RESIDUAL STRESS ANALYSIS OF CERAMIC COATINGS BY MEANS OF
SYNCHROTRON RADIATION XRD

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ABSTRACT
Synchrotron radiation XRD was used to study the residual stress field in two different ceramic coatings: polycrystalline diamond (~5 μm) on WC-Co and Y₂O₃-partially-stabilised-zirconia (~300 μm) on Al substrates. In both cases, the use of synchrotron radiation, and the possibility of changing wavelength in particular, permitted to study the residual stress trend inside the ceramic layers. For the diamond coated component, the stress analysis was extended also to the WC substrate, in the interface region with the coating.

INTRODUCTION
The control of the residual stress is a primary issue in ceramic coating technology. Both the deposition process and the service conditions may produce a residual stress, which may be particularly critical in applications where a large mismatch exists between structural, thermal and mechanical properties of layer and substrate.

A case of particular interest is that of protective coatings, like polycrystalline diamond anti-wear layers [1] and Partially-Stabilized-Zirconia (PSZ) Thermal Barrier Coatings (TBCs) [2], that are both deposited by high temperature processes, and must be designed to withstand severe working conditions. The protective action cannot be exploited if the adhesion between metal and substrate is not guaranteed, and adhesion is strongly influenced by the residual stress. Therefore, a residual stress analysis of the coated components is absolutely necessary.

XRD is known to be a valuable technique to measure residual strain in a non-destructive way [3]. However, the shallow penetration of X-ray and the need for a suitable diffraction geometry and for a careful control of several possible error sources may limit the applications of this technique. Errors may be relevant when studying low stress levels, as is frequently the case in plasma sprayed ceramic TBCs [4]. In addition, as traditional XRD methods involve the measurement of high angle reflections, it may be necessary to use different wavelengths to study different materials or polyphasic components.

Station 2.3 of the Daresbury (UK) synchrotron radiation facility may help to overcome part of these limitations. Even if it was designed for high resolution powder diffraction, the parallel beam geometry is perfectly suited to the X-ray Residual Stress Analysis (XRSA), being almost unaffected by typical errors arising from sample positioning and roughness. The
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principal advantages offered by this facility are essentially three: the high X-ray flux permits to
detect even very weak reflections, that frequently occur when studying thin films or polyphasic
samples (a); the appropriate wavelength may be selected in a wide range (\(-0.5 \div -3.5\) Å), by
simply changing the angle of the Si double crystal monochromator located in the incident beam,
without moving the sample (b); the perfectly monochromatic radiation and the goniometer
geometry give a narrow instrumental profile, even at high 2θ angle, which is the angular region
where data for XRSA are collected (c).

Profiting from these remarkable potentialities, we studied the stress distribution in two
completely different coating systems: thin polycrystalline diamond layers on WC-Co
substrates, and thick PSZ coatings deposited on Al components by Plasma Spray.

EXPERIMENTAL

Ceramic coatings

The diamond coating was produced by Hot Filament Chemical Vapour Deposition
(HFCVD) on a WC-6%Co (K10 alloy) 10x10x1 mm³ substrate. The diamond thickness after a
8 hour deposition at 750°C in H₂+0.5%CH₄ atmosphere was ~5 µm. Further details on the
deposition process and coating microstructure may be found elsewhere [5].

The 300 µm PSZ coatings were plasma sprayed in Ar atmosphere on commercial Al
bars (130x10x5 mm³). An Ar (liquid+gas) fog was used as a cooling medium, in order to
control the temperature during the spraying (155°C for the sample of the present study) [4].
Other details on the spraying process may be found in the cited literature. The reducing spraying
conditions caused a high oxygen defect in the ceramic, which was responsible for the formation
of two zirconia polymorphs (tetragonal + cubic) [6]. This phase composition was metastable,
with the cubic phase that tended to transform to tetragonal by low temperature (~150°C) or even
room temperature (RT) ageing [6]. Since a considerable volume expansion is associated with
the transformation, a residual strain was introduced in the coating. In particular, the ceramic

Figure 1. Measurement geometry for the 300 µm PSZ coatings.
was expected to be in a compressive state after the transformation, and preliminary measurements using CuKα radiation gave a residual stress value of about -15 and -40 MPa for samples aged 15 months at RT and 48 hours at 155°C, respectively.

