effective elastic moduli of materials with anisotropic pore arrangements were modelled by Kachanov et al. [MK96, KT00]. A nonlinear elastic behavior in the compression of thermally sprayed materials was observed by Kroupa et al. [KP02].

The elastic anisotropy in plasma sprayed alumina coatings was investigated by ultrasonic techniques by Parthasarathi et al. [PTSO95]. An increase of the thermal expansion coefficient with increasing deposit density was observed by Rohan et al. [RCCN00]. The anisotropy of the microstructure of thermally sprayed deposits and its influence on deposit properties have been discussed mainly on ceramic yttria-stabilized zirconia (YSZ) thermal barrier coatings (TBCs). The reduction of elastic anisotropy at increasing annealing temperatures was correlated to a reduction in intersplat pore surface area [AIL+01]. An extensive discussion on anisotropic microstructure characterization and property modelling is given by Kulkarni et al. [KSGH00, KWN+03] and Margadant et al. [MSP+01].

Also, process-property relationships for YSZ TBCs were established by relating an increasing deposition temperature to a large increase in (through-thickness) thermal conductivity, hardness and oxide content. Similar to bulk ceramic materials, where the pore morphology is known to significantly influence materials properties [Ric77], a reduction in thermal conductivity of deposits was related to an increased amount of total pore volume [KSGH00]. Process-property relationships were also discussed by Jiang et al. [JMK+00], who found for
Mo deposits that the thermal conductivity and hardness increase with increasing particle velocity, whereas the oxygen content and the porosity decrease.

In recent years, simulations of the plasma (thermal) [MBV01] and deposition (kinetic) [GMC01] process, of the deformation and solidification of particles [IIGZ01, HB01] and of the development of the deposit microstructure [WFM01] as a function of the particle trajectories, the particle temperature and velocity distribution have all been performed. Beauvais et al. [BGB+01] and Lugaresi et al. [LPJ02] modelled process-microstructure-property relationships for different spray techniques. Neural network concepts have been applied by Guessasma et al. [GMC02] to describe the thermal spray deposition process. Kundas et al. [KKH+02] used 3D finite element methods to describe the heat transport into the deposit and the buildup of residual stresses.

The present work focuses on the microstructure characterization of thermally sprayed metallic NiCrAlY deposits of the standard chemical composition 67 wt.% Ni, 22 wt.% Cr, 10 wt.% Al, 1 wt.% Y. Employed spray techniques comprise vacuum plasma spray (VPS), atmospheric plasma spray (APS), water-stabilized plasma spray (WSP), flame spray (FS) and wire-arc spray (WAS) using different spray parameter sets to generate a wide range of “sample” pore morphology. The aim is to gain insight into generic relations between the processing parameters of thermally sprayed deposits, the developing pore morphology and resulting materials properties. Such relationships are not yet well established or understood owing to their complex nature and the lack of appropriate methods for the characterization of the pore morphology. Up to now, similar investigations are known only for the ceramic YSZ system [AIL+01, KWN+03]. Characterization of microstructure by means of anisotropic small-angle neutron scattering (SANS) combined with standard techniques like image analysis and X-ray diffraction is expected to lead to a new level of understanding of microstructure-property relationships. SANS in the Porod regime offers non-destructive quantitative results on the total amount of surface area combined with a measure of microstructural anisotropy within the deposits. The relation between pore surface area obtained by small-angle Porod scattering and microstructure was established by Ilavsky et al. [IAL+97, IBK97]. A recently refined multiple SANS technique (MSANS) extends the range of accessible information to pore sizes of up to a few micrometers and the corresponding mean pore sizes, shape and orientation distributions [AIL+01, ABIL02, BAL+03]. This method is also expected to help in separating dominant sub-systems of coarse globular pores and fine-scaled oblate spheroid-shaped pores, and the determination of volume and surface area fractions within these pore sub-systems. Characterizations of pore systems by the SANS and MSANS method in the field of thermal spray are known from investigations on ceramic deposits. The capabilities of the techniques were demonstrated by Ilavsky et al. [ILA+98], who also compared the scattering methods with conventional methods of characterization of the pore system such as mercury intrusion porosimetry (MIP) and image analysis of optical or electron micrographs, each with its specific potentials but also limitations: MIP only yields the open, i.e. interconnected porosity [IBK97], and in optical analysis the resolution is limited and care has to be taken to avoid preparational artefacts [KLKB00]. By SANS investigations, it has become possible to relate a variation in the specific surface area of pores between different samples to specific
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Spray parameter settings like the spray distance [ILA+96] and the spray angle [IALK97] with respect to the deposition plane. Open and closed porosity were distinguished by the technique of contrast mixing [IAL+97] that showed 60% of the total specific surface area of the ceramic deposits investigated to be attributed to closed porosity. Microstructural details of pores as obtained by the MSANS technique, and their influence on materials properties are discussed by Allen et al. [AIL+01] and are imbedded in a comprehensive study including X-ray tomographic mapping of the pores by Kulkarni et al. [KWN+03]. Since thermally sprayed NiCrAlY is often used as bond coating material for TBCs in turbine applications, one aspect of the present work is the extension of the microstructural investigations from the TBCs to their bond coatings.

Besides the identification of the relevant microstructural parameters for the NiCrAlY deposits capable of describing macroscopic materials properties [MSP+01, MSK+03], a further issue of the present work is to understand the relation of microstructure [KW1+01, KWA+02] and anisotropy of properties. Since the SANS and MSANS techniques in principle yield information on the anisotropy of the pore morphology, it is of special interest to determine how this anisotropy is reflected in the materials properties, especially in those properties that vary themselves with direction. As the SANS and MSANS investigations provide average information on the pore morphology, they are complemented by local imaging techniques like scanning (SEM) and transmission (TEM) electron microscopy. Additionally, oxide phases and ternary intrasplat features like intermetallic precipitates are discussed with respect to their influence on the materials properties.

The main features of the pore morphology specific to the spray techniques, as determined by the SANS technique and by MSANS modelling, are outlined and qualitatively confirmed by SEM images. The microstructure-property relationships and microstructure-property anisotropy relations are discussed on the basis of measurements of the electrical and thermal conductivities and the sound velocity. Also, the impact of pore microstructure on the mechanical properties such as the residual stress state and the elastic modulus as well as on technological properties like the abrasive and the erosive wear rates are discussed. From the spray-technique dependent pore morphology, spray-technique independent microstructure-property relationships are proposed, and - where possible - models for the description are applied and verified.

In section 4, details on the applied spray techniques and spray parameter settings as well as the feedstock material NiCrAlY are given. In section 5, the principles of the applied SANS and MSANS methods with their theoretical background are outlined. The experimental results from SANS and MSANS are given in section 6 together with results from other experimental techniques applied for deposit characterization such as X-ray diffraction, TEM, SEM and energy dispersive X-ray spectroscopy (EDX), as well as oxygen concentration determination by hot gas extraction. Section 7 deals with the interpretation of the experimental MSANS results by pore-microstructure modelling. In section 8 the determined quantitative microstructural parameters are discussed with respect to their influence on deposit properties that were primarily measured at the EMPA Thun in the framework of the EUREKA / KTI - supported project Σ!1973 “THERMETCOAT” [SIW99].
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Materials and processing

4.1 The deposit NiCrAlY

NiCrAlY belongs to the so called “MCrAlY” alloys, where “M” stands for a metal like Fe, Ni or Co. These alloys are known to be highly hot-corrosion resistant (Co-base) or oxidation resistant (Ni-base) [Nic00]. The primary protective scales against oxidation are passivating layers of aluminum oxide (alumina, Al\(_2\)O\(_3\)), preventing further oxidation. The inward diffusion of oxygen is slowed down by the alumina corundum structure. The aluminum in the solid solution alloy serves as a reservoir to repeatedly replenish the oxide scales. The alumina film determines the durability of the coating. If it spalls, new oxide scales have to be built up by aluminum diffusion from the reservoir in the matrix. The addition of chromium promotes the diffusion of aluminum and therefore permits a reduction of aluminum, which is known to cause brittleness. Yttrium is one of the frequently used oxygen-active elements like Si, Ta or Hf. These active elements enhance the oxide-scale adhesion and decrease the oxidation rate [Nic00]. The oxide film must be tightly adherent and resist spalling, since only a certain amount of aluminum is available from the metallic matrix. If the matrix is aluminum-depleted, a major failure may occur. The limited solubility of yttrium in the matrix leads to precipitation of needle-like yttria (Y\(_2\)O\(_3\)) at the grain boundaries, outward from the alloy into the alumina film, thereby pinning it to resist spalling [Her99]. “MCrAlY” forms a tenacious protective oxide scale that inhibits any interactions between the host surface and the outside corrosive environment. It is thermally and chemically compatible with steel or Ni-superalloy substrates. Interdiffusion with the substrate has not been considered as a major failure mode [Nic00], since the “MCrAlY” coatings are diffusionally stable. Applications are limited to temperatures of 927\(^\circ\)C for CoCrAlY and 982\(^\circ\)C for NiCrAlY.

The major application by far of NiCrAlY is for bond coating between Ni superalloy substrates and ceramic Y\(_2\)O\(_3\) - ZrO\(_2\) (yttria-stabilized zirconia) thermal barrier coatings, but also for protective plasma sprayed coatings exposed to hot corrosive or high-temperature oxidizing environments [IIZK97a], e.g. to protect valve chambers in marine diesel engines. In gas turbine engines, the excellent oxidation resistance and the diffusional stability of NiCrAlY are advantageous properties [Her99].
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4.2 Spray process and applications

Spray techniques

Nowadays, several thermal spray techniques are widely applied. The optimal choice depends on the particular application, sample geometry and desired coating properties. Within this work, coatings were deposited by the following spray techniques:

- Vacuum plasma spraying (VPS)
- Atmospheric plasma spraying (APS)
- Water-stabilized plasma spraying (WSP)
- Flame spraying (FS)
- Wire-arc spraying (WAS)

Further important spray techniques to be mentioned here for completeness are high velocity oxygen fuel (HVOF), detonation gun spray (DGS) and the cold spray (CS) techniques. A detailed description and overview of most of the aspects of thermal spraying is given e.g. by Pawlowski [Paw95], including descriptions of set-ups for the different spray techniques, typical spray parameter settings and substrate treatments prior to deposition. A thermal spray facility comprises a spraying gun by which the feedstock material is heated, melted and accelerated towards the substrate. The gun is often fixed on a robot that moves periodically to ensure a homogeneous deposition rate on the surface at a fixed spraying distance. Usually, the spraying process is controlled by a control unit. Specific surrounding atmospheres (inert gas, vacuum) may require a chamber. Additionally, the facility might comprise diagnostic tools to monitor on-line the inflight particle properties like particle temperature and velocities as well as the substrate temperature.

Spray parameters

To generate variations in the microstructure obtained by each spraying technique, the spray parameter settings were varied according to Table 4.1. The parameters and their variations have been selected especially for this study to obtain a wide range of microstructures and therefore do not necessarily reflect commercial settings.

Sample preparation

The thermally sprayed coatings were deposited on mild steel substrates (ST37-2) of size $25 \times 25 \times 4.6 \text{mm}^3$ and $25 \times 100 \times 4.6 \text{mm}^3$. Prior to the deposition, the substrates were machined, chamfered, annealed in \text{N}_2 atmosphere at 690°C for 1 h and cooled down to room temperature overnight to relax residual stresses introduced by the preparation. The substrates were grit blasted with corundum particles of size $400 - 600 \mu\text{m}$, impinging within an angle of about $60^\circ - 90^\circ$ to the substrate surface. After the grit blasting procedure, the average surface roughness was $Ra = 6 - 12 \mu\text{m}$. Finally, the prepared substrate was coated using NiCrAlY feedstock material.
Table 4.1: Spray parameters for production of samples with different spray techniques and spray parameter settings (slpm: standard liter per minute).

<table>
<thead>
<tr>
<th>Process</th>
<th>Spray parameters</th>
<th>Electrical energy (kW)</th>
<th>Spray distance (mm)</th>
<th>Chamber pressure (10^2 Pa)</th>
<th>Plasma gas H₂ (slpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPS</td>
<td></td>
<td>43</td>
<td>275</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>44</td>
<td>275</td>
<td>150</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>275</td>
<td>150</td>
<td>4</td>
</tr>
<tr>
<td>APS</td>
<td></td>
<td>46</td>
<td>140</td>
<td>160</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>41</td>
<td>140</td>
<td>170</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46</td>
<td>160</td>
<td>160</td>
<td>4.7</td>
</tr>
<tr>
<td>WSP</td>
<td></td>
<td>160</td>
<td>350</td>
<td>310</td>
<td>270</td>
</tr>
<tr>
<td>FS</td>
<td></td>
<td>250</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WAS</td>
<td></td>
<td>3</td>
<td>160</td>
<td>100</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Powder composition

The employed NiCrAlY feedstock material used for VPS, APS, WSP and FS is a prealloyed powder produced by an atomization process. The powder is designated Sulzer Metco AMDRY 962. Two different particle ranges were used for the different spray techniques, as given in Table 4.2. The nominal powder chemical composition is 67 wt.% Ni, 22 wt.% Cr, 10 wt.% Al, 1 wt.% Y.

Table 4.2: Feedstock material according to specifications.

<table>
<thead>
<tr>
<th>Spray technique</th>
<th>shape</th>
<th>(particle/wire) diameter $d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPS, APS</td>
<td>powder</td>
<td>$d &lt; 40 \mu m$</td>
</tr>
<tr>
<td>WSP, FS</td>
<td>powder</td>
<td>$56 \mu m &lt; d &lt; 106 \mu m$</td>
</tr>
<tr>
<td>WAS</td>
<td>wire</td>
<td>1.6 mm</td>
</tr>
</tbody>
</table>
5

Methods of microstructural pore characterization

5.1 Imaging by transmission and scanning electron microscopy

TEM and SEM were applied to qualitatively compare local imaging results with the average information on the pore morphology obtained by SANS. SEM analysis was carried out on cross-section samples of the deposits. Assuming isotropy in the surface plane perpendicular the spray direction, the cross-section images allow qualitative information on the 3D pore shape to be obtained. The TEM analysis focused on the detection and visualization of existing narrow cracks with opening dimensions of the order of 100 nm. TEM samples were prepared for TEM analysis with the electrons parallel to the spray direction (planar view). Owing to the preferred splat alignment, there is thus a higher probability of finding narrow cracks.

Sample preparation, TEM

A cylinder of 3 mm diameter with its axis parallel to the spray direction was prepared by electric wire discharge machining from the deposit attached to its substrate. A disc of 200 µm was cut by electric wire discharge within the deposit. The disc was thinned by grinding with SiC grinding paper (grit size P200-P4000), reducing the thickness to a foil of 40 µm. The foil was thinned by ion milling (PIPS: Precision Ion Polishing System, Gatan, Inc., with 2 Ar⁺ guns, 5 keV, 3 – 6 µA, chamber pressure: 6.5 × 10⁻⁵ Pa), with a low angle of incidence of 5° to the foil that was furthermore rotated by 360° for homogeneous thinning. Each side was thinned for about 45 min, until local transparency indicated sufficient thinning. The final quality was achieved by alternating guns from either the top or the bottom direction, at ±5°, at 2 keV, 4 µA for 11 min, in 2 opposite sectors covering ranges of 60° to retain a base for foil handling. TEM investigations were performed on a JEOL 2010 instrument.
5. METHODS OF MICROSTRUCTURAL PORE CHARACTERIZATION

Sample preparation, SEM

SEM cross-section samples were prepared by cutting and subsequent grinding with SiC grinding paper (grit size P200-P4000), diamond polishing and finishing with colloidal silica [MSP+01]. Partially, the finishing was performed using ion polishing to compare the quality of sample preparation. SEM investigations were performed on a LEO 440 instrument (operating voltage: 20 kV) with the option for energy dispersive X-ray spectroscopy.

5.2 (Small-angle) neutron scattering

Owing to the high penetration depth of up to a few centimeters in many materials, neutrons are a unique probe to obtain microstructural information. SANS can be used to obtain size distributions and volume fractions of inhomogeneities in a size range between a few nanometers and a few micrometers. Inhomogeneities could be pores or precipitates that generate a scattering contrast in a surrounding matrix. In thermally sprayed deposits, SANS has been shown [IAL+97] to be particularly useful in determining the total sum of internal surface area, e.g. the sum of interfaces between splats and pores of different sizes (see section 5.2.3). Furthermore, from modelling of the pore morphology, detailed information on the pore sizes, shape and orientations can be deduced, as discussed in detail in section 5.3. The information obtained by SANS is an average for a sampling volume of the order of 10 mm$^3$. In the wide-angle region, (crystalline) phase analysis or (residual) stress analysis [MSBP99, KPM+01, KMP+] provide valuable information on thermally sprayed deposits.

5.2.1 Neutron scattering

Neutrons interact with condensed matter by absorption, magnetic or nuclear scattering. When a neutron is scattered by a nucleus, in general it can change its energy $E$ and momentum $\hbar \vec{k}$, $\vec{k}$ being the wave vector of the neutron. The scattering process is called elastic, if the energy of the neutron remains unchanged, i.e. the modulus of the incident neutron momentum, $|\hbar \vec{k}_0|$, is equal to the modulus of the scattered neutron momentum, $|\hbar \vec{k}|$; the neutron may only change its direction. Scattering is called coherent, when a phase relation exists between the incident neutron and the scattered neutron [Hec87], in which case the scattering amplitudes are superimposed and the phase information is retained. In sufficiently thick samples, neutrons scattered in layers nearest to the incident surface act as incident neutrons for scattering in subsequent layers. Since no phase relation exists between different scattering centers, from the electron diffraction literature [Cow81], this scattering is called incoherent multiple scattering. The multiple small-angle scattering discussed in the following section 5.3 is an incoherent multiple superposition of coherent scattering events, and therefore called incoherent [SB99].
In the time-independent scattering theory, the stationary-state scattering process is described by an incident plane wave

\[ \Psi_0(\vec{x}) = \frac{1}{(2\pi)^{3/2}} \exp(i \vec{k}_0 \cdot \vec{x}) \]  

that is scattered at a potential \( V(\vec{x}) \). This is described by

\[ [\Delta + \frac{\hbar^2 k_0^2}{2m} + V(\vec{x}) - E] \Psi(\vec{x}) = 0, \]  

where \( \Delta \) is the Laplace operator, \( \vec{k}_0 \) and \( \vec{k} \) are the wave vectors of the incident and scattered neutrons of mass \( m \), and \( k = |\vec{k}| = |\vec{k}_0| \). Once the potential is further specified, this differential equation may be solved by a partial wave expansion (see, e.g. [Sch93]) or by perturbation theory (see, e.g. [Sak94]). The resulting wave \( \Psi(\vec{x}) \) is a superposition of the transmitted incident and the scattered spherical wave and can be expressed in the far field (Fraunhofer diffraction regime) as

\[ \Psi(\vec{x}) = \Psi_0(\vec{x}) + f(\theta) \frac{\exp(i k r)}{r}, \]  

where \( f(\theta) \) is the scattering amplitude and measures the strength of interaction. It depends on the scattering angle \( 2\theta \) as shown in Fig. 5.1, where \( \vec{Q} \) is the scattering vector defined as

\[ \vec{Q} = \vec{k} - \vec{k}_0, \]  

and

\[ |\vec{Q}| = (4\pi \sin \theta)/\lambda, \]  

The scattering amplitude can be denoted as

\[ f(\theta) = -\frac{m}{2\pi \hbar^2} \int d^3 \vec{x} \exp(-i\vec{k} \cdot \vec{x}) V(\vec{x}) \Psi(\vec{x}) \]  

and the microscopic scattering cross-section \( \sigma \) for a neutron to be scattered into the solid angle \( \Omega \) is then given by

\[ \frac{d\sigma}{d\Omega}(\vec{Q}) = |f(\theta)|^2 \]  

A partial wave expansion for a spherically symmetric particle is given by [Wei51], where \( \nu_l \) is the phase shift of the \( l \)th partial wave

\[ \sigma(\theta) = \frac{1}{4k^2} \sum_{l=0}^{\infty} (2l + 1) |1 - \exp(2i\nu_l)|^2 P_l(\cos \theta) \]  

If the potential is weak, the wave-function \( \Psi(\vec{x}) \) in eqn. 5.6 can be replaced by the unperturbed state \( \Psi_0(\vec{x}) \). This corresponds to the expansion of the potential \( V(\vec{x}) \) up to first order
and is called first order Born approximation. In this case, the scattering amplitude is the Fourier transformation of the scattering potential:

\[
f(\bar{Q}) = -\frac{m}{2\pi\hbar^2} \int d^3\vec{x} V(\vec{x}) \exp(i \bar{Q} \cdot \vec{x}),
\]

The true neutron-nucleus interaction \( V(\vec{x}) \) is a short range and very strong attractive interaction. As was shown by Fermi, in a solid material this can be approximated by the much weaker Fermi pseudopotential \([Fer36]\):

\[
\tilde{V}(\vec{x}) = \frac{2\pi\hbar^2}{m} b \delta^3(\vec{x}),
\]

\( b \) being the total neutron scattering length of a nucleus. Then, eqn. 5.6 reduces to

\[
f(\theta) = -b.
\]

Within the kinematic theory, the basic equation for the microscopic coherent scattering cross-section from an assembly of \( N \) nuclei is \([FS87]\)

\[
\frac{d\sigma}{d\Omega} (\bar{Q}) = \sum_{j} \sum_{j'}^{N-1} b_j b_{j'} \exp(i \bar{Q} \cdot (\vec{r}_j - \vec{r}_{j'}))
\]

5.2.2 Small-angle scattering

Coherent scattering is restricted to small angles only when \( kR \gg 1 \), i.e. the linear extent of the scattering object is much larger than the wavelength of the incident radiation see, e.g. \([BH85]\). Small-angle scattering deals with structures large in size compared with the interatomic spacings. Therefore, the sum over several scattering centers \( j \) of scattering length \( b_j \) can be replaced by the neutron scattering length density \( \rho_{n,M}(\vec{r}) \) in the matrix (M) and \( \rho_{n,P}(\vec{r}) \) within the particle (P), the latter being approximately zero in the case of a pore. The difference in scattering length density is then:

\[
\Delta \rho_n(\vec{r}) = \rho_{n,P}(\vec{r}) - \rho_{n,M}(\vec{r})
\]

and its square \( |\Delta \rho_n(\vec{r})|^2 \) is called the scattering contrast. In sufficiently dense samples with a high scattering cross-section, a superposition from scattering between neighboring particles leads to interparticle interference. As long as the interparticle distance remains much larger than the particle size, only at low \( Q \) interference effects will contribute to the scattering cross-section see, e.g. \([Kos79]\). The scattering information is contained in the angular region near the zero order reflection or the transmitted incident beam. At small angles, the approximation \( \sin \theta = \theta \) is sufficient. For \( N_P \) homogeneous, uncorrelated particles of volume \( V_P \) embedded in a homogeneous matrix (dilute limit, no interparticle interference), the macroscopic scattering cross-section \( d\Sigma/d\Omega \) is given by

\[
\frac{d\Sigma}{d\Omega} (\bar{Q}) = \frac{N}{V} \frac{d\sigma}{d\Omega} (\bar{Q}) = \frac{V_P}{V} \left| \Delta \rho_n \right|^2 \left| \int_{V_P} \exp(i \bar{Q} \cdot \vec{r}) d^3\vec{r} \right|^2,
\]
5. METHODS OF MICROSTRUCTURAL PORE CHARACTERIZATION

Fig 5.1: Scattering geometry.

where

\[ S(\vec{Q}) = \frac{1}{V_P} \left| \int_{V_P} \exp(i\vec{Q} \cdot \vec{r}) d^3r \right| \]  

(5.15)

is the form factor of a single particle. \( |\Delta \rho_n|^2 \) is the mean neutron scattering contrast between the matrix and the particle, and \( d\sigma/d\Omega \) denotes the microscopic scattering cross-section. \( N/V \) is the average nuclear density in the sample volume \( V \). For spheres of radius \( R \) in the diffraction limit, \[ S(QR) = \frac{3 (\sin(QR) - (QR) \cos(QR))/QR^3}{(QR)^3} \]  

(5.16)

Often, a particle size distribution \( N(R, R_0) \) is found around a mean particle radius \( R_0 \). Then, assuming no interparticle interference contribution, eqn. 5.14 becomes

\[ \frac{d\Sigma}{d\Omega}(\vec{Q}) = |\Delta \rho_n|^2 \frac{1}{V} \int_{R}^{R_0} N_P(R) V_P(R)^2 |S(\vec{Q}, R)|^2 dR \]  

(5.17)

5.2.3 Specific surface area of a pore morphology

At sufficiently large \( Q \), the tail of the particle scattering curve is a function of the surface area of the scattering particles. For statistically isotropic (randomly oriented) particles with smooth surfaces, the macroscopic scattering cross-section behaves as a function of \( \vec{Q} \) as \[ S(QR) = 3 (\sin(QR) - (QR) \cos(QR))/(QR)^3 \]  

(5.16)

Often, a particle size distribution \( N(R, R_0) \) is found around a mean particle radius \( R_0 \). Then, assuming no interparticle interference contribution, eqn. 5.14 becomes

\[ \frac{d\Sigma}{d\Omega}(\vec{Q}) = |\Delta \rho_n|^2 \frac{1}{V} \int_{R}^{R_0} N_P(R) V_P(R)^2 |S(\vec{Q}, R)|^2 dR \]  

(5.17)

with the Porod constant

\[ P = 2\pi|\Delta \rho_n|^2 S_T. \]  

(5.19)

A necessary condition for Porod scattering is \( LQ \geq 3 \), \( L \) being the smallest dimension of the scatterers e.g., [Por82, Kos79]. The \( S_T \) obtained is the sum of surface areas of all particles of different sizes larger than \( L \) (and therefore theoretically of particle sizes as large as the sample dimension). The Porod law was originally derived for particles with random orientation giving rise to isotropic small-angle scattering. For anisotropic coherent precipitates within a matrix, the analysis has recently been extended by Ciccarello et al. [CGB88, CSSK00, CSSK02, SCSK02], who showed that the area of the interphase surface must be substituted by the area of that portion of the interface which has its normals inside the considered solid angle. For anisotropically shaped particles in non-random orientation (like anisotropic
pores with preferred alignment in thermally sprayed coatings), it is therefore appropriate to
determine the Porod constant by orientationally averaging the scattering contributions from
different directions of $\vec{Q}$:

$$\lim_{Q \to \infty} \langle d\Sigma(\vec{Q})/d\Omega \rangle = 2\pi |\Delta \rho_n|^2 S_T Q^{-4}$$ (5.20)

$\langle \rangle$ denoting the orientational average of the sectors over the azimuthal angle.

