MECHANICAL PROPERTIES OF PLASMA SPRAYED COATINGS - MEASURED BY DIFFRACTION

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Abstract
The elastic constants of one metallic and one ceramic plasma sprayed coating were investigated by diffraction. Free standing pieces of yttria stabilized zirconia (YSZ) coating and NiCrAlY bond coat were subjected to compressive loads in a stress rig and the lattice strain was measured both normal and parallel to the coating surface. Due to the nature of the diffraction measurements and the anisotropic defect structure of the coatings, the values of Young's modulus $E_{hkl}$ and Poisson's ratio $\nu_{hkl}$ depend both on the Miller indices $hkl$ of the reflection and on the measurement direction. Furthermore, the results for $E_{hkl}$ and $\nu_{hkl}$ differ both from common zero porosity bulk values and bulk coating values obtained by bending or indentation measurements on these coatings. All coatings exhibit a hexagonal anisotropy with the coating surface as basal plane.

1. INTRODUCTION
Plasma spraying is a process for depositing coatings as protection against thermal loads, wear and corrosion. As a result of the deposition process, the coatings have properties quite different from bulk materials of the same composition. Key parameters in that context are porosity, mechanical anisotropy and residual stress.

An important characteristic of the coating is residual stress, which influences its adhesion, integrity, fatigue life and overall performance in service \cite{1,2}. In thermal spraying, residual stress develops in two stages: during the deposition and during cooling after the deposition. In the deposition stage, quenching stress arises due to rapid cooling and solidification of molten particles upon impact. As the solidified particles adhere to the substrate, they cannot contract freely and tensile quenching stress develops. However, the determination of stress is based on the measurement of strain so that the knowledge of the generally anisotropic elastic constants is required.

The presence of pores and cracks, their orientation and the distribution of their shapes is recognized as responsible for the mechanical anisotropy in the absence of preferred orientation both of metallic and ceramic coatings \cite{3-6}. Key effects are a general decrease of the elastic moduli compared to the bulk material, and differences of the elastic moduli parallel and perpendicular to the coating surface. Direct evidence for the elastic anisotropy can be obtained by a simple $\sin^{2}\psi$-measurement in which lattice strains are
recorded from d-spacings that have different angles $\psi$ with respect to the coating surface (Fig. 1).

![Figure 1: Principle of a lattice strain measurement vs. $\sin^2\psi$.](image)

The result of such a surface-measurement by x-rays for a NiCrAlY coating is shown in Fig. 2.

![Figure 2: Lattice strain distribution of the (0 2 10) and (2 6 8) reflection. Both have the same d-spacing so that the result is a mixture of both.](image)

Other results give evidence that the weak depth dependence of stresses can be disregarded as reason for the non-linear behavior shown in fig. 2 [10]. The distinct non-linearity of $\varepsilon$ vs. $\sin^2\psi$ gives evidence that the elastic moduli change from the direction perpendicular to the surface ($\psi = 0$) to the direction parallel to the surface ($\psi = \pi/2$) because the same stress will cause different strains in different directions.

The characterization of elastic properties is usually done by means of indentation, bending and ultrasonics. Indentation yields only values for the Young’s modulus $E$ in-plane and out-of-plane, provided that Poisson’s ratio $\nu$ is known. This is generally not the case so that bulk values for $\nu$ have to be used. Bending tests provide only in-plane values for $E$ and $\nu$ for which surface strain measurements have to be performed. So far, only ultrasonics testing was under certain conditions capable of measuring the full set of five independent elastic constants. Still, experimental results are scarce and work has been focused on ceramic coatings [7-9]. This work focuses on a new approach for obtaining
aggregate constants by means of diffraction measurements on coatings under external stresses.

2. EXPERIMENTAL PROCEDURE

Coating preparation. Relevant parameters as composition and porosity are listed in Tab.1. Steel substrates of 50 x 25 x 2.5 mm³ dimensions were used; substrate temperatures were kept below 150 °C.

Table 1: Composition of the feedstock powders prior to plasma spraying.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Composition</th>
<th>Porosity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Ni + 5wt.% Al</td>
<td>10.0 (±1.0)</td>
</tr>
<tr>
<td>YSZ</td>
<td>ZrO₂ + 8 wt.% Y₂O₃</td>
<td>11.0 (±0.1)</td>
</tr>
</tbody>
</table>

