Origin and Measurement of Stresses in Thin Layers

J.-D. Kamminga
Stellingen behorend bij het proefschrift

**Origin and Measurement of Stresses in Thin Layers**

door J.-D. Kamminga

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2. Difractie spanningsanalyse kan betrouwbaarder worden verricht op basis van de mechanische elastische constanten dan op basis van de difractie elastische constanten (zie hoofdstuk VI van dit proefschrift).

3. In de spanningsanalyse van een eenfasiëge gesputterde laag kan het van nut zijn de laag als een composiet te beschouwen (zie hoofdstukken II en IV van dit proefschrift).

4. Voor de slijtage-eigenschappen van dunne keramische lagen op gereedschappen voor omvormende bewerkingen zijn de spanningen in de lagen van onderschikt belang.

5. De onlangs ingevoerde salarisverhoging van promovendi aan de TU Delft zal leiden tot beter promotieonderzoek.

6. De rechtsongelijkheid van arm en rijk in Nederland zou afnemen als advocaten standaardtarieven in rekening zouden brengen, zoals dat nu bijvoorbeeld al het geval is bij tandartsen.

7. Het verlagen van het abstractieniveau maakt een probleem niet noodzakelijkerwijs eenvoudiger. Zo is het twijfelachtig of de recente vervanging van "plus" door "erbij" in het basisonderwijs de rekenkunst van de basisscholier zal verbeteren.

8. Het feit dat het geboortedorp van Hielke en Sietse Klinkhamer niet bestaat, zou een les moeten zijn voor archeologen die op zoek zijn naar de resten van Troje.

H. de Roos, *Op reis met de Kameleon*, Uitgeverij Kluitman Alkmaar BV.

9. De uitdrukking *al ons weten is stukwerk* wordt treffend geïllustreerd met het financiële verdeelmodel zoals dat binnen de TU Delft wordt toegepast.
Origin and Measurement of Stresses in Thin Layers

Proefschrift

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Chapter I

General introduction

Thin layers are often applied to improve the surface properties of materials. For example: tools for the processing of materials can be covered with a thin ceramic surface layer to enhance the wear resistance. Thereby service life is increased. As the (mechanical) properties of the tool are determined to a large extent by the properties of the layer, there is a large need to understand the properties of thin layers in a fundamental way. One of the characteristic features of thin layers that has large effects on their properties is the occurrence of large residual stresses. This thesis is devoted to the analysis and understanding of stress in thin layers.

Stress can cause a film to crack, in the case of tensile stress, or to peel off, in the case of compressive stress (see Figs. 1,2). On the other hand, if a tool during use is e.g. loaded by external tensile forces, a pre-engineered compressive residual internal stress may prevent the layer from cracking. This illustrates that it is important to be able to predict and to control the stress in thin layers.

From a scientific point of view, stresses in thin layers are also particularly interesting. Stress values measured in thin layers are often much higher than those encountered in bulk materials. Substantial numbers of publications considering the origin and the measurement of the stress in thin layers exist. However, these investigations have not yet led to satisfactory quantitative models for the stress. Only if the stress is of only thermal origin (see below), measured stress values could be explained quantitatively (e.g. see Ref. [1]). In particular the origins of so-called growth stresses, that develop during growth, are not well understood.

Part I of the current thesis aims to arrive at a better understanding of the stress in thin layers.

![Crack pattern in a CVD TiN layer on Mo. The cracks are caused by tensile stress in the layer (top view, taken from Ref. [1]).](image)

Fig.1: Crack pattern in a CVD TiN layer on Mo. The cracks are caused by tensile stress in the layer (top view, taken from Ref. [1]).
Fig. 2: Blistering of a magnetron sputtered TiN layer on silicon, caused by compressive stress in the TiN layer (top view).

Distinction is made between thermal stress and growth stress. Because the thermal expansion coefficients of the thin layer and the substrate are in general different, any change in temperature induces a misfit between the substrate and the thin layer that, if the substrate can be considered as infinitely thick, is accommodated by the thin layer. The corresponding thermal stress in the layer is quantitatively understood. The difference between the total stress and the thermal stress is called growth stress. The sign and size of the growth stress strongly depends on the process used for thin layer deposition.

Stresses in two types of thin layers have been investigated, namely magnetron sputtered TiN layers and evaporated Ni layers.

Growth stress parallel to the surface in sputtered layers is often of compressive nature and can be extremely high. It has been suggested that such compressive growth stress is due to the energetic bombardment, by ions and/or atoms, of the growing surface of the layer during deposition. The impinging particles get trapped or shoot surface atoms deeper into the confined layer, thus causing compressive stress. This mechanism has been called atomic peening [2] (see Fig. 3). The results of an investigation of a set of magnetron sputtered TiN layers are presented in Chapters II, III and IV. A model is proposed that describes the state of stress in thin layers as induced by the trapped particles (Chapter II). Predictions from the model are experimentally validated. The stress depth profile that is present in the layers has been determined (Chapter III). A quantitative description of the type and number of the trapped particles in the TiN layers is given in Chapter IV.

Growth stress parallel to the surface in evaporated layers is often of tensile nature. Such growth stress is thought to be due to porosities at an atomic scale in the layer. The attractive interatomic forces acting across the porosities would lead to the tensile stress [3]. In a layer with a columnar microstructure (see Fig. 4), the grain-boundaries, that are perpendicular to the surface, act as aggregates of tensile stress causing porosities: the columns attract each other [4].
Clearly, strong elastic interaction of the grains occurs in the in-plane directions of a layer with tensile stress (without this interaction significant tensile stress would impossible). However, due to the space between the columns of the layer the columns are believed to be (more or less) free to move in a direction perpendicular to the layer surface, independent of each other. Thus elastic interaction between the columns can be neglected in the direction perpendicular to the surface. This direction dependence of the elastic interaction is indeed found for the evaporated Ni layers investigated in this work (Chapter V).

X-ray diffraction, the experimental technique mainly used to characterise the thin layers in the current thesis, is treated in detail in Chapter V and in Part II of this thesis. Due to the very high precision at which lattice spacings can be measured with X-ray diffraction, strains in the investigated specimens can be revealed. For polycrystalline materials of which the crystallites are elastically anisotropic, the interpretation of the strains measured with diffraction in terms of macroscopic stress is however by no means straightforward.

Elastic anisotropy implies that the elastic behaviour is different for different directions in the crystal (see Fig. 5); there are relatively stiff and relatively compliant directions in the crystal. For example, in cubic materials the <111> and <100> are the most stiff and the most compliant directions, respectively, or vice versa. X-ray diffraction is very sensitive to these differences

---

**Fig. 3: Schematic representation of the atomic peening mechanism.** a) Atoms and ions advance to and hit the surface of the growing layer and b) knock surface atoms in the confined layer, and/or get trapped in the growing layer.
Fig. 4. Schematic representation of a layer with a columnar microstructure. The attractive interatomic forces acting across the grain-boundaries (arrows) are believed to cause tensile stress parallel to the surface; the interaction of the grains in the in-plane directions is large. However, because of the space between the columns, the elastic interaction in directions perpendicular to the layer surface can be neglected.

Because each measured lattice spacing refers to a specific (set of) crystallographic direction(s) $<hkl>$.

Apart from the above mentioned $hkl$ dependency of the strains in a single crystal, the elastic anisotropy also brings about that the corresponding strains in the differently oriented crystallites of a (massive) polycrystalline material, as induced by a given macrostress (i.e. the mechanical stress imposed on the aggregate of crystals) are different.

Because the measured strain depends on the $<hkl>$ reflection used in the diffraction experiment, the measured strain is not a direct measure for the macroscopic (mechanical) strain. This complicates the interpretation of the measured strains in terms of (macro) stress. The calculation of the stress from the reflection dependent strains must be performed using the so-called diffraction elastic constants, which are different for different $hkl$. If, for the specimen to be investigated, the diffraction elastic constants have been determined experimentally, the stress can be accurately calculated from the measured strain. However, in most cases the diffraction elastic constants must be calculated from the single crystal elastic constants by use of a grain interaction model [5,6]. This calculation involves assumptions for the elastic interaction of the differently oriented grains. These assumptions are in general not justified: the actual grain interaction depends on the microstructure of the specimen concerned. Thus, the use of such calculated diffraction elastic constants can lead to unreliable stress values.

New methods for diffraction stress analysis are presented in Chapter VI. These new methods involve stress analysis on the basis of mechanical elastic constants. Mechanical elastic constants can be measured more easily than diffraction elastic constants and, if they have to be calculated
Fig. 5: Diffraction can be used to measure lattice spacings that belong to specific directions \(<hkl>\) in the crystal. As an example, two \((111)\) lattice planes are depicted in a cubic crystal structure (shaded). Using diffraction it is possible to measure the distance between the successive \((111)\) lattice planes in the \([111]\) direction: the lattice spacing \(d^{(111)}\).

from the single crystal elastic constants, the values obtained are not very sensitive to the assumptions used for the elastic interaction of the differently oriented crystallites, in contrast with the diffraction elastic constants. Also in contrast with the diffraction elastic constants, theoretical upper and lower boundaries can be given for the mechanical elastic constants [7]. Hence methods for stress analysis on the basis of mechanical elastic constants provide several advantages.

One of the diffraction methods of stress analysis proposed in Chapter VI is compared in Chapter VII with the so-called bending foil measurement [8,9] for an investigation of stress in a series of magnetron sputtered TiN layers. In the bending foil measurement a layer is deposited on a foil. The stress in the layer causes the foil to bend. From the radius of curvature of a strip taken from the foil, the stress in the layer can be deduced. Combining the result of the bending foil stress measurement with the result of the diffraction stress measurement allows determination of Young’s modulus of the TiN layer.

Finally, a practical problem that often occurs performing X-ray diffraction experiments with thin layers on substrates is dealt with in Chapter VIII. Because the information depth of the diffraction experiment is typically of the order of the layer thickness, the diffraction patterns obtained consist of diffraction peaks of both the layer and the underlying substrate. The associated peak overlap in the diffraction pattern recorded can hinder an accurate evaluation of the parameters of the diffraction peaks of the layer. A method is given by which the substrate peaks are removed from the diffraction pattern of the \((\text{layer/substrate})\) specimen, employing a separate measurement of the uncovered substrate.
References


Chapter II

A model for stress in thin layers induced by misfitting particles

An origin for growth stress

J.-D. Kamminga, Th.H. de Keijser, R. Delhez, E.J. Mittemeijer

ABSTRACT
The stress caused by misfitting particles in thin layers adherent to substrates is modelled. The model assumes an elastically isotropic matrix with holes in which the misfitting particles are introduced. The stress field generated in the matrix consists of a hydrostatic stress resulting directly from the misfitting particles and a biaxial state of stress resulting from the condition that the layer should remain attached to its substrate. The model and its implications for diffraction stress measurements are illustrated using magnetron sputtered TiN layers.

I. Introduction

Although residual stress in thin layers is widely researched, only thermal stress in supported thin layers is fully understood. Much is unclear about other types of stress. In sputtered layers often high compressive stresses exist which are ascribed to the implantation of sputter gas atoms and self interstitials [1]. A quantitative understanding of the stress caused by such particles has not yet been obtained. In this paper the volume change in a body of finite size caused by misfitting particles as calculated by Eshelby [2] is used to model stresses in thin layers containing misfitting particles.

II. Model

The stresses occurring in a supported layer with misfitting particles are calculated in two steps (see Fig. 1). Starting from a free-standing, strain-free, hole containing layer of equal lateral dimensions as the substrate, the stress and volume change caused by introducing particles into the holes are derived. Secondly, the stress required to fix the expanded layer onto its substrate is calculated.