### 5.3 Multiple small-angle neutron scattering

Typical pore sizes in thermally sprayed deposits are beyond the maximum size accessible
by conventional SANS instruments. A larger size could in principle be accessed on an ul-
tra small-angle neutron scattering (USANS) Bonse-Hart type instrument [GRL85, AWT97,
ACD+98, IALJ02, SEH+97], a perfect crystal diffractometer, usually covering the range in
reciprocal space of $10^{-4}$ nm$^{-1} < Q < 10^{-2}$ nm$^{-1}$. Difficulties arise, however, since towards
lower scattering angles scattering from individual particles (single scattering regime) - at
constant sample thickness - is modulated by a broadening from multiple small-angle scat-
tering processes. The single scattering regime is accessed by a low scattering probability
per particle, a low particle density and a sufficiently thin sample, leaving the latter as the
only tunable parameter to reach the single scattering regime. For thermally sprayed coat-
ings, typical pore densities and scattering cross-sections require a sample thickness of less
than $100 \mu$m to avoid significant multiple small-angle scattering contributions, reducing the
statistical relevance for the average bulk deposit, and introducing difficulties and artifacts
due to sample thinning. Therefore, it is not possible to directly extract structural informa-
tion from neutron scattering from thermally sprayed deposits with pores in this size regime.

When dealing with multiple small-angle scattering, the following two regimes should be
distinguished:

- Weak multiple small-angle scattering. The single scattering information is retained by
careful application of multiple small-angle scattering corrections [SS80, Cop88, MJS97].

- Strong multiple small-angle scattering. From the experimentally determined broad-
  ening of the beam as a function of wavelength or sample thickness, information on
  the particle size or shape is extracted. Several formalisms are found in the literature
  [BH85, MS92b, SB99].

The latter approach to multiple small-angle neutron scattering (MSANS), as originally de-
veloped by Berk et al. [BH85, HB85, BH86, BH88] is followed here. The MSANS ana-
lysis was first developed for randomly distributed, uniform, monodisperse spheres [HB85,
BH86, BH88] and for that experimentally confirmed [BH85, HFB86, LKGP91]. The MSANS
method was then expanded to treat multiple small-angle scattering from spheroidally shaped
 pores [AB94, ABK+94, AFF+99] and later to treat multi-component anisotropic pore sys-
tems [AIL+01], as occur in many thermally sprayed deposits [KWN+03].
Methods of Microstructural Pore Characterization

In a thick sample with sufficient scattering probability, the neutrons scattered once after entering the sample serve as incident neutrons for subsequent scattering events. Depending on the size of the scatterer, its scattering contrast with the matrix, and the neutron wavelength, the neutrons are diffracted or refracted many times during passage through the sample. These copious scattering events lead to a wavelength-dependent broadening of the primary beam. Generally, the inhomogeneities causing multiple small-angle scattering could be pores, large precipitates or ferromagnetic domains [BM00]. Since within the present work, MSANS is used to describe the pore morphology in thermally sprayed deposits, in the following the inhomogeneities are referred to as pores.

The MSANS beam broadening is the result of stochastic multiple small-angle scattering on successively encountered pores. Therefore, the multiple small-angle scattering is an incoherent superposition of coherent scattering from single pores. The wavelength or sample thickness dependence of the MSANS beam broadening is a signature of multiple events regardless of the nature of the process, i.e. diffractive or refractive [BH88]. Dexter and Beeman [DB49] and Warren [War49] for example employed multiple diffraction from X-rays to extract a particle size from the gaussian broadening of the primary beam by means of variation of sample thickness. Von Nardroff [Nar26] described the effect of multiple refraction from spheres on the broadening of the incident beam.

The diffractive or refractive nature of the single scattering process is determined by the magnitude of the phase shift $\nu_0$ that a neutron experiences when crossing a pore with respect to a second neutron crossing the embedding matrix. For spherical pores, the phase shift parameter is given by

$$\nu = 2R \Delta \rho_n \lambda.$$  \hspace{1cm} (5.21)

$\nu$ affects the amount of multiple small-angle scattering through the mean number of scattering events $\bar{z}$, which is the ratio of the sample thickness $\tau$ to the mean free path $l$ of the neutrons

$$\bar{z} = \tau/l = n \tau \Sigma_T(\nu) = \Phi_T \tau \Sigma_T(\nu)/V_P.$$  \hspace{1cm} (5.22)

The mean free path $l$ depends on the total macroscopic scattering cross-section of the pores, $\Sigma_T(\nu)$ as $l = 1/n \Sigma_T(\nu)$, and $n = \Phi_T/V_P$ is the number density of scatterers with $V_P$ being the volume of a single pore and $\Phi_T$ being the total volume of all pores. $\Sigma_T(\nu)$ is a function of the mean phase shift $\nu$ and is obtained by integrating the macroscopic scattering cross-section $\Sigma(Q, \nu)$ over all possible orientations of the scattering vector:

$$\Sigma_T(\nu) = (2\pi/k^2) \int_0^\infty \Sigma(Q, \nu) Q dQ.$$  \hspace{1cm} (5.23)

As outlined in section 5.2, $\Sigma(Q, \nu)$ depends on the scattering contrast $|\Delta \rho_n|^2$ of the pore with respect to the matrix, the pore size and its shape. The MSANS beam broadening profile is determined by $\Sigma(Q, \nu)$, the wavelength $\lambda$ of the incident neutrons and the sample thickness $\tau$. Since variation in $\lambda$ implies also a varying $\nu$, measurements at several wavelengths will
5. METHODS OF MICROSTRUCTURAL PORE CHARACTERIZATION

Differently weight the refraction and diffraction behavior of the pores, and therefore more information on the pore morphology is inherently available. Since the pore morphology in thermally sprayed deposits usually consists of pores with dimensions between a few 10 nanometers up to a few micrometers, a general MSANS formalism capable of describing such a pore system has to include both, diffraction and refraction. In the following, scattering cross-sections and their relations to the beam broadening are discussed for the extreme cases of refraction and diffraction. Subsequently, the more complex general case is discussed.

**Refraction**

In the regime of geometrical optics, $\nu \gg 1$, refraction is dominant and the total macroscopic scattering cross-section is given by [Nar26]

$$\Sigma^\text{geo}_T = \lim_{\nu \to \infty} \Sigma(\nu) = 2 \pi R^2.$$  \hspace{1cm} (5.24)

An incident beam experiencing a mean number of $\bar{z}$ impacts from refracting spheres undergoes an average total bend [Nar26]

$$\alpha_0 = (4 \delta^2 \bar{z} (\log(2/\delta) + 1))^{1/2},$$  \hspace{1cm} (5.25)

where $\mu = 1 - \delta = 1 - \Delta \rho_n \lambda^2/2\pi$ is the index of refraction for neutrons [Bac75]. $\alpha_0$ is obtained from integrating over all possible displacements, from vertical incidence with no directional change to a maximum displacement related to the angle of total reflection, $2\sqrt{2}\delta$. For a gaussian incident beam profile of a width $\omega_0$, the total width $\omega$ after passage of the sample is

$$\omega = (\omega_0^2 + 2\alpha_0^2)^{1/2},$$  \hspace{1cm} (5.26)

leading to

$$\omega^2 - \omega_0^2 = 8 \delta^2 \bar{z} (\log(2/\delta) + 1),$$  \hspace{1cm} (5.27)

and $\bar{z} = 3\tau \Phi_T/4R$ with $\tau$ being the penetrated sample thickness, from that the pore radius $R$ may be determined.

Expressed in the macroscopic single scattering cross-section, von Nardroff’s formula for spheres reads [BH85]

$$\Sigma^\text{geo}(Q) = \lim_{\nu \to \infty} \Sigma(Q, \nu) = (\nu/2\mu)^2 (1 + (Q/2 \Delta \rho_n \lambda)^2)^{-2}.$$  \hspace{1cm} (5.28)
5. METHODS OF MICROSTRUCTURAL PORE CHARACTERIZATION

Diffraction
In the diffraction regime, \( \nu \ll 1 \). The Rayleigh-Gans single scattering macroscopic cross-section for spheres, eqn. 5.14 - 5.16 can be expressed as e.g., [Kos79]

\[
\Sigma_{\text{diff}}(Q, \nu) = 8 \pi^3 \Delta \rho^2 R^6 J_{3/2}^2(QR)/(QR)^3,
\]

with \( J_n \) being the n-th order Bessel function. The total macroscopic scattering cross-section can be determined from 5.29 by integration according to 5.23 as [Ray11, Gan25]

\[
\Sigma_{\text{diff}}^T(\nu) = \lim_{\nu \to 0} \Sigma(\nu) = \pi R^2 \nu^2/2 = 2 \pi \Delta \rho^2 \lambda^2 R^4
\]

The Born approximation has been applied to particles of shapes other than spheres by Kratky and Porod [KP49] and Shull and Roess [SR47]. A collection of structure and form factors for various particle shapes can be found in [GF55, Por82, FS87, Ped97].

General case
Weiss [Wei51] in his treatment combined the diffraction and the refraction regime of the single scattering and multiple-scattering. The single scattering cross-section for an arbitrary phase shift \( \nu_0 \) for monodisperse spheres of radius \( R_0 \), exact in the small-angle region \( kR_0 \gg 1 \), is given by [Hul46, Wei51, BH85]

\[
\Sigma(Q, \nu_0) = n k^2 R_0^4 \times \left[ \frac{J_1(QR_0)}{QR_0} \right]^2 - 2 \frac{J_1(QR_0)}{QR_0} \times \Re(F(Q, R_0, \nu_0)) + |F(Q, R_0, \nu_0)|^2
\]

(5.31)

where \( \Re(F) \) denotes the real part of \( F \), and

\[
n = \frac{\Phi_T}{V_P} = \frac{3 \Phi_T}{4 \pi R_0^3}
\]

(5.32)

with \( V_P = 4 \pi R_0^3/3 \) the single sphere volume and \( \Phi_T \) the volume of all spheres in the sample volume, and

\[
F(QR_0, \nu_0) = \int_0^1 J_0(QR_0 \xi) \left\{ \exp(i \nu_0(1 - \xi^2)^{1/2}) \right\} \xi d\xi.
\]

(5.33)

The first term in eqn. 5.31 is interpreted as diffraction, the second is an interference term between diffraction and refraction, and the third term is interpreted as refraction [Wei51]. In lowest order \( \nu_0 \), eqn. 5.31 reduces to eqn. 5.29. The total single scattering cross-section was derived as [Wei51]

\[
\Sigma_{T, \nu_0 \sim 1} = 2 \pi R^2 \left[ 1 - (2 \sin \nu_0/\nu_0) + (2/\nu_0^2)(1 - \cos \nu_0) \right],
\]

(5.34)
which reduces to eqns. 5.30 and 5.24 for small and large \( \nu_0 \), respectively. Since large pore radii enter the total refraction cross-section as \( R^2 \) (eqn. 5.24), often refraction is a multiple refraction. On the other hand, scattering from small pores often remains in the single scattering regime, since the total diffraction cross-section depends on the pore size as \( R^4 \) (eqn. 5.30).

Multiple small-angle scattering analysis
The multiple small-angle scattering can be described in terms of a Boltzmann transport equation [Mol48, SS49, Bet53], or equivalently by a diffusion process in the plane of \( \theta \). Alternatively, \( W(\vec{Q}, \tau) \) can be expressed as an infinite series of convolution products of the single scattering products [SS80]. The diffusion equation describing multiple small-angle scattering from monodisperse, randomly distributed homogeneous spheres in the small-angle approximation is given by Snyder and Scott as [SS49]

\[
\frac{\partial}{\partial z} + \eta \frac{\partial}{\partial x} + \epsilon \frac{\partial}{\partial y} W(\eta, \epsilon, x, y|z) = n \int_{-\infty}^{+\infty} d\eta' \int_{-\infty}^{+\infty} d\epsilon' \Sigma\left((\eta - \eta')^2 + (\epsilon - \epsilon')^2\right)^{1/2} \times \left[W(\eta', \epsilon', x, y|z) - W(\eta, \epsilon, x, y|z)\right],
\]

(5.35)

where \( W(\eta, \epsilon, x, y|z) \) is the probability that a neutron (at \( z = 0 \) initially travelling along the z-axis as indicated by the separate notation) passing through the point \((x, y, z)\) is scattered into a direction determined by \( \eta \) to \( \eta + d\eta \) and \( \epsilon \) to \( \epsilon + d\epsilon \). The spatial gradient of the probability \( W(\eta, \epsilon, x, y|z) \) is the difference of what is scattered at \((x, y, z)\) in any direction \((\eta', \epsilon')\) and what remains to be scattered into the direction \((\eta, \epsilon)\). \( \eta \) and \( \epsilon \) are the angles made with the z-axis by projecting the track into the \( xz \) and \( yz \) planes, \( n \) denotes the density of scattering centers and \( \Sigma \) is the macroscopic single scattering cross-section. The single scattering angle is given by \( 2\theta = ((\eta - \eta')^2 + (\epsilon - \epsilon')^2)^{1/2} \). \( z \) denotes the distance from the sample surface parallel to the incident beam. \( z = 0 \) is the plane of incidence and \( z = \tau \) the plane after the passage of the sample. The solution of eqn. 5.35 in pinhole geometry in the plane of a two-dimensional position-sensitive detector can be expressed as a function of the scattering vector \( \vec{Q} \) by [BH85]

\[
W(Q|\tau) = \exp(-\bar{z}) \delta(\vec{Q}) + \Delta W(QR_0|\tau)
\]

\[
= \exp(-\bar{z}) \delta(\vec{Q}) + \frac{kR_0}{2\pi} \int_0^2 d\zeta \zeta J_0(QR_0\zeta) \times (\exp(-\bar{z}(1 - q(\zeta))) - \exp(-\bar{z})),
\]

(5.36)

where the first term reflects the transmitted primary beam, and the second term \( \Delta W(QR_0|z) \) describes the \( Q \)-dependent multiple small-angle scattering profile. \( R_0 \) is the volume-weighted mean radius of the scattering pores, \( J_0(x) \) is the zero order Bessel function, and \( \delta(\vec{Q}) \) is the
5. METHODS OF MICROSTRUCTURAL PORE CHARACTERIZATION

delta function. The $Q$-dependence of the single scattering event enters the multiple small-angle scattering profile in the exponential by the expression $q(\zeta)$

$$q(\zeta) = \frac{2\pi}{k^2\Sigma_T} \int_0^{\infty} J_0(QR_0\zeta)\Sigma(Q, \nu_0)QdQ$$ (5.37)

The first term of 5.36 can be incorporated into the integral of the second multiple-scattering term, and the profile expressed in terms of $QR_0$ is given by

$$W(QR_0|\tau) = \frac{k^2 R_0^2}{2\pi} \int_0^{\infty} d\zeta \zeta J_0(QR_0\zeta) \exp[-\bar{z}(1 - q(\zeta))],$$ (5.38)

Anisotropically shaped pores
For anisotropically shaped pores, $\Sigma(Q, \nu_0)$ in $q(\zeta)$ of eqn. 5.37 has to be replaced by an orientationally-averaged single scattering cross-section [AB94]:

$$\Sigma(Q, \nu_0) \rightarrow \left\langle \Sigma(\vec{Q}, \nu_0) \right\rangle_{\text{Orientation}}$$ (5.39)

For spheroids with radii $R_0$, $R_0$ and $\beta R_0$, it is possible to derive $\Sigma(Q, \nu_0)$ for each spheroid orientation with respect to $Q$ by coordinate transformation and applying the Jacobian volume-element matrix in the orientational averaging integral [Pat39, SR47, AB94]. $\Sigma(Q, \nu_0)$ in eqn. 5.31 becomes

$$\left\langle \Sigma(\vec{Q}, \nu_0) \right\rangle_{\text{Orientation}} = \frac{4\pi \beta R_0^3}{3\Phi_T} \times k^2 R_0^4 \int_0^{1} \left\{ \frac{J_1(QR_0K(\beta, \chi))}{QR_0K(\beta, \chi)} \right\}^2 \left( -2 \frac{J_1(QR_0K(\beta, \chi))}{QR_0K(\beta, \chi)} \times \Re(F(Q, R_0, \nu_0)) + |F(Q, R_0, \nu_0)|^2 \right\} [K(\beta, \chi)]^2 d\chi$$ (5.40)

with the orientation factor

$$K(\beta, \chi) = [1 + (\beta^2 - 1)\chi^2]^{1/2},$$ (5.41)

and $\chi = \cos(\eta)$, $\eta$ being the angle between $\vec{Q}$ and the spheroid $\beta R_0$ axis,

$$n = \frac{\Phi_T}{V_P} = \frac{3 \Phi_T}{4\pi \beta R_0^3}$$ (5.42)

with $V_P = 4\pi \beta R_0^3/3$ the single spheroid volume, $\Phi_T$ the volume of all spheroids in the sample volume, and

$$F(QR_0, \chi, \beta, \nu_0) = \int_0^{1} J_0(QR_0K(\beta, \chi)\xi) \{ \exp(i\nu_0(1 - \xi^2)^{1/2}/K(\beta, \chi)) \} \xi d\xi.$$ (5.43)
The integration in eqn. 5.40 adds incoherently the contributions from all possible orientations \( d\mathcal{X} \) with respect to \( \vec{Q} \).

The total single scattering cross-section of a spheroid in orientation \( \mathcal{X} \) with respect to \( \vec{Q} \) is

\[
\Sigma_{T;\beta,\mathcal{X}} = \frac{3 \Phi_T}{4\pi \beta R_0} \pi R_0^2 A(\beta, \mathcal{X}),
\]

(5.44)

where

\[
A(\beta, \mathcal{X}) = K(\beta, \mathcal{X}) \left\{ 2 + \frac{4}{c^2} [1 - \cos(c) - c \sin(c)] \right\}
\]

(5.45)

and \( c = \beta v_0 K(\beta, \mathcal{X}) \).

While the beam profile \( W(Q|\tau) \) can in principle be calculated for each \( \lambda \), the present analysis [AB94, AIL+01] employs the beam profile width, which is related to the radius of curvature of the scattering profile for a given direction of \( \vec{Q} \) as

\[
r_c(\lambda) = \lim_{\vec{Q} \to 0} \left[ \frac{d^2 W(\vec{Q}|\tau) / d\vec{Q}^2}{W(\vec{Q}|\tau)} \right]^{-1/2}
\]

(5.46)

Non-random orientation and multi-component pore systems

Eqns. 5.38 and 5.39 can be generalized to non-random orientation distributions of anisotropically shaped pores. In eqn. 5.39 the non-random orientation distribution has then to be incorporated in the orientational averaging.

A pore morphology as encountered in thermally sprayed deposits often consists of different dominant pore systems, i.e. interlamellar pores (\( \nu \)), fine-crack type pores (\( \nu \)) and globular pores (\( \nu \)). In general, these pore systems have different mean sizes and consist of non-spherical elements (\( \nu \) and \( \nu \)) with non-random orientation distribution. Separate pore systems are incorporated by taking the weight of each pore system on the beam broadening into account. The SANS cross-section in eqn. 5.39, \( \left\langle \Sigma(\vec{Q}, v_0) \right\rangle_{\text{Orientation}} \) now combines the (weighted) scattering of all pore components, and equally the total scattering cross-section in eqn. 5.37 becomes \( \Sigma_T = \Sigma_P + \Sigma_C + \Sigma_G \), resulting in a \( \bar{z} \) weighting of the contributions of the separate pore systems [AIL+01, BAL+03].