Measurement of Elastic Constants. Diffraction methods probe the interatomic lattice spacings from which strains are readily obtained. First, the position of the measured diffraction peak is translated into a d-spacing by means of Bragg's law

\[ n\lambda = 2d_{hkl} \sin \theta_{hkl} \quad \text{a)} \]

in which \( n \) is an integer, \( \lambda \) is the wavelength, \( d_{hkl} \) is the d-spacing and \( \theta_{hkl} \) is the diffraction angle. The strain/stress relationship for in-plane isotropy applied here is

\[ \varepsilon = \frac{d_{\psi} - d_0}{d_0} = -\frac{\nu(hkl,\psi)}{E(hkl,\psi)}\sigma + \frac{1+\nu(hkl,\psi)}{E(hkl,\psi)}\sigma \cos^2 \psi \quad \text{b)} \]

in which \( \varepsilon \) is the strain, \( \sigma \) is the applied stress, \( \nu \) and \( E \) are Poisson's ratio and Young's modulus for the crystal direction \( hkl \) and the specimen direction \( \psi \), respectively, which is the angle between the load direction and the bisector of the incident and reflected neutron beam (see Fig. 1). Since only the slope of the stress/strain curves is of interest, any one of the measured d-spacings can be used as reference value \( d_0 \). From eq. (2) follows also that the determination of \( \nu \) (where \( \psi=\pi/2 \)) requires the preceding measurement of \( E \) for which is \( \psi=0 \).

General considerations [3-6] demand that the elastic constants of sprayed coatings exhibit hexagonal symmetry so that the stiffness matrix becomes

\[
S = \begin{pmatrix}
S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\
S_{12} & S_{11} & S_{13} & 0 & 0 & 0 \\
S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & S_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & S_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & 2(S_{11} - S_{12})
\end{pmatrix} \quad \text{c)}
\]
The relationship between the aggregate constants in eq. (3) and the elastic constants obtained by diffraction for a certain $hkl$ is [11]

$$
\overline{z}_{ijkl} = \frac{1}{2\pi} \int_{0}^{2\pi} s_{ijkl} - u_{ijmn} \left( c^{*}_{mnop}(\varphi_B) - c_{mnop} \right) s_{ijkl} d\varphi_B
$$

where $s_{ijkl}$ is the orientation dependent (i.e. dependent on the direction $\psi$) aggregate stiffness tensor in fourth rank tensor notation, $c^{*}_{ijkl}$ are the orientation-dependent (on $hkl$) single crystal elastic constants of the respective material, and $w_{ijkl}$ is the generalized Eshelby-tensor. Eq. (4) requires that no preferred orientation is present. The results of the texture measurements are shown in Fig. 3.

![Figure 3: Pole figures for the Ni (002) reflection (a) and for the YSZ (022) reflection (b). The maximum value is about 1.1 \times random.](image)

The crystallite orientations of both samples are almost ideally random so that preferred orientation can be disregarded.

The relationship between $\nu(hkl,\psi)$, $E(hkl,\psi)$ and $\overline{z}_{ijkl}$ is

$$
E^{\perp}(hkl,\psi = 0) = 1/\overline{z}_{3333}(hkl,\psi = 0)
$$

$$
E^{\parallel}(hkl,\psi = \pi/2) = 1/\overline{z}_{3333}(hkl,\psi = \pi/2)
$$

$$
\nu^{\perp} = \frac{\overline{z}_{3311}(hkl,\psi = \pi/2)}{\overline{z}_{3333}(hkl,\psi = \pi/2)}
$$

$$
\nu^{\parallel} = \frac{\overline{z}_{3322}(hkl,\psi = \pi/2)}{\overline{z}_{3333}(hkl,\psi = \pi/2)}
$$

$$
\nu^{\parallel} = \frac{\overline{z}_{3311}(hkl,\psi = 0)}{\overline{z}_{3333}(hkl,\psi = 0)}
$$
These constants are measured by diffraction. The principle of their measurement is shown in Fig. 4.

Figure 4: Measurement of Poisson’s ratio and Young’s modulus in various specimen directions.

The macroscopic elastic constants $S_{ij}$ are independent on hkl. They are obtained by means of a least-square fit of $s_{ijkl}$ in eq. (4). The relationships between the $S_{ij}$ (contracted notation of the $S_{ijkl}$) and Young’s modulus/Poisson’s ratio in various directions are

$$E^\perp = 1/S_{33} \quad \text{6a)}$$
$$E^\parallel = 1/S_{11} = 1/S_{22} \quad \text{6b)}$$
$$\nu^\perp = S_{13} / S_{33} \quad \text{6c)}$$
$$\nu^\parallel = S_{13} / S_{11} \quad \text{6d)}$$
$$\nu^{\parallel\perp} = S_{12} / S_{11} \quad \text{6e)}$$

where $E^\perp$ and $E^\parallel$ are Young’s modulus perpendicular and parallel to the surface, respectively. $\nu^\perp$ is Poisson’s ratio for a load perpendicular to the surface. $\nu^\parallel$ and $\nu^{\parallel\perp}$ describe Poisson’s ratio for a load parallel to the surface in a parallel ($\nu^\parallel$) and normal ($\nu^{\parallel\perp}$) direction.
3. RESULTS

Lattice strain was measured for about 20-30 different loads. An example for these measured stress/strain curves is shown in Fig. 5.

![Graphs showing stress/strain relations for nickel coating and reflection (002).](image)

Figure 5: Experimentally obtained stress/strain relations for the nickel coating and the reflection (002).