A. Stress and volume change caused by misfitting particles in a matrix
The theory suitable for this problem is fully explained in [3].
1. One particle in an infinite matrix

An elastically isotropic matrix $M$ of infinite size containing a spherical hole is considered. The insertion of a spherical misfitting particle $P$ causes a radial displacement in the infinite matrix of:

$$w^\omega_M(r) = \frac{C^\omega}{r^2}$$  \hspace{1cm} (1)

where $r$ is the distance from the centre of the particle and $C^\omega$ is given by:

$$C^\omega = \frac{3\epsilon r^3_M K_P}{3K_P + \frac{2E}{1+\nu} \frac{r^3_M}{r^3_M+P}}$$  \hspace{1cm} (2)

where $r_M$ is the radius of the hole before and $r_{M+P}$ the radius of the hole after insertion of the particle. The misfit is given by $\epsilon = (r_p - r_M) / r_M$ where $r_p$ is the particle radius before insertion. $E$ is the Young's modulus of the matrix and $\nu$ is its Poisson ratio. $K_P$ denotes the bulk modulus of the particle. The effective bulk modulus of particles of atomic size is not known. Although the theory is believed to hold for particles of atomic scale, $C^\omega$ can only be calculated from the elastic constants of bulk materials for relatively large particles.

From spherical symmetry and using Eq. (1), it follows for the dilatation of the infinite matrix:

$$\Delta^\omega_M = \frac{\partial w^\omega_M}{\partial r} + 2\frac{w^\omega_M}{r} = 0$$  \hspace{1cm} (3)

$\sigma_M = 0$  \hspace{2cm} $V$

$\sigma_M = \sigma^h_M$  \hspace{2cm} $V + \Delta V$

$\sigma_M = \sigma^h_M + \sigma^{fs}_M$

**Fig. 1:** Steps involved in the calculation of stresses in a matrix $M$ of a layer on a substrate containing misfitting particles. Step 1: introduction of particles into holes of a free-standing originally strain-free layer of lateral dimensions equal to those of the substrate. Step 2: fixing the expanded layer onto its substrate.
The stress in the radial direction obeys:

\[ \sigma^r_M(r) = \frac{2E}{1 + \nu} \frac{C^w}{r^3} \]  \hspace{1cm} (4)

On inserting the particle \( P \) into the hole in the infinite matrix \( M \), the volume within a closed surface that completely surrounds the hole increases by:

\[ \Delta V_{M+P} = 4\pi C^w \]  \hspace{1cm} (5)

which is independent of the size and shape of the closed surface.

2. One particle in a finite matrix

In a finite matrix the above does not hold because the stress normal to the free surface must be zero. To obtain the state of stress in a finite matrix a set of 'image' stresses is added to the stresses in the infinite matrix (Eq. (4)) such that a zero surface traction is obtained. For a spherical matrix of radius \( R \), it follows from Eq. (4) that a uniform hydrostatic stress \( \sigma' = -\sigma^r_M(R) \) has to be applied. This stress corresponds to a uniform dilatation of the matrix \( M \) and of the particle \( P \) (neglecting perturbations by the different elastic constants of particle and matrix):

\[ \Delta' = \Delta'_M = \Delta'_P = \frac{6(1 - 2\nu)}{1 + \nu} \frac{C^w}{R^3} \]  \hspace{1cm} (6)

For the volume change of the spherical system (= matrix + particle) caused by the image forces one obtains:

\[ \Delta V^{i}_{M+P} = \frac{4}{3} \pi R^3 \Delta' = \frac{2(1 - 2\nu)}{1 + \nu} 4\pi C^w \]  \hspace{1cm} (7)

The total volume change \( \Delta V^{i}_{M+P} \) of a finite spherical matrix containing one misfitting particle follows from Eqs (5) and (7):

\[ \Delta V^{i}_{M+P} = \Delta V^w_{M+P} + \Delta V^i_{M+P} = \frac{3(1 - \nu)}{1 + \nu} 4\pi C^w \]  \hspace{1cm} (8)

3. Many particles in a finite matrix

For a finite body of arbitrary shape containing a homogeneous distribution of \( n \) misfitting particles per unit volume the fractional change in volume of the body (= matrix + \( n \) particles) equals [2]:

\[ \]
\[
\left( \frac{\Delta V}{V} \right)_{\text{body}} = \frac{3(1-\nu)}{1+\nu} 4\pi n C^- \quad (9)
\]

and the dilatation of the matrix equals:

\[
\Delta_M = \frac{2(1-2\nu)}{1+\nu} 4\pi n C^-
\quad (10)
\]

Eqs (9) and (10) do not follow straightforwardly from Eqs (8) and (7).

The hydrostatic stress in the matrix of an (unbounded) finite body of arbitrary shape containing \( n \) misfitting particles per unit volume follows from Eq. (10):

\[
\sigma^h_M = \frac{E}{1-2\nu} \cdot \frac{\Delta_M}{3} = \frac{2E}{3(1+\nu)} 4\pi n C^-
\quad (11)
\]

**B. Stresses caused by fixing the expanded layer onto the substrate**

When the volume increase given by Eq. (9) is isotropic the layer has to undergo a lateral compression of \(-\frac{1}{3} (\Delta V/V)_{\text{body}}\) to match the substrate. Ignoring differences in elastic properties of matrix and particles, this compression corresponds to a rotationally symmetric biaxial state of stress in the matrix of the layer characterised by (see Eq. (9)):

\[
\sigma^{\text{fix}}_M = -\frac{E}{1-\nu} \cdot \frac{1}{3} \left( \frac{\Delta V}{V} \right)_{\text{body}} = -\frac{E}{1+\nu} 4\pi n C^-
\quad (12)
\]

From Eqs (11) and (12) it follows:

\[
\sigma^{\text{fix}}_M = -\frac{3}{2} \sigma^h_M
\quad (13)
\]

Eq. (12) is not necessarily always valid. When e.g. the growth of precipitates in a layer is the stress generating mechanism, the growth may be such that the spherical symmetry of the elastic problem is infringed and the necessary compression to match the layer to the substrate will not follow from Eqs (9) and (12).

**III. X-ray diffraction analysis**

To measure stresses by diffraction the \( \sin^2 \psi \) method is often used [4]. The lattice spacing \( d_\psi \) at an angle \( \psi \), where \( \psi \) is the angle between the specimen surface and the reflecting lattice plane, is used as an internal strain gauge. For \( \sigma^{\text{fix}}_M \) and \( \sigma^h_M \) together with a thermal stress \( \sigma^h_M \) (\( \sigma^{\text{fix}}_M \) and
$\sigma_M^{th}$ represent rotationally symmetric biaxial states of stress) the relation between the lattice spacing of the isotropic matrix $d_{M0}$ and $\sin^2 \psi$ is:

$$d_{M\psi} - d_{M0} = d_{M0} \left[ \frac{1 + v}{E} (\sigma_M^{fs} + \sigma_M^{th}) \sin^2 \psi - \frac{2v}{E} (\sigma_M^{fs} + \sigma_M^{th}) + \frac{1 - 2v}{E} \sigma_M^{th} \right]$$  (14)

where $d_{M0}$ is the lattice spacing of the strain-free matrix. By use of Eq. (13), Eq. (14) can be written with two stress parameters instead of three. The above form represents clearly the different contributions to the stress field. A plot of $d_{M\psi}$ versus $\sin^2 \psi$ yields a straight line and from its slope and intercept with the $d_{M\psi}$ axis, together with Eq. (13), the stresses $\sigma_M^{th}$, $\sigma_M^{fs}$ and $\sigma_M^{th}$ are obtained provided $v$, $E$ and $d_{M0}$ are known.

The value of $d_{M0}$ poses a serious problem in the analysis. Small errors in it introduce large errors due to the small difference between $d_{M\psi}$ and $d_{M0}$ on the left-hand side of Eq. (14) (a small error in $d_{M0}$ occurring in the slope of the $\sin^2 \psi$ curve is of little importance). Even if a literature value for $d_{M0}$ is available one still has to consider the errors in the $d_{M\psi}$ values originating from the instrumental aberrations. One has either to correct $d_{M\psi}$ or to measure $d_{M0}$ at each $\psi$ from a strain-free specimen.

Next some properties of Eq. (14) are discussed which can be of help in the stress analysis.

Actions of the stresses in Eq. (14) are illustrated in Fig. 2. A strain-free matrix yields a lattice spacing $d_{M0}$ for every $\psi$ (line I in Fig. 2). The hydrostatic stress $\sigma_M^{th}$ causes at every $\psi$ the same change in lattice spacing (line II).

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**Fig. 2: Graphical illustration of Eq. (14); see also text.**
\[
\sin^2 \psi_A = \frac{2\nu}{1 + \nu} \tag{15}
\]

the first two terms at the right-hand side of Eq. (14) cancel and
\[
d_{\nu_A} = d_{\nu_0} + d_{\nu_0} \frac{1 - 2\nu}{E} \sigma_M^{th} \tag{16}
\]

independent of \(\sigma_M^{fs}\) and \(\sigma_M^{th}\).

\(\sigma_M^{fs}\) gives an inclined line in the \(\sin^2 \psi\) plot, which can be thought to originate from line II by a rotation around point A (line III). Analogously, \(\sigma_M^{th}\) causes a further rotation around point A (line IV, which represents Eq. (14)). For the \(\sin^2 \psi\) value of point \(C\) the contributions of \(\sigma_M^{th}\) and \(\sigma_M^{fs}\) to \(d_{\nu_0} - d_{\nu_0}\) annul; by use of Eq. (13) it follows from Eq. (14):
\[
\sin^2 \psi_C = \sin^2 \psi_C = \frac{2}{3} \tag{17}
\]

It is noticed that \(d_{\nu_0}\) at point \(C\) on line IV is solely determined by \(\sigma_M^{th}\). In the absence of thermal stresses, the strain-free lattice spacing \(d_{\nu_0}\), can be read directly from the \(\sin^2 \psi\) curve at \(\psi = \psi_C\).

Point \(B\) on line IV occurs for the strain-free direction \(\psi_0\), where \(d_{\nu_0} = d_{\nu_0}\) independent of any of the stresses. It follows from Eq. (14) and Eq. (13):
\[
\sin^2 \psi_0 = \frac{2\nu(\sigma_M^{fs} + \sigma_M^{th}) - (1 - 2\nu)\sigma_M^{th}}{(1 + \nu)(\sigma_M^{fs} + \sigma_M^{th})} = \frac{2\nu\sigma_M^{th} - (1 + \nu)\sigma_M^{th}}{(1 + \nu)\sigma_M^{th} - \frac{3}{2}(1 + \nu)\sigma_M^{th}} \tag{18}
\]

\(d_{\nu_0}\) can be determined from Eq. (18) if \(\sigma_M^{th}\) is known. Then, \(\sin^2 \psi_0\) can be calculated from the slope of the \(\sin^2 \psi\) curve, giving \(\sigma_M^{fs} + \sigma_M^{th}\), and from \(\sigma_M^{th}\) as deduced from the slope by use of Eq. (13). Note that, if \(\sigma_M^{th}\) is known \(d_{\nu_0}\) need not to be known accurately because \(\sigma_M^{fs}\) and \(\sigma_M^{th}\) can then be determined directly using only the slope of the \(\sin^2 \psi\) curve and Eq. (13).

With a series of layers all having the same (unknown) thermal stress but different misfitting-particles induced stresses, extra possibilities arise.

(i) All \(\sin^2 \psi\) curves intersect at \(\sin^2 \psi = 2/3\) (see below Eq. (17)). This can be used as a check for the applicability of the present model.

(ii) For the slope \(S\) of the \(\sin^2 \psi\) curve (see Eq. (14)) one can write, using Eqs (13) and (16):
\[
S = d_{\nu_0} \left[ \frac{1 + \nu}{E} \sigma_M^{th} + \frac{3(1 + \nu)}{2(1 - 2\nu)} \right] - \frac{3(1 + \nu)}{2(1 - 2\nu)} d_{\nu_0} \tag{19}
\]
By plotting $S$ versus $d_{M\psi_A}$ in theory one can determine $\sigma^b_M$ from the intercept with the $S$ axis of the straight line fitted to the data points. Small errors in $d_{M0}$ do not cause serious errors in the stress. Unfortunately the procedure delivers a very inaccurate value for $\sigma^b_M$ because $\sigma^b_M$ has to be determined by the subtraction of two large numbers (the intercept and $d_{M0}3(1+\nu)/2(1-2\nu)$), of which the intercept contains a relatively large error (the range of $d_{M\psi_A}$ values available is always very small as compared to the distance to the origin). Yet the slope of the line can serve to check the value of $\nu$ used in the data evaluation.