5.4 Setup and data reduction

SANS and MSANS measurements were performed at the 38 m SANS instrument [KW00] at the Paul Scherrer Institut, Villigen, Switzerland and partly at the 8 m SANS instrument NG1 [GRL85] at the Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, USA. The schematic outline of the PSI SANS instrument in pinhole geometry is shown in Fig. 5.2. From the left, the neutron guide transports the
neutrons from the cold-D$_2$ moderator of the Swiss neutron spallation source SINQ to the velocity selector defining the wavelength at the sample position. For the determination of the total specific surface area at the PSI instrument, a wavelength $\lambda = 0.5 \text{ nm}$ and a wavelength-distribution $\Delta \lambda / \lambda = 0.10$ was selected. A collimation system defines the beam divergence on the sample, which was mounted between collimator and the detector vessel containing a moveable position sensitive detector of 128 x 128 pixels sized $7.5 \times 7.5 \text{ mm}^2$. The thermally sprayed deposits were oriented with respect to the incident neutrons as shown in Fig. 5.3. For the determination of the total specific surface area, the cross-section sample was investigated with the incident neutrons perpendicular to the spray direction (Fig. 5.3, left, $y$-orientation). The standard sample thickness for measurements in the Porod regime was 1 mm. The MSANS beam broadening was determined in both orientations, i.e. additionally from free-standing deposits with the incident neutrons parallel to the spray direction (Fig. 5.3, right, $x$-direction) with a thickness between 2.2-3.8 mm (see Table 6.9 in the following section). The macroscopic neutron scattering cross-section $d\Sigma$ from a sample into the solid angle element $d\Omega$ covered by a detector pixel $ij$ is e.g. [Kei00]:

$$
\left( \frac{d\Sigma}{d\Omega} \right)_{ij} = \left( \frac{I_{S,ij} - I_{Cd,ij}}{I_{S,EB}} \right) C_S - \left( \frac{I_{H_2O,ij} - I_{Cd,ij}}{I_{H_2O-EB}} \right) \frac{1 - P_S}{F_{H_2O}} F_{H_2O} \tag{5.47}
$$

where for the pixel $ij$, $I_{S,ij}$ denotes the normalized count rate of the sample, and similarly, $I_{S,EB,ij}$, $I_{H_2O,ij}$, $I_{H_2O-EB,ij}$ and $I_{Cd,ij}$ are the normalized count rates of the sample background, water, water background and Cd background, respectively. $C_S$ and $P_S$ are the attenuation factor and the scattering probability [SSK+00]. For all samples analyzed, $C_S = 1$ and $P_S = 0$ were used. The transmissions of sample, water and its background (cuvette), $T_S$, $T_{H_2O}$, $T_{H_2O-EB}$ were determined experimentally by separate transmission measurements by comparing the intensity within the primary beam position with and without sample, water
or cuvette, and $T_{\text{S-EB}} = 1$. The scaling factor of water was determined from its ideal incoherent scattering cross-section $\frac{d\Sigma}{d\Omega_{\text{H}_2\text{O},\text{id}}} = \frac{1-T_{\text{H}_2\text{O}}}{4\pi \tau_{\text{H}_2\text{O}} T_{\text{H}_2\text{O}}}$ through the effective incoherent scattering cross-section $\frac{d\Sigma}{d\Omega_{\text{H}_2\text{O},\text{eff}}} = g(\lambda) \frac{d\Sigma}{d\Omega_{\text{H}_2\text{O},\text{id}}}$ taking the inelastic and multiple scattering contributions into account by a factor $g(\lambda)$ [WB87, Lin00]. For the PSI SANS instrument, $g(\lambda)$ was determined and interpolated for the applied wavelength to be $g(\lambda = 0.5\text{nm}) = 1.325$. The scaling factors of water and sample are then

$$
F_{\text{H}_2\text{O}} = \frac{d\Sigma}{d\Omega_{\text{H}_2\text{O},\text{eff}}} \tau_{\text{H}_2\text{O}} A_{\text{H}_2\text{O}} = g(\lambda) \tau_{\text{H}_2\text{O}} A_{\text{H}_2\text{O}} \frac{1-T_{\text{H}_2\text{O}}}{4\pi \tau_{\text{H}_2\text{O}} T_{\text{H}_2\text{O}}},
$$

$$
F_{\text{S}} = \tau_{\text{S}} A_{\text{S}},
$$

(5.48)

$A$ and $\tau$ denoting the illuminated area and the penetrated thickness.

**SANS in the Porod regime**

For thermally sprayed coatings produced with the spray direction perpendicular to the surface plane to be coated, the pore morphology is isotropic about the spray direction [IALK97]. The spreading-out and partial dissociation of the impinging particles generate an anisotropic microstructure in the cross-sectional view.

From the anisotropic two-dimensional (2D) scattering pattern of the cross-section samples in orientation $y$ (see Fig. 5.3), the apparent Porod constant $\tilde{P}$ is obtained in the Porod regime by averaging with regard to the azimuthal angle in $15^\circ$ wide sectors around the incident beam in steps of $10^\circ$. $\tilde{P}$ is determined for each sector by fitting

$$
\frac{d\Sigma}{d\Omega} Q^4 = \tilde{P} + BQ^4,
$$

(5.49)
where $B$ denotes the background. The Porod constant $P$ is then determined by orientationally averaging $\hat{P}$ according to eqn. 5.20. Often, the distribution of $\hat{P}$ can be fitted to a sufficiently good approximation by an ellipse (or two perpendicularly oriented ellipses) with aspect ratio $\phi_{\text{Porod}}$ and axis $\hat{P}$. For an ellipse (each), the orientational average is deduced from geometrical considerations as

$$P = \int_0^{\pi/2} \frac{\hat{P}}{\sqrt{\cos^2 \alpha / \phi_{\text{Porod}}^2 + \sin^2 \alpha}} \sin \alpha d\alpha$$  \hspace{1cm} (5.50)

$\phi_{\text{Porod}}$ denoting the aspect ratio of the fitted ellipse, and $\hat{P}$ the apparent Porod constant parallel to the spray direction. The total specific surface area $S_T$ is determined from $P$ according to 5.19. Eqn. 5.50 exploits the symmetry of the microstructure about the spray direction [IALK97].

The 2D apparent surface area distribution (defined by Ilavsky et al. [IALK97]) is calculated from the 2D apparent Porod constant by applying eqn. 5.19 to a given direction of $\vec{Q}$. The 2D apparent specific surface area is a projection of the 3D specific surface area distribution in the deposits onto a plane with its normal perpendicular to the spray direction (and therefore contains projections of the specific surface area parallel and perpendicular to the spray direction).

**MSANS analysis**

The MSANS beam broadening at wavelengths between $\lambda = 1.2\text{ nm}$ and $\lambda = 1.9\text{ nm}$ was determined in steps of $\Delta \lambda = 0.1\text{ nm}$ in the two sample orientations $x$ and $y$ (Fig. 5.3). According to eqn. 5.46, the MSANS modelling requires the beam broadening to be expressed in the radius of curvature $r_c(\lambda)$ of the scattering curve at $Q = 0$. For a gaussian profile, $r_c$ is numerically equal to its standard deviation

$$FWHM = 2 r_c [2 \ln(2)]^{1/2}.$$  \hspace{1cm} (5.51)

Although the profile is not necessarily gaussian, experimentally this is often the case at sufficiently small $Q$, also for the NiCrAlY deposits. In practice, the data was fitted between about 95 – 40% of the maximum intensity. The sample broadening $r_{c,\text{sample}}$ is influenced by the incident beam width $r_{c,\text{beam}}$, which has to be taken into account by $r_{c,\text{sample}}^2 = r_{c,\text{measured}}^2 - r_{c,\text{beam}}^2$ [AB94]. For both sample orientations, the experimental data were azimuthally averaged around the incident beam to yield the MSANS beam broadening. The MSANS anisotropy $\phi_{\text{MSANS}}$ is deduced from the MSANS data of the cross-section samples by a sector-wise averaged analysis in $15^\circ$ wide sectors. An ellipse is fitted to the anisotropic $r_c$ data, and $\phi_{\text{MSANS}}$ is expressed in terms of the aspect ratio of the fitted ellipse (similarly as for the determination of $\phi_{\text{Porod}}$), and finally averaged over all wavelengths to obtain a mean $\phi_{\text{MSANS}}$. 

6

Results and microstructural analysis

6.1 Phase analysis by X-ray diffraction

Information on present secondary phases in the NiCrAlY deposits is important for interpretation of the SANS scattering data (e.g. for calculating scattering length densities). Since in metallic materials the phase composition may change during processing (for example by oxidation during spraying), for all samples an X-ray diffraction phase analysis was performed. A Siemens D500 X-ray diffractometer with Cu Kα radiation (operating voltage: 40 kV) was used. The scattering vector $\vec{Q}$ was oriented parallel to the spray direction. For standard $\theta$-2$\theta$-scans, a 2$\theta$-range $20^\circ - 155^\circ$ was chosen with an angular step-width $\Delta 2\theta = 0.1^\circ$. For $2\theta = 45^\circ$, the (2$\theta$-dependent) spot-size at the sample position was about 200 mm$^2$. Deposits were investigated from their surface side as well as from their interface side after removal of the substrate by electric wire discharge machining. The intensity due to the Cu Kα$_2$ peak was subtracted from the measured intensity.

$\gamma$–NiCrAlY and secondary crystalline phases

The primary identified phase is $\gamma$-NiCrAlY. Fig. 6.1 shows the X-ray diffraction patterns of the NiCrAlY deposits in different magnifications to show (a) the overall diffraction pattern, (b) the spray technique dependent lattice parameter and width of the $\gamma$–NiCrAlY phase by means of the 200 Bragg reflection as an example, (c) and (d) the secondary crystalline phases $\alpha$-Cr / $\beta$-NiAl. The lattice parameter of $\gamma$–NiCrAlY was calculated as average from the diffraction peaks. The results are given in Table 6.1, together with the Bragg peak width (FWHM) of the 200 NiCrAlY reflection.

The crystalline metallic and intermetallic phases $\alpha$-Cr and $\beta$-NiAl are presumably located inside the splats within the $\gamma$-NiCrAlY matrix. Their distinction by the X-ray crystallographic method is difficult due to their almost equal lattice parameters, as Taylor and Floyd [TF53] pointed out. The amount of $\alpha$-Cr / $\beta$-NiAl varies strongly with the spray technique: They are found in significant quantity mainly in the VPS deposits and the feedstock powder.
Fig 6.1: X-ray diffraction patterns for different spray techniques. Bragg peak positions for $\alpha$-Cr and $\beta$-NiAl indicated by a vertical line are literature values [ICD03]. The X-ray diffraction patterns recorded from different samples are displaced vertically for clarity. Further details are given in the text.
α-Cr /β-NiAl phases are found only in small amounts at the FS deposit surface and at the APS and WAS interfaces. Literature values on peak positions [ICD03] suggest the peaks from the VPS deposits and from the FS deposit surface belong to α-Cr (PDF-no. 01-1261 [ICD03]), whereas from the APS and WAS interfaces they belong to β-NiAl (PDF-no. 44-1188 [ICD03]). However, such an identification holds only for a pure Cr phase and a stoichiometric NiAl phase that would not introduce a lattice parameter deviation larger than the difference between the two phases.

Fig. 6.2 shows the presence of the intermetallic yttride Ni$_5$Y in the feedstock powder. After the deposition, Ni$_5$Y is found only in the VPS deposits, at a significantly decreased fraction. Ni$_5$Y was observed by TEM analysis of feedstock powder, often concentrated in the boundary between individual grains [IIZK97a].

**Table 6.1: Lattice parameter $a$ and FWHM of the γ−NiCrAlY 200 Bragg peak. Uncertainties in least significant digits given in parentheses are statistical errors obtained from the fit.**

<table>
<thead>
<tr>
<th>sample</th>
<th>$a_{\text{NiCrAlY}}$ (nm)</th>
<th>FWHM 200 reflection (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>0.36012 (4)</td>
<td>0.329 (3)</td>
</tr>
<tr>
<td>VPS-I</td>
<td>0.3590 (3)</td>
<td>0.47 (2)</td>
</tr>
<tr>
<td>APS-I</td>
<td>0.35985 (7)</td>
<td>0.57 (2)</td>
</tr>
<tr>
<td>WAS-I</td>
<td>0.35880 (7)</td>
<td>0.57 (3)</td>
</tr>
<tr>
<td>FS</td>
<td>0.3574 (1)</td>
<td>0.73 (3)</td>
</tr>
<tr>
<td>WSP-I</td>
<td>0.3560 (1)</td>
<td>0.59 (2)</td>
</tr>
</tbody>
</table>

**Through-thickness gradient in lattice parameter**

Diffraction patterns from the APS interface and surface (both taken from the same free-standing deposit) are shown in Fig. 6.3. Besides a reduced peak width at the interface, a shift in the γ-NiCrAlY lattice parameter of $\Delta a = 0.001$ nm from 0.3599 nm to 0.3609 nm was deduced (if not explicitly given, for the X-ray diffraction analysis the standard uncertainty in lattice parameter was 0.0001 nm). A shift in lattice parameter could also be due to residual stresses. However, it is supposed that residual stresses have mostly relaxed during the substrate removal. Also, the X-ray diffraction analysis as performed with the setup described above probes the lattice parameter parallel to the spray direction (normal component). In sufficiently thin deposits, the normal strain component is usually negligible, whereas the in-plane strain component parallel to the deposit plane can be significant [Sto09].

For an APS deposit attached to its substrate, a maximum gradient of the in-plane strain component across the deposit thickness corresponding to $\Delta a_{\text{residual-stress}} = 0.0004$ nm was determined by spatially resolved neutron diffraction strain scanning [KMP et al.].
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Fig 6.2: Background-subtracted X-ray diffraction pattern from feedstock powder, showing the presence of a crystalline Ni$_5$Y phase.

Fig 6.3: X-ray diffraction pattern from the interface and surface of an APS deposit.
Also, the detection of $\beta$-NiAl exclusively at the interface suggests a gradient of chemical composition over the deposit thickness that could be one reason for the through-thickness lattice parameter variation of the $\gamma$-NiCrAlY phase. The $\gamma$-NiCrAlY Bragg peaks of the FS and the WSP deposits at the surface are split, as shown in Fig. 6.4. This indicates the existence of two different crystallites of slightly different chemical composition with different lattice parameters, 0.3560 nm and 0.3596 nm, the latter near the lattice parameter of the feedstock powder. At the interface of the FS deposit, only a single $\gamma$-NiCrAlY phase is detected with an intermediate lattice parameter of 0.3574 nm.

Through-thickness lattice parameter variations as observed in the APS and also in the FS deposits - as well as a variation in $a$ between different spray techniques (see Table 6.1) - can in general be related to an element-selective depletion of the metallic matrix by the buildup of secondary metallic phases like the $\alpha$-Cr /$\beta$-NiAl, or by oxide formation. Indeed, as will be shown in section 6.7, the oxide content is correlated with the amount of these secondary metallic phases (oxide phases are quantified by hot gas extraction as discussed in the following section 6.2, since X-ray amorphous phases can not be detected by the X-ray diffraction technique). Physical reasons for an inhomogeneity of $a$ over the deposit thickness are different thermal histories during the spray process and subsequent cooling and the missing annealing effect by the deposition of subsequent layers on the top surface (the annealing effect also reduces the peak width). For different spray techniques, the feedstock particle temperature, dwell time and surrounding atmosphere could influence the oxide content.
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6.2 Oxygen and nitrogen content

The oxygen and nitrogen content of the deposits were measured by hot gas extraction in an electrically heated furnace of a LECO-TC-436 O/N analyzer (detection limit 1 µg/g) at a temperature of 2300 °C. The oxygen was quantified as CO$_2$ by infrared absorption after the release from its corresponding oxide and the conversion from CO in a rare earth oxide filter. Molecular nitrogen is thermally released and measured by thermal conductivity. The sample was placed in a graphite crucible that was outgassed prior to the sample load for 20 s at 2400 °C. Streaming helium served as inert carrier gas. As a melt-forming additive, a Sn capsule (300 mg) was added. For calibration, a reference “Leco 501-553” with a nominal weight of 500 mg per pin and an oxygen and nitrogen content of 0.0230 ± 0.0007 wt.% O; 0.0497 ± 0.0015 wt.% N was used. The specimens were placed in graphite cylinders, type crucible 776-247.

Fig. 6.5 shows the amount of oxygen extracted as a function of extraction time. The appearance of several peaks indicates the existence of different oxides: Oxygen is released from a specimen, if sufficient thermal energy is inserted to break the bonds to its parent compound, as in the case of the analyzed NiCrAlY deposits. The oxygen that is bound in different oxides is reflected in a typical release rate as a function of heat input or time. If the peaks are sufficiently separated, in principal the amount of oxygen bound in different oxides can be separately determined besides the total amount of oxygen [TM90]. For the analyzed thermally sprayed deposits, a quantitative separation of oxides is difficult. Nevertheless the extraction of oxygen from these specimens can be used to estimate the number of oxides present.

The total oxygen content is determined from the area under the extraction curves of Fig. 6.5 normalized to the reference and is given in Table 6.2 along with the nitrogen content. With significantly less than 1 wt.%, the VPS deposit exhibits the lowest oxygen content, as expected for the vacuum atmosphere. With more than 7 wt.%, the WSP specimens have the highest oxygen content. Since the feedstock powder contains only a low oxide content, the variation in oxygen content suggests the latter is introduced into the NiCrAlY deposits mainly during the spraying process. The oxygen content depends therefore on the feedstock particle temperature and the contact time with the surrounding air during spraying and subsequent cooling [HVMM01].

Fig. 6.6 shows the dependence of the lattice parameter $a$ as determined from X-ray diffraction as a function of the oxide content. A clear trend from the APS to the WSP deposit can be seen that indicates a reduction of the lattice parameter for an increasing amount of oxide in the deposit. The only exception is the VPS deposit, which exhibits a comparatively too low lattice parameter. This might be caused by the high amount of the α-Cr phase as detected by the X-ray analysis (section 6.1), which leads to a Cr depletion in the NiCrAlY matrix.
Fig 6.5: Oxygen determination by hot gas extraction for different spray techniques. (a) APS, (b) FS, (c) WAS, (d) WSP and (e) VPS. The graphs show the relative concentration of oxygen as a function of extraction time.
Table 6.2: Oxygen and nitrogen content of different NiCrAlY deposits (mean values from 3 separate measurements). Uncertainties in least significant digits given in parentheses are standard deviations from the mean value.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen content (wt.%)</th>
<th>Nitrogen content (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock ($d &lt; 40 \mu m$)</td>
<td>0.66 (2)</td>
<td>0.15 (2)</td>
</tr>
<tr>
<td>Feedstock ($56 \mu m &lt; d &lt; 106 \mu m$)</td>
<td>0.32 (1)</td>
<td>0.18 (1)</td>
</tr>
<tr>
<td>FS-I</td>
<td>4.44 (8)</td>
<td>0.04 (1)</td>
</tr>
<tr>
<td>VPS-I</td>
<td>0.38 (3)</td>
<td>0.13 (3)</td>
</tr>
<tr>
<td>VPS-II</td>
<td>0.34 (6)</td>
<td>n.a.</td>
</tr>
<tr>
<td>VPS-III</td>
<td>0.32 (6)</td>
<td>0.052 (1)</td>
</tr>
<tr>
<td>APS-I</td>
<td>2.1 (1)</td>
<td>0.037 (5)</td>
</tr>
<tr>
<td>APS-II</td>
<td>1.10 (3)</td>
<td>0.026 (3)</td>
</tr>
<tr>
<td>APS-III</td>
<td>1.40 (5)</td>
<td>0.034 (1)</td>
</tr>
<tr>
<td>WSP-I</td>
<td>6.9 (1)</td>
<td>0.060 (5)</td>
</tr>
<tr>
<td>WSP-II</td>
<td>7.2 (1)</td>
<td>0.052 (5)</td>
</tr>
<tr>
<td>WSP-III</td>
<td>5.3 (1)</td>
<td>0.043 (9)</td>
</tr>
<tr>
<td>WAS-I</td>
<td>2.88 (3)</td>
<td>0.039 (3)</td>
</tr>
<tr>
<td>WAS-II</td>
<td>2.88 (3)</td>
<td>0.033 (3)</td>
</tr>
<tr>
<td>WAS-III</td>
<td>2.86 (8)</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

6.3 Porosity

The pore volume fraction (porosity) $\Phi_T$ was determined by a mass and volume balance from the density of the deposits $\rho_{m,\text{Dep}}$ [IPC’00], considering the density of the metallic matrix $\rho_{m,\text{NiCrAlY}}$ approximated by the skeletal density of the feedstock powder as determined by He - pyknometry [MSP’01], the oxygen content as given in Table 6.2 and tabulated oxide densities [PW75]. The volume of the deposit consists of the volume fraction $\Phi_{\text{NiCrAlY}}$ of the NiCrAlY matrix, the total pore volume fraction $\Phi_T$ and the volume fractions $\Phi_{\text{Oxide}_i}$ of all $i$ oxides:

$$1 = \Phi_T + \Phi_{\text{NiCrAlY}} + \sum_i \Phi_{\text{Oxide}_i} \quad (6.1)$$

With the total mass $m_{\text{Dep}}$ of the deposit, the mass $m_{\text{NiCrAlY}}$ of the metallic matrix and the mass $m_{\text{Oxide}_i}$ of the $i$th oxide, the mass balance reads $m_{\text{Dep}} = m_{\text{NiCrAlY}} + \sum_i m_{\text{Oxide}_i}$, and therefore,

$$\Phi_T = 1 - \frac{m_{\text{NiCrAlY}} \rho_{m,\text{Dep}}}{\rho_{m,\text{NiCrAlY}} m_{\text{Dep}}} - \sum_i \frac{\rho_{m,\text{Dep}} m_{\text{Oxide}_i}}{m_{\text{Dep}} \rho_{m,\text{Oxide}_i}} \quad (6.2)$$

As oxides, $\text{Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$ and NiO have been considered. The mass densities of the NiCrAlY matrix and the oxides are given in Table 6.3.
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Fig 6.6: Lattice parameter of the $\gamma$-NiCrAlY matrix as a function of the oxygen content for different spray techniques. The line is a guide to the eye.

In Table 6.3, the calculated neutron scattering length densities are included that are used in the following sections. The intensity of SANS scattering depends on the scattering contrast between the present phases, i.e. between the NiCrAlY matrix and pores, between the NiCrAlY matrix and oxides and between oxides and pores (and between different oxides). The scattering length density of pores is negligible compared to that of the NiCrAlY matrix and of the oxides. Therefore, the pores have the highest contrast with their surrounding and predominantly cause the SANS scattering.

The neutron scattering length densities were calculated from the mass densities, the chemical composition and the coherent scattering cross-sections given in [Sea92]. The nominal NiCrAlY feedstock powder composition was used to calculate the NiCrAlY scattering length density (a wet-chemical elemental analysis of the deposits showed only slight deviations in chemical composition introduced by application of the different spray techniques).

In Table 6.4, the deposit densities are given along with the total oxide volume $\Phi_{\text{Oxides}}$ and total pore volume fractions $\Phi_T$ determined for the investigated spray techniques and spray parameter settings. The relative uncertainty in $\Phi_{\text{Oxides}}$ was assumed to be equal to the relative uncertainty of oxygen content given in Table 6.2, uncertainties of $\rho_{\text{m,Dep}}$ and $\Phi_T$ were estimated from repeated measurements to be less than 1% [MSP+01].
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Table 6.3: Mass densities $\rho_m$ for bulk NiCrAlY and the most likely oxides and neutron scattering length densities $\rho_n$ [Sea92].

<table>
<thead>
<tr>
<th></th>
<th>$\rho_m$ (g/cm$^3$)</th>
<th>$\rho_n$ ($10^{-4}$ nm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCrAlY bulk</td>
<td>7.25</td>
<td>6.43</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>4.02</td>
<td>5.77</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>5.35</td>
<td>5.23</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>5.03</td>
<td>4.41</td>
</tr>
<tr>
<td>NiO</td>
<td>6.80</td>
<td>8.83</td>
</tr>
</tbody>
</table>

6.4 Imaging by transmission and scanning electron microscopy

Microstructure characterization was performed by SEM and TEM. Instrumental details and specimen preparation are described in section 5.1.

TEM analysis

The microstructures of the APS and VPS deposits were investigated by TEM in planar view with the incident electron beam parallel to the spray direction. The TEM images are presented to elucidate the prominent microstructural features complementing the analysis by the neutron diffraction technique. Fig. 6.7 shows an overview of the pore morphology next to the central hole introduced from the thinning process, as well as a fine, approximately 80 nm wide crack. The overview indicates the intersplat pore system. The splats are identified by their circular shape. Images (a) and (b) of Fig. 6.8 are bright and dark field images of a splat boundary region. On the upper right of (a), a splat can be seen separated from another splat at the bottom by an intersplat pore. At positions (1) and (2), oxides fill the space to the neighboring splat. Within a ring of up to 300 nm thickness surrounding the splat at position (2) partial recrystallization has taken place, whereas in the middle of the oxide region, the structure remains amorphous, as can be seen from the diffraction images (c) and (d) indexed correspondingly. In the inset, the diffraction pattern of the amorphous region displays the intensity distribution along the indicated line. The ring in the diffraction pattern of the partially recrystallized region marks the reflection used for the dark field image.