**XRD measurements**

All measurements were conducted in a ψ-tilting geometry. The parallel beam geometry of Synchrotron Radiation (SR) station 2.3 of Daresbury has already been described in detail in the past [7]. Concerning our measurements, the important point was the reliability of the goniometer after the ψ-tilting, also considering the non-standard operating conditions: in particular, samples were mounted on a 4-circle goniometer head, by means of a custom-designed adapting ring. Figure 1 shows sample position during the measurements. To check the instrument we measured the position of the (531) Si peak of a NBS 640b powder sample. In spite of the residual roughness and the relatively low precision positioning, Figure 2 shows that no shift was measured after a 70° ψ-tilting.

**RESULTS AND DISCUSSION**

**XRSA in diamond coated WC-Co**

The residual strain in diamond coated components is the resultant of an intrinsic (ε_i) and a thermal (ε_r) term. The relative amount of ε_i and ε_r depends on several factors, including surface morphology, substrate properties, growth modality and, in general, process parameters. The intrinsic component may be difficult to evaluate [8]. Most theoretical modelling consider the thermal stress only, which should be prevailing in several cases (e.g., the diamond/WC-Co system). In any case, a sharp transition from tension to compression is expected at the diamond/substrate interface [9,10]. In addition, theoretical speculations usually assume zero stress as a substrate starting condition, and also that no plasticity effects or chemical reactions occur. These conditions are quite ideal, and limit the real usefulness of such calculations. The real need, in fact, is for a method which is able to measure the actual stress distribution in...
finished coated components. If we consider experimental methods, XRSA is probably the best non-destructive technique to measure the strain field in both coating and substrate, provided that a sufficient penetration depth may be achieved.

Before starting the SR measurements, XRSA was done by a conventional laboratory instrument (Huber 4030), using CuKα radiation. A sin²ψ plot of the (331) diamond peak showed the presence of a high compressive stress in the coating; there was no data splitting for positive/negative ψ-tilting nor for 0, 90° φ- (in-plane) rotation. From these preliminary measurements a simple axially symmetric uniform stress field could be assumed:

\[ \sigma_{11} = \sigma_{22}, \sigma_{33} = 0, \sigma_{ij} = 0 \quad (i \neq j) \]  

SR XRSA was done on the diamond layer first, along both [331] and [311], using λ=1.506 and λ=1.900 Å, respectively. XECs (X-ray Elastic Constants) were calculated (as Hill averages) from single crystal data (c_{11} = 1079 GPa; c_{12} = 124 GPa; c_{44} = 578 GPa [11]). As shown in Figure 3, the measured residual stress was compressive (~ -1.7 GPa) and didn’t depend on the crystallographic direction or wavelength. This result supports the hypothesis of a constant (or slowly varying) stress within the diamond layer. However, due to the very low absorption of carbon, a stress gradient could hardly be detected by changing λ.

On the contrary, as shown in Figure 4, the absorption coefficient of the WC phase (for the wavelength range considered) is high, and varies considerably by changing the wavelength. Therefore we selected three different λ values to study the residual strain in the WC interface region. To have an approximate value of the thickness of the sampled volume, we may refer to the information depth, \( \xi \) [12], defined as:

\[
\xi_i = \frac{\int_{0}^{\infty} z \cdot \exp(-\mu k z) \cdot dz}{\int_{0}^{\infty} \exp(-\mu k z) \cdot dz} = \frac{1}{\mu k}
\]  

Figure 3. Results of synchrotron radiation XRSA. The sin²ψ plot refers to the (311) (λ=1.506 Å, slope=1.59x10⁻³, R=0.9996, σ= -1.75(8) GPa) and (331) (λ=1.9 Å, slope=1.56x10⁻³, R=0.9963, σ= -1.69(5) GPa) diamond reflections.
Table I. Absorption coefficient ($\mu$) and information depth, $\xi_i$ (calculated at $\psi=0$, $45^\circ$ and $75^\circ$), for the wavelengths used in the XRSA of the WC phase.