IV. Experimental illustration

Magnetron sputtered TiN layers are used to illustrate the model. These layers are known to possess high growth stresses, believed to be induced by argon implantation and/or self interstitials [1].

Five pairs of layers with thicknesses of 1.0, 2.0, 3.0, 4.0 and 6.2 μm were deposited onto (i) high-carbon high-chromium cold work tool steel and (ii) WC based cermet substrates, using identical sputter parameters for all layers. Argon was used as sputter gas. The nitrogen pressure

![Graph showing $\sin^2\psi$ plots of TiN layers of different thicknesses deposited on tool steel and cermet substrates. The error in the $d_\psi$ values equals 0.02 pm. The dotted lines represent linear least squares fits forced to intersect at $\sin^2\psi = 2/3$.](image_url)

Fig. 3: $\sin^2\psi$ plots of TiN layers of different thicknesses deposited on tool steel and cermet substrates. The error in the $d_\psi$ values equals 0.02 pm. The dotted lines represent linear least squares fits forced to intersect at $\sin^2\psi = 2/3$. 

13
during deposition, and thus the stoichiometry of the TiN was controlled by monitoring optical emission of the plasma during deposition. The substrate temperature was about 350 °C (for details see [5,6]).

X-ray diffraction measurements were performed employing CuKα radiation. Positions of the TiN 422 peaks were determined after isolating the {422} reflection from diffractograms by means of a profile fitting program (reflections overlap, see [6]). Different slopes of the \( \sin^2 \psi \) curves were found for layers of equal thickness on different substrates and also for layers of different thickness on the same substrate (see Fig. 3). Because layers of equal thickness were deposited simultaneously onto the two substrates the growth stresses of the layers in a thickness pair are expected to be identical and then the difference in slope is due to a difference in thermal stress. Therefore \( \sin^2 \psi \) curves of each layer pair should intersect at \( \sin^2 \psi_A = 2v/(1+v) \) (see Eqs (15) and (16)). From the five intersections it is obtained \( v = 0.24 \pm 0.02 \), which seems a reasonable value (cf. [7]). From the difference of the slopes of the \( \sin^2 \psi \) curves of each pair, the difference in linear thermal expansion coefficients \( \Delta \alpha \) of the substrates can be obtained (see Eq. (14) and [11]). It is found that \( \Delta \alpha = (7.6 \pm 0.6) \times 10^{-6} \text{K}^{-1} \), which compares well with the ranges of \( \alpha \) reported for the substrates [8,9]. From these two findings it is concluded that layers of equal thickness indeed exhibit the same growth stress and that the thermal stress is the same for all layers on the same substrate.

Hence for layers deposited on the same substrate differences in slopes of the \( \sin^2 \psi \) curves (see Fig. 3) are due to (yet not understood) differences in growth stress. \( \sin^2 \psi \) curves for layers on the same substrate should therefore intersect at \( \sin^2 \psi_c = 2/3 \) (cf. Eq. (17)). On this basis the full lines in Fig. 3 were obtained. The lines fit the data to within experimental error. Hence the proposed model may be applicable to the present layers. This is stated prudently since in the model it is assumed that plastic deformation is absent and that the strain-free lattice spacing of all layers is the same, which it is difficult to verify in this case.

Anxw, the proposed model offers an explanation for an effect that is often observed but hitherto not understood: for differently stressed layers of the same material \( \sin^2 \psi \) curves do not intersect at the naively expected \( \sin^2 \psi \) value for the strain-free direction (here \( 2v/(1+v) \); cf. Eq. (15)) but at a significantly higher value (as \( \sin^2 \psi_c \); cf. Eq. (17)).

References


Chapter III

Stress and stress gradients in magnetron sputtered TiN layers

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ABSTRACT
Magnetron sputtered TiN layers of various thicknesses have been deposited using equal deposition parameters. By a comparison of X-ray diffraction measurements from layers deposited simultaneously on two different substrate materials the Poisson ratio of the TiN layer material has been determined. Comparison of stresses in layers of different thicknesses suggested the presence of stress gradients. The state of stress could be described accurately by a depth independent thermal stress and a depth dependent, substrate independent, growth stress. Several expressions for the depth dependence of growth stress have been evaluated. The results obtained agree with a recently proposed model according to which the state of growth stress consists of a compressive biaxial component and a tensile hydrostatic component.

I. Introduction

Compressive growth stress in sputtered thin layers is commonly ascribed to atomic peening [1]. With this mechanism in mind, a model has been proposed recently [2] that describes the state of stress in a thin layer on a substrate as obtained by inserting misfitting particles into the thin layer. The state of stress was shown to consist of a tensile hydrostatic component and a compressive planar component. Experiments corresponded well with the model, but also revealed that the stress depends on layer thickness. This paper provides an analysis of this thickness dependence assuming stress gradients to be present in these layers using X-ray diffraction (XRD) measurements. The results are discussed in terms of the model mentioned.

II. Theory

For elastically isotropic and homogeneous material subjected to (i) a rotational symmetric state of stress characterised by the stress $\sigma_{\parallel} (= \sigma_{11} = \sigma_{22})$, parallel to the specimen surface, and (ii) a hydrostatic state of stress characterised by the stress $\sigma^h$, it can be shown [3]:

$$\frac{d\psi - d_\lambda}{d_{\text{ref}}} = \sigma_{\parallel} \left[ \frac{1 + \nu}{E} \sin^2 \psi - \frac{2\nu}{E} \right]$$

(1a)
with

\[
\frac{d_A - d_x}{d_{ref}} = \sigma^a \frac{1 - 2\nu}{E}
\]  

(1b)

where \(d_x\) denotes the spacing of the diffracting lattice planes inclined at an angle \(\psi\) to the surface of the specimen, \(\nu\) is the Poisson ratio and \(E\) is Young’s modulus. The spacing \(d_x\) is the strain-free lattice spacing of the material; \(x\) refers to the material composition, which is allowed to vary in this paper. Unlike to what is common use in XRD stress analysis a reference spacing \(d_{ref}\), which is permitted to deviate somewhat from \(d_x\), is introduced in order to obtain a tractable method of analysis. With \(d_x\) varying, \(d_{ref}\) will be taken constant at a value very close to the values occurring for \(d_x\) and therefore the deviations in the stresses to be determined will be very small (see Eqs (1a) and (1b)). Note that once true strains are not used (as in the above equations), small errors in the strain (i.e. left-hand side of Eqs (1a) and (1b)) are involved anyway.

When a set of \(d_x\) values is obtained for various tilt angles \(\psi\) from a specimen with a constant \(d_x\), it follows from Eqs (1a) and (1b) that a plot of \(d_x\) versus \(\sin^2 \psi\) yields a straight line with slope \(d_{ref} \sigma^a (1 + \nu)/E\).

Now a thin layer on a substrate is considered in which \(\sigma_x, \sigma^g\) and the composition \(x\) are a function of \(z\), the distance from the substrate-layer interface into the layer. If \(x\) varies with \(z\), then \(d_x\), \(\nu\) and \(E\) may also vary with \(z\). For the moment the \(z\) dependencies of \(\nu\) and \(E\) are ignored.

The X-ray averaged (= measured) lattice spacing \(\langle d \rangle_x\) for a layer of thickness \(D\) containing a lattice spacing \(d_x\) varying with \(z\) (\(z = D - \tilde{z}\)) can be calculated by:

\[
\langle d \rangle_x = \frac{1}{D} \int_0^D d_x(z) e^{-\mu z} dz = \frac{\mu k}{e^{\mu D} - 1} \int_0^D d_x(z) e^{\mu z} dz
\]  

(2)

where \(\mu\) is the linear absorption coefficient and \(k\) denotes a geometry factor, which for an \(\omega\)-type diffractometer reads: \(k = 2 \sin \theta \cos \omega / (\sin^2 \theta - \sin^2 \omega)\), where \(\theta\) is the Bragg angle and, for the present geometry, \(\omega\) equals \(\psi\) (see [4]). From Eq. (1a) one then obtains:

\[
\langle d \rangle_x = \langle d_A \rangle + \langle \sigma_x \rangle d_{ref} \left[ \frac{1 + \nu}{E} \sin^2 \psi - \frac{2\nu}{E} \right]
\]  

(3a)

where \(\langle d_A \rangle\) and \(\langle \sigma_x \rangle\) denote an averaging analogous to that of \(d_x\) (see Eq. (2)). On the basis of Eq. (3a), supposed functions for the dependencies of \(d_A\) and \(\sigma_x\) on \(z\) can be tested on a set of measured \(\langle d \rangle_x\) values for various \(\psi\) and \(D\).

From Eq. (1b) it follows for the X-ray averaged value of \(d_A:\)
\[ <d_A> = <d_i> + <\sigma^h> d_{nf} \frac{1-2\nu}{E} \]  

(3b)

However, to avoid too many parameters in the testing, instead of separate functions for \(d_i\) and \(\sigma^h\) only (overall) functions for \(d_A\) were applied. These functions are analysed afterwards from the point of view expressed in Eq. (3b).

The thermal misfit imposed at the layer-substrate interface e.g. by cooling down from deposition temperature \(T_{dep}\) to room temperature \(T_{room}\), leads to a biaxial state of stress \(\sigma^{th}\) in the thin layer, that in case all misfit is elastically absorbed by the elastically isotropic thin layer is given by:

\[ \sigma^{th} = \frac{E}{1-\nu} (\alpha_s - \alpha_L)(T_{room} - T_{dep}) \]  

(4)

where \(\alpha_s\) and \(\alpha_L\) are the linear thermal expansion coefficients of substrate and layer respectively. The depth independent thermal stress \(\sigma^{th}\) contributes to \(<\sigma_i>\) in Eq. (3a).

### III. Experimental

Detailed descriptions of the deposition process and the XRD measurements are given in [5].

Five pairs of TiN layers with thicknesses of 1.0, 2.0, 3.0, 4.0 and 6.2 µm were magnetron sputtered on (i) high-carbon high-chromium cold work tool steel and (ii) WC based cermet substrates, using identical sputter parameters for all layers and deposition times of 15, 30, 45, 60 and 90 min. Layers of equal thickness were deposited at about 620 K simultaneously on the

![Graph showing TiN on tool steel and TiN on cermet](image)

Fig. 1: \([422]\) X-ray averaged lattice spacings \(<d>_\psi\) versus \(\sin^2\psi\) for TiN layers of various thicknesses deposited on a tool steel and a WC based cermet. Dotted lines represent the fit assuming exponential depth dependencies (see text).
two types of substrate. XRD measurements were performed employing CuKα radiation for which the linear absorption coefficient \( \mu \) of TiN is 8.26·10⁴ m⁻¹. Values for the TiN \{422\} lattice spacings \(<d>\) were obtained using Bragg's law, after isolating the \{422\} reflection from the diffractograms by means of a profile fitting program, because of overlap with substrate reflections. The thinnest of the layers (1.0 \( \mu \)m) was annealed successively for 15 min and 60 min at 620 K using nitrogen (99.998% pure) as protective gas.

**IV. Results**

The experimental values for the \{422\} lattice spacings \(<d>\) are plotted as a function of \( \sin^2 \psi \) in Fig. 1 for the two types of substrate.