SEM analysis

The microstructure was characterized by SEM on cross-section samples with the incident electrons perpendicular to the spray direction. Fig. 6.9 shows SEM backscattered electron images (BEI) [FH01] of (a) APS, (b) VPS, (c) WSP, (d) FS, and (e) WAS deposits, all with the same magnification. As indicated in the BEI images, different features are identified:
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Table 6.4: Deposit density $\rho_{m,\text{Dep}}$, total oxide volume fraction $\Phi_{\text{Oxides}}$ and total pore volume fraction $\Phi_T$ (given in % of total sample volume) for different spray techniques and spray parameter settings. Standard uncertainties in least significant digits are given in parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_{m,\text{Dep}}$ (g cm$^{-3}$)</th>
<th>$\Phi_{\text{Oxides}}$ (%)</th>
<th>$\Phi_T$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FS</td>
<td>6.40 (6)</td>
<td>5.9 (1)</td>
<td>8.0 (2)</td>
</tr>
<tr>
<td>VPS-I</td>
<td>6.88 (7)</td>
<td>0.5 (1)</td>
<td>6.9 (2)</td>
</tr>
<tr>
<td>VPS-II</td>
<td>6.89 (7)</td>
<td>0.5 (1)</td>
<td>6.8 (2)</td>
</tr>
<tr>
<td>VPS-III</td>
<td>6.91 (7)</td>
<td>0.4 (1)</td>
<td>6.5 (2)</td>
</tr>
<tr>
<td>APS-I</td>
<td>6.63 (7)</td>
<td>2.8 (1)</td>
<td>8.1 (1)</td>
</tr>
<tr>
<td>APS-II</td>
<td>6.49 (6)</td>
<td>1.5 (1)</td>
<td>11.2 (1)</td>
</tr>
<tr>
<td>APS-III</td>
<td>6.62 (7)</td>
<td>1.9 (1)</td>
<td>9.1 (1)</td>
</tr>
<tr>
<td>WSP-I</td>
<td>6.37 (6)</td>
<td>9.1 (2)</td>
<td>5.2 (2)</td>
</tr>
<tr>
<td>WSP-II</td>
<td>6.45 (6)</td>
<td>9.4 (2)</td>
<td>3.7 (2)</td>
</tr>
<tr>
<td>WSP-III</td>
<td>6.57 (6)</td>
<td>7.2 (2)</td>
<td>4.5 (2)</td>
</tr>
<tr>
<td>WAS-I</td>
<td>6.66 (7)</td>
<td>3.9 (1)</td>
<td>6.5 (1)</td>
</tr>
<tr>
<td>WAS-II</td>
<td>6.66 (7)</td>
<td>3.9 (1)</td>
<td>6.5 (2)</td>
</tr>
<tr>
<td>WAS-III</td>
<td>6.74 (7)</td>
<td>4.0 (1)</td>
<td>5.4 (2)</td>
</tr>
</tbody>
</table>

The metallic $\gamma$-NiCrAlY matrix, interlamellar and globular pores, two different oxide phases mainly consisting of a combination of $Y_2O_3$ and $Al_2O_3$ (Oxide I) and of $Al_2O_3$ (Oxide II) (further discussed in the following section 6.5), and the substrate on the top or bottom.

6.5 Chemical element mapping by energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDX) was performed on polished cross-section samples with the incident electrons perpendicular to the spray direction on a SEM instrument. Instrumental details and specimen preparation are described in section 5.1. The spatial resolution of the elemental distribution is limited to a few micrometers by the sample volume excited by the electron beam. Exemplary for all spray techniques, a chemical element mapping by EDX of the wire-arc sprayed deposit is shown in the images of Fig. 6.10. The images include mappings for the elements Ni, Al, Y and O overlayed with the corresponding SEM backscattered electron image to attribute the preferential location of elements to different microstructural features. The distribution of Cr is similar to that of Ni in Fig. 6.10(e) and therefore not separately presented.

In Fig. 6.10(d), the metallic $\gamma$-NiCrAlY matrix inside the splats is marked along with the regions I and II located at the splat boundaries. Comparing the elemental distributions in
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Fig 6.7: Low and high magnification transmission electron micrographs of an APS deposit in planar view with the electron beam parallel to the spray direction, showing (a) an overview of the pore system and (b) a narrow crack.

Figs. 6.10(c-f), the metallic $\gamma$-NiCrAlY matrix shows a homogeneous spatial distribution of mainly Ni (and Cr) and, in smaller amounts, of Al and Y. Fig. 6.10(f) shows that O is detected mainly in regions I and II, but to a minor extent also within the $\gamma$-NiCrAlY matrix, which is attributed to surface oxidation after the sample preparation. Regions I and II exhibit a strong Ni and Cr depletion. Besides O, region I contains mainly Y and Al, whereas region II contains mainly Al. Therefore, it is likely that region I consists mainly of $\text{Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$, whereas region II consists mainly of $\text{Al}_2\text{O}_3$.

The preferential location of $\text{Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$ at the splat boundaries shows that Al and Y indeed protect the metallic splat matrix, strengthen the intersplat adhesion and constitute an $\text{Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$ corrosion barrier, as outlined in section 4.
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Fig 6.8: TEM analysis of a splat boundary region in an APS deposit. (a) bright field image, (b) dark field image, (c) and (d) diffraction patterns of an amorphous oxide region (1) and region (2), where partial recrystallization has taken place. Further details are given in the text.
Fig 6.9: SEM-BEI images of cross-section samples: (a) APS, (b) VPS, (c) WSP, (d) FS and (e) WAS deposits. The spray direction is vertical within the plane of observation.
Fig 6.10: Chemical element mapping by EDX. (a) and (b) are overview and magnification SEM-BEI images. (c)-(f) show image (b) overlayed with elemental distributions in yellow for (c) Al, (d) Y, (e) Ni and (f) O. In (d), the metallic NiCrAlY matrix is marked along with two different oxide regions I and II. The spray direction is vertical within the plane of observation.
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6.6 Anisotropic Porod scattering

In Fig. 6.11, the small-angle neutron scattering data are presented for all spray techniques and spray parameter settings. The data are shown as obtained from the experiment after correcting for background and transmission according to eqn. 5.47 and azimuthally averaging around the incident beam. All deposits were oriented with the incident neutrons perpendicular to the spray direction (Fig. 5.3 a).

For all deposits, at low $Q$, the intensity decreases following Porod's law, $I(Q) \propto Q^{-4}$. At large $Q$, the Porod regime is superposed by a constant background from isotope or spin incoherent scattering. At intermediate $Q$, a hump in the SANS scattering, most pronounced for the VPS deposits and the feedstock powder, indicates a nanometer sized structure, which will be discussed in section 6.7.

Fig. 6.12 shows the small-angle scattering of an APS cross-section sample in two directions parallel and perpendicular to the spray direction from $15^\circ$ wide sectors around the incident beam. In the low and intermediate $Q$ region, the constant shift between the two directions reflects the anisotropy of surface area distribution. At high $Q$, the scattering data merges into an isotropic background.

In Fig. 6.13, the direction-dependent apparent surface area (defined in section 5.4) for the different spray techniques is presented. The apparent surface area is obtained with eqn. 5.19 for different orientations by fitting eqn. 5.49. The direction of $Q$ parallel to the spray direction (through-thickness direction) corresponds to $0^\circ$, whereas the direction perpendicular to it (in-plane direction) is $90^\circ$.

While the apparent surface area anisotropy of the VPS, APS and WAS deposits could be described by a single ellipse (see Fig. 6.13), for the WSP and FS deposits two perpendicularly oriented ellipses were needed to fit the data. In Table 6.5 the data obtained from the evaluation of Fig. 6.13 are collected. The lengths of the axes of the ellipses in direction $0^\circ$ are denoted by $r_1$ and $r_2$, $r_1$ being normalized to 1 for each deposit for clarity. Where it applies, $r_2$ is given as ratio to $r_1$. The related aspect ratios are denoted by $\eta_1$ and $\eta_2$. The total SANS anisotropy is determined by $\phi_{\text{Porod}} = (\eta_1 r_1 + \eta_2 r_2)/(r_1 + r_2)$, and is also given in Table 6.5. In Fig. 6.13(d), the ellipses $(\eta_1, r_1)$ and $(\eta_2, r_2)$ are shown for the FS deposit. In Fig. 6.14, the total specific surface areas of the different spray techniques and spray parameter settings are plotted as calculated according to eqn. 5.20 and 5.50 [KWI+01]. The total specific surface area $S_T$ of deposits from different spray techniques differ by up to 50% of the maximum value, whereas for a single spray technique, the influence of spray parameter settings on $S_T$ is significantly less (< 15 %).
Fig 6.11: SANS scattering curves for different spray techniques and spray parameter settings: (a) VPS, FS and the NiCrAlY feedstock powder (b) WSP and APS, (c) WAS and (d) Porod regime of the different spray techniques with the fitted line indicating $I(Q) \propto Q^{-4}$. 
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Fig 6.12: Small-angle neutron scattering of an APS deposit, averaged over 15° wide sectors around the incident beam direction, for two perpendicular sectors at angles of 0° and 90°.

6.7 Precipitates within the NiCrAlY matrix

The “hump” in the SANS data in the Q-range around 0.2 – 2 nm⁻¹, most pronounced for the VPS deposits and the feedstock powder (Fig. 6.11), indicates a nanostructured phase with particle diameters of a few nanometers. In principle, nanometer sized precipitates can grow and freeze when subjected to heat input and subsequent rapid cooling during thermal spraying, as was for instance observed by Jing et al. [GMG03] in HVOF sprayed AlFe deposits. A broadened X-ray diffraction peak of the crystalline α-Cr phase of the VPS deposits (Fig. 6.1) suggests that this phase is precipitated in nanometer-sized crystallites. In the following, a detailed analysis of the nanometer sized particles is presented.

X-ray phase and peak width analysis

The size of small crystalline precipitates can be determined by a peak shape analysis of the corresponding X-ray Bragg reflections. The peak width of Bragg peaks as shown in Figs. 6.1 - 6.4 arises from a convolution of profiles caused by the finite crystallite size and variations in lattice parameter introduced by local residual stresses [War69]. The broadening due to finite crystal sizes is described by the Scherrer formula

\[
\delta(2\theta_{hkl}) = \frac{\lambda}{(L_{\text{X-ray}} \cos(\bar{\theta}_{hkl}))},
\]

(6.3)
Fig 6.13: 2D apparent specific surface area projections from SANS for different spray parameter settings of (a) APS, (b) VPS, (c) WSP, (d) FS and (e) WAS deposits. The spray direction corresponds to 0°. In (d), the horizontal and vertical ellipses, described by \((\eta_1, r_1)\) and \((\eta_2, r_2)\), are shown for the FS deposit. The origin of the main scattering contributions for 0° and 90° are indicated on the graphs on the bottom right.
Table 6.5: Apparent surface area anisotropies. The aspect ratios of the two ellipses are $\eta_1$ and $\eta_2$, and the lengths of their axes oriented along the direction $0^\circ$ are $r_1$ and $r_2$. The ratio of the apparent surface area in direction $0^\circ$ and $90^\circ$ is $\phi_{Porod}$. For clarity, $r_1$ is set to 1. Uncertainties in least significant digits given in parentheses are statistical errors obtained from the fit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta_1$</th>
<th>$r_1$</th>
<th>$\eta_2$</th>
<th>$r_2/r_1$</th>
<th>$\phi_{Porod}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FS-I</td>
<td>1.61 (5)</td>
<td>1</td>
<td>0.21 (3)</td>
<td>0.49 (4)</td>
<td>1.15 (9)</td>
</tr>
<tr>
<td>VPS-I</td>
<td>1.68 (1)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1.68 (1)</td>
</tr>
<tr>
<td>VPS-II</td>
<td>1.39 (1)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1.39 (1)</td>
</tr>
<tr>
<td>VPS-III</td>
<td>1.59 (1)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1.59 (1)</td>
</tr>
<tr>
<td>APS-I</td>
<td>1.58 (2)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1.58 (2)</td>
</tr>
<tr>
<td>APS-II</td>
<td>1.65 (2)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1.65 (2)</td>
</tr>
<tr>
<td>APS-III</td>
<td>1.57 (3)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1.57 (3)</td>
</tr>
<tr>
<td>WSP-I</td>
<td>1.31 (2)</td>
<td>1</td>
<td>0.15 (2)</td>
<td>0.28 (2)</td>
<td>1.06 (9)</td>
</tr>
<tr>
<td>WSP-II</td>
<td>1.29 (2)</td>
<td>1</td>
<td>0.16 (2)</td>
<td>0.24 (2)</td>
<td>1.07 (9)</td>
</tr>
<tr>
<td>WSP-III</td>
<td>1.33 (2)</td>
<td>1</td>
<td>0.18 (2)</td>
<td>0.33 (4)</td>
<td>1.04 (9)</td>
</tr>
<tr>
<td>WAS-I</td>
<td>1.43 (1)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1.43 (1)</td>
</tr>
<tr>
<td>WAS-II</td>
<td>1.47 (1)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1.47 (1)</td>
</tr>
<tr>
<td>WAS-III</td>
<td>1.46 (1)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1.46 (1)</td>
</tr>
</tbody>
</table>

where $L_{X-ray}$ is the mean volume weighted column length of grains perpendicular to the lattice planes ($hkl$) (i.e. parallel to the spray direction) that allows coherent diffraction. $\lambda$ is the wavelength and $2\theta_{hkl}$ the Bragg peak position. With $\epsilon$ being an approximate upper strain value, the strain broadening is given by

$$\delta(2\theta_{hkl})^{strain} = 4\epsilon \tan(\theta_{hkl})$$

(6.4)

By the Warren-Averbach method [War69, KA74], the total peak width can be attributed to these two main contributions, when the the different dependencies of the crystallite size broadening and the microstrain broadening on $2\theta_{hkl}$ are exploited. For a set of reflections, a mean volume weighted column length $L_{X-ray}$ can be deduced from the total integral breadths $\delta(2\theta)_{hkl}$ of a set of Bragg reflections with Miller indices ($hkl$), defined as the ratio between the total peak area and the peak height. For the precise determination of the integral breadth of the convoluted experimental profile, a Pearson-VII function was fitted that includes both Gaussian and Cauchy functions for different limits of the profile shape factor $\mu$

$$P(2\theta) = P_0 \left[ 1 + 4 \frac{\left(2^{(1/\mu)} - 1\right)}{\delta_p^2} \left(2\theta - 2\theta_{hkl}\right)^2 \right]^{-\mu},$$

(6.5)

where $P_0$ is the amplitude and $\delta_p$ is related to the total integral breadth $\delta(2\theta_{hkl})$ as

$$\delta(2\theta_{hkl}) = \frac{\sqrt{\pi\mu}}{\delta_p} \times \frac{\Gamma(\mu - 1/2)}{\Gamma(\mu)},$$

(6.6)
6. RESULTS AND MICROSTRUCTURAL ANALYSIS

Γ being the Gamma-function. With $s = 2 \sin(\theta)/\lambda$, $\delta(s_{hkl})_{\text{size}} = 1/L_{\text{X-ray}}$ and $\delta(s_{hkl})_{\text{strain}} = 2 \epsilon_s$, the total integral breadth $\delta(s_{hkl})$ corresponds to the $s$-independent size broadening and the $s$-dependent strain broadening. According to Klug and Alexander [KA74], the profile induced by the finite crystallite size can be well approximated by a Cauchy function, and the strain profile by a Gaussian function. For a convolution of a Gaussian and a Cauchy function,

$$\frac{(\delta s_{hkl})_{\text{size}}}{(\delta s_{hkl})} = 1 - \left[ \frac{(\delta s_{hkl})_{\text{strain}}}{(\delta s_{hkl})} \right]^2,$$

from which in the following size and strain contributions were determined.

The integral breadths $\delta(2\tilde{\theta}_{hkl})$ are given in Table 6.6 for the feedstock powder and a VPS deposit together with the Bragg peak positions $2\tilde{\theta}_{hkl}$ for different $(hkl)$ reflections. From eqn. 6.7, the mean volume weighted column length and microstrain are calculated and given in Table 6.7.

**TEM analysis**

TEM specimens of a VPS deposit were prepared as described in section 5.1. The TEM images in Fig. 6.15 show two splats in the planar view with the electron beam in spray direction. The shape of the droplets is circular, in agreement with the expectation that parallel to the deposit surface no preferred orientation exists. The diameters of the two splats are approximately 375 nm and 130 nm, indicating that a fraction of droplets were partially dissociated by splashing, as suggested by Izdinsky et al. [IIZK97b]. Izdinsky et al.
Table 6.6: X-ray Bragg peak positions and corresponding integral breadths from the feedstock powder and from the surface of the VPS deposit. Standard uncertainties in least significant digits obtained from the fit are given in parentheses.

<table>
<thead>
<tr>
<th>hkl</th>
<th>Feedstock</th>
<th>VPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2\theta$ (°)</td>
<td>$\delta(2\theta)$ (°)</td>
</tr>
<tr>
<td>110</td>
<td>44.67 (2)</td>
<td>3.36 (9)</td>
</tr>
<tr>
<td>200</td>
<td>64.99 (2)</td>
<td>4.3 (3)</td>
</tr>
<tr>
<td>211</td>
<td>82.37 (1)</td>
<td>3.9 (1)</td>
</tr>
<tr>
<td>220</td>
<td>99.00 (6)</td>
<td>5.7 (3)</td>
</tr>
<tr>
<td>310</td>
<td>116.7 (4)</td>
<td>3.7 (8)</td>
</tr>
</tbody>
</table>

Table 6.7: Crystallite size and microstrain in the feedstock material and the VPS deposit. Standard uncertainties in least significant digits obtained from the fit are given in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>Feedstock</th>
<th>VPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{X\text{-ray}}$ (nm)</td>
<td>2.9 (4)</td>
<td>4.1 (3)</td>
</tr>
<tr>
<td>$\epsilon$ (%)</td>
<td>0.8 (6)</td>
<td>0.5 (3)</td>
</tr>
</tbody>
</table>

also stressed the higher probability of small particles to oxidize. Indeed, an up to 15 nm thick oxide ring surrounding the splat can clearly be identified in the first two images, although it was sprayed under vacuum conditions. The third image of Figure 6.15 shows fine dispersed inhomogeneities in the size regime below 10 nm with the corresponding diffraction pattern in the inset. These inhomogeneities most likely are the same fine particles identified by X-ray diffraction as nanometer-sized $\alpha$-Cr phase (see previous section). A topological contrast mapping by atomic force microscopy (AFM) showed inhomogeneities of a similar size in the VPS deposit, and significantly less inhomogeneities in the APS deposit in agreement with SANS.

**SANS from precipitates**

As indicated in Fig. 6.11, the SANS curves partially deviate from the power law behavior of the Porod law, $I(Q) \propto Q^{-4}$. In the magnified Fig. 6.16 showing the scattering data of all deposits investigated, a strong deviation of the radially averaged $I(Q)$ from the power law is visible in the approximate range $0.2 \text{ nm}^{-1} < Q < 2 \text{ nm}^{-1}$, most pronounced for the feedstock powder and the VPS deposit. No or only weak scattering of the same type is seen for the other spray techniques (Fig. 6.11 and Fig. 6.16).
Fig 6.15: TEM analysis of a VPS deposit, showing in (a) and (b) fine oxide layers surrounding metallic splats. Inside the metallic splat of (a), the dark spots indicate precipitates. The image (c) shows the precipitates in high magnification together with the corresponding diffraction pattern.
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Assuming the scattering to be within the single scattering regime, originating from homogeneous spherical particles of radius $R$ distributed by a size distribution $N_{pr}(R)$ with scattering length $\rho_{pr}$ embedded in a matrix of scattering length $\rho_M$, eqn. 5.17 was applied to fit this part of the scattering curves. In Fig. 6.16, the fits to the data obtained for the VPS deposits are plotted as solid curves.

![Graph showing small-angle neutron scattering from precipitates. The solid lines are fits to data of the VPS deposits (details are given in the text).](image)

For the particle size, a log-normal size distribution $N_{pr}(R)$ with mean radius $R_0$ and width $s$ was assumed

$$N_{pr}(R) = n \exp\left(-\left(\ln(R) - \ln(R_0)\right)^2/s^2\right)$$

which is normalized by

$$\int_0^\infty N_{pr}(R) \, dR = n.$$  \hspace{1cm} (6.9)

With the volume $V(R) = 4\pi R^3/3$ of a single particle and the volume distribution $\Phi(R) = N_{pr}(R) V(R)$, the total volume fraction of precipitates becomes

$$\Phi_{pr} = \int_0^\infty \Phi(R) \, dR$$

The mean radius $\bar{R}$ and the volume weighted mean radius $\bar{R}_v$ are obtained by integration:

$$\bar{R} = \frac{\int_0^\infty N_{pr}(R) R \, dR}{\int_0^\infty N_{pr}(R) \, dR}$$

$$\bar{R}_v = \frac{\int_0^\infty \Phi(R) R \, dR}{\int_0^\infty \Phi(R) \, dR}$$

(6.11)
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\[ \bar{R} = \frac{\int_0^\infty N_{pr}(R) V(R) R dR}{\int_0^\infty N_{pr}(R) V(R) dR} \]  

(6.12)

\( \bar{R} \) and \( \bar{R}_V \) can be determined from the SANS curves without knowledge of the scattering contrast \(|\Delta \rho_n(\vec{r})|^2\), i.e. without knowing the chemical composition of the particle or the matrix.

The SANS mean radii derived from the fit are collected in Table 6.8. Comparing them to the results of the X-ray diffraction peak broadening analysis (section 6.1, Table 6.7), it is evident that very similar particle sizes are obtained from both techniques. Since the X-ray diffraction peaks stem from \( \alpha \)-Cr, the SANS scattering in the approximate range 0.2 nm\(^{-1} < Q < 2 \) nm\(^{-1}\) is caused most likely by nanometer-sized \( \alpha \)-Cr precipitates.

Precipitates of \( \alpha \)-Cr have for example been found in Ni-based alloys by Yang et al. [YLC92]. Also, a cubic \( \alpha \)-Cr phase was found by Wilkes and Lagedrost [WL86, Paw95] in the vacuum plasma sprayed deposit 32.3 wt.% Ni, 36 wt.% Co, 21 wt.% Cr, 8.8 wt.% Al, 1 wt.% Y, 0.9 wt.% Si containing a similar amount of chromium. The agreement with tabulated values [ICD03] of the Bragg peak positions of the \( \alpha \)-Cr suggests the precipitates to mainly consist of chromium. Thus, the scattering length density of the precipitates was assumed to be equal to the coherent scattering cross-section of \( \alpha \)-Cr, \( \rho_{n,pr} = \rho_{n,Cr} = 3.03 \times 10^{14} \text{ m}^{-2} \), calculated from tabulated values for the mass density of \( \alpha \)-Cr, \( \rho_{m,Cr} = 7.239 \text{ g cm}^{-3} \). For the scattering length density of the matrix, two estimations were made: NiCrAlY matrix with nominal composition of the feedstock powder (negligible chromium reduction due to precipitation), \( \rho_{n,M} = \rho_{n,NiCrAlY} = 6.43 \times 10^{14} \text{ m}^{-2} \), and NiCrAlY matrix completely depleted in chromium, \( \rho_{n,M} = \rho_{n,NiAlY} = 7.35 \times 10^{14} \text{ m}^{-2} \). The uncertainty in the chemical composition of the matrix results in an uncertainty in the scattering contrast between precipitates and matrix, \( 11.6 \times 10^{28} \text{ m}^{-4} < |\Delta \rho_{n}|^2 = |\rho_{n,M} - \rho_{n,pr}|^2 < 18.9 \times 10^{28} \text{ m}^{-4} \), and in a similar uncertainty for the determined volume fractions \( \Phi_{pr} \). For the fit, the chromium depleted limit of the scattering contrast was used to calculate the total volume fraction of the precipitates \( \Phi_{pr} \) given in Table 6.8. Volume fractions calculated with the nominal feedstock NiCrAlY composition are 1.64 times the given values of \( \Phi_{pr} \).

The SANS scattering related to the precipitates was found to be isotropic. This SANS isotropy of the precipitates obtained from the VPS cross-section samples with the incident neutrons perpendicular to the spray direction indicates a spherical shape or random orientation distribution of the precipitates.

