Internal Stress Distribution Analysis in Thin Textured Coatings by X-Ray Diffraction - Problems and Attempts at Their Solution

Christoph Genzel
Hahn-Meitner-Institut Berlin, Department of Structural Research
Glienicker Str. 100, D - 14109 Berlin, Federal Republic of Germany

Abstract

X-ray stress analysis (XSA) at thin polycrystalline layers with marked textures involves a series of difficult problems, because the material becomes anisotropic on the macroscopic scale. This applies especially to the detection of non-uniform residual stress distributions within layers, the thickness of which is small with respect to the penetration depth $\tau$ of the X-rays. By the example of thin and highly <111> textured PVD coatings of Ti$_{1-x}$Cr$_x$N, the paper compares several methods of the XSA concerning their suitability for the detection of stress gradients in thin layers. The best results are obtained by means of the scattering vector method, where the lattice spacing depth profiles $d_{\psi}(hkl,\tau)$ are measured after stepwise rotation of the sample around the scattering vector $g_{\psi}$ near the intensity poles of the texture. Individual stress profiles $\sigma(\tau)$ are then obtained directly from the $d_{\psi}(hkl,\tau)$-distributions with the so-called stress factors $F_{\psi}(hkl,\psi,\sigma_{\text{max}})$ acting as proportionality constants, which reflect the macroscopic elastic anisotropy of the material.

Introduction

Thin hard coatings on the basis of TiN, for example, deposited by physical vapor deposition methods (PVD) are well-known today to influence the properties of technical parts like resistance to abrasive wear and corrosion to a large extend. In many cases, high compressive stresses up to some GPa develop during the coating process within the layers, which may contribute to the mechanical behavior in a positive manner. Since the amount and even the sign of these stresses depend strongly on the process parameters like temperature, bias voltage, process pressure or layer thickness [1]-[3], efforts are made to produce coatings with defined internal stress gradients in order to combine favorable mechanical properties like high hardness on the top of the coatings with a sufficient adhesiveness at its interface.

Therefore, the knowledge of both, the amount and the distribution of the residual stresses within the coatings, is of great practical interest. However, due to the small diffracting volume as well as texture, X-ray diffraction at thin polycrystalline coatings often leads to line profiles of rather weak intensity and, therefore, stress analysis involves a series of difficulties. Especially for the second reason, the techniques of the XSA derived from the $\sin^2\psi$-method [4] are restricted to a few discrete $\psi$-positions for
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

Sponsored by the International Centre for Diffraction Data (ICDD).

This document is provided by ICDD in cooperation with the authors and presenters of the DXC for the express purpose of educating the scientific community.

All copyrights for the document are retained by ICDD.

Usage is restricted for the purposes of education and scientific research.

DXC Website – www.dxcicdd.com

ICDD Website - www.icdd.com
strain evaluation, which only yields an average value with respect to the layer thickness [5]-[7]. Nevertheless, there are some hints in the literature for non-uniform stress distributions in such hard coatings from \( \sin^2 \psi \)-measurements after stepwise sublayer removal [8], the use of radiations with different penetration depths \( \tau \) [9], from curved \( d \) versus \( \sin^2 \psi \)-distributions [10] as well as from depth profiling methods using grazing incidence X-ray diffraction [11].

Recently, a new formalism for X-ray stress gradient analysis was proposed, by means of which the stress profiles \( \sigma_i(\tau) \) of individual components of the stress tensor can be obtained directly from the measured strain depth profiles, \[ \varepsilon_{\psi}(hkl, \tau) = [d_{\psi}(hkl, \tau) - d_0]/d_0 \] (\( d_0 \) - lattice spacing of the stress-free material), if the penetration depth \( \tau \) is varied by stepwise rotation of the sample around the scattering vector \( g_{\psi} \) for fixed positions \((\varphi, \psi)\) with respect to the sample reference system [12]. Theoretical predictions for applying this method to stress gradient analysis in thin layers were made in [13].