<table>
<thead>
<tr>
<th>$\lambda$ (Å)</th>
<th>$\mu$ (µm$^{-1}$)</th>
<th>$\xi_i(\psi=0^\circ)$ (µm)</th>
<th>$\xi_i(\psi=45^\circ)$ (µm)</th>
<th>$\xi_i(\psi=75^\circ)$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>0.580</td>
<td>0.767</td>
<td>0.54</td>
<td>0.20</td>
</tr>
<tr>
<td>0.9</td>
<td>0.249</td>
<td>1.76</td>
<td>1.25</td>
<td>0.46</td>
</tr>
<tr>
<td>0.65</td>
<td>0.105</td>
<td>4.18</td>
<td>2.96</td>
<td>1.08</td>
</tr>
</tbody>
</table>

where $k = 2/(\sin \theta \cos \psi)$. Since $\xi_i$ depends on $\psi$, we report the value calculated for several $\psi$ values in Table I.

From Figure 4 it can be seen that CuK$\alpha$ is not adequate because is too close to the Co absorption edge (1.608 Å). The exact Co content on the surface is not known, as it varies depending on the process conditions. In particular, some Co was found on the surface, above the diamond [13], because of the diffusion process during deposition. The absorption coefficients for the selected wavelengths are less sensitive to small variation of Co.

Figure 5 shows the $\sin^2 \psi$ plots for the three wavelengths. The zero strain interplanar distance was calculated from the Poisson modulus, assuming a relation that is verified for biaxial stress fields ($\sin^2 \psi(\psi=0) = 2\psi/(\psi+1)$ [3]). The different slopes suggest the presence of a strain gradient. Considering a simple model of linear stress gradient, for a biaxial stress field we may write[3,14]:

$$\sigma_{ij}(z) = \begin{bmatrix} \sigma_{11} & \sigma_{12} \\ \sigma_{12} & \sigma_{22} \end{bmatrix} + \begin{bmatrix} A_{11} & A_{12} \\ A_{12} & A_{22} \end{bmatrix} \cdot z = \sigma_{ij} + A_{ij} \cdot z \quad (3)$$

The residual stress averaged over the sampled volume may be obtained by considering the X-ray absorption effect:

![Figure 4. Linear absorption coefficient for WC-6wt%Co. The arrows in (b) indicate the $\mu$ values for the wavelengths used in the synchrotron radiation XRSA.](Copyright (C) JCPDS-International Centre for Diffraction Data 1997; ISSN 1097-0002, Advances in X-ray Analysis, Volume 40)
According to the results for the diamond layer, we may introduce a further simplification, by assuming that Eq. 1 holds for the interface region of WC too. In this case ($\sigma_{11} = \sigma_{22}, \sigma_{12} = 0$) we may write the following expression for the measured strain:

$$<\varepsilon_{ij}> = XEC_1 \cdot \sigma_{11} \cdot \sin^2(\psi) + 2XEC_2 \cdot \sigma_{11} + [XEC_1 \cdot A_{11} \cdot \sin^2(\psi) + 2XEC_2 \cdot A_{11}] \cdot \xi_i =$$

$$= [XEC_1 \cdot \sin^2(\psi) + 2XEC_2] \cdot [\sigma_{11} + \frac{A_{11} \cdot \sin(\theta) \cdot \cos(\psi)}{2\mu_\lambda}]$$

(5)

where

$$XEC_1 = \left(\frac{1+\nu}{E}\right)_{x-ray} \quad XEC_2 = \left(-\frac{\nu}{E}\right)_{x-ray}$$

(6)

are the X-ray elastic constants.

Eq. 5 is analogous to the traditional $\sin^2\psi$ equation [3], but contains a $\cos(\psi)$ term that accounts for the gradient effect. Actually, Eq. 5 is a system of $n$ equation, where $n$ is the number of different wavelengths employed for the measurements (3 in this case). The system may be
solved with the help of a least square algorithm to process simultaneously all the data of Figure 5. The result is shown in Figure 6. From the best fit of the data we can obtain the stress trend (intercept ($\sigma_{11}$) and slope ($A_{11}$)) in the WC phase, which is reported in Figure 7 together with the results for the diamond phase.

The question as to what is the maximum depth that contributed to the results may be answered by considering the information depth. The dashed line in Figure 7 extends beyond 3 $\mu$m, which is the value of $\xi$ (at $\psi=45^\circ$) for the shorter wavelength (Table I): little information comes from deeper layers. It is worth noting that the present analysis referred to the interface region. The stress trend in the rest of the substrate is not directly accessible by XRSA, but it certainly changes, in order to equilibrate the observed stress field at the interface.