Fig. 6.17 shows the integrated X-ray intensity and peak width of the 211 \( \alpha \)-Cr Bragg reflection versus the volume fraction of the precipitate phase as derived from SANS, given in Table 6.8. Although low statistics due to missing deposits with an “intermediate” \( \alpha \)-Cr volume fraction hamper the interpretation, the identification of the SANS scattering to be due to the \( \alpha \)-Cr seems justified. Fig. 6.18 relates the SANS - \( \alpha \)-Cr volume fraction in different spray techniques to the oxide volume fraction (as given in Table 6.4 along with corresponding standard uncertainties). Note the logarithmic scale. The observed dependence suggests that...
Table 6.8: Volume fractions $\Phi_{pr}$ of $\alpha$-Cr precipitates and mean radii $\bar{R}_V$ and $\bar{R}$. Standard uncertainties in least significant digits are given in parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume fraction $\Phi_{pr}$ (%)</th>
<th>Mean volume weighted radius $\bar{R}_V$ (nm)</th>
<th>Mean radius $\bar{R}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPS-I</td>
<td>5.5 (2)</td>
<td>2.1 (2)</td>
<td>1.7 (2)</td>
</tr>
<tr>
<td>VPS-II</td>
<td>5.9 (2)</td>
<td>2.0 (2)</td>
<td>1.5 (2)</td>
</tr>
<tr>
<td>VPS-III</td>
<td>6.6 (2)</td>
<td>2.8 (2)</td>
<td>1.9 (2)</td>
</tr>
<tr>
<td>APS-I</td>
<td>0.66 (3)</td>
<td>0.99 (9)</td>
<td>0.86 (9)</td>
</tr>
<tr>
<td>APS-II</td>
<td>1.00 (5)</td>
<td>0.98 (9)</td>
<td>0.89 (9)</td>
</tr>
<tr>
<td>APS-III</td>
<td>0.52 (3)</td>
<td>1.08 (9)</td>
<td>0.89 (9)</td>
</tr>
<tr>
<td>WAS-I</td>
<td>0.26 (2)</td>
<td>3.4 (3)</td>
<td>1.75 (2)</td>
</tr>
<tr>
<td>WAS-II</td>
<td>0.21 (1)</td>
<td>3.5 (3)</td>
<td>1.40 (2)</td>
</tr>
<tr>
<td>WAS-III</td>
<td>0.71 (3)</td>
<td>2.0 (2)</td>
<td>1.23 (2)</td>
</tr>
<tr>
<td>WSP-I</td>
<td>0.14 (1)</td>
<td>11.7 (8)</td>
<td>7.55 (8)</td>
</tr>
<tr>
<td>WSP-II</td>
<td>0.16 (1)</td>
<td>20.0 (9)</td>
<td>8.58 (9)</td>
</tr>
<tr>
<td>WSP-III</td>
<td>0.18 (1)</td>
<td>13.8 (9)</td>
<td>6.76 (5)</td>
</tr>
<tr>
<td>FS-I</td>
<td>0.35 (2)</td>
<td>1.84 (7)</td>
<td>1.65 (2)</td>
</tr>
</tbody>
</table>

Fig 6.17: Integrated intensity and peak width of $\alpha$-Cr 211 X-ray Bragg reflection versus SANS volume fraction.
the precipitation of $\alpha$-Cr and the formation of oxides suppress each other. This may be caused by the reduction of chromium in the matrix due to $\alpha$-Cr precipitates. Less chromium in the NiCrAlY matrix is related to a lower diffusivity of Al (as outlined in section 4). Hence, less oxides (alumina) can be formed. The SANS scattering from the precipitates does not affect the determination of the pore surface area, which can be separately determined as long as a sufficiently large region of the Porod power law scattering at smaller scattering vectors can be accessed.

![Graph showing oxide volume fraction versus $\alpha$-Cr volume fraction obtained from SANS.](image)

Fig 6.18: Oxide volume fraction (given in Table 6.4 along with standard uncertainties) versus $\alpha$-Cr volume fraction obtained from SANS.

### 6.8 Beam broadening analysis

Fig. 6.19 shows the 2D detector images of the MSANS beam broadening of an APS deposit for wavelengths $\lambda$ between $1.3\text{ nm} < \lambda < 1.9\text{ nm}$ in linear intensity scale. The isotropic images in Figs. 6.19(a) are determined from free-standing deposits with the incident neutron beam parallel to the spray direction, the corresponding images in Figs. 6.19(b) reflect the anisotropy of the pore morphology in the cross-sectional view with the neutron beam perpendicular to the spray direction. The analyzed $Q$-range varied with $\lambda$ between $2.3\times10^{-3}\text{ nm}^{-1} < Q < 4.0\times10^{-1}\text{ nm}^{-1}$ at $1.3\text{ nm}$ and $1.6\times10^{-3}\text{ nm}^{-1} < Q < 2.8\times10^{-1}\text{ nm}^{-1}$ at $1.9\text{ nm}$. The MSANS beam broadening is reflected in an increasing width of the approximately gaussian profile with increasing $\lambda$ as shown in Fig. 6.20 for the radially averaged $I(Q)$.

The experimentally determined circularly-averaged MSANS beam broadening is shown in Fig. 6.21 for the cross-section and free-standing deposits of different APS spray parameter settings. A change in the slope or curvature is related to a change in the mean phase shift $\nu$ and therefore a measure of the diffractive or refractive nature of the scattering.
Overall shift towards higher $r_c$ reflects the two different projections of the pore arrangement probed by the neutrons, and also the different sample thickness as given in Table 6.9 used in orientations $x$ and $y$ to obtain sufficient broadening. The noise seen in the fits to the MSANS data of the APS-II deposit in Fig. 6.21(b) is primarily due to rounding errors associated with interpolation issues and should not affect the overall fit.
Fig 6.20: MSANS beam broadening with increasing wavelength, radially averaged around the incident beam, linear scale.

Table 6.9: Boundary values for the MSANS modelling: Experimental total specific surface area $S_T$ from SANS and MSANS anisotropy $\phi_{MSANS}$, total pore volume $\Phi_T$ and thickness in sample orientations $x$ and $y$. Standard uncertainties in least significant digits are given in parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_T$ ($10^6$ m$^{-1}$)</th>
<th>$\phi_{MSANS}$</th>
<th>$\Phi_T$ (Vol. %)</th>
<th>$\tau_x$ (mm)</th>
<th>$\tau_y$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAS-I</td>
<td>1.17 (3)</td>
<td>1.34 (2)</td>
<td>6.5 (1)</td>
<td>2.56 (5)</td>
<td>2.43 (5)</td>
</tr>
<tr>
<td>WAS-II</td>
<td>1.02 (3)</td>
<td>1.34 (2)</td>
<td>6.5 (2)</td>
<td>2.74 (5)</td>
<td>2.42 (5)</td>
</tr>
<tr>
<td>WAS-III</td>
<td>0.93 (3)</td>
<td>1.40 (2)</td>
<td>5.4 (2)</td>
<td>2.75 (5)</td>
<td>2.30 (5)</td>
</tr>
<tr>
<td>APS-I</td>
<td>0.77 (2)</td>
<td>1.35 (2)</td>
<td>8.1 (1)</td>
<td>3.76 (8)</td>
<td>2.30 (5)</td>
</tr>
<tr>
<td>APS-II</td>
<td>0.76 (2)</td>
<td>1.30 (2)</td>
<td>11.2 (1)</td>
<td>2.28 (5)</td>
<td>2.28 (5)</td>
</tr>
<tr>
<td>APS-III</td>
<td>0.71 (2)</td>
<td>1.28 (2)</td>
<td>9.1 (1)</td>
<td>2.63 (5)</td>
<td>2.48 (5)</td>
</tr>
<tr>
<td>VPS-I</td>
<td>0.86 (2)</td>
<td>1.17 (2)</td>
<td>6.9 (2)</td>
<td>3.82 (8)</td>
<td>2.26 (5)</td>
</tr>
<tr>
<td>WSP-I</td>
<td>1.26 (3)</td>
<td>1.25 (2)</td>
<td>5.2 (2)</td>
<td>2.95 (5)</td>
<td>2.27 (5)</td>
</tr>
<tr>
<td>FS-I</td>
<td>0.90 (3)</td>
<td>1.50 (3)</td>
<td>8.0 (2)</td>
<td>3.58 (8)</td>
<td>2.28 (5)</td>
</tr>
</tbody>
</table>
6. RESULTS AND MICROSTRUCTURAL ANALYSIS

Fig 6.21: (a)-(c). Experimentally determined wavelength-dependent MSANS beam broadening along with model results in two sample orientations $x$ and $y$ for different spray parameter settings of APS. (a) shows additionally the mean number of scattering events $\bar{z}$ for the orientations $x$ and $y$, related to the model of the APS-I deposit. For details on the modelling, see section 7.2.
6. RESULTS AND MICROSTRUCTURAL ANALYSIS

The anisotropic distribution of $r_c$ obtained from the sector-wise averaged analysis (see section 5.4) for different $\lambda$ is shown for the APS-I deposit in the polar plot of Fig. 6.22. The standard deviations of the experimental data in Fig. 6.22 shown for $\lambda = 1.2$ nm indicate the fit uncertainty in determining the gaussian width. Within the varied wavelength range, the

![Anisotropic MSANS beam broadening as measured and predicted by the model for different wavelengths, APS-I. Standard deviations of the experimental data are indicated for $\lambda = 1.2$ nm. For details on the modelling, see section 7.2.](image)

MSANS anisotropy $\phi_{MSANS}$ is rather independent of $\lambda$ [AIL+01], and was therefore determined as a mean for different $\lambda$ from the aspect ratios of the ellipses fitted to the anisotropic distribution of gaussian widths, as described in section 5.4.

In Table 6.9, the results are given along with the pore volume fractions $\Phi_T$, the specific surface area from Porod SANS $S_T$, and the sample thickness $\tau$ parallel to the incident neutron beam in orientations $x$ and $y$ (c.f. Fig. 5.3). These parameters together with the MSANS beam broadening $r_c(\lambda)_{x,y}$ serve as input for the MSANS modelling of the pore system.
7

Modelling of the pore morphology

For each deposit, a pore morphology consistent with the measured total specific surface area $S_T$ and total pore volume $\Phi_T$ derived as described before was modelled to fit the experimentally determined wavelength-dependent MSANS beam broadening and MSANS anisotropy. The modelling is based on the multiple small-angle neutron scattering analysis outlined in section 5.3 and the experimental results given in section 6.8. The model of the pore system with simplified model pores is described in section 7.1. Model results in terms of mean pore shape, orientation and size and volume and surface area fractions in different pore sub-systems are given in section 7.2 and discussed in terms of validity in section 7.3.

7.1 The model of the pore system

Motivated by the TEM and SEM observations in section 6.4, the pore systems of the NiCrAlY deposits were modelled by three major pore sub-systems, each represented by a pore species of either spherical or spheroidal shape. These pore species are classified in a spherical globular pore system, and two spheroidal pore systems, the latter two representing an interlamellar and a crack-type pore system. The spheroidal pore systems are distinguished mainly by their orientation distribution: Crack-type pores are mainly aligned with their short opening dimension perpendicular to the spray direction, and interlamellar pores with their short opening dimension parallel to it. Each spheroid is characterized by a radius $R_0$ and an aspect ratio $\beta$. With $R_0$ and $\beta$, the short axis $\beta R_0$ and the mean opening dimension (O.D.) $= 4\beta R_0/3$ are defined. The spherical pores are described by their radii $R_{0G}$. In Fig. 7.1, these model pore species are schematically illustrated. Each pore system contributes a fraction $\Phi_{C,P,G}$ to the total pore volume $\Phi_T$, where $c$ represents the fine crack-type pore system, $p$ the interlamellar pore system and $g$ the globular pore system. Likewise, it generates the fraction $S_{C,P,G}$ of the total specific surface area $S_T$ [AB94],

$$S_{C,P,G} = 3 \chi_{C,P,G} \Phi_{C,P,G}/R_{0C,P,G},$$

(7.1)

where by geometrical considerations

$$\chi(\beta) = 1/(2\beta)(1 + \beta^2 \ln\{1 + (1 - \beta^2)^{1/2}/\beta\}/(1 - \beta^2)^{1/2}); \quad (\beta \leq 1)$$

(7.2)
7. MODELLING OF THE PORE MORPHOLOGY

Fig 7.1: Pore models for the three dominant pore systems. The spray direction is vertical. The arrows indicate the physically relevant mean opening dimensions \( \langle O.D. \rangle \). (C) Crack, mainly aligned with the opening dimension perpendicular to the spray direction, (P) interlamellar pore, mainly aligned with the short opening dimension parallel to the spray direction, (G) globular pore.

To model the pore morphology in the investigated NiCrAlY deposits, for the crack and interlamellar pore system \( \beta_C = 1/10 \) and \( \beta_P = 1/5 \) were used (see below). Then, \( \chi_C = 5.15 \) for the crack pore system, \( \chi_P = 2.73 \) for the interlamellar pore system, and \( \chi_G = 1 \) for the globular pore system.

The orientation distributions of the spheroidal pores are parameterized by grouping all possible orientations into 3 angular sectors with respect to the spray direction: \( 0^\circ - 30^\circ \) (l), \( 30^\circ - 60^\circ \) (m) and \( 60^\circ - 90^\circ \) (h). Fig. 7.2 shows the model pore orientations with respect to the spray direction. The orientation probability of finding a crack or interlamellar pore within one of these sectors is given by \( g_l \), \( g_m \) and \( g_h \), respectively. Due to the solid angle distribution over the sectors l, m and h, for random distribution, \( g_l = 0.136 \), \( g_m = 0.364 \), and \( g_h = 0.500 \). For clarity, these orientation probabilities are expressed in terms of probabilities over random, denoted \( p_l \), \( p_m \) and \( p_h \), where the random distribution now corresponds to \( p_l = p_m = p_h = 1 \). Note that \( p > 1 \) when the probability is higher than random, and \( p < 1 \) when the probability is less than random.

Fig 7.2: Classification of orientations of the short spheroid axis (\( \beta R_0 \)) in three angular sectors with respect to the spray direction, \( (0-30)^\circ \) (l), \( (30-60)^\circ \) (m), and \( (60-90)^\circ \) (h).
The scope of the modelling of the pore morphology was to fit the orientationally-averaged experimental MSANS beam broadening \( r_c(\lambda) \) (shown in Fig. 6.21 for the APS deposits) for the two sample orientations \( x \) and \( y \) (Fig. 5.3). Constraints for the model fit are the total specific surface area, \( S_T \), determined experimentally from SANS in the Porod regime (section 6.6), and the observed MSANS anisotropy \( \phi_{\text{MSANS}} \) (section 6.8). Further given parameters are the sample thickness in \( x \) and \( y \) orientation, the total pore volume fraction \( \Phi_T \) determined from precision density measurements and the scattering contrast between the metallic matrix with scattering length density \( \rho_{\text{NiCrAlY}} = 6.43 \times 10^{-4} \text{nm}^{-2} \) (Table 6.3) and the pores, \( \rho_{\text{Pore}} = 0 \text{nm}^{-2}, |\Delta \rho_n|^2 = 41.34 \times 10^{-8} \text{nm}^{-4} \). The individual model boundary conditions are summarized in Table 6.9.

The dimensions of the pore species belonging to different sub-systems were parameterized in terms of fractions of the crack radius \( \langle R_0C \rangle \), i.e. \( \langle R_{0P} \rangle/\langle R_{0C} \rangle \) and \( \langle R_{0G} \rangle/\langle R_{0C} \rangle \) trial values were estimated and iteratively optimized. The functional dependence of \( r_c(\lambda) \) on the parameters of the model pore system is given by eqn. 5.46, the curvature of the neutron beam profile in the limit \( Q \to 0 \). The orientationally-averaged single scattering cross-section \( \langle \Sigma(Q, \nu_0) \rangle_{\text{Orientation}} \) is obtained by averaging \( \Sigma(Q, \nu_0) \) over each pore sub-system considering their volume fractions \( \Phi_{C,P,G} \) and the orientation distributions of the spheroids, \( p_{l,m,h} \). Values of \( q(\zeta) \) for the range of \( \zeta \) needed here are determined by computational methods as described in literature [BH86]. From the resulting tabulated values, \( q(\zeta) \) is inserted into eqn. 5.37 to calculate \( r_c(\lambda) \).

For each iteration step \( i \), the single-parameter fit for \( \langle R_{0C} \rangle \) is performed separately for each sample orientation \( x \) and \( y \). The first requirement for the model fit is the agreement in the obtained mean radii \( \langle R_{0C} \rangle_{i,x} \) and \( \langle R_{0C} \rangle_{i,y} \). From \( \langle R_{0C} \rangle_i \), the model specific surface area \( S_T \) is calculated according to eqn. 7.1. The model MSANS anisotropy \( \phi_{\text{MSANS}} \) is determined in a separate calculation from the MSANS parameters and \( \langle R_{0C} \rangle_i \) obtained from the fit by numerically averaging the anisotropy factors \( 1/K(\beta, \chi) \) (see eqn. 5.41) for each spheroidal pore system over the orientation distributions with respect to \( Q \) and applying an appropriate weighting that takes the volume fractions \( \Phi_{C,P,G} \) as well as the total cross-sections of each pore sub-system into account [AIL+01].

### 7.2 Modelling results

The detailed modelling procedure is exemplified by means of the APS-I deposit (see also [KWA+02, KWI+02]). From Table 6.9, the total volume fraction and its total specific surface area are \( \Phi_T = 8.1 \% \) and \( S_T = 0.77 \times 10^6 \text{m}^{-1} \). The model results of the circularly-averaged MSANS beam broadening are plotted for the cross-section and free-standing deposit in Fig.
6.21(a) along with the experimental values.

Also, Fig. 6.21(a) shows the mean number of scattering events, $\bar{z}$, for the sample orientations $x$ and $y$. For the APS-I deposit, $\bar{z} > 60$ for all wavelengths applied to determine the beam broadening. $\bar{z}$ is calculated from the model parameters based on eqn. 5.22. Generally, $\bar{z} > 20$ was obtained for all investigated deposits, which is sufficiently large for the transport approach (eqn. 5.35) to be justified and the MSANS modelling procedure to be applicable, i.e. $\bar{z} > 5$, [AB94, MS92a].

Model and experimental MSANS anisotropies for the APS-I deposit for different $\lambda$ are shown in the polar plot of Fig. 6.22. The resulting model MSANS anisotropy of 1.38 is within the uncertainty in agreement with the experimentally determined MSANS anisotropy $\Phi_{\text{MSANS}} = 1.35 \pm 0.3$.

Fitting the average crack radius resulted in $\langle R_{0C} \rangle = (0.728 \pm 0.010) \mu m$. The relative model pore radii $\langle R_{0P} \rangle / \langle R_{0C} \rangle$ and $\langle R_{0G} \rangle / \langle R_{0C} \rangle$ as given in Table 7.1 were used. With regard to

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\beta_C$</th>
<th>$\beta_P$</th>
<th>$\langle R_{0P} \rangle / \langle R_{0C} \rangle$</th>
<th>$\langle R_{0G} \rangle / \langle R_{0C} \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAS-I</td>
<td>0.1</td>
<td>0.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>WAS-II</td>
<td>0.1</td>
<td>0.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>WAS-III</td>
<td>0.1</td>
<td>0.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>APS-I</td>
<td>0.1</td>
<td>0.2</td>
<td>1.0</td>
<td>1.3</td>
</tr>
<tr>
<td>APS-II</td>
<td>0.1</td>
<td>0.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>APS-III</td>
<td>0.1</td>
<td>0.2</td>
<td>1.0</td>
<td>1.3</td>
</tr>
<tr>
<td>VPS-I</td>
<td>0.1</td>
<td>0.2</td>
<td>1.0</td>
<td>1.3</td>
</tr>
<tr>
<td>WSP-I</td>
<td>0.1</td>
<td>0.2</td>
<td>1.0</td>
<td>1.3</td>
</tr>
<tr>
<td>FS-I</td>
<td>0.1</td>
<td>0.2</td>
<td>1.0</td>
<td>1.3</td>
</tr>
</tbody>
</table>

the aspect ratios $\beta_C$ and $\beta_P$ of the spheroidal model pores, for all deposits, $\beta_C = 0.1$ and $\beta_P = 0.2$ turned out to be suitable values for the aspect ratios of the spheroidal interlamellar and crack-type pore systems, and especially $\langle R_{0P} \rangle / \langle R_{0C} \rangle = 1.0$ was required for a stable fit, implying the mean crack opening dimension to be half the opening dimension of the interlamellar pores. For the APS-I deposit, $\langle R_{0G} \rangle / \langle R_{0C} \rangle = 1.3$, whereas for other deposits $\langle R_{0G} \rangle / \langle R_{0C} \rangle = 1.0$ resulted in stable fits.

From the mean pore radii $\langle R_{0, C,P,G} \rangle$ and aspect ratios $\beta_{C,P}$, the mean opening dimensions $\langle \text{O.D.} \rangle_{C,P} = 4\beta_{C,P} \langle R_{0, C,P} \rangle / 3$ and the mean globular pore diameter $\langle 2R_{0G} \rangle$ were deduced as given in Table 7.2. For the APS-I deposit, $\langle \text{O.D.} \rangle_P = 0.193 \mu m$, $\langle \text{O.D.} \rangle_C = 0.097 \mu m$, and $\langle 2R_{0G} \rangle = 1.88 \mu m$.
7. MODELLING OF THE PORE MORPHOLOGY

Table 7.2:

Fit parameter $\langle R_{0C} \rangle$, mean opening dimensions $\langle \text{O.D.} \rangle_{C,P}$ and pore diameter $2\langle R_{0G} \rangle$ of the different pore systems, as obtained from the MSANS modelling.

Standard uncertainties in least significant digits are given in parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fit parameter $\langle R_{0C} \rangle$ (µm)</th>
<th>Cracks $\langle \text{O.D.} \rangle_C$ (µm)</th>
<th>Interl. Pores $\langle \text{O.D.} \rangle_P$ (µm)</th>
<th>Glob. Pores $2\langle R_{0G} \rangle$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAS-I</td>
<td>0.32 (2)</td>
<td>0.043 (2)</td>
<td>0.086 (4)</td>
<td>0.65 (3)</td>
</tr>
<tr>
<td>WAS-II</td>
<td>0.36 (2)</td>
<td>0.048 (2)</td>
<td>0.096 (5)</td>
<td>0.72 (4)</td>
</tr>
<tr>
<td>WAS-III</td>
<td>0.33 (2)</td>
<td>0.044 (2)</td>
<td>0.088 (4)</td>
<td>0.67 (3)</td>
</tr>
<tr>
<td>APS-I</td>
<td>0.73 (4)</td>
<td>0.097 (5)</td>
<td>0.193 (9)</td>
<td>1.88 (9)</td>
</tr>
<tr>
<td>APS-II</td>
<td>0.96 (5)</td>
<td>0.128 (6)</td>
<td>0.26 (1)</td>
<td>1.92 (9)</td>
</tr>
<tr>
<td>APS-III</td>
<td>0.70 (4)</td>
<td>0.093 (5)</td>
<td>0.186 (9)</td>
<td>1.82 (9)</td>
</tr>
<tr>
<td>VPS-I</td>
<td>0.39 (2)</td>
<td>0.052 (3)</td>
<td>0.104 (5)</td>
<td>1.01 (5)</td>
</tr>
<tr>
<td>WSP-I</td>
<td>0.32 (2)</td>
<td>0.042 (2)</td>
<td>0.083 (4)</td>
<td>0.81 (4)</td>
</tr>
<tr>
<td>FS-I</td>
<td>0.84 (4)</td>
<td>0.112 (6)</td>
<td>0.22 (1)</td>
<td>2.2 (1)</td>
</tr>
</tbody>
</table>

The orientation distributions obtained from the modelling expressed in probabilities over random, $p_{l,m,h}$, are given in Table 7.3.