In the present paper, experimental results obtained by means of the scattering vector method at thin PVD - coatings of TiN and \( Ti_{0.86}Cr_{0.14}N \) are reported. The elastic anisotropy of the layers due to the more or less pronounced <111> fiber texture is regarded by means of the stress factors \( F_v(hkl, \varphi, \psi, s_{\text{amp}}) \). Their calculation for the case of materials with strong fiber textures is described in [14]. The results of the stress evaluation performed in the scattering vector mode are compared with those obtained by conventional \( \sin^2 \psi \)-measurements. Further, a simple formalism is proposed for the transformation of the experimentally determined "Laplace stress" profiles, \( \alpha(\tau) \), into the real z- space profiles, \( \sigma(z) \), which takes into account the finite layer thickness and, therefore, is more practicable for the inversion problem in the case of thin layers than the method described in [15], which is valid for thick samples.

**Basic Principles**

The fundamental equation (1) in X-ray residual stress analysis of polycrystalline materials reflects the two sides of XSA concerning the macroscopic isotropy of the material in form of the formal equivalence of all measuring directions \((\varphi, \psi)\) on one hand, and the anisotropy of the individual crystallites in form of the hkl-dependence of the X-ray elastic constants (XEC), \( s_i \) and \( 1/2s_2 \), on the other hand:

\[
\varepsilon_{\psi}(hkl, \tau) = \frac{1}{2}s_2(hkl) \left\{ \left[ \sigma_{11}(\tau) \cos^2 \varphi + \sigma_{22}(\tau) \sin^2 \varphi + \sigma_{12}(\tau) \sin 2\varphi \right] \sin^2 \psi + s_{1}(hkl) \left[ \sigma_{11}(\tau) + \sigma_{22}(\tau) + \sigma_{33}(\tau) \right] \right\} 
\]

(1)
The strains and stresses in eq. (1) are the exponentially weighted averages ("Laplace profiles") of the actual depth profiles, $\varepsilon_{\psi}(hkl,z)$ and $\sigma(z)$, with respect to the penetration depth $\tau$ of the X-rays [16] [17]:

$$
\varepsilon_{\psi}(hkl,\tau) = \int \varepsilon_{\psi}(hkl,z) e^{-z/\tau} dz / \int e^{-z/\tau} dz, \quad \sigma(\tau) = \int \sigma(z) e^{-z/\tau} dz / \int e^{-z/\tau} dz
$$

(2)

In the case of highly textured materials, however, the macroscopic behavior becomes anisotropic as well because of the preferred orientation of the crystallites, and consequently, the possible measuring directions are essentially restricted to the intensity poles of the texture. Residual stress analysis in such materials cannot be performed on the basis of the $\sin^2\psi$- method [4], because the assumption of a quasi-isotropic material with a statistical orientation distribution of the crystallites is no longer fulfilled. In this case, the crystallite group method in which the textured material is considered to consist of a few ideal orientations of the crystallites may be applied for stress analysis [18][19]. Thus, rewriting eq. (1) in the form

$$
\varepsilon_{\psi}(hkl,\tau) = F_{ij}(hkl,\varphi,\psi, s_{mnop}) \sigma_{ij}(\tau)
$$

(3)

where the $F_{ij}$ are the so-called stress factors depending on the reflection $hkl$, the measuring direction $(\varphi,\psi)$ as well as on the single crystal elastic compliances $s_{mnop}$, the individual components of the stress tensor $\sigma_{ij}$ in the sample reference system can be evaluated by the least squares method, if the lattice strains $\varepsilon_{\psi}$ are measured for a sufficient large number of available directions. This procedure, however, only yields uniform values for the stresses and is therefore unsuitable for the detection of residual stress gradients in the near surface region of the material.

The idea of the stress factors can be applied to the analysis of steep stress gradients which vary significantly within the penetration depth $\tau$ of the X-rays, if the strain depth profiles are measured in the scattering vector mode, where $\tau$ is adjusted by stepwise rotation of the sample around the scattering vector $g_{\psi \varphi}$ at fixed positions of $\varphi$ and $\psi$ with respect to the sample reference system. In the case of strongly textured materials, these positions should correspond to the intensity poles. Denoting the angle of rotation by $\eta$, a general formulation of the penetration depth is given by

$$
\tau = (\sin^2 \theta - \sin^2 \psi + \cos^2 \theta \sin^2 \psi \sin^2 \eta) / (2 \mu \sin \theta \cos \psi)
$$