The important point is that the stress did not change abruptly from compressive to tensile at the interface. Despite most theoretical predictions, the residual stress in WC is tensile at the very interface and in the first ~1 $\mu$m. Unfortunately, the result of Figure 7 cannot be regarded as the residual stress in the outer layer of the whole component, because we could not measure the stress in the Co phase (the signal was too weak and confused by diamond and WC reflections), which is the metal binder in the composite substrate. The main comment that can be done concerns the diffusion process of C in Co, taking place during the deposition. This effect was
described by the shift of a low angle reflection (200) of Co in both coated [5] and uncoated (with diamond coating removed after deposition [15]) samples. The Co cell volume tends to increase with the C content (in the outer region accessible to X-ray, where diffusion is active) and this effect should add a progressively bigger compressive component to the stress field in the Co phase. Further studies will be necessary to define this point. In any case it seems clear that the real stress distribution may be quite different from the predictions of most theoretical speculations [9,10]. A similar statement is valid for some very popular experimental methods, like curvature change or cantilever bending [8,16,17], which generally assume a simple elastic behaviour of two continuous and uniform solids (substrate and coating) which is probably an oversimplification in the present case.

**XRSA in PSZ plasma sprayed coatings**

The same kind of approach was used for the measurement of the stress field in the outer layers of a 300 µm PSZ coating on Al. To measure the residual stress gradient across the surface of the ceramic, XRSA was performed with two different wavelengths: corresponding absorption coefficients and information depths are reported in Table II (a 16% TBC porosity [4,18] was considered to calculate μ and ξ). The SR measurements were done on the sample aged 15 months at RT. Measured reflections were {620} (with λ=1.5Å) and {840} (with λ=0.94Å) of the tetragonal phase, i.e., (206)/(602)/(620) and (408)/(804)/(840), respectively (using an indexing based on the distorted cubic fluorite structure). Due to the peak overlapping, profile fitting was necessary to find peak positions, as shown in Figure 8 for the{620} peaks (at ψ=0°). The XECs along the different crystallographic directions({620} and{840}) were calculated from single crystal data using a pseudo-cubic approximation [19]: c_{11}= 412 GPa; c_{12}= 110 GPa; c_{44}= 55 GPa.

Like in the case of the diamond coated WC-Co component, biaxial stress field and linear gradient (Eq. 3-5) were assumed for the coating region interested by the XRSA. Even though these simplifying assumptions may be not completely verified in this case, the quality of the data did not allow for the use of more complex models. Main causes of low quality are inherent to these ceramic coatings, and include the tetragonal symmetry of PSZ and the broad profiles, which lead to a considerable peak overlapping, as visible in Figure 8 (overlapping is even more severe for shorter wavelengths). In addition, the strain to be measured is quite low, because of the low stress and high elastic modulus of PSZ. Therefore, the present model may be considered as a reasonable (and necessary) approximation to the real stress field.

<table>
<thead>
<tr>
<th>λ (Å)</th>
<th>μ (µm⁻¹)</th>
<th>ξ(ψ=0°) (µm)</th>
<th>ξ(ψ=45°) (µm)</th>
<th>ξ(ψ=75°) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.0243</td>
<td>19.1</td>
<td>13.5</td>
<td>4.9</td>
</tr>
<tr>
<td>0.94</td>
<td>0.00665</td>
<td>62.7</td>
<td>44.3</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Table II. Absorption coefficient (μ) and information depth, ξ (calculated at ψ=0, 45 and 75°), for the wavelengths used in the XRSA of the PSZ coating.
CONCLUSIONS

The use of synchrotron radiation may considerably improve the X-ray residual stress analysis. In addition to the obvious advantages of SR, i.e., highly collimated, intense, monochromatic and parallel beam, an important feature is the possibility of varying the wavelength during experiments on the same sample. As shown in this work, the stress trend...
inside coated components could be studied by means of a simultaneous processing of XRSA data obtained with different wavelengths, without any changes in the diffraction geometry or in the sample positioning during the measurements.

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REFERENCES