The actual list of measured diffraction elastic constants $E_{hkl}, \nu_{hkl}, E_{hkl}^\|, \nu_{hkl}^\|$ and $E_{hkl}^\perp$ includes the hkl (200), (311), (220) (111) for nickel and (400), (311), (220) and (422) for YSZ) and will be published elsewhere. These constants are the input parameters for a least square process from which the aggregate compliances are obtained (see Tab. 2).

<table>
<thead>
<tr>
<th>specimen</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>217 (22)</td>
<td>137 (10)</td>
<td>125 (4)</td>
<td>97 (10)</td>
</tr>
<tr>
<td>YSZ</td>
<td>231 (20)</td>
<td>60 (10)</td>
<td>74 (10)</td>
<td>59 (10)</td>
</tr>
</tbody>
</table>

The anisotropy of the metallic coating is reversed compared to that of the ceramic YSZ coating, i.e. the metallic coating is elastically stiffer perpendicular to the surface while for the ceramic coating the opposite is the case. These findings indicate differences in the crack and pore structure of the metallic and the ceramic coating. The theoretical analysis in ref. [4] shows that two classes of pores and cracks have the most influence on the elastic properties. The first consists of voids having a high aspect ratio which extend between splats in the horizontal plane. The second group includes cracks and pores that have on average a lower aspect ratio and they are aligned with their long axis vertical to the surface plane. Among these two, the horizontal voids with the large aspect ratio have the stronger effect because they decrease the effective cross section to a larger extend. The results in Tab. 2 indicate that their fraction is lower for the metallic coating. This may be attributed to the low viscosity of metallic melts above the liquidus which, on the
other hand, increases the contact area upon impact of the molten droplet and improves bonding between splats.

The results in Tab. 2 can be used to calculate Young's modulus and Poisson's ratio normal and parallel to the coating surface which are listed in Tab. 3. Table 3: Calculated values for Young’s modulus and Poisson’s ratio in specimen directions normal (⊥) and parallel (∥) to the coating surface. Values are given in units of GPa.

<table>
<thead>
<tr>
<th>specimen</th>
<th>( E_{\text{calc}}^\perp )</th>
<th>( E_{\text{calc}}^\parallel )</th>
<th>( \nu_{\text{bd}}^\perp )</th>
<th>( \nu_{\text{bd}}^\parallel )</th>
<th>( \nu_{\text{bd}}^\perp\parallel )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>149 (15)</td>
<td>118 (14)</td>
<td>0.35 (0.1)</td>
<td>0.28 (0.1)</td>
<td>0.47 (0.1)</td>
</tr>
<tr>
<td>YSZ</td>
<td>83 (20)</td>
<td>185 (20)</td>
<td>0.25 (0.12)</td>
<td>0.49 (0.2)</td>
<td>0.1 (0.1)</td>
</tr>
</tbody>
</table>

The directional dependence of all elastic constants is very pronounced. On top of that there is also a general decrease of the values for Young’s modulus by 30-60% when compared to the bulk values with no porosity (see Tab. 4).

Table 4: Values for Young’s modulus as obtained by other methods. Values are given in units of GPa. Those marked with an asterisk were taken from ref. [9], the value marked with a ‘+’ was obtained by bending. \( E_{\text{bulk}} \) was calculated for isotropic polycrystals.

<table>
<thead>
<tr>
<th>specimen</th>
<th>( E_{\text{meas}}^\perp )</th>
<th>( E_{\text{meas}}^\parallel )</th>
<th>( E_{\text{bulk}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>-</td>
<td>78 (6)</td>
<td>232</td>
</tr>
<tr>
<td>YSZ</td>
<td>21.9 (1.9)</td>
<td>37.0 (4.5)</td>
<td>219</td>
</tr>
</tbody>
</table>

The differences between indentation and diffraction values amount up to a factor five for YSZ. By nature, diffraction ‘sees’ only the coating material and records therefore only the strain in nickel and YSZ, respectively. The total strain, however, consists of the elastic deformation of the crystallites and the shape change of the voids and pores which is not detected directly by diffraction. The porosity merely acts as a decrease of the effective cross section and, therefore, increases the effective stress on the crystallites. This, however, is not the case for indentation where the indenter size is of the order of the splats and pores. Thus, a larger part of the strain may go directly into the deformation of a few voids, hence the low values for \( E \).

4. CONCLUSIONS

Diffraction measurements of elastic moduli both of the ceramic and the metallic plasma sprayed coating show strong anisotropy normal and parallel to the coating surface. Although of comparable porosity, the elastic anisotropy is reversed in the metallic coating and the effect is more distinct in the ceramic YSZ. This is a strong indication that the horizontal voids with high aspect ratio play a major role for the elastic anisotropy. It can also be concluded that their fraction is lower in the metallic coating than in YSZ.
REFERENCES