(4)

[12], where $\mu$ and $0$ are the linear attenuation coefficient of the radiation and the Bragg angle, respectively. In eq. (4), the positions $\eta = 0^\circ$ and $90^\circ$ correspond to the limiting cases of the $\Omega$- and the $\Psi$- mode in the conventional X-ray residual stress analysis (Fig. 1). Because the inclination angle $\psi$ is not used for the variation of $\tau$ in the scattering vector mode, it becomes a usual parameter in the same sense as the azimuth angle.
φ. Consequently, individual components $\sigma_\phi(\tau)$ of the stress tensor can be separated from eq. (1) or eq. (3), if the $d_{\psi h} h k l, \tau(\eta)]$ - depth scans obtained in the scattering vector mode for suitable positions of φ and ψ are combined in an appropriate way. In the case of a biaxial stress state, for example, this procedure yields for the azimuth $\phi = 0^\circ$:

$$
\sigma_{11}(\tau_{\eta}) = \left[ d_{\psi 0} h k l, \tau_{\eta} - d_{\psi 2} h k l, \tau_{\eta} \right] / \left[ d_0 \left[ F_{11}(h,0,\psi_1) - F_{11}(h,0,\psi_2) \right] \right].
$$

In eq. (5), h stands for h k l, τ indicates that τ is varied by means of η, and ψ₁, ψ₂ are two neighboring positions of the inclination angle. For quasi-isotropic materials according to eq. (1), the stress factor of the $\sigma_{11}$ component is formally given by $F(h,0,\psi) = 1/2s_s(h) \cos^2 \phi \sin^2 \psi + s_1(h)$. For $\phi = 90^\circ$, an equivalent relation is obtained for $\sigma_{22}(\tau_{\eta})$. From the conventional point of view, (5) may be considered as "depth resolved" $\sin^2 \psi$-method performed at two discrete ψ-positions.

Fig. 1. Schematic view of the diffraction geometry in the XSA and the correlation of the penetration depth $\tau$ in Ψ-, Ω- and η-goniometry; PB, SB - primary and secondary (diffracted) beam, respectively.

For finite values of $\sigma_\phi(\tau_\eta), i = 1,2,3$ which may occur in form of phase-specific "pseudo-macro" stresses (PMS) between the individual components of multiphase materials [17], the situation becomes more complicated. Considering the evaluation of $\sigma_{33}(\tau_{\eta})$-gradients in more detail, η-scans have to be performed in the azimuths $\phi = 0^\circ, 90^\circ, 180^\circ$ and $270^\circ$. Denoting the average by $d_{\psi h}^+(h, \tau_\eta) = \left[ d_{\psi h} + d_{\psi 0} + d_{\psi 180} + d_{\psi 270} \right]/4$ [20] and taking the differences of two ψ-positions again, one obtains

$$
\sigma_{33}(\tau_{\eta}) = \frac{F_{33}(h,\psi_1) d_{\psi 0}(h, \tau_\eta) - F_{33}(h,\psi_2) d_{\psi 0}(h, \tau_\eta)}{d_0 \left[ F_{33}(h,\psi_1) F_{33}(h,\psi_2) - F_{33}(h,\psi_1) F_{33}(h,\psi_2) \right]}.
$$

\[\text{Copyright (C) JCPDS-International Centre for Diffraction Data 1999}
\]
where $F_{11}$ and $F_{33}$ are the stress factors of the in-plane and the normal stress component, respectively. By means of the eq.s (5) and (6), the "Laplace"-stresses $\sigma(\tau)$ are obtained directly from the measured $d_{ov}(h,\tau)$-profiles without any assumption in form of an analytical expression to describe the depth profiles. A formalism for calculating the actual stress profiles in the $z$-space, $\sigma(z)$, from their discrete Laplace transforms, is given in [15].