For the crack pore system of the APS-I deposit, $p_l = 0.30$, $p_m = 0.59$, $p_h = 1.50$, for the interlamellar pore system, $p_l = 4.80$, $p_m = 0.84$, $p_h = 0.094$. This implies that for the crack elements only one third from random distribution is oriented parallel to the spray direction, the short dimension lying within $0^\circ$ - $30^\circ$ to the spray direction (Fig. 7.2), and 50 % above random lie perpendicular to it within $60^\circ$ - $90^\circ$. For the interlamellar pores, the orientations are reversed and more extreme with almost five times the random distribution within $0^\circ$ - $30^\circ$ and only 1 % of it in the angular sector $60^\circ$ - $90^\circ$.

The distribution of pore volume to the three pore sub-systems is given in Table 7.4. For the APS-I deposit, $\Phi_P = 5.0\%$ pore volume is contained in the interlamellar pore system, $\Phi_G = 2.5\%$ in the globular pore system and only $\Phi_C = 0.6\%$ in the crack pore system, adding up to the experimentally determined total pore volume of $\Phi_T = 8.1\%$.

Similarly, Table 7.5 lists the distribution of total specific surface area $S_T$ to the three pore sub-systems on absolute scale and in fractions of $S_T$, calculated according to eqn. 7.1. The model total specific surface area obtained by summing all three components was tuned to fit the experimental result. For the APS-deposit, $S_T = 0.77 \times 10^6$ m$^{-1}$, which is obtained from $S_C = 0.12 \times 10^6$ m$^{-1}$, $S_P = 0.57 \times 10^6$ m$^{-1}$ and $S_G = 0.08 \times 10^6$ m$^{-1}$.

Fractional standard deviations were estimated by variation of the model pore parameters with constraints on $S_T$ and $\phi_{\text{MSANS}}$ [AIL+01] to be ±10 % for the component porosities, and ±5 % for the orientation probabilities, surface areas of the pore sub-systems, (O.D.) values,
Table 7.3:

Orientation distributions in terms of probabilities over random, \( p_{l,m,h} \) of the fine crack-type pores \( c \) and the interlamellar pores \( p \). The orientations represent angles between the short \( \beta R \) axis and the spray direction. Standard uncertainties in least significant digits are given in parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore system</th>
<th>Orientation (°)</th>
<th>( p_l )</th>
<th>( p_m )</th>
<th>( p_h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAS-I</td>
<td>c</td>
<td>0 - 30</td>
<td>0.00020 (1)</td>
<td>0.039 (2)</td>
<td>1.97 (9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 - 60</td>
<td>7.4 (4)</td>
<td>0.037 (2)</td>
<td>0.00020 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 - 90</td>
<td>0.00020 (1)</td>
<td>0.039 (2)</td>
<td>1.97 (9)</td>
</tr>
<tr>
<td>WAS-II</td>
<td>p</td>
<td>0 - 30</td>
<td>7.4 (4)</td>
<td>0.037 (2)</td>
<td>0.00020 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 - 60</td>
<td>0.00020 (1)</td>
<td>0.039 (2)</td>
<td>1.97 (9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 - 90</td>
<td>7.4 (4)</td>
<td>0.037 (2)</td>
<td>0.00020 (1)</td>
</tr>
<tr>
<td>WAS-III</td>
<td>c</td>
<td>0 - 30</td>
<td>7.4 (4)</td>
<td>0.037 (2)</td>
<td>0.00020 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 - 60</td>
<td>0.00020 (1)</td>
<td>0.039 (2)</td>
<td>1.97 (9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 - 90</td>
<td>7.4 (4)</td>
<td>0.037 (2)</td>
<td>0.00020 (1)</td>
</tr>
<tr>
<td>APS-I</td>
<td>c</td>
<td>0 - 30</td>
<td>0.30 (2)</td>
<td>0.59 (3)</td>
<td>1.50 (8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 - 60</td>
<td>4.8 (2)</td>
<td>0.84 (4)</td>
<td>0.094 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 - 90</td>
<td>0.00020 (1)</td>
<td>0.039 (2)</td>
<td>1.97 (9)</td>
</tr>
<tr>
<td>APS-II</td>
<td>p</td>
<td>0 - 30</td>
<td>7.4 (4)</td>
<td>0.037 (2)</td>
<td>0.00020 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 - 60</td>
<td>0.00020 (1)</td>
<td>0.039 (2)</td>
<td>1.97 (9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 - 90</td>
<td>7.4 (4)</td>
<td>0.037 (2)</td>
<td>0.00020 (1)</td>
</tr>
<tr>
<td>APS-III</td>
<td>c</td>
<td>0 - 30</td>
<td>0.83 (4)</td>
<td>0.99 (5)</td>
<td>1.05 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 - 60</td>
<td>5.3 (3)</td>
<td>0.78 (4)</td>
<td>0.00100 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 - 90</td>
<td>0.00020 (1)</td>
<td>0.039 (2)</td>
<td>1.97 (9)</td>
</tr>
<tr>
<td>WPS-I</td>
<td>p</td>
<td>0 - 30</td>
<td>3.4 (2)</td>
<td>1.18 (6)</td>
<td>0.23 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 - 60</td>
<td>0.00020 (1)</td>
<td>0.039 (2)</td>
<td>1.97 (9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 - 90</td>
<td>7.1 (4)</td>
<td>0.071 (4)</td>
<td>0.036 (2)</td>
</tr>
<tr>
<td>VPS-I</td>
<td>c</td>
<td>0 - 30</td>
<td>0.075 (4)</td>
<td>0.97 (5)</td>
<td>1.27 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 - 60</td>
<td>7.3 (4)</td>
<td>0.046 (2)</td>
<td>0.0020 (1)</td>
</tr>
</tbody>
</table>

and the mean globular pore diameter (see also the following section 7.3).

7.3 Reliability of modelling the pore morphology

The following conditions have to be fulfilled for the MSANS model to hold: The model results on \( r_c(\lambda) \) in both sample orientations \( x \) and \( y \) must agree with the experimental MSANS beam broadening, reflected in low \( \chi^2 \) values of the fit. The fitted radius \( R_{0C} \) in sample orientation \( x \) has to be recovered in sample orientation \( y \). The sum of the component surface areas \( S_c + S_p + S_G \) is required to agree with the experimentally determined total specific surface area \( S_T \) within the experimental error. Similarly, the model MSANS anisotropy has to agree with the experimental value \( \phi_{MSANS} \).

In Table 7.6 the deviations of the model results from the experimental values for all investigated deposits are listed and compared. Note, that for \( S_T \) and \( \phi_{MSANS} \) the experimental
Table 7.4:
Pore volume fractions in the pore sub-systems as obtained from the MSANS modelling. The total pore volume $\Phi_T$ corresponds to the values given in Table 6.9. Standard uncertainties in least significant digits are given in parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Phi_C$</th>
<th>$\Phi_P$</th>
<th>$\Phi_G$</th>
<th>$\Phi_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAS-I</td>
<td>0.27 (3) %</td>
<td>2.9 (3) %</td>
<td>3.3 (3) %</td>
<td>6.5 (1) %</td>
</tr>
<tr>
<td>WAS-II</td>
<td>0.13 (1) %</td>
<td>3.0 (3) %</td>
<td>3.4 (3) %</td>
<td>6.5 (2) %</td>
</tr>
<tr>
<td>WAS-III</td>
<td>0.16 (2) %</td>
<td>2.4 (2) %</td>
<td>2.8 (3) %</td>
<td>5.4 (2) %</td>
</tr>
<tr>
<td>APS-I</td>
<td>0.56 (6) %</td>
<td>5.0 (5) %</td>
<td>2.5 (3) %</td>
<td>8.1 (1) %</td>
</tr>
<tr>
<td>APS-II</td>
<td>1.8 (2) %</td>
<td>3.3 (3) %</td>
<td>6.1 (6) %</td>
<td>11.2 (1) %</td>
</tr>
<tr>
<td>APS-III</td>
<td>0.18 (2) %</td>
<td>4.5 (5) %</td>
<td>4.4 (4) %</td>
<td>9.1 (1) %</td>
</tr>
<tr>
<td>VPS-I</td>
<td>0.48 (5) %</td>
<td>1.9 (2) %</td>
<td>4.5 (5) %</td>
<td>6.9 (2) %</td>
</tr>
<tr>
<td>WSP-I</td>
<td>0.66 (7) %</td>
<td>3.1 (3) %</td>
<td>1.4 (1) %</td>
<td>5.2 (2) %</td>
</tr>
<tr>
<td>FS-I</td>
<td>2.6 (3) %</td>
<td>3.8 (4) %</td>
<td>1.6 (2) %</td>
<td>8.0 (2) %</td>
</tr>
</tbody>
</table>

errors are around 3% (Table 6.9). Table 7.6 indicates deviations from the experimental values that exceed the experimental error only for the MSANS anisotropy of the APS-II and the WAS-III deposits, while $S_T$ was tuned to fit the experimental value throughout. The $\chi^2$ values remained significantly high only for the $x$ orientation of the APS-II deposit fit, together with the deviation in $\phi_{\text{MSANS}}$ leaving the latter as the only deposit with a major uncertainty in the model of the pore system.

Once the model surface area and MSANS anisotropy agree with the experimental values within the experimental error, for the multiparameter pore model the unambiguity of the parameters entering the model has to be ensured. Therefore a systematic parameter variation study was performed to investigate the model behavior in the vicinity of the accepted solution. For 600 systematically varied input parameter sets, $\langle R_{0C}\rangle_{x,y}$ was fitted in sample orientations $x$ and $y$ as described in section 7.1 for the APS-III deposit as an example. For all parameter sets, from the weighted mean $\langle R_{0C}\rangle = 1/3\langle R_{0C}\rangle_x + 2/3\langle R_{0C}\rangle_y$, the model $\phi_{\text{MSANS}}$ and the model $S_T$ were calculated.

In Figs. 7.3-7.5 the results of the parameter study are presented for the APS-III deposit. Histograms are used to graphically display the systematic input model parameter variations (Fig. 7.3). For each model parameter set, the obtained model surface areas and model MSANS anisotropies are shown (Fig. 7.4) along with the fit result, $\langle R_{0C}\rangle_{x,y}$ (Fig. 7.5).

As an example for all varied input model parameters, Fig. 7.3 shows on the left the range of varied interlamellar pore volume fractions $\Phi_P/\Phi_T$ (a) and globular pore volume fractions $\Phi_G/\Phi_T$ (b). On the right, only those values of $\Phi_P/\Phi_T$ (c) and $\Phi_G/\Phi_T$ (d) are plotted that result in a model total specific surface area and a model MSANS anisotropy in agreement
Table 7.5:
Specific surface areas $S_{C,P,G}$ in the pore sub-systems as suggested by the MSANS modelling results: absolute values and fractions of the model total specific surface area $S_T$. Standard uncertainties in least significant digits are given in parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_C$</th>
<th>$S_P$</th>
<th>$S_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAS-I</td>
<td>0.13 (1)</td>
<td>0.74 (7)</td>
<td>0.30 (3)</td>
</tr>
<tr>
<td>WAS-II</td>
<td>0.054 (5)</td>
<td>0.69 (7)</td>
<td>0.28 (3)</td>
</tr>
<tr>
<td>WAS-III</td>
<td>0.074 (7)</td>
<td>0.61 (6)</td>
<td>0.25 (3)</td>
</tr>
<tr>
<td>APS-I</td>
<td>0.12 (1)</td>
<td>0.57 (6)</td>
<td>0.080 (8)</td>
</tr>
<tr>
<td>APS-II</td>
<td>0.29 (3)</td>
<td>0.28 (3)</td>
<td>0.19 (2)</td>
</tr>
<tr>
<td>APS-III</td>
<td>0.040 (4)</td>
<td>0.53 (5)</td>
<td>0.14 (1)</td>
</tr>
<tr>
<td>VPS-I</td>
<td>0.19 (2)</td>
<td>0.41 (4)</td>
<td>0.27 (3)</td>
</tr>
<tr>
<td>WSP-I</td>
<td>0.33 (3)</td>
<td>0.83 (8)</td>
<td>0.10 (1)</td>
</tr>
<tr>
<td>FS-I</td>
<td>0.49 (5)</td>
<td>0.37 (4)</td>
<td>0.044 (4)</td>
</tr>
</tbody>
</table>

Table 7.6: Comparison of experimental data and MSANS model results. $\Delta S_T$ and $\Delta \phi_{MSANS}$ indicate relative deviations between model results and experimental values in total specific surface area $S_T$ and MSANS anisotropy $\phi_{MSANS}$, respectively. $\Delta \langle R_{0C})_{x,y}$ denotes the relative deviation between the model radii in $x$ and $y$ orientation. $\chi^2_{x,y}$ are the minimized least-squares values of the fits in $x$ and $y$ orientation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta \phi_{MSANS}$</th>
<th>$\Delta S_T$</th>
<th>$\Delta \langle R_{0C})_{x,y}$</th>
<th>$\chi^2_x$</th>
<th>$\chi^2_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAS-I</td>
<td>1.3%</td>
<td>-0.1%</td>
<td>0.0%</td>
<td>0.55</td>
<td>0.39</td>
</tr>
<tr>
<td>WAS-II</td>
<td>0.6%</td>
<td>-0.1%</td>
<td>-0.6%</td>
<td>0.62</td>
<td>3.92</td>
</tr>
<tr>
<td>WAS-III</td>
<td>5.7%</td>
<td>-0.3%</td>
<td>0.1%</td>
<td>0.59</td>
<td>0.47</td>
</tr>
<tr>
<td>APS-I</td>
<td>-2.2%</td>
<td>0.5%</td>
<td>4.2%</td>
<td>2.63</td>
<td>1.31</td>
</tr>
<tr>
<td>APS-II</td>
<td>8.2%</td>
<td>-0.7%</td>
<td>-1.1%</td>
<td>19.9</td>
<td>0.60</td>
</tr>
<tr>
<td>APS-III</td>
<td>-1.2%</td>
<td>-0.7%</td>
<td>1.1%</td>
<td>0.91</td>
<td>0.37</td>
</tr>
<tr>
<td>VPS-I</td>
<td>0.3%</td>
<td>-0.6%</td>
<td>-0.3%</td>
<td>0.63</td>
<td>0.78</td>
</tr>
<tr>
<td>WSP-I</td>
<td>0.1%</td>
<td>0.1%</td>
<td>-0.6%</td>
<td>0.23</td>
<td>1.32</td>
</tr>
<tr>
<td>FS-I</td>
<td>-0.6%</td>
<td>0.0%</td>
<td>-0.7%</td>
<td>0.31</td>
<td>0.93</td>
</tr>
</tbody>
</table>
with the experimental values within the experimental errors.

In Fig. 7.4, the total specific surface area (a) and MSANS anisotropy (b) determined for the whole set of varied parameters are plotted along with the experimental errors indicated by the dashed vertical lines. Model parameter sets resulting in a surface area or MSANS anisotropy outside the experimental error are disregarded. In (c) and (d), those values of the surface area and MSANS anisotropy are plotted that agree in both, the total specific surface area and the MSANS anisotropy with the experiment within the experimental error.

Similarly, in Fig. 7.5 the model radii $\langle R_{0C} \rangle_{x,y}$ (a) and the resulting $\chi^2$ of the fits in orientations $x$ and $y$ (b) are shown obtained from the whole set of varied parameters, along with $\langle R_{0C} \rangle_{x,y}$ values (c) and $\chi^2_{x,y}$ (d) obtained from model parameters only resulting in a model total specific surface area and a model MSANS anisotropy in agreement with the experimental values within the experimental errors.

The model parameter variation study for the APS-III deposit shows a “smooth” model behavior in the vicinity of the accepted solution. By the requirement of the model total specific surface area and the model MSANS anisotropy to agree with the experimental values within the experimental uncertainty, the initial set of values for $\Phi_P/\Phi_T$ and $\Phi_G/\Phi_T$ is reduced to an uncertainty range of the model parameters that is typically less than the uncertainty estimates given before (section 7.2) and reflects the experimental uncertainty. The uncertainty tends to be higher for model parameters with a low weight on the total pore system, like the orientation distribution of the fine crack pore system not shown here that generates only a minor fraction of the pore volume. Also, the deviations in $\langle R_{0C} \rangle$ between the sample orientations $x$ and $y$ and the corresponding $\chi^2$ values are reduced.
Fig 7.3: Input parameters for model parameter variation study, deposit APS-III: (a) Systematic variation of interlamellar pore volume fraction $\Phi_P/\Phi_T$ and (b) globular pore volume fraction $\Phi_G/\Phi_T$. (c) and (d) show those values of $\Phi_P/\Phi_T$ and $\Phi_G/\Phi_T$ that result in a pore model complying with the experimental specific surface area and MSANS anisotropy within the experimental errors (c.f. Fig. 7.4).
Fig 7.4: Results of model parameter variation study, deposit APS-III: (a) Model specific surface area and (b) model MSANS anisotropy calculated from the systematically varied input parameters. In Fig. (c) and (d), the model surface area and model anisotropy are shown that comply both with the experimental total surface area and MSANS anisotropy within the experimental error. The vertical lines indicate the experimental result and corresponding errors.
Fig 7.5: Results of model parameter variation study, deposit APS-III: (a) Mean model radii \(<R_C>\) in orientations \(x\) and \(y\), and (b) \(\chi^2\) for orientations \(x\) and \(y\), obtained from the fit with systematically varied input parameters. In (c) and (d), \(<R_C>\) and \(\chi^2\) are shown that result in a model pore system complying with the experimental specific surface area and MSANS anisotropy within the experimental errors.
8

Summary and Discussion

In the following, the results of the microstructural analysis (section 6) and modelling of the pore morphology (section 7) are summarized. Microstructure characteristics specific to a single spray-technique are outlined and their influence on deposit properties is discussed.

In section 8.1, the specific features of the pore morphology are described in relation to the applied spray techniques. The overall picture is developed from various microstructural investigations including the Porod-SANS analysis and the MSANS modelling as well as TEM, SEM and X-ray diffraction. The impact of the pore morphology on the deposit properties is discussed in section 8.2, also referring to influences from ternary oxidic and intermetallic phases. The microstructure-property relationships are presented including properties like the electrical and thermal conductivity and the sound velocity in the thermally sprayed NiCrAlY deposits. The influence of the pore morphology on mechanical properties like average residual stresses and elastic moduli are discussed thereafter.

Experimental data on macroscopic deposit properties were determined in close collaboration with EMPA Thun (N. Margadant) within the framework of the KTI-supported project THERMETCOAT Σ1973!.

8.1 Description of the pore morphology

8.1.1 Spray-technique specific features

VPS

The VPS NiCrAlY deposits are the most dense coatings with the lowest oxygen content (Table 6.2). For VPS and APS the fine feedstock powder size (particle diameter \( d < 40 \mu m \), Table 4.2) was used resulting in a finer pore morphology. The total specific surface area is comparatively small \( (S_T = 0.86 \times 10^6 m^{-1} \) for VPS-I, Fig. 6.14 and Table 6.9) and varies by \( \pm 10\% \) for different spray parameter settings. The total pore volume \( (\Phi_T = 6.9 \% \) for VPS-I, Table 6.4) varies by \( \pm 4\% \) and is intermediate compared with the other spray
techniques. According to Table 7.4, for the VPS-I, the largest pore volume fraction (i.e. 65%) is found in the globular pore system ($\Phi_G = 4.5\%$), but the interlamellar pore system contains the highest amount (47%) of specific surface area ($S_P = 0.41 \times 10^6 \text{m}^{-1}$), whereas 22% is located in the crack system. The mean opening dimension is comparatively small (for interlamellar pores, $\langle O.D. \rangle_P = 0.1 \mu\text{m}$ and for the globular pores, the mean diameter is $2\langle R \rangle_G = 1 \mu\text{m}$, Table 7.2). The cracks and interlamellar pores are strongly aligned parallel and perpendicular to the spray direction, respectively (Table 7.3).

The results of the MSANS modelling are qualitatively confirmed by the VPS SEM image Fig. 6.9(b), which shows that a large fraction of the pore volume is located in globular pores. Only a few globular pores at a maximum diameter of approximately 3 $\mu\text{m}$ are found, whereas many are smaller than 1 $\mu\text{m}$.

APS

The APS NiCrAlY deposits have a coarser pore morphology than the VPS deposits, although for the APS deposits the same feedstock powder was used. This is also reflected in a lower deposit density (still intermediate compared with the other spray techniques) and a significantly higher pore volume fraction ($\Phi_T = 8.1\%$ for APS-I) with variations up to 15% for different spray parameter settings. The APS deposits have a similar amount of surface area than the VPS deposits ($S_T = 0.77 \times 10^6 \text{m}^{-1}$ for APS-I) with only 7% deviation between different spray parameter settings. The oxide content is between 1-2 wt.% and therefore significantly higher than for the VPS deposits but still low than for the other spray techniques. The largest amount of pore volume (48 – 61%) is found in the interlamellar pore system. There are only a few cracks. The mean opening dimension of the interlamellar pores is $\langle O.D. \rangle_P = 0.2 \mu\text{m}$ (APS-I) and varies by $\pm15\%$ for the different spray parameters. The interlamellar pores and cracks are not as strongly oriented as in the VPS deposits, which is indicated by a significant fraction $p_m$ with the opening dimension in the intermediate angular range $30 – 60^\circ$ with respect to the spray direction.

Comparing the SEM micrograph of the APS deposit, Fig. 6.9(a), to the VPS, the coarser pore morphology and the dominant interlamellar pores can be identified. Also, the oxides are visible in the APS deposit.

WAS

The WAS NiCrAlY deposits are sprayed from a wire feedstock. This results in a similar pore morphology to the APS technique. They have a higher oxide content (2.8 wt.%), but also a higher deposit density. The WAS deposits have a total specific surface area of $S_T = 0.93 \times 10^6 \text{m}^{-1}$ (for WAS-I) and a variation of 13% for different spray parameter settings. The pore volume is $\Phi_T = 6.5\%$ with a variation of 16% within the applied spray parameter settings. The interlamellar and globular pores have a similar weight on the total pore volume (50 – 52% of the pore volume is interlamellar, 44 – 46% is globular). For all
WAS deposits, more than 60% of the total surface area is interlamellar. Only a few cracks are found. The mean interlamellar opening dimensions are 0.09 µm (WAS-I), which is similar to the VPS deposits, and vary by 8% for the different spray parameters. Comparing the MSANS model results of different spray techniques, cracks in the WAS deposits have the strongest alignment parallel to the spray direction. Similarly, the interlamellar pores are aligned most strongly perpendicular to the spray direction.

In the SEM micrograph of the WAS-I deposit, Fig. 6.9(e), a pore morphology similar to the APS deposit can be seen. Interlamellar and globular pores can be identified as indicated in the image. However, the interlamellar pores do not seem to be as strongly oriented perpendicular to the spray direction as the MSANS analysis suggests. The small mean opening dimensions predicted by the MSANS model can not be understood from the WAS micrograph.

FS

For the WSP and FS NiCrAlY deposits, the large feedstock powder size was used (particle diameter 56 µm < d < 106 µm, Table 4.2). The FS deposit has a significant oxygen content (4.4 wt.%, Table 6.2) and a low deposit density (Table 6.4). The total specific surface area, \( S_T = 0.90 \times 10^6 \text{ m}^{-1} \) (Table 6.9) is similar to the WAS deposits. The total pore volume \( \Phi_T = 8.0% \) is comparatively high (Table 6.4). The FS exhibits the highest crack pore volume from all deposits, \( \Phi_C = 2.6% \), and only a small fraction in the globular pore system (\( \Phi_G = 1.6% \)), c.f. Table 7.4. The mean crack opening dimension is 0.11 µm (Table 7.2). The interlamellar pores are strongly aligned perpendicular to the spray direction, whereas less strongly oriented cracks are indicated by a significant fraction \( p_m \) with the opening dimension in the angular range 30 – 60° with respect to the spray direction (Table 7.3).