The cooling of the layer-substrate assemblies from the deposition temperature to room temperature will induce thermal stresses. Because of the difference in linear thermal expansion coefficient for the two types of substrate (\( \Delta \alpha_{SS} \)) the layers deposited on the tool steel and the cermet experience different thermal stresses. Since the same state of growth stress should exist in pairs of layers simultaneously deposited on the two substrates, it follows from Eqs (3a) and (4) that plots of the difference of \(<d>\) values versus \( \sin^2 \psi \) for all layer-thickness pairs yield straight lines, that intersect the \( \sin^2 \psi \)-axis at \( \sin^2 \psi = 2 \sqrt{1+\nu} \). The slopes of these lines equal \( d_{ref} \Delta \alpha_{SS}(T_{room}-T_{dep})(1+\nu)/(1-\nu) \), if no relaxation of thermal stresses occurs. The results shown in Fig. 2 for the layers of 3.0, 4.0 and 6.2 \( \mu \)m thickness agree well, which shows that the thermal stress does not depend on layer thickness (the results for the 1.0 \( \mu \)m and 2.0 \( \mu \)m layers are omitted because their \(<d>\) values scatter considerably, which is ascribed to the more pronounced overlap with substrate peaks). From the point of intersection with the \( \sin^2 \psi \)-axis

![Graph showing differences in X-ray averaged \{422\} lattice spacings \( \Delta <d> \) for three layer-thickness pairs versus \( \sin^2 \psi \). The dotted line represents the linear least squares fit (see text).](image)

*Fig. 2: Differences in X-ray averaged \{422\} lattice spacings \( \Delta <d> \) for three layer-thickness pairs versus \( \sin^2 \psi \). The dotted line represents the linear least squares fit (see text).*
of the straight line fitted to these data it is obtained: $v = 0.255 \pm 0.016$, which seems reasonable (see [6]). From the slope of the straight line, using $d_{ef} = 8.657 \cdot 10^{-11}$ m ([7]; see discussion) and the $v$ found it is obtained: $\Delta \alpha_{SS} = (6.2 \pm 0.4) \cdot 10^{-6}$ K$^{-1}$, which agrees with the values reported for the thermal expansion coefficients of the two substrates: $\alpha_{WC} = (4.6-8.9) \cdot 10^{-6}$ K$^{-1}$ and $\alpha_{TS} = (11.9-12.9) \cdot 10^{-6}$ K$^{-1}$ [8,9]. The values for $\sigma_{th}$, calculated from Eq. (4) using $\Delta T_n = 8.6 \cdot 10^{-6}$ K$^{-1}$ [8] and the above values of $\alpha_{TS}$ and $\Delta \alpha_{SS}$, $E = 640$ GPa [6] and $\alpha_{WC} = \alpha_{TS} - \Delta \alpha_{SS}$ (because of the large range reported for $\alpha_{WC}$, see above), are $\sigma^d_{TS} = -1.1$ GPa and $\sigma^{th}_{WC} = 0.7$ GPa for the TiN layers on the tool steel and the cermet respectively.

In view of Eq. (3a) and the value determined for $v$ it can be seen from Fig. 1 that $<\sigma_{\|}>$ and $<d_{\|}> = <d>_{\psi}$ at $\sin^2 \psi = 2v/(1+v) = 0.407$ vary with layer thickness. This effect cannot be ascribed to a relatively more pronounced annealing of the bottom parts of the layers during deposition, because the annealing experiments did not lead to changes in $<d>_{\psi}$ values. Therefore it is assumed that for the layers on the same substrate $\sigma_{\|}$ and $d_{\|}$ are identical for identical distances to the layer-substrate interface. In view of Fig. 1 this implies that the (compressive) stress $\sigma_{\|}$ and the lattice spacing $d_{\|}$ decrease for increasing distance to the substrate-layer interface.

The procedure described below Eq. (3a) has been applied to evaluate several functions assumed for $\sigma_{\|}$ and $d_{\|}$ by fitting to the $<d>_{\psi}$ data obtained for variable $\psi$ and $D$. For $\sigma_{\|}$ and $d_{\|}$ the following functions were applied:

(i): $\sigma_{\|} = A_1 + A_2 \tilde{z}$  
(ii): $\sigma_{\|} = A_1 + A_2 \exp(A_3 \tilde{z})$  
(iii): $d_{\|} = B_1 + B_2 \tilde{z}$  
(iv): $d_{\|} = B_1 + B_2 \exp(B_3 \tilde{z})$

![Graph](image)

**Fig. 3:** Results for the depth dependencies of $\sigma^{growth}$ and $d_{\|}$ as a function of the distance to the substrate-layer interface $\tilde{z}$. Fit results:

$A_1$ (tool steel) = -4.9 GPa, $A_1$ (WC cermet) = -3.0 GPa, $A_2$ = -6.6 GPa,

$A_3 = B_3 = -7.47 \cdot 10^5$ m$^{-1}$, $B_1 = 8.6603 \cdot 10^{-11}$ m, $B_2 = 1.75 \cdot 10^{-13}$ m (see text).
The constant $A_1$ in (i) and (ii) was allowed to take two different values for the two substrates, to take into account the difference in ($\tilde{x}$ independent) thermal stress for the different substrates, whereas $A_2$, $A_3$, $B_1$, $B_2$ and $B_3$ were taken equal for all layers, assuming that the state of growth stress does not depend on the type of substrate. In the fits on the basis of the above functions the error-of-fit, defined as the sum of the squared deviations of measured $<d>_\varphi$ values from the fitted ones, divided by the number of degrees of freedom (= the number of data points minus the number of fit parameters) was minimised.

For each of the four possible combinations of functions (i) to (iv) fits were performed on all measured lattice spacings simultaneously. The four minimised error-of-fit values showed that the best fit was obtained using the exponential behaviours for $\sigma_{//}$ and $d_A$, which was also clear from visual inspection of the resulting plots. This fit yielded almost equal values for $A_3$ and $B_3$. Consequently the same quality of fit could be obtained by taking $A_3 = B_3$ (note that equality of $A_3$ and $B_3$ implies a linear relation between $\sigma_{//}$ and $d_A$). The resulting fit and the corresponding depth profiles for the biaxial component of the growth stress ($\sigma_{\text{growth}} = \sigma_{//} - \sigma_{\text{th}}$) and $d_A$ are shown in Figs 1 and 3 respectively. Note that the depth dependence of $\sigma_{//}$ causes a slight curvature in all dotted lines in Fig. 1.

V. Discussion

The quality of the fits obtained for the adopted depth profiles shown in Fig. 3, validates the assumption that the state of stress in the layers consists of a depth independent thermal component and a depth dependent, substrate independent growth component.

- **Origin of growth stress**

Growth stresses in the layers are believed to be caused by atomic peening; accelerated ions hit the surface during deposition, knocking surface atoms deeper into the layer. The associated introduction of additional volume in the constrained layer induces compressive stress. A model for the stress development caused by this introduction of extra volume in a thin layer [2] shows that the introduction of misfitting particles in a free-standing layer leads to a hydrostatic, tensile stress $\sigma^h$ and a volume expansion which is proportional to $\sigma^h$. Fixing the expanded layer on an infinitely stiff substrate then requires a rotationally symmetric biaxial state of stress $\sigma^{\text{fix}}$ which is proportional to the volume expansion and therefore to $\sigma^h$. In addition with the thermal stress $\sigma_{\text{th}}$, the total biaxial component of the stress becomes:

$$\sigma_{//} = \sigma_{\text{th}} + \sigma^{\text{fix}}.$$

- **Origin of depth dependence of lattice spacing $d_A$**

The lattice parameter of TiN, increases for increasing $x$ to a maximum of $4.241 \cdot 10^{-10}$ m at $x = 1$ (corresponding to a [422] lattice spacing $d_{x=1}$ of $8.657 \cdot 10^{-11}$ m, used for $d_{\text{ref}}$ in this paper) and then decreases for values of $x > 1$ [7]. The values of $d_A$ determined for the present layers exceed this maximum value for $d_{x=1}$ (see Fig. 3). The presence of a tensile hydrostatic
stress $\sigma^h$, as predicted above, can explain the occurrence of $d_A$ values larger than the maximum value for $d_s$. Because $\sigma^h$ is proportional to $\sigma^f$, Eq. (1b) implies a linear relation between $d_A$ and $\sigma^f$, in agreement with the results obtained by fitting: $A_j = B_j$.\(^1\) Thus the depth dependence of $d_A$ is directly linked to the depth dependence of growth stress.

- **Origin of depth dependence of growth stress**
  Several suggestions can be given as causes for a depth dependent growth stress.

  (i) *Decrease of deposition temperature*
  Because the layer depositions were preceded by intense sputter cleaning of the substrate, temperature decreased during the depositions. The results shown in Fig. 2 indicate that for layers thicker than 3 $\mu$m a change in temperature is not significant, whereas for the thinnest layers $\Delta\alpha_{cd}(T_{room}-T_{dep})$ could not be determined accurately. Anyhow, it is not clear how a small temperature change during deposition can strongly affect the growth stress.

  (ii) *Depth dependence of elastic moduli*
  It has been suggested that $E$ depends on the chemical composition of TiN, \([6]\). The apparent $\sigma^f$ gradient could therefore originate from a depth dependence of $E$ and $v$. However, to ascribe the gradients fully to the elastic moduli, $E$ should vary at least by a factor of 2. This is improbable in view of the constancy of the deposition parameters.

  (iii) *Depth dependence of morphology*
  SEM analysis shows that the grains in the present layers grow out to a columnar structure in the first 1.5 $\mu$m. Such a columnar structure has been reported to exhibit a texture in which densely packed planes are preferentially oriented parallel to the surface \([e.g. 10]\). The dense packing of these planes may hinder atoms to be sputtered forward into the layer and a developing preferential orientation could thus be associated with a decreasing growth stress \((\text{see also [11]})\). Further, recognising the relatively low density of grain-boundaries, a decrease of grain-boundary area during growth can lead to a decreasing growth stress similarly. Because plastic flow is more likely for relatively coarse grained material, it has been suggested that stress gradients in TiN layers can develop as a consequence of a coarsening of the grains during layer growth \([11]\). Because no plastic relaxation of thermal stress occurred \((\text{see results})\) plastic flow is unlikely in the present case \((\text{note that for the layers on tool steel both } \sigma^h \text{ and } \sigma^{\text{growth}} \text{ are compressive})\).

\(^1\) From the depth dependencies of $\sigma^f$ and $d_s$, using Eq. (1b), the proportionality constant $\gamma$ in $\sigma^f = \gamma \sigma^f$ can be derived. It follows: $\gamma = -0.40$. This result should be compared with the theoretical value of $\gamma = -2/3$ as derived in \([2]\) \((\text{see [5]})\).
VI. Conclusions

- The state of stress in the layers considered can be described by a depth independent thermal stress and a depth dependent, substrate independent, growth stress.
- The growth stress can be described accurately by a combination of a tensile hydrostatic stress and a compressive planar stress, in accordance with a recently proposed model based on atomic peening as stress causing mechanism.
- Depth dependence of stress is most likely correlated to a changing morphology during layer deposition, although other mechanisms cannot completely be ruled out.

References

Chapter IV

On the origin of stress in magnetron sputtered TiN layers

J.-D. Kamminga, Th.H. de Keijser, R. Delhez, E.J. Mittemeijer

ABSTRACT
A recently proposed model has been used to describe the state of stress in magnetron sputtered TiN layers in which the stresses are believed to be caused by atomic peening. The state of stress in the layer is described by a combination of (i) a hydrostatic state of stress, caused by the introduction of the misfitting atoms, and (ii) a biaxial state of stress induced by the equalisation of the lateral dimensions of the substrate and the layer, dilated due to the misfitting atoms and the thermal misfit due to the cooling down of the layer/substrate assembly to room temperature. The implications of the thus obtained total state of stress on X-ray diffraction measurements have been clarified and a quantitative elaboration of the growth stress as a function of the amount and type of misfitting particles has been given. It has deduced that the growth stresses are caused by about 1 wt.% Ti atoms on nitrogen sites in the TiN lattice. By comparing X-ray diffraction results of layers of different thickness, deposited simultaneously on two different substrates, it has been concluded that the growth stress in the layers depends on the layer thickness, whereas the thermal stress is equal for all layers on a given substrate. The observed layer thickness dependence of the growth stress has been associated with a (macro) strain depth profile in the layers. The distinct diffraction line broadening observed for all layers can not be due to smallness of crystallite size and the macro strain depth profiles, it is ascribed to (localised) lattice defects as dislocations and low angle grain-boundaries.