**Experimental Procedure**

**Samples**

The TiN coatings (thickness 1.3...2.3µm) were deposited by the ion plating process (bias voltage 300V, deposition temperature 450°C, process pressure 1.0 Pa) on high speed steel substrates (German grade: S 6-5-2). The process parameters were maintained constant during the deposition. The Ti$_{0.85}$Cr$_{0.15}$N coatings (thickness 2.0...4.0µm) were produced by arc-PVD (bias voltage 200V, deposition temperature 450°C) on high speed steel (German grade: M 42). One part of the coatings was deposited using a constant process pressure of 1.0 Pa, whereas for the second part the pressure was increased continuously during the deposition from 0.4 up to 2.0 Pa in order to get gradient layers with respect to the residual stress distribution. The chemical homogeneity of the layers over the thickness was proved by means glow discharge optical spectroscopy (GDOS).

**X-Ray Diffraction**

The X-ray investigations were performed on a HUBER $\psi$- diffractometer using CuKα and CoKα radiation. For texture and stress gradient analysis, the diffractometer was equipped with a $\varphi$ - rotation table as well as with a parallel beam unit consisting of a horizontal soller-slit followed by a (001) LiF- analyzer crystal in order to suppress fluorescence as well as the large horizontal divergence of the diffracted beam for measurements performed near the grazing incidence. All coatings were pre-characterized by means of the conventional $\sin^2\psi$ - method performed in the $\Psi$-goniometry using the reflections 311 (for CoKα: $2\theta = 88.7^\circ$), 222 and 422 (for CuKα: $2\theta = 78^\circ$ and 125.7°, respectively) up to $\sin^2\psi = 0.93$.

For evaluating the depth distribution of the residual stresses within the coatings, the scattering vector technique was applied. The stepwise $\eta$- rotation of the sample around the scattering vector (cf. Fig. 1) was realized by means of a combined $\varphi$ - $\omega$ - $\psi$ - rotation. In each $\eta$- position the diffraction profile was recorded. The polarization-, absorption- and Lorentz- correction of the intensities was performed by means of the equations given in [12]. Further, the centroid of the intensity distribution was used for the determination of the peak position in order to take into account line asymmetries due to steep strain gradients within the penetration depth of the X-rays [13].
This way, the depth profiles of the lattice spacings, \( d_{\psi}(hkl, \tau) \), were measured in the intensity poles 311 (\( \psi = 29.5^\circ \)), 3\( \bar{1} \)1 (\( \psi = 58.5^\circ \)), 4\( \bar{2} \)2 (\( \psi = 62^\circ \)) and 3\( \bar{1} \)1 (\( \psi = 80^\circ \)) themselves (the values refer to the pole distances for a <111> fiber texture), as well as for neighboring positions (35\(^\circ\), 53\(^\circ\), 59\(^\circ\) and 75\(^\circ\)). In dependence on the inclination angle \( \psi \), the increment of the rotation angle, \( \Delta \eta \), was varied between 1\(^\circ\) and 10\(^\circ\), in order to achieve increments of the penetration depth of about \( \Delta \tau = 0.1 \mu m \). The stress profiles were determined by taking the differences of the two \( d_{\psi}(hkl, \tau) \) - depth profiles obtained in neighboring positions, in order to minimize errors due to an insufficient knowledge of the exact lattice parameter \( d_0 \) of the stress-free material.

**Results**

*Conventional Stress Analysis by means of the sin\(^2\psi\)-Method*

A preliminary pole figure analysis revealed a more or less strong <111> fiber texture for all coatings investigated (Fig. 2). Nevertheless, the \( d_\psi \) versus sin\(^2\psi\)-distributions remain strictly linear up to large values of \( \psi \) and show no splitting (Fig. 3a), which would indicate a triaxial stress state with shear components \( \sigma_\phi \) (\( i = 1,2 \)). In the case of the Ti\(_{0.85}\)Cr\(_{0.15}\)N- layers, the texture was so strong that the \( d_\psi \) versus sin\(^2\psi\)-distribution could only be measured near the intensity poles of the texture (Fig. 3b), and therefore, the number of measuring points remains rather small.