The SEM micrograph of the FS NiCrAlY deposit, Fig. 6.9(d), shows a coarse microstructure. The larger splat sizes clearly indicate the larger feedstock powder size. Only a few globular pores are seen, and the interlamellar pores are mostly well aligned perpendicular to the spray direction. The cracks can not be resolved in the micrograph.

WSP

The WSP NiCrAlY deposits have the highest oxide content (6.9 wt.%, ±18% for different spray parameter settings) and a very low deposit density. Also, the WSP have the highest total specific surface area \( S_T = 1.26 \times 10^6 \text{ m}^{-1} \) (for WSP-I), with a variation of ±9% for different spray parameter settings. The pore volume is \( \Phi_T = 5.2% \), and varies by ±17% for different spray parameter settings. 59% of \( \Phi_T \) are interlamellar pores, 13% are cracks and 27% are globular pores. The mean opening dimension of the interlamellar pores is 0.08 µm (WSP-I). Both cracks and interlamellar pores are less strongly oriented, as indicated by a significant fraction \( p_m \) with the opening dimension in the angular range 30 – 60° with respect to the spray direction.
The SEM micrograph of the WSP deposit, Fig. 6.9(c), shows a similarly coarse pore morphology as the FS deposit. Compared with the FS, the interlamellar pores are less oriented. Large oxide particles can be identified.

8.1.2 Microstructural anisotropy

For a single population of oblate spheroids with radii \((R_0, R_0, \beta R_0)\) and an orientation \(\mathbf{X}\) (eqn. 5.40), the width of the single scattering profile in the diffraction limit is proportional to \([R_0 K(\beta, \mathbf{X})]^{-1}\) [RS47] and therefore its anisotropy should be proportional to \(1/\beta\). It is assumed [AIL+01] that the anisotropy of the MSANS beam broadening follows the single scattering anisotropy \(1/\beta\), whereas the Porod anisotropy is proportional to \(1/\beta^4\).

The experimentally observed anisotropy of a real pore system with pores of different size, anisotropy and orientation distribution will depend on the characteristic length scale that is probed. SANS and MSANS differently weight specific features of the overall pore morphology. Therefore, by experimentally determining both, SANS and MSANS anisotropy, more information on the pore morphology is inherently available.

The SANS anisotropy \(\phi_{\text{Porod}}\) is a measure of surface area distribution independent of pore size, but sensible to small orientational variations due to the high area/volume ratio of small particles. The MSANS beam broadening anisotropy is a volume-weighted measure of the mean orientations and aspect ratios of the interlamellar pores (\(P\)) and cracks (\(C\)), with the weight of the elements given by their contribution \(\Sigma_P\) and \(\Sigma_C\) to the total cross-section \(\Sigma_T = \Sigma_C + \Sigma_P + \Sigma_G\). The orientation of a pore itself has a weight on the beam broadening, which is taken into account by the orientational average of its scattering cross-section, \(\langle \Sigma(\vec{Q}, \nu_0) \rangle_{\text{Orientation}}\) (see eqn. 5.39).

In Fig. 8.1 the MSANS anisotropy of the NiCrAlY deposits is plotted versus the Porod anisotropy. For all deposits except the WSP deposit, a high MSANS anisotropy is associated with a low Porod anisotropy. This reflects the different size regimes of pores present in the deposits and their different weighting in the Porod scattering and the MSANS beam broadening.

Fig. 8.1 shows for the VPS deposit a high Porod SANS anisotropy and a low MSANS anisotropy. This is in agreement with the corresponding SEM micrograph, Fig. 6.9(b), which shows on the large scale a microstructure consisting of mainly isotropic pores assigned to the globular pore system. These pores cause a rather isotropic MSANS beam broadening, giving rise to a low MSANS anisotropy \(\phi_{\text{MSANS}}\). The well aligned, mainly interlamellar fine pores suggest a strong orientation of surface area perpendicular to the spray direction and therefore a high Porod anisotropy \(\phi_{\text{Porod}}\).

As the other extreme, the SEM micrograph of the FS deposit, Fig. 6.9(d), exhibits a coarser pore system than the VPS deposit. With the increased splat size, in the FS deposit also the microstructural features are larger, and therefore the characteristic anisotropy is found at a different length scale, resulting in the lowest \(\phi_{\text{Porod}}\) but highest \(\phi_{\text{MSANS}}\).
Fig. 8.2 shows the Porod aspect ratio $\eta_1$ obtained from the horizontal ellipse needed to describe the anisotropic surface area distribution that is associated with the interlamellar pore system (Table 6.5) versus the mean interlamellar opening dimension $\langle \text{O.D.}\rangle_P$. Fig. 8.2 suggests that $\eta_1$ increases with $\langle \text{O.D.}\rangle_P$, except the VPS deposit. Note that $\eta_1$ is determined from the Porod scattering and enters the MSANS model parameter $\langle \text{O.D.}\rangle_P$ only indirectly through the total specific surface area, $S_T$. Fig. 8.2 shows a pore sub-system-specific dependence of the apparent surface area anisotropy on the mean opening dimension that becomes apparent for the dominant interlamellar pore system. The correlation between $\eta_1$ and $\langle \text{O.D.}\rangle_P$ may serve as justification for terming $\eta_1$, the “interlamellar” Porod anisotropy.

### 8.2 Microstructure-property relationships

The following section focuses on microstructure-property relationships. Cross-property correlations - relating different deposit properties to each other - are for example discussed in [MSK+03]. In the present work, cross-property correlations are mentioned only where it is necessary to understand underlying principles.
8. SUMMARY AND DISCUSSION

Fig 8.2: Experimental interlamellar Porod anisotropy $\eta_1$ versus model mean opening dimension of the interlamellar pore system. The dotted curve is a guide to the eye.

8.2.1 Electrical conductivity

The electrical conductivity was determined by N. Margadant, EMPA Thun, Switzerland. The in-plane electrical conductivity [MSK+03] was measured on free-standing deposits by a 4-electrode measurement based on the “Van de Pauw” method [Pau58] modified for application to anisotropic thermally sprayed coatings [IPC+00].

Fig. 8.3 shows the experimentally determined in-plane electrical conductivity $\sigma_{el, EFF}$ in relation to the microstructural parameters (a) deposit density $\rho_{m-Dep}$, (b) oxide content $o$, (c) total specific surface area $S_T$ and (d) total pore volume $\Phi_T$. Fig. 8.3 suggests $o$ and $\rho_{m-Dep}$ to be the two major microstructural features that determine the in-plane electrical conductivity over a wide range of spray techniques and spray parameter settings. There is no obvious correlation to $S_T$ nor $\Phi_T$. For example, for the APS deposits $\sigma_{el, EFF}$ is insensitive with respect to variation in $\Phi_T$, whereas for the VPS deposits $\sigma_{el, EFF}$ varies by 30 % at almost constant $\Phi_T$. This shows that for these NiCrAlY deposits, the pore volume fraction is an inappropriate microstructural parameter to predict the in-plane electrical conductivity. A systematic dependence on $S_T$ is only found for the VPS deposits, which have the highest density (94 - 100 %) and the lowest oxide content (< 1%). Since only for the “high-density” and “low-oxide content” VPS deposits a systematic dependence of electrical conductivity on the total surface area $S_T$ is observed, it is likely that in the other coatings a dependence on the detailed pore morphology is masked by the dominant microstructural features.
Fig 8.3: Dependence of the in-plane electrical conductivity $\sigma_{el, \text{EFF}}$ on (a) the deposit density, (b) the oxide content, (c) the total specific surface area $S_T$ and (d) the total pore volume $\Phi_T$. 
The in-plane electrical conductivity is proportional to the in-plane thermal conductivity (discussed in the following section 8.2.2) within the experimental error [MSP+01, MSK+03], in agreement with the Wiedemann-Franz law, stating a proportionality between both conductivities for metals. One exception are the WSP deposits with the highest oxide content, indicating an additional heat transport contribution from the oxide phase. This behavior is an indication for the reliability of the measurement. Contact problems are thought to have been minimized owing to the 4-electrode “Van de Pauw” technique. Also, a dramatic decrease of the electrical conductivity with an increasing oxide content, e.g. Fig. 8.3b, can be expected.

To understand the influence of the oxide content on the electrical conductivity in more detail, not only the overall amount of oxides may be important, but also the arrangement, size and shape of the oxide phases. For this, an approach of Weber, Dorn and Mortensen [WDM03] and Weber, Fischer and Mortensen [WFM03] is followed. They tested the applicability of different predictive schemes to describe the electrical conductivity of metallic matrix composites containing high volume fractions of non-conducting inclusions like oxides or pores. Applying this approach to the NiCrAlY deposits investigated here, two different cases were distinguished:

- **(a)** The oxide volume $\Phi_{\text{Oxides}}$ is the primary non-conducting phase determining the in-plane electrical conductivity, or

- **(b)** the non-conducting phase determining the in-plane electrical conductivity consists equivalently of pores and oxides: $\Phi_{\text{Pores}} + \Phi_{\text{Oxides}}$.

The electrical conductivity of the pores and oxide phases $\sigma_{\text{el, P}}$ and $\sigma_{\text{el, O}}$ were assumed to be zero, and $\sigma_{\text{el, M}}$ is the NiCrAlY matrix electrical conductivity. The predictive schemes are based on the solution of the intensity field within an ellipsoidal inclusion embedded in a matrix subjected to a remotely applied field [WDM03]. Bounding schemes determine the maximum or minimum value of $\sigma_{\text{el, M}}$.

**Predictive schemes:**
- The two-phase self-consistent scheme (SCS) is based on the fact that the volume-fraction weighted sum of the local polarization fields in the two phases has to vanish.
- The mean field approach (MF) assumes that in the dilute case the intensity field in the inclusion is proportional to the average intensity field in the matrix.
- In the differential effective medium approach (DEM), the composite of a certain volume fraction of inclusion phase is replaced by a homogeneous material having the same effective properties.

**Bounding schemes:**
- The Hashin-Shtrikman bound scheme (HS) results in an upper and lower bound to $\sigma_{\text{el, EFF}}$ by taking into account the probability distribution function of finding two arbitrary points in the composite within the same phase.
8. SUMMARY AND DISCUSSION

- The three-point upper bound scheme (3-UB) is an improvement of the Hashin-Shtrikman bounds by taking a three-point correlation function into account. Only the upper bound to $\sigma_{el, \text{EFF}}$ can be given in an analytical expression.

Details on all employed schemes are given in Table 1 of [WDM03] and references cited therein.

Table 8.1 lists the functional dependencies suggested by [WDM03] for different predictive schemes, and fitting parameters obtained by applying the latter to the NiCrAlY deposits. The fitting results are shown in Fig. 8.4 for all predictive schemes for the in-plane electrical deposit conductivity $\sigma_{el, \text{EFF}}$ (a) as a function of the total oxide volume and (b) as a function of the sum of pore and oxide volume to be the determining non-conducting phase.

For the first approach, the best fit in terms of minimum $\chi^2$ was obtained for the differential scheme based on randomly oriented spheroids [Tor91], with (c.f. Table 8.1)

$$\frac{\sigma_{el, \text{EFF}}}{\sigma_{el, M}} = (1 - \Phi_{\text{Oxides}})^{1/(1 - S)},$$

(8.1)

$S$ being the equivalent Eshelby polarization factor [WFM03] given by

$$\frac{1}{1 - S} = \frac{1 + 3S_\perp}{6S_\perp(1 - S_\perp)},$$

(8.2)

with $S_\perp$ standing for the polarization factor perpendicular to the short axis of an oblate spheroid. For the second approach, a minimum $\chi^2$ is achieved for the three-point upper bound scheme and the differential scheme for random spheroids. For the first, only the upper bound to the electrical conductivity can be given in an analytical expression. However, extrapolating to $\Phi = 0$ results in an unrealistically high $\sigma_M = 15.3 \mu\Omega^{-1}m^{-1}$, which is more than one order of magnitude higher than the electrical conductivity of all deposits including the low oxide and low porosity VPS deposits. The differential scheme based on randomly oriented spheroids results in a similarly low $\chi^2$ and yields a realistic value of $\sigma_{el, M} = 1.27 \mu\Omega^{-1}m^{-1}$. Since also for the first approach the minimum $\chi^2$ was achieved for this scheme, the latter seems to be the most appropriate one to describe the electrical conductivity in thermally sprayed NiCrAlY deposits. The second approach is favored by the lower $\chi^2$ and the more realistic assumption, that oxide and pore volume both reduce the electrical conductivity. A similar conclusion was made by Weber et al. [WDM03] who identified the differential scheme to be most capable of predicting the effective electrical conductivity in two-phase materials, whereas other microscopic models partially lead to large discrepancies to the electrical conductivity of the NiCrAlY deposits.
Table 8.1: Fitting results for $\sigma_{el, eff} = F(\Phi)$, where $F$ is the functional dependence suggested by [WDM03] for different predictive schemes, and $\Phi$ = oxide volume or the sum of the pore and oxide volume, respectively. Abbreviations for the predictive schemes are given in the text. The bold face indicates a selection of predictive schemes resulting in fits with lowest $\chi^2$ values.

<table>
<thead>
<tr>
<th>predictive scheme</th>
<th>$\sigma_{el, M} = F(\Phi_{Oxides})$</th>
<th>parameter</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>symm 2-phase (SCS)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = (1 - \frac{3}{2} \Phi)$</td>
<td>$\sigma_M = 0.27$</td>
<td>0.111</td>
</tr>
<tr>
<td>spheres (MF)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = \frac{1}{1 + \frac{3}{2} \Phi}$</td>
<td>$\sigma_M = 0.73$</td>
<td><strong>0.061</strong></td>
</tr>
<tr>
<td>spheroids (MF)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = \frac{1}{(1 + \frac{1}{1 - \Phi})}$</td>
<td>$\sigma_M = 4.74, S = 0.94$</td>
<td>0.116</td>
</tr>
<tr>
<td>spheres (DEM)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = (1 - \Phi)^{3/2}$</td>
<td>$\sigma_M = 0.27$</td>
<td>0.111</td>
</tr>
<tr>
<td>random spheroids (DEM)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = (1 - \Phi)^{1/(1-S)}$</td>
<td>$\sigma_M = 0.42, S = 0.95$</td>
<td><strong>0.051</strong></td>
</tr>
<tr>
<td>spheres (HS)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = \frac{2(1-\Phi)}{3(1-\Phi)}$</td>
<td>$\sigma_M = 0.27$</td>
<td>0.108</td>
</tr>
<tr>
<td>(3-UB)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = \frac{(2(1-\Phi)(1-\xi))}{\Phi+2(1-\xi)}$</td>
<td>$\sigma_M = 0.47, \xi = 0.99$</td>
<td><strong>0.062</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>predictive scheme</th>
<th>$\sigma_{el, M} = F(\Phi_{Pores} + \Phi_{Oxides})$</th>
<th>parameter</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>symm 2-phase (SCS)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = (1 - \frac{3}{2} \Phi)$</td>
<td>$\sigma_M = 0.29$</td>
<td>0.109</td>
</tr>
<tr>
<td>spheres (MF)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = \frac{1}{1 + \frac{3}{2} \Phi}$</td>
<td>$\sigma_M = 4.79$</td>
<td>0.086</td>
</tr>
<tr>
<td>spheroids (MF)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = \frac{1}{(1 + \frac{1}{1 - \Phi})}$</td>
<td>$\sigma_M = 5.04, S = 0.94$</td>
<td>0.117</td>
</tr>
<tr>
<td>spheres (DEM)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = (1 - \Phi)^{3/2}$</td>
<td>$\sigma_M = 0.29$</td>
<td>0.109</td>
</tr>
<tr>
<td>random spheroids (DEM)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = (1 - \Phi)^{1/(1-S)}$</td>
<td>$\sigma_M = 1.27, S = 0.93$</td>
<td><strong>0.049</strong></td>
</tr>
<tr>
<td>spheres (HS)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = \frac{2(1-\Phi)}{3(1-\Phi)}$</td>
<td>$\sigma_M = 0.31$</td>
<td>0.109</td>
</tr>
<tr>
<td>(3-UB)</td>
<td>$\frac{\sigma_{el, eff}}{\sigma_M} = \frac{(2(1-\Phi)(1-\xi))}{\Phi+2(1-\xi)}$</td>
<td>$\sigma_M = 15.3, \xi = 1.00$</td>
<td><strong>0.047</strong></td>
</tr>
</tbody>
</table>
Fig 8.4: Predictive schemes for the effective in-plane electrical conductivity $\sigma_{el, EFF}$ [WDM03], (a) as a function of the total oxide volume, and (b) as a function of the total pore and oxide volume.
8. SUMMARY AND DISCUSSION

8.2.2 Thermal conductivity

The thermal conductivity data is kindly provided by A. Kulkarni, Center for Thermal Spray Research, State University of New York, Stony Brook, USA. The thermal diffusivity in through-thickness and in-plane directions was measured using a Holometrix laser flash thermal diffusivity instrument. The specific heat was separately determined by differential scanning calorimetry ("TA Instruments", DSC2910). From the diffusivity and the heat capacity along with the deposit density, the thermal conductivity was deduced as described in detail in [MSK+03].

To identify the dominant property-determining parameters for the thermal conductivity of the NiCrAlY deposits, in Fig. 8.5 the dependence of the through-thickness and in-plane thermal conductivity, $\kappa_{\text{through-thick}}$ and $\kappa_{\text{in-plane}}$, on the oxide content $o$, the deposit density $\rho_{\text{m-Dep}}$, the total specific surface area $S_T$ and the total pore volume $\Phi_T$ are shown. Independent of the direction of $\kappa$, the thermal conductivity tends to increase with increasing $\rho_{\text{m-Dep}}$ (Fig. 8.5 (a)). The influence of the oxide phases is less pronounced (Fig. 8.5(b)) than in the electrical conductivity because of their non-zero thermal conductivity. This suggests that the pore morphology has a stronger influence on the thermal conductivity. However, a comparison (Fig. 8.5 (c) and (d)) shows that there is no obvious influence of $S_T$ and $\Phi_T$ on $\kappa$.

In Fig. 8.6 the through-thickness and in-plane thermal conductivities are therefore plotted versus the interlamellar pore volume fraction $\Phi_P$, the crack pore volume fraction $\Phi_C$ and the globular pore volume fractions $\Phi_G$. Although no obvious influence of $S_T$ and $\Phi_T$ on $\kappa$ has been observed, Fig 8.6(a) and 8.6(b) show the trend of $\kappa_{\text{through-thick}}$ and $\kappa_{\text{in-plane}}$ to decrease with increasing interlamellar pore volume $\Phi_P$ and crack pore volume $\Phi_C$. Fig 8.6(c) shows an inverse trend of increasing $\kappa_{\text{through-thick}}$ and $\kappa_{\text{in-plane}}$ with increasing globular pore volume $\Phi_G$. In order to illustrate these trends, the data were fitted by a linear function, $f(\Phi_{P,C,G}) = m \Phi_{P,C,G} + \text{const.}$ The fit results are given in Table 8.2. The decrease of $\kappa_{\text{through-thick}}$ and $\kappa_{\text{in-plane}}$ with an increasing volume fraction in the anisotropic interlamellar and crack-type components of the pore system, $\Phi_P$ and $\Phi_C$, resulting in negative slopes $m$, can be caused by the higher resistive cross-section of the anisotropic pore systems.

<table>
<thead>
<tr>
<th>pore sub-system</th>
<th>$m_{\text{through-thick}}$ ($10^2 \text{W m}^{-1}\text{K}^{-1}$)</th>
<th>$\chi^2_{\text{through-thick}}$ ($10^{-6} \text{W m}^{-1}\text{K}^{-1}$)</th>
<th>$m_{\text{in-plane}}$ ($10^2 \text{W m}^{-1}\text{K}^{-1}$)</th>
<th>$\chi^2_{\text{in-plane}}$ ($10^{-6} \text{W m}^{-1}\text{K}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_P$</td>
<td>$-0.75 \pm 0.45$</td>
<td>1.09</td>
<td>$-0.62 \pm 0.42$</td>
<td>0.91</td>
</tr>
<tr>
<td>$\Phi_C$</td>
<td>$-1.10 \pm 0.43$</td>
<td>0.66</td>
<td>$-0.82 \pm 0.48$</td>
<td>0.80</td>
</tr>
<tr>
<td>$\Phi_G$</td>
<td>$0.80 \pm 0.33$</td>
<td>0.71</td>
<td>$0.55 \pm 0.38$</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Fig 8.5: Through-thickness (left) and in-plane (right) thermal conductivity as a function of (a) deposit density, (b) oxide content, (c) total specific surface area and (d) total pore volume.
Fig 8.6: Through-thickness (left) and in-plane (right) thermal conductivity versus (a) the interlamellar pore volume $\Phi_P$, (b) the crack pore volume $\Phi_C$ and (c) the globular pore volume $\Phi_G$. The lines are weighted linear fits to visualize the tendencies, not necessarily implying a linear dependence.
The observed increase of $\kappa_{\text{through-thick}}$ and $\kappa_{\text{in-plane}}$ with a higher volume fraction in the isotropic globular pore component $\Phi_G$ may in principle be due to the fact that for a constant volume fraction, a larger mean pore diameter would imply a smaller number density of obstacles and therefore less reduction in thermal conductivity. However, Fig. 8.7(a) shows a reduction of $\kappa_{\text{through-thick}}$ with the mean globular pore diameter $\langle 2R_0G \rangle$, and Fig. 8.7(b) finally implies the opposite trend, i.e. a decrease of $\kappa_{\text{through-thick}}$ with the inverse number density of globular pores, $V_G/\Phi_G$, where $V_G = 4\pi(\langle 2R_0G \rangle/2)^3/3$. Therefore, the increase of $\kappa$ with increasing $\Phi_G$ can also not be caused by the number density of globular pores, leaving the observed dependence still unexplained.

Fig. 8.7: Through-thickness thermal conductivity versus (a) mean globular pore diameter $\langle 2R_0G \rangle$ and (b) inverse number density of globular pores, $1/n = V_G/\Phi_G$.

Fig. 8.8 shows the through-thickness thermal conductivity $\kappa_{\text{through-thick}}$ versus the in-plane thermal conductivity $\kappa_{\text{in-plane}}$. The in-plane thermal conductivity tends to be higher than the through-thickness conductivity, as expected because the interlamellar pores and a possible bad interlamellar thermal contact should reduce the through-thickness thermal conductivity more than the in-plane thermal conductivity.

Furthermore, Fig. 8.8 shows a rather constant reduction from $\kappa_{\text{in-plane}}$ to $\kappa_{\text{through-thick}}$ for a wide range of pore morphologies. This implies that the thermal conductivity anisotropy, i.e. the ratio $\kappa_{\text{through-thick}}/\kappa_{\text{in-plane}}$, is insensitive to detailed pore microstructural features like the distribution of volume fractions to the spheroidal pore systems, $\Phi_P$ and $\Phi_C$.

Indeed, $\kappa_{\text{through-thick}}$ is expected to be strongly reduced with an increasing amount of interlamellar pores, whereas $\kappa_{\text{in-plane}}$ is expected to be reduced mainly with the amount of

![Graph](image)
crack-type pores. In contrast, $\kappa_{\text{through-thick}}$ ($\kappa_{\text{in-plane}}$) should be influenced only to a minor extent by the crack-type (interlamellar) component.

However, Figs. 8.6(a) and 8.6(b) show that $\kappa_{\text{through-thick}}$ and $\kappa_{\text{in-plane}}$ decrease simultaneously with an increasing anisotropic pore volume regardless of orientation (interlamellar or crack pore volume). This simultaneous decrease of $\kappa_{\text{through-thick}}$ and $\kappa_{\text{in-plane}}$ is an indication for the strong weight of a single anisotropic pore sub-system - presumably the interlamellar one - on the thermal conductivity. This observation is in agreement with the insensitivity of the thermal conductivity anisotropy to the details of the pore morphology, as suggested by Fig. 8.8.