I. Introduction

A few decades ago the atomic peening mechanism was introduced as an explanation for the compressive stress occurring in thin layers that are deposited under ionic or atomic bombardment [1]. The bombarding ions or atoms are believed to knock surface atoms deeper into the growing layer, or they get themselves trapped in the layer. The associated additional volume in the constrained layer induces compressive stress. A generally valid quantitative description for the whole process of the atomic peening has not been given yet. For the theoretical modelling, good descriptions are required of (i) the energy and type of the atoms or ions hitting the surface (ii) the interaction between the advancing/penetrating particles and the (sub)surface and (iii) the state of stress induced by the knocked-in species. The present paper focuses on the last of these three problems. A previously reported model for the state of stress in thin layers induced by misfitting particles [2] can be used to understand the resulting state of stress and to determine the type and
quantity of the trapped species in thin layers deposited under atomic or ionic bombardment. To this end the thin layer is conceived as an assembly of a matrix and particles that have a certain misfit with the matrix. The state of stress induced in the matrix is shown to be triaxial.

The model is applied to a set of magnetron sputtered TiN layers. TiN layers are not only of importance in almost any area of thin layer technology, but the extremely high, mostly compressive, stresses that are often observed to be present in these layers makes TiN also an interesting material to study stress development in thin layers from a scientific point of view.

In this work X-ray diffraction has been used to measure the stress in these thin layers. X-ray diffraction is especially sensitive to the near surface region of a specimen and is therefore particularly suited for thin layer research. Furthermore, in contrast to mechanical methods to measure stress in thin layers (e.g. by means of curvature measurements), in principle the whole stress tensor in the layer can be determined by X-ray diffraction. Hence, X-ray diffraction is in particular suitable to verify the above model that predicts a state of stress not only consisting of biaxial components. Moreover, additional microstructural information can be extracted from the shape of the diffraction peaks.

The minute atomic size of the (misfitting) particles (i.e. the knocked-in atoms) complicates the application of the model and thereby the interpretation of the diffraction results: one has to ascribe a misfit and elastic constants to single atoms. Furthermore, in the interpretation of the diffraction data it is not evident whether the misfitting particles (atoms) should be considered as diffracting either coherently or incoherently with the matrix. Suggestions how to deal with these problems are presented in this paper.

II. Theory

Recently, a model has been developed that describes the state of (macro-) stress in thin layers caused by the introduction of misfitting particles [2]. In what follows, first this model is summarised briefly. Then the effects for the shape and position of X-ray diffraction profiles are discussed. The treatment given below is intended for diffraction stress analysis of sputtered thin layers, of which the stresses are caused by misfitting particles of atomic size.

A. State of stress in thin layers induced by misfitting particles

The stress occurring in a supported layer containing misfitting particles can be calculated in two steps. First, for a free-standing, hole containing layer of lateral dimensions equal to those of the (infinitely stiff) substrate, its volume change and stress caused by the introduction of misfitting particles into the holes is calculated. Secondly, the stress required to equalise the lateral dimensions of the dilated layer and the substrate is determined.

Distinction will be made between the notions ‘matrix’ and ‘body’ of the layer. The ‘matrix’ of the layer refers to the material without possibly present particles and holes (in which the particles can be inserted); the volume of possibly present particles and holes is thus not included in the volume of the matrix. The notion ‘body’ refers to the layer as a whole; its volume comprises the volume of the matrix and the volumes of the possibly present inserted particles and holes.
For the first step (i.e. the introduction of the misfitting particles into the holes of the free-standing layer) the calculation can be performed easily for a system of matrix and particles with different elastic constants (see Ref. [2,3]). However, in the second step of the treatment (i.e. the equalisation of the lateral dimensions of layer and substrate) the calculation of the stress in the matrix becomes complicated if particles and matrix have different elastic constants. In this paper the calculation will be performed for the matrix and misfitting particles having equal elastic constants; this treatment already provides an explanation of the observations.

**Step 1: Volume change of the free-standing body and the stress in its matrix induced by the insertion of the misfitting particles**

The volume change of a finite body caused by inserting misfitting particles into holes in the body has been derived by Eshelby [3]. Consider an elastically isotropic free-standing layer composed of a matrix (total matrix volume: \( V_M \)) and holes (volume of one hole: \( V_H \)). Particles (volume of one particle: \( V_P \)) with the same elastic constants as the matrix are introduced into the holes. The sum of the volumes of the matrix and the particles (both having the same elastic properties) is constant (because the volume of a free-standing elastically homogeneous solid consisting of cubic or elastically isotropic material is independent of its (internal) state of stress (see Ref. [3])). Consequently, the volume change of the free-standing body equals the difference in the total volumes of the particles before insertion and the holes before insertion. For \( n \) particles per unit volume it follows for the dilatation of the body:

\[
\left( \frac{\Delta V}{V} \right)_{\text{body}} = n V_{\text{MIS}} \tag{1}
\]

where \( V_{\text{MIS}} = V_P - V_H \) \(^1\) (volume changes are denoted by \( \Delta V \)).

Whereas the sum of the volumes of matrix and particles remains constant upon introduction of the misfitting particles into the holes, the separate volumes of matrix and particles alter. For example, for particles initially larger than the holes (\( V_{\text{MIS}} > 0 \)) the volumes of the particles decrease and consequently, the volume of the matrix increases. For spherical particles and spherical holes it follows for the dilatation of the matrix [3]:

\[
\left( \frac{\Delta V}{V} \right)_{\text{m}} = \frac{2}{3} \frac{1 - 2\nu}{1 - \nu} n V_{\text{MIS}} \tag{2}
\]

where \( \nu \) is the Poisson ratio. When the particles are randomly distributed throughout the body, the dilatation given by Eq. (2) corresponds to a hydrostatic stress \( \sigma^h_M \) in the matrix:

\(^1\) In Ref. [2] the treatment was given for spherical holes and spherical particles in terms of \( C^w \) instead of \( V_{\text{MIS}} \). For elastically isotropic matrix and particles with equal elastic constants it holds: \( 12\pi C^w (1 - \nu) = V_{\text{MIS}} (1 + \nu) \) (see also Refs [3,4]).
\[ \sigma_h^b = \frac{E}{3(1-2\nu)} \left( \frac{\Delta V}{V} \right)_{M} = \frac{2}{9} \frac{E}{1-\nu} nV_{\text{MIS}} \]  \hspace{1cm} (3) 

where \( E \) is Young’s modulus.

**Step 2: Stress required to equalise the lateral dimensions of the dilated body and the substrate**

For a substrate that is much thicker than the layer it can be assumed that the substrate is infinitely stiff. Then the misfit between the lateral dimensions of the layer and the substrate is fully accommodated by the thin layer. The correspondingly imposed strain, i.e. \(-\frac{1}{3} \left( \frac{\Delta V}{V} \right)_{\text{body}}\), pertains to a rotationally symmetric biaxial state of stress parallel to the specimen surface characterised by \( \sigma_{\text{body}}^{\text{fs}} \). Since it has been adopted here that matrix and particles have equal elastic properties, this stress is equally present in both the matrix and the particles and one obtains, using Eq. (1):

\[ \sigma_{\text{body}}^{\text{fs}} = \sigma_{M}^{\text{fs}} = \frac{1}{3} \frac{E}{1-\nu} \left( \frac{\Delta V}{V} \right)_{\text{body}} = \frac{1}{3} \frac{E}{1-\nu} nV_{\text{MIS}} \]  \hspace{1cm} (4)

Thus the state of stress in the matrix is triaxial, characterised by the hydrostatic stress \( \sigma_{h}^b \) and the biaxial stress \( \sigma_{M}^{\text{fs}} \) with (cf. Eqs (3) and (4)):

\[ \sigma_{h}^b = -\frac{2}{3} \sigma_{M}^{\text{fs}} \]  \hspace{1cm} (5)

**B. Diffraction stress analysis**

1. **Biaxial state of stress; the \( \sin^2 \psi \) analysis**

To measure stresses by diffraction the lattice spacing determined for a certain specimen orientation is used as an internal strain gauge. For a macroscopically isotropic specimen that consists of a cubic material, subjected to a rotationally symmetric biaxial state of stress parallel to the specimen surface (\( \sigma_{\parallel} = \sigma_1 = \sigma_2 \)) diffraction stress analysis is based on the equation [5,6]:

\[ \frac{d_{\psi}^{hkl}}{a_{\text{ref}}} \sqrt{h^2 + k^2 + l^2} - a_\chi = \left( 2S_1^{\text{hkl}} + \frac{1}{2} S_2^{\text{hkl}} \sin^2 \psi \right) \sigma_{\parallel} \]  \hspace{1cm} (6)

where \( d_{\psi}^{hkl} \) is the lattice spacing determined from the peak position of an \( \{hkl\} \) reflection recorded at a specimen tilt angle \( \psi \) (\( \psi \) is the angle between the specimen surface and the reflecting lattice plane, and \( a_\chi \) is the lattice parameter of the diffracting material in the absence of stress. The subscript \( x \) refers to the appropriate material composition and recognises that the lattice parameter may depend on the material composition \( x \).

Distinction between the reference parameter \( a_{\text{ref}} \) and \( a_\chi \) is made in recognition of their different effects on the precision of the stress obtained; whereas an error in \( a_{\text{ref}} \) of several percent leads to an equally small relative error in the obtained stress, the error induced by a
similar error in \( a_x \) is much larger. Consequently, \( a_{ref} \) can be considered as a known constant, contrary to \( a_x \). Also, a single value for \( a_{ref} \) can be used in a comparison of the stresses in layers with slightly different \( a_x \).

\( S_1^{hkl} \) and \( \frac{1}{2} S_2^{hkl} \) are the so-called diffraction elastic constants for the \( hkl \) lattice planes employed in the diffraction measurements, which are taken here independent of the orientation of the diffracting lattice plane (i.e. independent of \( \psi \) in Eq. (6)).

Stress analysis is often applied on the basis of the so-called \( \sin^2 \psi \) method. Then a set of \( d_{\psi}^{hkl} \) values is measured at different \( \psi \) angles using the same type of reflection \( hkl \). A plot of \( d_{\psi}^{hkl} \) versus \( \sin^2 \psi \) (the so-called \( \sin^2 \psi \) plot) yields a straight line and from its slope the stress \( \sigma_{\parallel} \) can be obtained when \( \frac{1}{2} S_2^{hkl} \) is known, without a precise knowledge of \( a_x \) (cf. Eq. (6)).

2. Superimposed biaxial and hydrostatic states of stress

For a homogeneous cubic material subjected to (i) a rotational symmetric biaxial state of stress parallel to the specimen surface (\( \sigma_{\parallel} \)), and (ii) a hydrostatic state of stress (\( \sigma^h \)), Eq. (6) transforms to [2,5,6]:

\[
\frac{d_{\psi}^{hkl}}{a_{ref}} \sqrt{h^2 + k^2 + l^2} - a_A = \left( 2S_1^{hkl} + \frac{1}{2} S_2^{hkl} \sin^2 \psi \right) \sigma_{\parallel}
\]

(7a)

with

\[
\frac{a_A - a_x}{a_{ref}} = \left( 3S_1^{hkl} + \frac{1}{2} S_2^{hkl} \right) \sigma^h
\]

(7b)

Using the \( \sin^2 \psi \) method, no precise \( a_A \) value is needed to yield a proper value for \( \sigma_{\parallel} \) (see Eq. (7a)). However, an accurate value for \( \sigma^h \) can only be obtained if an accurate and precise value for \( a_x \) is available, which is generally not the case.