![Fig. 2. Texture analysis of an arc-PVD Ti\(_{0.85}\)Cr\(_{0.15}\)N- layer (sample K49, thickness 2.4\( \mu m \)), experimental pole figures.](image)

The rotational symmetry of the in-plane stress state was proven in all cases by measurements at various azimuths \( \phi \). The values of \( \sigma_{||} \) obtained for the different reflections hkl agree satisfactorily within the error bars (Fig. 4). What else is striking, is that the absolute values for the thin TiN layer are significantly larger than those of the thicker layer.
Fig. 3. $d_\psi$ versus $\sin^2 \psi$-distributions obtained for a) TiN (sample T4, thickness 1.3 \mu m) and b) Ti\textsubscript{0.85}Cr\textsubscript{0.15}N (sample K12, thickness 3.0 \mu m). CuK\alpha, 422 - reflection.

Fig. 4. In-plane stresses $\sigma_{||}$ obtained by means of the $\sin^2 \psi$-method for the different reflections used; a) TiN and b) Ti\textsubscript{0.85}Cr\textsubscript{0.15}N.

**Lattice Spacing Depth Profile Analysis by means of the Scattering Vector Method**

In order to analyze the depth distribution of the stresses in more detail, the scattering vector technique was applied to measure the depth profiles of the lattice spacings, $d_{\psi}(hkl, \tau)$ after stepwise rotation of the sample around the scattering vector at the individual texture poles. Examples for the $d_{\psi}(hkl, \tau)$-profiles obtained at the 311- and the 311- pole of a Ti\textsubscript{0.85}Cr\textsubscript{0.15}N-layer are shown in Fig. 5. It should be noted that a uniform stress distribution over the layer thickness, i.e. $\sigma \neq f(x)$, would result in straight horizontal $d_{\psi}(hkl, \tau)$-profiles, because $\psi$ is kept fixed for the individual $\eta$-scans.

In the present case, however, finite slopes were observed for the individual curves, the signs of which depend on whether the scans were performed on the low- or the large-angle side with respect to the strain-free direction. A schematic representation of the
situation is given in Fig. 5c. For a plane-stress state of rotational symmetry this direction is related to the X-ray elastic constants by \( \sin^2 \psi = -2s_y/(1/2s_x) \). For the 311- reflection of TiN, this corresponds to a \( \psi \)-value of approximately 35°. Therefore, the clear increase of the lattice spacings towards the interface, which was found for the 311- pole (Fig. 5b), indicates a decrease of the compressive stresses in the same direction. On the other hand, one realizes from Fig. 5a that the same stress gradient leads to the opposite run of the lattice spacings in the 311- pole at \( \psi = 29.5^\circ \), whereas a nearly horizontal distribution is observed at \( \psi = 35^\circ \), which corresponds to the strain-free direction of the plane-stress state.

Fig. 5. XSA performed in the scattering vector mode (Ti_{0.85}Cr_{0.15}N, sample K12, thickness 3.0 \( \mu \)m); a) and b) lattice spacing depth distributions, \( d(311,\tau) \), obtained at different \( \{311\} \)-poles, the straight lines are linear least squares fit approximations; c) schematic view of the correlation between an in-plane stress gradient \( \sigma_{||}(z) \) and the corresponding gradients of the lattice spacing depth profiles for different inclination angles \( \psi \). See text for details.
Laplace Stress Analysis

The evaluation of the Laplace stress profiles from the measured $d_\psi(hkl, \tau)$- depth distributions was performed by the formalism described in [12]. Because the strain state within the layers was found in all cases by preliminary investigations in the conventional $\sin^2 \psi$ - mode as well as in the scattering vector mode to be of rotational symmetry, i.e. $d_\psi(hkl, \tau) = f(\psi)$, the in-plane stress component $\sigma_{\|}(\tau)$ is related to the lattice spacing depth distributions by

$$
\sigma_{\|}(\tau) = \left[ d_{\psi_1}(h, \tau) - d_{\psi_2}(h, \tau) \right] / \left[ d_0[F_{\|}(h, \psi_1) - F_{\|}(h, \psi_2)] \right]
$$

(cf. eq. (5)). The anisotropic stress factors $F_{\|}$ in eq. (7) were determined from the 111-pole figures by means of the formalism described in [14], for a quasi-isotropic material they are formally given by $F_{\|}(h, \psi) = 1/2a_0(h) \sin^2 \psi + 2a_1(h)$. The lattice parameters of the stress-free material, $d_0$, were assumed by 0.424 nm and 0.4227 nm for TiN and Ti$_{0.85}$Cr$_{0.15}$N, respectively, where the latter value was calculated from the corresponding data of TiN and CrN assuming the validity of Vegard's law. It should be emphasized that uncertainties in $d_0$ are only of minor importance in the stress analysis by means of eq. (7) for the same reason as in the case of the conventional $\sin^2 \psi$ - method [4], since the stresses are determined from the differences or, more precisely, from the slopes of the lattice spacing (depth) distributions.