### 8.2.3 Sound velocity

The sound velocity data were determined by Jürg Neuenschwander EMPA Dübendorf, Switzerland, and by N. Margadant, EMPA Thun, Switzerland. The longitudinal sound velocity in through-thickness and in-plane direction was determined in transmission mode on free standing deposits by the run time of the transmission signal and the sample geometry. For the contact mode measurements, a Krautkrämer USIP 2 instrument and Harisonic transducers type HLI-CM1002 (10 MHz) and V212BB (20 MHz) were used. Further details are described in [IPC+00, MSK+03].

Fig. 8.9 shows the dependence of the through-thickness and in-plane longitudinal sound velocity on...
velocity $v_{\text{through-thick}}$ and $v_{\text{in-plane}}$ on the oxide content $o$, the deposit density $\rho_{\text{m-Dep}}$, the total specific surface area $S_T$ and the total pore volume $\Phi_T$. Both $v_{\text{through-thick}}$ and $v_{\text{in-plane}}$ tend to increase with increasing $\rho_{\text{m-Dep}}$ and decreasing $\Phi_T$. There is no obvious correlation to $o$. Regarding the $S_T$-dependence, a general, spray-technique independent trend cannot be observed. At most, Fig. 8.9(c) suggests a reduction of $v_{\text{through-thick}}$ with increasing $S_T$ within each set of different spray techniques, WAS, WSP and VPS. The APS deposits exhibit only a low variation of $S_T$ and $v_{\text{through-thick}}$ for varying spray parameters. $v_{\text{through-thick}}$ is more sensitive to variations of $S_T$ than $v_{\text{in-plane}}$ due to the larger amount of surface area oriented perpendicular to the spray direction (mostly as interlamellar surface area).
8. SUMMARY AND DISCUSSION

Fig. 8.10 shows the dependence of the in-plane and through-thickness sound velocity on the interlamellar, crack and globular pore volume fractions, Φ_P, Φ_C and Φ_G. In order to illustrate trends, the data were fitted by a linear function, \( f(Φ_{P,C,G}) = m Φ_{P,C,G} + \text{const} \) (similar to the discussion of the thermal conductivity in section 8.2.2).

The corresponding fit results are collected in Table 8.3. No statement can be made on the influence of the globular pore volume because of the high fit uncertainty. The dominance of the interlamellar pore fraction is expressed by the simultaneous reduction of \( v_{\text{through-thick}} \) and \( v_{\text{in-plane}} \) with \( Φ_P \). The linear fits in Figs. 8.10(a) and 8.10(b) along with the fit results suggest that an increasing interlamellar pore volume mostly reduces \( v_{\text{through-thick}} \), whereas an increasing crack pore volume mainly reduces \( v_{\text{in-plane}} \). This indicates the different influence of the interlamellar and crack pore sub-systems on the direction-dependent sound velocity. The main reduction of \( v \) is due to the anisotropic pore sub-system oriented with the largest cross-sectional area perpendicular to the direction of measurement. In Fig. 8.11, the dependence of

<table>
<thead>
<tr>
<th>pore sub-system</th>
<th>( m_{\text{through-thick}} ) (10^5 m s(^{-1}))</th>
<th>( \chi^2_{\text{through-thick}} ) (10(^3) (m s(^{-1}))^2)</th>
<th>( m_{\text{in-plane}} ) (10^5 m s(^{-1}))</th>
<th>( \chi^2_{\text{in-plane}} ) (10(^3) (m s(^{-1}))^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Φ_P )</td>
<td>-635 ± 224</td>
<td>375</td>
<td>-459 ± 125</td>
<td>117</td>
</tr>
<tr>
<td>( Φ_C )</td>
<td>-30 ± 371</td>
<td>805</td>
<td>-309 ± 212</td>
<td>262</td>
</tr>
<tr>
<td>( Φ_G )</td>
<td>-67 ± 211</td>
<td>794</td>
<td>7 ± 138</td>
<td>342</td>
</tr>
</tbody>
</table>

the in-plane sound velocity \( v_{\text{in-plane}} \) on the mean crack opening dimension \( ⟨O.D.⟩_C \) is shown. A decrease of \( v_{\text{in-plane}} \) with an increase of \( ⟨O.D.⟩_C \) is observed, except for the VPS deposit, which exhibits a comparably high in-plane sound velocity. The correlation of \( v_{\text{in-plane}} \) on \( ⟨O.D.⟩_C \) shows the sensitivity of the sound velocity on the mean size of the crack pore system. The interfaces between splats and cracks are transition regions between different media in terms of transport of ultrasonic waves. Therefore, they presumably cause a dispersion of the ultrasonic wave and thereupon a reduction in the mean sound velocity. \( v_{\text{in-plane}} \) is less reduced towards larger mean crack dimensions, which shows the interface region to be relevant for the reduction.
Fig 8.10: Through-thickness (left) and in-plane (right) sound velocity versus (a) the interlamellar pore volume $\Phi_P$, (b) the crack volume $\Phi_C$ and the globular pore volume $\Phi_G$. The lines are weighted linear fits to visualize the tendencies, not necessarily implying a linear dependence.
8. SUMMARY AND DISCUSSION

8.2.4 Residual stress and Young’s modulus

Residual stress

Macroscopic average residual stress values in the coatings were determined by mechanical profilometry (curvature method) on samples with substrate dimensions of approximately 103x25x4.5 mm$^3$. Line scans were performed on a mechanical profilometer (“Wänzel Präzision”, resolution of 0.001 mm). For each spray technique and spray parameter setting, bending profiles were recorded at three stages of preparation; the first one after grinding and annealing, the second one after subsequent grit blasting, and the final one after deposition of the coating.

From the bending profiles, the curvature of the substrate-deposit system was determined by fitting a circle to the profilometric data. The average macroscopic in-plane residual stress in the deposit $s_{\text{in-plane}}$ was calculated according to Stoney’s formula [Sto09], with $r$ being the radius of bending due to residual stresses introduced during the spray process:

$$s_{\text{in-plane}} = \frac{1}{r} \frac{E_S H_S^2}{6 h_D (1 - \nu_S)} \quad (8.3)$$

$E_S$ and $\nu_S$ are the elastic constant and the Poisson’s ratio of the substrate, respectively, and $H_S$ and $h_D$ are the substrate and deposit thickness. Values of $s_{\text{in-plane}}$ calculated from the
curvature of the substrate-deposit system obtained by eqn. 8.3 are given in Table 8.4. Each value was determined as a mean from three samples of the same spray-parameter setting.

The WAS and APS samples have the highest residual stress values. For these samples the direction of bending has reversed during the deposition. Residual stresses are lower in the WSP samples, and lowest in the FS sample. Here the direction of curvature remained the same before and after spraying.

Table 8.4: Average in-plane residual stress $s_{\text{in-plane}}$ in the deposits as determined by curvature measurements (uncertainties in least significant digits given in parentheses are standard deviations from the mean value).

<table>
<thead>
<tr>
<th>Spray Parameter</th>
<th>VPS</th>
<th>APS</th>
<th>WSP</th>
<th>FS</th>
<th>WAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-plane residual stress (MPa)</td>
<td>68 (27)</td>
<td>205 (27)</td>
<td>103 (42)</td>
<td>32 (27)</td>
<td>269 (50)</td>
</tr>
<tr>
<td>II</td>
<td>69 (37)</td>
<td>189 (20)</td>
<td>97 (27)</td>
<td>284 (41)</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>24 (23)</td>
<td>227 (38)</td>
<td>110 (20)</td>
<td>319 (86)</td>
<td></td>
</tr>
</tbody>
</table>

In Figure 8.12, $s_{\text{in-plane}}$ is plotted versus the surface area of the fine crack-type pore sub-system, $S_C$. It can be observed that a low residual stress state is correlated with a high surface area in the crack pore sub-system. A possible cause for the different average residual stress levels determined for the investigated spray techniques could be a relaxation of residual stresses by generating fine cracks. The residual stress level can be decreased by formation of cracks with their opening dimension mainly aligned perpendicular to the spray direction, i.e. parallel to $s_{\text{in-plane}}$.

In contrast to ceramic coatings, in the more ductile metallic coatings crack formation is not expected to be the primary mechanism of residual stress relief. However, Fig. 8.12 implies a clear correlation between the average in-plane residual stress and the specific crack surface area, i.e. the tendency to find reduced overall residual stress in samples with a high amount of fine cracks. Obviously, an initially high residual stress has been relieved by the formation of cracks with their fine opening dimension along the in-plane stress direction. The residual stress state in the NiCrAlY deposit-substrate systems has been investigated by the curvature method and complemented by neutron strain scanning measurements on identical samples [KPM$^+$01, KMP$^+$]. By neutron strain scanning, a spatially resolved residual stress profile over the sample thickness is obtained.

Young’s modulus

The Young’s moduli were determined by J. Matejicek, Institute of Plasma Physics, Prague, Czech Republic. The macroscopic average in-plane Young’s moduli were determined by 4-point bending measurements. The measurements were performed using an "Instron" 1362
8. SUMMARY AND DISCUSSION

Fig 8.12: Average residual in-plane (tensile) stress \( \sigma_{\text{in-plane}} \) versus surface area in the fine crack-type pore sub-system.

Fig. 8.13 shows the Young’s modulus \( E \) versus the surface area in the crack system \( S_C \). For all spray techniques except the VPS, Fig. 8.13 suggests a slight reduction of the Young’s modulus with an increasing crack surface area \( S_C \). The VPS deposit exhibits by far the highest Young’s modulus. This extreme value cannot be correlated to the crack surface area as for the other spray techniques. Also, the Young’s modulus of the VPS deposit seems to be too high to be the “limit” of low oxide content and small pore volume. A possible reason for the high value of \( E \) may be a significantly improved intersplat contact, that might be facilitated by the low oxide content.

8.2.5 Abrasive and erosive wear rates

The abrasive and erosive wear rates were determined by N. Margadant, EMPA Thun, Switzerland. The abrasive wear was determined according to [ASTM, G75]. The deposits were tested in a slurry of alumina abrasive (grain size 45 to 75 \( \mu \)m) in distilled water. The weight loss was determined as a function of time, corresponding to sliding distance. The mechanical 4-point bending device with an inner span of 47 mm and an outer span of 94 mm. The displacement rate was chosen to be 0.1 mm/min up to a maximum load of 800 N. Further details are given in [MSK+03].
particle erosion wear was determined by a mixed mode of liquid impingement similar to [ASTM, G73] and particle jet erosion similar to [ASTM, G76] [MSK+03]. Alumina particles of the same grain size were used as for the abrasive wear. Details on the abrasive and erosive wear measurements are given in [MSK+03].

Fig. 8.14 shows the particle erosive wear rate for the investigated NiCrAlY deposits versus the total surface area $S_T$. Except for the FS deposit, Fig. 8.14 shows an increasing particle erosion with an increasing amount of total surface area $S_T$. The reduced erosion resistance at increased $S_T$ suggests that by particle erosion, material is removed from the deposit surface mainly at places of low adhesion related to a high surface area. Since the surface area mainly separates single splats (interlamellar pores) or fractions of a splat (intralamellar cracks), Fig. 8.14 suggests the deposit material to be removed as complete splats or parts of single splats. The FS deposit exhibits a significantly higher erosive wear rate that is attributed to a significantly lower interlamellar bonding quality achieved by the flame spray technique.

In contrast, Fig. 8.15, showing the abrasive wear rate versus $S_T$ [KWI+01], indicates the reverse trend. A reduction of the abrasive wear rate with an increasing total specific surface area $S_T$ is observed. The abrasive wear is supposed to remove deposit material more continuously than the erosive wear, i.e. not by partial breakouts. The increase of abrasive wear rate with decreasing pore surface area may be due to fine oxide layers at the splat boundaries that mainly generate the surface area. These oxide layers are harder than the $\gamma$-NiCrAlY
8. SUMMARY AND DISCUSSION

matrix inside the splats and therefore could reduce the abrasive wear rate. It is important to note that rather the distribution of oxides than the total amount of oxides influence the wear behavior.

8.3 Property anisotropy and impact from microstructural anisotropy

Thermal conductivity

Fig. 8.16(a) shows the dependence of the in-plane and through-thickness thermal conductivity $\kappa$ on the MSANS anisotropy $\phi_{\text{MSANS}}$, and Fig. 8.16(b), the aspect ratio $\kappa_{\text{ar}} = \kappa_{\text{in-plane}}/\kappa_{\text{through-thick}}$ versus $\phi_{\text{MSANS}}$. Both $\kappa_{\text{in-plane}}$ and $\kappa_{\text{through-thick}}$ decrease with increasing $\phi_{\text{MSANS}}$. Fig. 8.16(b) shows that the resulting aspect ratio $\kappa_{\text{ar}}$ of the macroscopic thermal conductivity tends to increase with an increasing MSANS anisotropy, whereas no obvious correlation of $\kappa_{\text{ar}}$ with the Porod anisotropy $\phi_{\text{Porod}}$ was found.

Whereas the distribution of surface area expressed in $\phi_{\text{Porod}}$ was expected to be reflected in the direction-dependence of the thermal conductivity, Fig. 8.16 suggests rather the MSANS anisotropy $\phi_{\text{MSANS}}$ to be the appropriate measure of the pore morphology over a length scale influencing the thermal conductivity of the investigated thermally sprayed NiCrAlY deposits.
8. SUMMARY AND DISCUSSION

Fig 8.15: Abrasive wear rate versus total surface area $S_T$. The straight line is a guide to the eye.

Sound velocity

Fig. 8.17(a) shows the through-thickness sound velocity, $v_{\text{through-thick}}$, versus the Porod anisotropy $\phi_{\text{Porod}}$. For the deposits WSP, FS, WAS and APS, $v_{\text{through-thick}}$ clearly decreases with increasing $\phi_{\text{Porod}}$. A decrease of similar slope is observed for the VPS deposits at an approximately 50% higher $v_{\text{through-thick}}$. The in-plane sound velocity $v_{\text{in-plane}}$ is not significantly influenced by $\phi_{\text{Porod}}$. Therefore the dependence of $v_{\text{through-thick}}$ on $\phi_{\text{Porod}}$ is reciprocally reflected in the aspect ratio of the sound velocity $v_{\text{ar}} = v_{\text{in-plane}} / v_{\text{through-thick}}$ (Fig. 8.17(b)).

$v_{\text{ar}}$ proportionally increases with $\phi_{\text{Porod}}$ for all spray techniques except the VPS deposits. The latter exhibit a similar behavior for different spray-parameter settings. Therefore Fig. 8.17(b) suggests that for all investigated NiCrAlY deposits, the microstructural anisotropic distribution of surface area expressed in $\phi_{\text{Porod}}$ is generally reflected in the macroscopic property anisotropy of the direction-dependent sound velocity $v_{\text{ar}}$. However, the VPS deposits deviate from all other spray techniques with a significantly higher through-thickness sound velocity. Whereas the overall highest magnitude of $v$ is associated with the high density, low oxide content and an improved bonding quality and intersplat contact (see section 8.2.4) of the VPS deposits the deviation in $v_{\text{ar}}$ from the values obtained for other spray techniques most likely is related to the small amount of interlamellar pore volume, $\Phi_G$, in the VPS deposit as determined by the MSANS modelling (Table 7.4).
Fig 8.16: Thermal conductivity $\kappa$ versus MSANS anisotropy $\phi_{\text{MSANS}}$. (a) $\kappa_{\text{in-plane}}$ and $\kappa_{\text{through-thick}}$, and (b) aspect ratio $\kappa_{\text{ar}}$. In (a), the lines are linear weighted fits, in (b) the line indicates the case $\kappa_{\text{ar}} = \phi_{\text{MSANS}}$. 
Fig 8.17: (a) Through-thickness sound velocity $v_{\text{through-thick}}$ versus Porod anisotropy $\phi_{\text{Porod}}$, and (b) aspect ratio of sound velocity $v_{\text{ar}} = v_{\text{in-plane}}/v_{\text{through-thick}}$ versus $\phi_{\text{Porod}}$.
The various microstructural and property anisotropies of the thermally sprayed NiCrAlY deposits discussed above suggest correlations between microstructural anisotropies at different length scales. Whereas the SANS anisotropy in the Porod regime is a measure of surface area distribution and is sensitive to details of the pore microstructure, the MSANS anisotropy is a volume weighted average reflecting the mean opening dimensions and their orientation distribution.

Pores, cracks and oxides change macroscopic properties by specific mechanisms. For example, electron or phonon scattering and therefore the electrical and thermal conductivities are reduced. The sound velocity is reduced by similar defects, but the interaction mechanism with each defect varies. Also, defects of different length scales are probed. Although a single microstructural (i.e. SANS or MSANS) anisotropy needs not necessarily to be reflected in a macroscopic property anisotropy, for both, $\kappa$ and $\nu$, their aspect ratio of the in-plane and through-thickness components are correlated with these microstructural anisotropies accessed by small angle neutron scattering. Whereas $\nu_{ar}$ is sensible to the specific surface area distribution (i.e. $\phi_{\text{Porod}}$), $\kappa_{ar}$ is influenced by the pore morphology on a larger scale (i.e. $\phi_{\text{MSANS}}$). In both, $\nu$ and $\kappa$, it is rather one direction, that depends on a microstructural anisotropy, i.e. the through-thickness component of $\nu$ and the in-plane component of $\kappa$.

The reduction of $\nu_{\text{through-thick}}$ with the total specific surface area shows that $\nu$ is sensitive to (a) the amount of interlamellar pores mainly influencing the through-thickness direction (b) to the (interlamellar) surface area and therefore to the low interlamellar contact, possibly also reduced by the mean opening dimensions of the interlamellar pores.

### 8.4 Conclusions - microstructure-property correlations

The properties of thermally sprayed NiCrAlY deposits discussed in section 8.2 depend in a complex manner on various microstructural features. Various parameters of the pore system along with the oxide content and the deposit density are found to be most relevant for many properties of the NiCrAlY deposits.

The influence of the pore morphology may be different for any specific macroscopic property and is reflected in correlations with one or more parameters of the pore system like total surface area ($S_T$), total pore volume ($\Phi_T$), anisotropies of the pore system ($\phi_{\text{Porod}}$ and $\phi_{\text{MSANS}}$), mean pore opening dimensions ($\langle O.D. \rangle$) or pore volume and surface area fractions in the interlamellar, the crack and the globular pore sub-systems ($\Phi_{P,C,G}$ and $S_{P,C,G}$).

The electrical conductivity is reduced mostly by the oxide content, superposing correlations with the pore morphology. Both, oxide and pore volume were used to describe the reduction in electrical conductivity.
Complex technological properties like abrasive and erosive wear are well correlated with the total specific surface area and show the potential of characterizing the pore morphology in terms of total specific surface area.

The anisotropies of thermal conductivity and sound velocity are related to anisotropies of the pore system at different length scales, expressed in $\phi_{\text{Porod}}$ and $\phi_{\text{MSANS}}$. Whereas mainly the in-plane component of the thermal conductivity increases with the MSANS anisotropy $\phi_{\text{MSANS}}$, the through-thickness sound velocity is sensitive to the Porod anisotropy, $\phi_{\text{Porod}}$ that is related to the distribution of surface area. The microstructure-property anisotropy correlations are essentially general trends for all spray techniques.

However, also spray-technique specific correlations like the reduction of the through-thickness sound velocity with increasing specific total surface area $S_T$ are observed, which hold separately for a small range of microstructures achieved by spray parameter variation of each single spray technique. In practice, such relations are often important when only a limited choice of spray-techniques are available.
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Conclusions and outlook

The aim of the present study was the establishment of microstructure-property relationships from an extensive microstructural analysis of NiCrAlY deposits of different pore morphology as generated by the application of various thermal spraying techniques. Correlations between microstructural parameters and properties are observed both, for variations of spray-parameter settings within a single spray technique, and also as general trends for all investigated spray techniques. Such general trends have potential in predicting properties of microstructures of other spray techniques which were not investigated. Abrasive and particle-erosive wear rates are influenced by the total specific surface area of the pores rather independently of the employed spray technique. However, a correlation of the through-thickness sound velocity with the total specific pore surface area is observed only within a narrow range of pore morphology obtained by spray-parameter variations within a specific spray technique. Therefore a quantitative microstructure characterization and identification of the relevant microstructural parameters is essential to develop microstructure-property relationships in thermally sprayed NiCrAlY deposits.

The total specific pore surface area determined by small-angle neutron scattering (SANS) in the Porod regime varies by up to 50% of the maximum value for different spray techniques, and by less than 15% for variations in spray parameter settings of a single spray technique. This confirms the total specific surface area to be a sensible measure of the pore microstructure. In addition, the MSANS technique provides unique microstructural information over length scales between a few nanometers and micrometers, which allows relevant microstructural details with respect to specific macroscopic properties to be determined. The interlamellar pore sub-system is shown to have the largest impact on several macroscopic deposit properties for all investigated thermally sprayed NiCrAlY deposits. The largest fraction of the intersplat boundary is the surface area of the interlamellar pores. This is reflected in a reduction of the through-thickness thermal conductivity to about 75% of the value for the in-plane direction. Formation of a large amount of microcracks as known from ceramic coatings is not observed in NiCrAlY deposits, owing to the higher ductility of the metallic splats. However, a minor fraction of fine-scale cracks generated presumably near brittle oxide phases was identified and related to a reduction of the average residual stress in the
9. CONCLUSIONS AND OUTLOOK

Deposits. These results on the NiCrAlY bond coats complement the extensive investigations on the pore morphology performed so far on the ceramic top coats of the TBCs.

For a deposit sprayed by a specific spray technique, a deviation from a general trend relating a microstructural feature to a macroscopic property is attributed to a variation in splat bonding quality and the underlying bonding mechanism. An example is the dependence of the erosive wear rate on the total specific surface area for the flame sprayed deposit. However, up to now it is experimentally difficult to quantify the bonding quality on a microstructural scale in order to take the latter into account in a microstructure-property model.

An important aspect in thermally sprayed deposits is the microstructural anisotropy, which was quantified by detailed analysis of anisotropic SANS and MSANS scattering. The anisotropic pore morphology is reflected in the direction-dependence of macroscopic deposit properties. For this purpose, the parameters of the pore morphology with an inherent anisotropy or preferred orientation were associated with direction-dependent macroscopic deposit properties like electrical and thermal conductivity and sound velocity. The significance of the SANS and MSANS technique is reflected in the correlation between the deduced microstructural anisotropies and property-anisotropies. The sound velocity anisotropy is related to the surface area anisotropy expressed in the Porod anisotropy, whereas, at a larger length scale, the MSANS anisotropy is correlated with the thermal conductivity anisotropy, which on a larger length scale reflects the size and orientation of anisotropic pores.

From SANS, the volume fraction of the \( \alpha \)-Cr precipitates observed in the VPS deposits was determined to be 5.5 - 6.5 vol.\%. TEM analysis showed the \( \alpha \)-Cr precipitates to be an intrasplat feature located within the \( \gamma \)-NiCrAlY matrix. A still open question is a possible influence of these precipitates on deposit properties like hardness, that could not be unambiguously shown. The precipitates are found with a significant volume fraction most likely in the VPS deposits. At the same time, these deposits differ from other spray techniques by their highest density and lowest oxide content. Therefore, outstanding properties of the VPS deposit like highest thermal and electrical conductivity, highest sound velocity and highest hardness [MSK+03] that often differ from other correlations can not be related to a single microstructural feature like the \( \alpha \)-Cr precipitates.

Within the present work, correlations between microstructural parameters and deposit properties are interpreted in terms of "relevant microstructural" parameters. A complementary approach by a statistical correlation was followed by Margadant et al. [MSK+03]. The combination of these approaches to establish microstructure-property relationships led to an improved understanding and may allow thermally sprayed deposits with optimized pore morphology to be developed. The comprehensive database of microstructural parameters and macroscopic properties collected within the framework of the EUREKA / KTI - supported project \( \Sigma 1973 \) "THERMETCOAT" may serve as basis to gain further insights into the thermal spraying technology.
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