C. Application to thin layers with misfitting particles

In this subsection it is explained how the model that describes the state of stress in thin layers with misfitting particles (subsection A) can be verified by means of diffraction analysis (subsection B).

1. Elastic constants

In subsection A, the modelling was done for elastically isotropic materials. For such materials, the elastic behaviour of both single crystals and macroscopic aggregates can be completely described by the Young’s modulus \( E \) and the Poisson’s ratio \( \nu \). Then the diffraction elastic constants, \( S_1^{hkl} \) and \( \frac{1}{2} S_2^{hkl} \), are \( hkl \) independent and equal to the (macroscopic) mechanical elastic constants \( S_1^{mech} \) and \( \frac{1}{2} S_2^{mech} \). \( E \) and \( \nu \) are related to \( S_1^{mech} \) and \( \frac{1}{2} S_2^{mech} \) through [5,6]:

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\[
E = \frac{1}{S_{1}^{\text{mech}} + \frac{1}{2} S_{2}^{\text{mech}}} \\
\nu = \frac{-S_{1}^{\text{mech}}}{S_{1}^{\text{mech}} + \frac{1}{2} S_{2}^{\text{mech}}}
\]  

(8)  

(9)

2. Diffraction analysis of thin layers with misfitting particles

Depending on the misfit and the size of the particles different approaches can be followed for the diffraction stress analysis, leading to different results.

a. Misfitting macroscopic particles

For macroscopic particles two cases can be set apart. First, if the particles and the matrix yield separate diffraction peaks, the diffraction stress analysis of the matrix reflections should be performed on the basis of Eq. (5) and Eqs (7a) and (7b). This is for example the case when particles and matrix consist of a different phase. Secondly, if it is not possible to separate the particle and matrix diffraction peaks (e.g. when particles and matrix consist of the same material), composite diffraction peaks are obtained whose centroids correspond to the volume average of the lattice spacings of particles and matrix. Due to the constant sum of volumes matrix and particles (cf. section II.A), the measured dilatation after the introduction of the particles in the free-standing layer is then zero. Hence, a purely biaxial rotational symmetric state of stress is measured in the layer after the equalisation of the lateral dimensions of the dilated layer and the substrate and stress analysis must be performed on the basis of Eq. (6).

b. Misfitting particles of atomic size: large misfit

Consider an atom that is inserted into a perfect matrix structure. Due to its misfit the matrix atoms surrounding the inserted atom are moved from their original sites. If this displacement is sufficiently large the contribution of these matrix atoms to the diffraction peaks from the matrix disappears. Then the inserted atom plus the surrounding (matrix) atoms can be considered as an entity playing the role of a macroscopic misfitting particle whose diffraction does not contribute to the diffraction peaks of the matrix. Diffraction analysis of the matrix reflections should be performed on the basis of Eq. (5) and Eqs (7a) and (7b).

c. Misfitting particles of atomic size: small misfit

If, due to the small misfit of the inserted atom, the displacements of the matrix atoms surrounding the inserted atom are thus small that the contribution of these matrix atoms to the diffraction peaks does not disappear, a different procedure should be followed. Clearly, in this case the number of unit cells of which the matrix consists is unaltered by the insertion of the particle. The dilatation measured from the matrix diffraction peaks now equals the dilatation of the body (see step 1 in Section II.A). This dilatation corresponds to a hydrostatic stress \( \sigma^h \):

\[
\sigma^h = \frac{E}{3(1-2\nu)} \left( \frac{\Delta V}{V} \right)_{\text{body}} = \frac{E}{3(1-2\nu)} nV_{\text{MIS}}
\]

(10)
and it follows (cf. Eq. (4)):  
\[ \sigma^{\text{fit}} = \sigma^{\text{fit}}_{\text{body}} = -\frac{1}{3(1-\nu)} \frac{E}{V} \left( \frac{\Delta V}{V} \right)_{\text{body}} = -\frac{1}{3(1-\nu)} \frac{E}{n} V_{\text{fit}} \]  
(11)

Consequently:

\[ \sigma^{\text{th}} = -\frac{1-\nu}{1-2\nu} \sigma^{\text{fit}} \]  
(12)

The diffraction analysis for particles with small misfit should be performed on the basis of Eq. (12) and Eqs (7a) and (7b).

**d. Small or large misfit?**

To predict which of the above diffraction analyses should be used for thin layers with misfitting atoms, it is necessary to establish if a case of small or large misfit occurs. In our opinion a precise criterion cannot be given. In analogy to what is common use in dislocation theory it is convenient to define a ‘core’ inside which the displacements of the atoms are ‘large’. In this work a limiting misfit of 10% is used to define the core-matrix boundary (cf. Ref. [7]). Theoretical estimates for the corresponding core radius for inserted misfitting atoms in a matrix relevant for the present paper are given in Appendix A. If the core radius is significantly larger than the radius of the misfitting atom, the misfit can be considered to be large and the stress analysis for large misfit should be used. For a core radius significantly smaller than the misfitting atom radius, the misfit can be considered to be small and the stress analysis for small misfit should be used.

**3. Thermal stress**

In the analysis of the state of stress in the matrix of thin layers with misfitting particles the possible presence of a thermal stress will be accounted for as well. The thermal misfit imposed at the layer-substrate interface, e.g. by cooling down from deposition temperature (\( T_{\text{dep}} \)) to room temperature (\( T_{\text{room}} \)), leads to an additional biaxial state of stress in the thin layer, characterised by the stress component \( \sigma^{\text{th}} \). To calculate this stress from the thermal misfit imposed at the layer/substrate interface, one has to employ the mechanical elastic constants \( S^\text{mech} \) and \( \frac{1}{2} S^\text{mech} \) or \( E \) and \( \nu \) of the layer (cf. Eqs (8) and (9)). In case all thermally induced misfit is elastically accommodated by the thin layer the thermal stress is given by:

\[ \sigma^{\text{th}} = \frac{E}{1-\nu} \int_{T_{\text{dep}}}^{T_{\text{room}}} \alpha_s(T) - \alpha_l(T) dT \]  
(13)

where \( \alpha_s \) and \( \alpha_l \) are the linear thermal expansion coefficients of substrate and layer respectively.
4. Complete state of stress in thin layers with misfitting particles of atomic size

Summarising, the state of stress of the matrix of an elastically isotropic thin layer with misfitting particles of atomic size can be described by a biaxial stress $\sigma_{\parallel} = \sigma^{fix} + \sigma^{th}$ and a hydrostatic stress $\sigma^h$. In the analysis of the stresses distinction will be made between thermal stress ($\sigma^{th}$) and growth stresses, i.e. stresses caused by misfitting particles introduced by bombarding particles during growth ($\sigma^h$ and $\sigma^{fix}$).

a. Layers with different thermal stress and equal growth stress

The lattice spacing of the matrix of a given specimen measured at $\sin^2 \psi = -2S_{1}^{hkl} / \frac{1}{2} S_{2}^{hkl}$ does not depend on the biaxial component of the stress (i.e. the right-hand side of Eq. (7a) cancels). Consequently, plots of matrix spacing versus $\sin^2 \psi$ of layers with different thermal stress and equal growth stress and composition show lines that intersect at $\sin^2 \psi = -2S_{1}^{hkl} / \frac{1}{2} S_{2}^{hkl}$. It follows for the difference in lattice spacings measured at a certain $\psi$ from two layers (I and II) of equal composition having different thermal stress and equal growth stress:

$$\frac{d_{\psi}^{hkl}(I) - d_{\psi}^{hkl}(II)}{d_{ref}^{hkl}} = \left(2S_{1}^{hkl} + \frac{1}{2} S_{2}^{hkl} \sin^2 \psi\right)\left(\sigma^{th}(I) - \sigma^{th}(II)\right)$$  \hspace{1cm} (14)

Consequently, a plot of such difference in matrix lattice spacings versus $\sin^2 \psi$ yields a straight line that intersects the $\sin^2 \psi$ axis at $-2S_{1}^{hkl} / \frac{1}{2} S_{2}^{hkl}$. From the slope the difference between the thermal stresses in layers I and II can be obtained.

b. Layers with equal thermal stress and different growth stress

(i) Large misfit

For atomic particles with a sufficiently large misfit (see above) it follows from Eqs (5), (7a) and (7b) that at $\sin^2 \psi = 2/3$ the lattice spacing at the corresponding angle $\psi$ is solely determined by $a_s$ and the thermal stress (the growth components of the stress cancel). Consequently, $\sin^2 \psi$ plots of layers of equal matrix composition having equal thermal stress and different growth stress show lines that intersect at $\sin^2 \psi = 2/3$.

(ii) Small misfit

For atomic particles with a small misfit (see above) it follows from Eqs (7a), (7b) and (12), using Eqs (8) and (9) that at $\sin^2 \psi = 1$ the growth components of the stress cancel and the lattice spacing at the corresponding angle $\psi$ is solely determined by $a_s$ and the thermal stress. Consequently, $\sin^2 \psi$ plots of layers of equal matrix composition having equal thermal stress and different growth stress show lines that intersect at $\sin^2 \psi = 1$. 

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III. Experimental

A. Specimen preparation

TiN layers were reactively sputtered on high-carbon, high-chromium cold work tool steel (X155CrVMo12 1) and WC based cermet cuboids of dimensions 40x15x8 mm and 20x20x3 mm, respectively. Prior to deposition the substrates were mechanically polished (final step 1 µm diamond paste) and ultrasonically cleaned in 96% ethanol.

The layers were deposited in a Teer UDP 350 4-RF system [8]. The apparatus consists of a cylindrical sputter chamber (height and diameter approximately 0.5 m) in which a cylindrical specimen mill is placed such that the axes of both cylinders coincide. The mill was rotated at about 5 rpm around its cylinder axis. Two titanium sputter targets (Teer, 99.5 wt.% Ti) of lateral dimensions of 130x240 mm were placed opposite to each other, along the cylindrical chamber wall. When the substrates on the rotating specimen mill were in front of the target, the substrate-target distance was approximately 130 mm. The glow in front of the sputter targets was monitored using an optical emission unit tuned such that the intensity of the 502 nm Ti line was recorded.

Prior to the deposition of TiN the chamber was evacuated to a pressure below 0.001 Pa, followed by inlet of argon to a pressure of 0.3 Pa. A so-called bias voltage of -750 V (DC) was applied to the substrates and a plasma was initiated between the negatively charged substrates and the chamber wall.

Due to the bombardment of the substrates with the Ar⁺ ions the initial oxides and other impurities were removed from the substrate surface. A current of 0.2 A was set between the chamber wall and the sputter targets (using the targets as cathode) to remove contaminants from the targets, also leading to the ejection of sputtered titanium atoms into the plasma and consequently to gettering of contaminants sputtered from the targets and the substrates. This sputter cleaning procedure was maintained for 30 minutes leading to the removal of up to several hundreds of nanometers material from the substrate surface and an increase of the substrate temperature to approximately 620 K. After sputter cleaning the bias voltage was set to -150 V, the current between the sputter plates and the chamber wall was increased to 7.5 A and a titanium (inter)layer was sputtered on the substrates. This was done for 1-2 min until a stable Ti signal was acquired with the optical emission unit. At the substrate a titanium interlayer with a thickness of about 200 nm was obtained. Subsequently the bias voltage was set at -65 V, nitrogen was led into the chamber and upon sputtering continuously the Ti targets, a TiN layer was deposited on the substrate.

The nitrogen inlet was controlled by means of the optical emission unit and a rapidly responding piezo valve in the following way. Because the presence of nitrogen in the sputter chamber leads to TiN formation on the target (which decreases the titanium sputter yield), the intensity of the recorded titanium line decreases with increasing nitrogen pressure. Hence, the ratio of the intensity of the titanium line recorded during TiN deposition and the intensity of the titanium line recorded during deposition of the titanium interlayer can be used as a measure for the nitrogen pressure in the sputter chamber. The piezo valve was controlled such that the so-
called relative titanium line intensity was kept at a value that could be tuned accurately between 20 and 100%.