Fig. 6. Piecewise linear Laplace- stress profiles $\sigma_{\|}(\tau)$ calculated by means of eq. (7) for the lattice spacing depth distributions measured in the scattering vector mode at individual intensity poles of the texture, Ti$_{0.85}$Cr$_{0.15}$N. The profiles for sample K12 correspond to the $d_\psi(311, \tau)$- and $d_\psi(3\bar{1}1, \tau)$- distributions shown in Fig. 5a,b. The dashed horizontal lines denote the average stress obtained by means of the conventional $\sin^2 \psi$- method (cf. Fig. 4).
Fig. 6 and 7 show the Laplace stresses $\sigma_{11}(\tau)$ evaluated from the $d_\psi(hkl,\tau_\psi)$-distributions obtained at the distinct texture poles for the samples investigated. Therefore, the lattice spacing depth profiles were approximated by smooth curves (in the present case straight lines) within the $\tau$-range they were measured (cf. Fig. 5a,b) and then, $\sigma_{11}(\tau)$ was calculated for the respective depth using eq. (7). This procedure yields the Laplace stresses over the covered $\tau$-range in form of piecewise smooth functions which correspond to the individual texture poles.

Fig. 7. Piecewise linear Laplace-stress profiles $\sigma_{11}(\tau)$ obtained for the TiN-layers, cf. Fig. 6.

Real Space Stress Evaluation

By means of eq. (7), the scattering vector method in principle yields the Laplace stresses $\sigma_{11}(\tau)$ directly for discrete positions of the penetration depth $\tau$. The calculation of the actual stress distributions in the real space, $\sigma_{11}(z)$, from these experimentally determined Laplace profiles, however, involves some difficult problems. So the inverse numerical Laplace transform (INLT) is well-known to be one of the ill-posed inversion problems, because the experimental data always scatter to a certain amount, which leads to instabilities in the numerical systems [21]. Moreover, in the case of thin coatings, the classical methods of the INLT, which are based on a expansion of the real space function $f(z)$ into a series of orthogonal functions [22]-[24], would fail, because the upper limit in the integral transform (2) must be replaced by the finite layer thickness $D$:

$$\sigma(\tau) = \frac{1}{D} \int_0^D \sigma(z)e^{-z/\tau}dz$$

$$\int_0^D e^{-z/\tau}dz.$$  (8)
Thus, in order to get a first approximation of the real space stresses, \( \sigma_{11}(z) \), the following simple formalism is proposed. The real space stress profiles are described by polynomial functions \([25][26]\), i.e.

\[
\sigma(z) = a_0 + a_1 z + a_2 z^2 + \ldots \tag{9}
\]

Due to the simple form of eq. (9), the transforms \( \sigma(\tau) \) by means of eq. (8) yield rather simple expressions too, even for the finite upper integration limit:

\[
\sigma(\tau) = a_0 + a_1 \left( \tau - \frac{D e^{-D/\tau}}{1 - e^{-D/\tau}} \right) + a_2 \left( 2\tau^2 - \frac{D e^{-D/\tau}(D+2\tau)}{1 - e^{-D/\tau}} \right) + \ldots \tag{10}
\]

The first bracket term in eq. (10) represents the exponentially weighted "effective" penetration depth \([27]\) with regard to the finite layer thickness \( D \) (cf. eq. (12) in \([13]\)). The unknown parameters \( a_i (i = 0,1,2,\ldots) \) in eq. (10) are now to be calculated by means of a least squares fit from the experimentally determined Laplace stress profiles within the whole \( \tau \)-range covered. These profiles are given either in form of discrete depth distributions from the measured \( d_{j}(hkl,\tau) \) - profiles by eq. (7), or, like in the present case, in form of piecewise smooth segments, if the \( d_{j}(hkl,\tau) \) - distributions were approximated before by smooth curves themselves.

From the example shown in Fig. 8 it can be realized that even comparatively small gradients in the Laplace space are correlated to much steeper gradients in the real space.

![Fig. 8. Correlation between the experimentally obtained Laplace stresses \( \sigma_{11}(\tau)_{\text{exp.}} \) and the calculated real space stress profiles, \( \sigma_{11}(z) \), respectively (Ti_{0.85}Cr_{0.15}N, sample K49, cf. Fig. 6c). \( \sigma_{11}(z) \) was chosen by a polynomial of second order, the corresponding Laplace profile, \( \sigma_{11}(\tau)_{\text{calc.}} \), was calculated by means of eq. (8). See text for details](image-url)
The reason for this behavior lies in the nature of the transform (8), which indicates that the respective profiles \(\sigma(\tau)\) "follow" the actual profiles \(\sigma(z)\) more or less slowly in an exponentially damped form. Furthermore, a comparison of eq. (9) and eq. (10) shows that the slope of the \(\sigma(\tau)\)-profile depends on the layer thickness, i.e. the smaller \(D\) (compared to \(\tau\)) the more flat becomes the \(\sigma(\tau)\)-curve, or, in other words, the more steep is the real space gradient which corresponds to the same Laplace profile.

It should be emphasized that the procedure applied here for the evaluation of the real space stresses from their Laplace transforms differs in an essential point from the stress gradient analysis by means of the \(\sin^2\psi\)-based methods [20][25][26][28][29]. In the latter case, the penetration depth \(\tau\) is varied by means of the tilt angle \(\psi\), and thus, all stress components \(\sigma_{ij}\) which contribute to the (more or less curved) \(\varepsilon_{\psi\psi}(hkl, \tau)\) versus \(\sin^\psi\)-distributions remain coupled in the basic equation (1) of the XSA. Therefore, the total number of unknown parameters which are necessary to describe the stress profiles \(\sigma_{ij}(z)\) becomes quite large, especially for in-plane stress states which are not of rotational symmetry. This often leads to numerical instabilities in the least squares fit procedure, which are avoided in the case of the scattering vector method, because individual stress components can be separated from the basic equation even for complicated triaxial stress states, if the lattice spacing depth scans \(d_{\psi\psi}(hkl, \tau)\) are combined in a suitable way.

**Discussion**

In all the layers investigated, the distribution of the in-plane residual stresses was found to be non-uniform over the layer thickness, even in such coatings which were deposited under homogeneous conditions. This remarkable result was obtained by means of the scattering vector method, where the depth profiles of the lattice spacings, measured at fixed positions \((\phi, \psi)\) with respect to the sample reference system, show a clear depth dependence (Fig. 5), which is directly related to those of the Laplace stresses by means of eq. (7).

The conventional \(\sin^\psi\)-method, on the other hand, gives no hints for these gradients in form of curved \(d_{\psi}\) versus \(\sin^\psi\) distributions. They remain linear up to large values of \(\psi\) (Fig. 3a), or, in the case of very strong textures, are only available near the intensity poles (Fig. 3b). This result agrees with theoretical predictions made in [13], where the small layer thickness compared with the large penetration of the X-rays was shown to be the reason for the linearity of the \(d_{\psi}\) versus \(\sin^\psi\) curves, even in the case of steep stress gradients within the layer.

Within the framework of the scattering vector method, the elastic anisotropy of the material due to the texture is regard by means of the stress factors \(F_\psi\), the calculation of which for the case of strong fiber textures is described in [14]. For TiN, the anisotropy ratio given by \(A = 2c_{1212}/(c_{1111} - c_{1122})\) (\(c_{\text{sat}}\) - single crystal elastic constants) is close to
unity (A = 0.86) and the differences between the anisotropic stress factors and their quasi-isotropic equivalents, which contain the usual X-ray elastic constants, are small. For this reason, the average stress values obtained by means of the conventional sin²ψ - method, which assumes quasi-isotropic elastic behavior of the polycrystalline material, fit into the non-uniform Laplace stress distributions evaluated by means of the scattering vector method, despite of the strong texture within the layers (Fig.s 6 and 7).