A series of TiN layers was deposited using deposition times of 15, 30, 45, 60 and 90 minutes and a relative intensity of 55%; layers were deposited simultaneously on both substrate types.

B. Morphology and thickness
The morphology of the coatings was studied using a JEOL 6400 F scanning electron microscope (SEM). Cross sections of the layers were obtained by grinding and polishing mechanically a side of the specimens (last step 1 μm diamond paste).

Layer thicknesses were measured by grinding a spherical crater through the layers using a grinding sphere with a radius of 20 mm. The diameters of the circular intersections of the sphere with the upper layer surface and the layer-substrate interface were measured using an optical microscope. The thicknesses of the layers were then calculated using straightforward geometry (cf. Ref. [9]).

C. Electron probe micro analysis
Electron probe micro analysis (EPMA) was employed for a quantitative assessment of the overall composition and composition gradients in the TiN coatings. A Jeol JXA 733 electron probe X-ray micro analyser equipped with four wavelength-dispersive spectrometers and one energy-dispersive system was used. This instrument is provided with Tracer Nothern TN 5500 and 5600 systems for instrument control, data acquisition and analysis. A beam of 10 keV electrons and a current of 20 nA was used. The intensities of the Ti Kα, Ar Kα, Fe Kα, Cr Kα, C Kα and O Kα radiations were measured and compared with intensities for these radiations recorded from standard specimens. The N Kα line (392 eV) overlaps with the Ti LL line (395 eV), which hinders a direct determination of the N Kα intensity. Nitrogen contents were determined using a method described by Bastin and co-workers [10,11]. The obtained nitrogen weight fraction should be considered as an underestimate, because surface contamination by carbon and oxygen decreases the thus acquired nitrogen content.

D. X-ray diffraction analysis
X-ray diffraction measurements were performed with a Siemens D-500 θ-2θ type diffractometer, equipped with a diffracted-beam monochromator set to select the Cu Kα radiation. Because of the small TiN layer thicknesses (< 6.2 μm), the observed diffraction patterns consisted of overlapping reflections of substrate and layer. Overall θ-2θ scans were recorded for all layers in the range from 30 to 160 °2θ, to obtain a rough indication of texture and to select the diffraction peaks with which the stress measurements could best be performed.

1. Stress measurements
For the layers on both substrate types the {422} TiN reflection turned out to be favourable for the stress analysis (reasonable intensity, high diffraction angle (about 124 °2θ), minimum overlap).
For the sin^2ψ stress measurements 20 scans of the \{422\} TiN reflection were recorded at specimen tilt angles ψ (for an α-type diffractometer it holds ω = ψ) corresponding to sin^2ψ values of 0, 0.1, 0.2, 0.3, 0.4, and 0.5. The 2θ range used for the scans of the \{422\} TiN reflection was chosen according to the following criteria: (i) the starting angle and ending angle were taken at 2θ values where the observed intensity was minimal, (ii) the measurement range covered at least 2.5 - 3 times the full width at half maximum (FWHM) of the α1 component of the \{422\} TiN peak to both the low angle side and the high angle side of the \{422\} TiN peak position. For both substrates the above criteria yielded 2θ ranges of typically 112-150 °2θ. The step size for the \{422\} TiN scans was 0.05 °2θ and the counting time was chosen such that at the peak maximum of the \{422\} TiN reflection at least 1000 counts were collected.

TiN and substrate reflections were fitted simultaneously using the profile fitting program ProFit [12] adopting a pseudo Voigt function for both the α1 component and the α2 component, and a linear background. A value of 0.5 was used for the ratio of the intensities of the α2 and the α1 components.

For the thinner TiN layers the overlapping of the weak \{422\} TiN reflection by strong substrate reflections hindered a direct evaluation of the quality of the fit by visual inspection. Therefore the following procedure was adopted for all peaks. From the overall fit the background and all fitted reflections but the \{422\} TiN reflection were subtracted from the measured pattern. Thus only the \{422\} TiN reflection remained. For some of the thinner layers the shape of the remaining TiN peak was not realistic. These peaks were excluded from further analysis.

Positions of the thus isolated \{422\} TiN reflections were obtained (i) by stripping the α2 component [13] and fitting a parabola through the top of the remaining α1 peak (using data points with intensities above 70% of the top intensity) and also (ii) by fitting pseudo Voigt functions to the α1 and α2 components of the peak and taking the middle of the peak at half height of the α1 component as peak position. These two methods yielded equal values for the peak position within 0.05 °2θ. Values obtained with the latter method (ii) are used in this paper.

Lattice spacings were obtained from the positions of the diffraction peaks using Bragg’s law. Because all peaks used for the sin^2ψ analysis are measured at approximately the same diffraction angle, the 2θ dependence of the diffractometer error can be neglected, because an instrumental error that is equal for all d^thickψ values does not interfere with the sin^2ψ analysis (i.e. the slope of the straight line in the d^thickψ-sin^2ψ plot). Further, it was verified that the ψ dependence of the diffractometer error is negligible with respect to shifts associated with the measured strains. Consequently, no correction for instrumental errors was necessary for the lattice spacings used in the sin^2ψ analysis.

2. Line width measurements
The profile fitting programme provides two measures for the breadth of the α1 component of the fitted peaks; the integral breadth β, which is the ratio of the peak area and the peak maximum, and the full width at half maximum (FWHM). The relatively high background and the large width of the peaks causes inaccuracy in the values of β, especially for diffraction peaks at relatively large diffraction angles recorded from the thinner layers. From the overall θ-2θ scans accurate β
values could be determined for the \{111\}, \{200\}, \{220\}, \{311\} and \{222\} reflections for all layers but the thinnest. For the \{422\} reflections used for the stress measurements the $\beta$ values turned out to be inaccurate and corresponding FWHM values have been used.

IV. Results

A. Morphology and thickness
The layers are brightly gold coloured. The deposition times and the corresponding layer thicknesses are shown in Table 1. A growth rate of approximately 4.0 $\mu$m per hour occurred for all layers. A cross section of the 4.0 $\mu$m layer on tool steel is shown in Fig. 1. The first $\sim 0.2$ $\mu$m of the layer contrasts with the other parts of the layer, which indicates the titanium interlayer. The equiaxed grains of the TiN layer near the substrate appear to have grown out to a columnar structure in the first 1.5 $\mu$m. After the first 1.5 $\mu$m the column diameter remains constant at a

<table>
<thead>
<tr>
<th>Deposition time (min.)</th>
<th>Thickness ((\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.0</td>
</tr>
<tr>
<td>30</td>
<td>2.0</td>
</tr>
<tr>
<td>45</td>
<td>3.0</td>
</tr>
<tr>
<td>60</td>
<td>4.0</td>
</tr>
<tr>
<td>90</td>
<td>6.2</td>
</tr>
</tbody>
</table>
value of approximately 0.2 μm.

B. Composition

The results of a cross section EPMA measurement for the 4 μm thick layer deposited on the tool steel are shown in Fig. 2. In the predominant upper part of the layer the composition is constant. The measured Ti concentration of (79 ± 1) wt% is slightly higher than for stoichiometric TiN (77 wt%). From Fig. 2 it is clear that the corresponding nitrogen concentration is constant but lower than the expected 21 wt% (on the basis of the Ti content: 100 wt% - 79 wt%), which is attributed to carbon and oxygen contamination on the surface of the analysed cross section during EPMA analysis (see section III.C).

The argon content in the coating increases from 0.08 wt% in the upper part of the layer to about 0.65 wt% near the substrate. This is ascribed to the higher bias voltage used for the deposition of the titanium interlayer than used for the deposition of the TiN layer, causing a higher argon concentration in the titanium interlayer than in the TiN layer. In this way also argon concentrations above 1 wt% can be understood, as previously reported for TiN layers sputtered using the same sputter parameters and a bias of -120 V for both interlayer and toplayer [9].

![Figure 2](link_to_image)

Fig. 2: Ti and N content and Ar content in the Ti interlayer/TiN layer of 4.0 μm thickness on tool steel.
extent of the range of gradual change of composition near the substrate/layer interface (larger than the 0.2 μm thickness of the interlayer) is caused by the limited lateral resolution of the EPMA measurements (for the measurement presented here about 0.5 μm).

C. Stress measurements
The measured lattice spacings are plotted versus $\sin^2 \psi$ in Fig. 3. In view of the negative slopes of the $\sin^2 \psi$ plots, the sum of the biaxial components of the stress are compressive in all layers (see Eqs (6) and (7a)). These compressive stresses decrease with increasing layer thickness and are higher in the layers deposited on the tool steel than in the layers deposited on the cermet. To determine the stresses the elastic constants should be known. Selection of values for the diffraction elastic constants is dealt with first.

1. Elastic constants
The diffraction elastic constants and the mechanical elastic constants have been calculated here from the single crystal elastic constants. In several studies elastic constants have been deduced from the sound velocity in single crystal TiN by means of acoustic microscopy [14,15] and inelastic neutron scattering [16,17]. In the literature mostly the constants reported in Ref. [17] have been used. However, the determination of the elastic constants from the phonon dispersion curves requires an extrapolation which induces considerable statistic uncertainties. In Ref. [14]

![Graph showing $\sin^2 \psi$ plots for the TiN layers deposited on the tool steel and the cermet.]

Fig. 3: $\sin^2 \psi$ plots for the TiN layers deposited on the tool steel and the cermet.
not all the constants have been measured independently. The elastic constants reported by Ref. [15] seem the most reliable ones and these will be used in the present paper.

Different models exist to calculate the diffraction and mechanical elastic constants from the single crystal elastic constants. Due to the relatively small elastic anisotropy of TiN, the difference between the diffraction and mechanical elastic constants as derived from the various models is relatively small. In the present paper the Neerfeld-Hill elastic constants are used for all layers. In Table 2 the results for the diffraction elastic constants for the $\{422\}$ reflection and for the mechanical elastic constants, together with the corresponding values of $E$ and $\nu$ (cf. Eqs (8) and (9)), have been gathered (formulas to be used for these models can be found in e.g. Ref. [6]).

Table 2: Diffraction elastic constants and mechanical elastic constants for TiN calculated using the Neerfeld-Hill model from the single crystal elastic constants reported in Ref. [15]: $s_{11} = 1.80$ TPa$^{-1}$, $s_{12} = -0.38$ TPa$^{-1}$ and $s_{44} = 6.14$ TPa$^{-1}$.

<table>
<thead>
<tr>
<th>$S_4^{422}$ (TPa$^{-1}$)</th>
<th>$\frac{1}{2} S_5^{422}$ (TPa$^{-1}$)</th>
<th>$S_1^{meh}$ (TPa$^{-1}$)</th>
<th>$\frac{1}{2} S_2^{meh}$ (TPa$^{-1}$)</th>
<th>$E$ (GPa)</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.56</td>
<td>2.84</td>
<td>-0.54</td>
<td>2.67</td>
<td>470</td>
<td>0.254</td>
</tr>
</tbody>
</table>

2. Thermal stress

Reported values for the linear thermal expansion coefficients of the tool steel ($\alpha_{TS}$) and the cermet ($\alpha_{WC}$) are $\alpha_{TS} = (11.9-12.9) \times 10^{-6}$ K$^{-1}$ [18] and $\alpha_{WC} = (4.6-8.9) \times 10^{-6}$ K$^{-1}$ [19]. Consequently, from Eq. (13) different thermal stresses are expected for the layers deposited onto the tool steel and the cermet substrates. In the treatment it is assumed that the growth stresses in simultaneously deposited layers are equal.