The sin²ψ - investigations at the TiN - layers yield significantly higher compressive stresses for the layer with the smaller thickness (Fig. 4). This is in good agreement with the results concerning the scattering vector method, where a clear increase of the compressive stresses towards the interface between the layer and the substrate was found in the case of the thicker layer (Fig. 7b). Similar results are reported, for example, in [10]. Hence, it may be assumed that the highest compressive stresses in the present case are concentrated near the interface. This conclusion is supported by the results of the texture analysis. Here, an increase in the texture strength characterized by the intensity ratio $I_{\text{max}}/I_{\text{random}}$ for the 111 - pole figures was observed from 2.66 for the 1.3 µm thick layer up to 6.15 for the 2.3 µm thick layer, which indicates that the texture only develops during the deposition. Thus, the texture may be assumed to exist in form of a gradient over the layer thickness, which can explain the distribution of the stresses, because a strong texture is generally assumed to reduce the residual stresses due to the preferred orientation of the crystallites which lowers their mutual distortion.

In the case of the Ti$_{0.66}$Cr$_{0.15}$N - layers, significant differences in the depth profiles of the Laplace stresses were found between those layers deposited under homogeneous conditions with respect to the process pressure (samples K41 and K49, Fig. 6b,c) and the layer, which was produced with variation of the process pressure during the deposition (sample K12, Fig. 6a). In the latter case, a clear decrease of the compressive Laplace stresses towards the interface between layer and substrate was observed. This result confirms former investigations performed at Ti$_{0.66}$Cr$_{0.15}$N - layers, which were deposited under constant process pressures of 0.4 Pa, 0.8 Pa and 2.0 Pa, respectively. In these layers, the microhardness as well as the lattice parameter $d_{111}$ perpendicular to the surface were found to increase remarkably with the process pressure [30], which is a hint for its direct relation to the compressive in-plane stresses in this case.

Furthermore, it is interesting to note that the values of the lattice spacings for the Ti$_{0.66}$Cr$_{0.15}$N- layers at $\psi = 35^\circ$, which corresponds approximately to the strain-free direction of a biaxial stress state of rotational symmetry, are significantly larger than the $d_0$ of 0.4227 nm calculated from the corresponding values of TiN and CrN. A triaxial stress evaluation by means of eq. (6), however, revealed only tensile stresses up to 150 MPa for $\sigma_{33}$, which are only of minor importance in the present case and cannot be the reason for the large lattice spacings. Therefore, they should mainly be attributed to the widening effect caused by interstitial atoms within the crystal lattice, which was investigated, for example, in [31].
Conclusions

By the examples of PVD - coatings of TiN as well as Ti\(_{0.85}\)Cr\(_{0.15}\)N, the scattering vector method has proven to be suitable for the detection of even strongly non-uniform residual stress distributions in thin and highly textured layers. Compared with the sin\(^2\)\(\psi\) - based methods in X-ray stress gradient analysis, its main advantage with respect to the problems involved in thin film research consists in the possibility to measure the lattice spacing depth distributions even at fixed positions (\(\varphi,\psi\)) of the scattering vector in the sample reference system, which should be the intensity poles of the texture.

The extrapolation of the stress state towards the free surface represents one of the most difficult problems in X-ray stress gradient analysis. In order to minimize the uncertainties involved in this procedure, \(\tau\) should be kept as small as possible. This can be realized in grazing incidence geometry, which requires in the case of the scattering vector goniometry an excellent in-plane as well as out-of-plane resolution of the incoming beam. Therefore, use should be made of synchrotron radiation, since it provides both, a small beam divergence and intensities, which are some orders of magnitude higher than those of conventional X-ray tubes.

Acknowledgment

The author is obliged to Dipl.-Phys. K. Klein for the provision of the samples. Financial support of the German Research Foundation (DFG) for the investigations is gratefully acknowledged.

References

12  Ch. Genzel, phys. stat. sol. (a) 146, 629 (1994).