A plot as proposed below Eq. (14) has been given in Fig. 4 for the three thickest of the layers

![Graph showing differences in measured lattice spacings for layers deposited on different substrates](image)

**Fig. 4**: Differences in measured lattice spacings for the 3.0, 4.0 and 6.2 μm layers deposited on the two different substrates (see text).
on both substrates. For the thinner layers this analysis failed because of too large experimental errors. Clearly, the obtained data can be fitted well using a single straight line. This implies that the difference in thermal stress of the layers deposited on the different substrates is independent of the layer thickness, which suggests a constant deposition temperature (see Eq. (13)). The point of intersection with the $\sin^2 \psi$ axis in Fig. 4 occurs at $\sin^2 \psi = 0.407$, which should be compared with the theoretical value of $2S_1^{422} / \frac{1}{2}S_2^{422} = 0.412$; a good agreement exists.

From the slope of the line in Fig. 4, $(-2.95 \pm 0.21) \cdot 10^{-13}$ m, the difference in thermal stress is obtained (Eq. (14)). It holds, using $d_{ref} = 8.657 \cdot 10^{-11}$ m (cf. Ref. [20]):

$$\sigma_T^{th} - \sigma_w^{th} = 1.24 \pm 0.09 \text{ GPa}.$$  

For the present small temperature ranges the thermal expansion coefficients can be considered as constants. It holds (cf. Eq. (13)):

$$\alpha_T - \alpha_w = \frac{1 - v}{E} \frac{\sigma_T^{th} - \sigma_w^{th}}{T_{room} - T_{dep}}$$  

It can be obtained from the differences in thermal stress (see above), in linear thermal expansion coefficient for the two substrates and in deposition temperature (620 K) and room temperature (293 K): $\alpha_T - \alpha_w = (6.0 \pm 0.4) \cdot 10^{-6}$ K$^{-1}$, which is compatible with the values for $\alpha_w$ and $\alpha_T$ mentioned above.

3. Growth stress

From the $\sin^2 \psi$ plots in Fig. 3 and the constant thermal stress it follows that the growth stress decreases with increasing layer thickness. In view of section II.C.4 this implies that, depending on the misfit of the misfitting atoms, the $\sin^2 \psi$ plots for layers deposited on a certain substrate should intersect at either $\sin^2 \psi = 2/3$ or $\sin^2 \psi = 1$. Clearly the data can be accurately fitted with a point of intersection at $\sin^2 \psi = 2/3$. This shows that the model described in section II is compatible with the measured data and it can be concluded that the misfitting atoms experience a large misfit. From the slopes of the fits in Fig. 3 the total stress (i.e. $\sigma^{fix} + \sigma^{th}$) in all layers have been determined (see results given in Table 3). The values found for the compressive stresses are very large, several GPa; such overall biaxial stress values have been measured often in this type of

<table>
<thead>
<tr>
<th>Layer thickness (µm)</th>
<th>Stress (cermet) (GPa)</th>
<th>Stress (tool steel) (GPa)</th>
<th>Growth stress (tool steel) (GPa)</th>
<th>Growth stress (cermet) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-4.8</td>
<td>-6.5</td>
<td>-5.7</td>
<td>-5.2</td>
</tr>
<tr>
<td>2.0</td>
<td>-4.3</td>
<td>-5.9</td>
<td>-5.1</td>
<td>-4.7</td>
</tr>
<tr>
<td>3.0</td>
<td>-3.9</td>
<td>-5.3</td>
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<tr>
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<td>-4.1</td>
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<tr>
<td>6.2</td>
<td>-3.1</td>
<td>-4.5</td>
<td>-3.7</td>
<td>-3.5</td>
</tr>
</tbody>
</table>
layers. The thermal stress calculated from Eq. (13) in the layer deposited on the tool steel using $\alpha_{TS} = 12.4 \times 10^{-6}$ K$^{-1}$ and $\alpha_{TiN} = 8.6 \times 10^{-6}$ K$^{-1}$ [19] is $\sigma_{TS}^{th} = -0.8$ GPa. Then using the above value of $\sigma_{TS}^{th} - \sigma_{WC}^{th} = 1.24 \pm 0.09$ GPa, it follows: $\sigma_{WC}^{th} = 0.4$ GPa. Now the stress $\sigma^{fit}$ can be calculated for all layers by subtracting the thermal stress from the measured total stress. Results for the growth stress, $\sigma^{fit}$, are also shown in Table 3. The growth for layers deposited on the different substrates do not differ significantly, but they do depend on layer thickness.

D. Diffraction-line width

Diffraction-line broadening is often interpreted employing the so-called Williamson-Hall plot [21]. In the linear version of the Williamson-Hall plot the integral breadth $\beta$ (on a 2θ scale) multiplied by $\cos \theta$ (where $\theta$ is the Bragg angle of the corresponding peak) is plotted versus $\sin \theta$ for various peaks of a given sample. Such Williamson-Hall plots have been given in Fig. 5 for the 2.0, 3.0, 4.0 and 6.2 $\mu$m layers deposited on the tool steel.

The FWHM of the $\{422\}$ reflections have been plotted versus $\sin^2 \Psi$ in Fig. 6 for the layers deposited on the tool steel and the cermet, respectively. For the 1.0 $\mu$m and 2.0 $\mu$m layers deposited on the cermet the FWHM could not be determined accurately because of considerable overlap of the corresponding reflections of the TiN layer with reflections of the substrate. The FWHM of the diffraction lines decreases with increasing layer thickness and decreases with increasing specimen tilt angle $\Psi$. The FWHM values for layers of the same thickness deposited on

![Williamson-Hall plots](image)

**Fig. 5:** Williamson-Hall plots for the 2.0, 3.0, 4.0 and 6.2 mm layers deposited on the tool steel. Integral breath values $\beta$ have been measured at $\Psi = 0$. The lines shown have been drawn through the $\{111\}$ and $\{222\}$ data points; see discussion in section V.B.1.
Fig. 6: FWHM values versus \( \sin^2 \psi \), from TiN layers of various thicknesses deposited on the tool steel and the cermet.

the tool steel and on the cermet do not differ significantly. Thus the peak width for layers of equal growth stress and different thermal stress is the same.

V. Discussion

A. State of stress

1. Layer thickness dependence of growth stress
The state of stress in the layers consists of a substrate dependent, layer thickness independent thermal stress and a substrate independent, layer thickness dependent growth stress (see results shown in section IV). In a previous paper, the layer thickness dependence of the growth stress was explained by stress gradients in the layers, with the highest stress at the substrate-layer interface (Ref. [22]; see also Appendix B). Because the sampling depth of the diffraction experiment depends on the specimen tilt angle, deviations from the straight line behaviour in a \( \delta_{\psi}^{\text{int}} - \sin^2 \psi \) plot, as described in section II.B, may arise for specimens subject to a stress gradient. Accordingly, it is not directly evident whether the measured, ‘X-ray averaged’, data can be used in the manner discussed in section II.B, to verify the predictions given in section II.C.4.

Eq. (14) holds also if (substrate independent) gradients in growth stress occur (this follows from Eqs (7a), (7b) and (B2), recognising that the thermal stress is depth independent). Consequently, the above treatment of the thermal stress (see section IV.C.2.) is not affected by growth stress gradients.
To determine whether or not the gradients in the growth stress affect the current analysis of the growth stress, the layer is conceived as composed of a set of infinitely thin sublayers. For each of the sublayers, Eq. (5) holds. Clearly, for layers with equal thermal stress but different growth stresses, induced by misfitting atoms with large misfit, the lattice spacing measured at $\sin^2\psi = 2/3$ is equal for each sublayer (section II.C.4). Consequently, in the $\sin^2\psi$ plots of each sublayer, also the lines in the 'X-ray averaged' (i.e. representing an average over X-ray penetration depth range) $\sin^2\psi$ plots have a point of intersection at $\sin^2\psi = 2/3$. Furthermore, it was shown in Ref. [22] that for the current specimens the curvature of the lines in the $\sin^2\psi$ plots of all layers, as induced by the stress gradients, is very small.

From these two findings it follows that, the growth stress gradients present in the layers do not obstruct verification of the model proposed for the state of stress induced by misfitting particles.

The reason(s) for the stress gradients are yet unclear. Several suggestions have been given in Ref. [22].

It was also established [22] that the relation between $\sigma^h$ and $\sigma^{\rho_x}$ is best described experimentally by $\sigma^h = -0.40 \sigma^{\rho_x}$, in contrast with the theoretically expected relation: $\sigma^h = -\frac{1}{2} \sigma^{\rho_x}$ (Eq. (5); see section II.C.2.b). However, the proportionality constant relating $\sigma^h$ and $\sigma^{\rho_x}$ is very liable to experimental errors. Further, non-experimental deviations from Eq. (5) could e.g. be induced by the slight elastic anisotropy of the TiN or a non random distribution of the misfitting particles.

Anyhow, independent of the presence of gradients in growth stress, the general conclusion is that the growth stress consists of a tensile hydrostatic component and a compressive biaxial component.

2. Identification of misfitting particles

The type and the amount of misfitting particles have not yet been indicated. The application of the model to the case of misfitting particles of atomic size is not without complications because the elastic constants of a single atom are not known and it is not obvious what volume should be used for $V_{MIS}$ (cf. Eq. (1)). To deal with these complications, the following procedure has been adopted.

A small cluster of atoms (e.g. one unit cell) is taken from the TiN matrix and a misfitting atom is inserted in the centre of this cluster of atoms. The change in volume of the cluster is estimated using a hard sphere model (which requires estimations for the radii of the associated atoms). $V_{MIS}$ is given by the difference in volume of the dilated cluster and the original (undilated) cluster of atoms.

Misfitting particles in the sputtered TiN layers can be Ar, Ti and N atoms. To generate compressive biaxial stress in the matrix, the particle size has to be larger than the hole size (see Eq. (4)). Thus, because Ti has the largest radius of the three types of atom (see Appendix A), misfitting particles on Ti sites need not be considered. The following particle-hole systems remain: (i) Ar atoms on N-sites, (ii) Ti atoms on N-sites and (iii) N atoms on tetrahedral sites. Ar and Ti atoms on tetrahedral sites would also cause a compressive stress, but it is believed that in
the case that an Ar or Ti atom is forward sputtered on a tetrahedral site, the misfitting particle will change place with a neighbouring N atom and a combination of the above systems (i) or (ii) with (iii) occurs.

In appendix A the values for $V_{MIS}$ and the core radii (the core radius indicates the strain is 10%; see section II.C.2.d) in systems (i), (ii) and (iii) are calculated employing the procedure sketched above: the values found for $V_{MIS}$ are 0.010, 0.024 and 0.0016 nm$^3$ for the systems Ar on N-sites, Ti on N-sites and N on tetrahedral sites, respectively, corresponding to core radii of 0.21, 0.28 and 0.11 nm.

The first two of the core radii (corresponding to Ar and Ti atoms on nitrogen sites) are considerably larger than the radius of a neighbouring Ti atom (see Appendix A) and hence the adjacent atoms will be displaced severely. Thus for the Ar and Ti atoms on N-sites the treatment of ‘atomic particles with large misfit’ according to section II.C.2.b should be applied. For the nitrogen atoms on tetrahedral sites the core radius is much smaller and it is unclear whether the analysis for small misfit (section II.C.2.c) or for large misfit (section II.C.2.b) should be used. From the measurements it is clear that the current TiN layers correspond with the case of atomic particles with large misfit (see section IV.C.3).

The biaxial stress caused by a given amount of misfitting Ar, Ti on N-sites and N on tetrahedral sites has been estimated using Eq. (4) and appendix A: concentrations of the order of one at% misfitting atoms can already lead to stresses of several GPa.

In view of the very low Ar concentrations measured in the 4.0 μm thick layer on tool steel exhibiting a growth stress of -4.1 GPa (Fig. 2: Ar concentration about 0.1 wt%) the major part of the growth stress cannot have been caused by Ar. Further, considerable amounts of misfitting N atoms on tetrahedral sites should be present to cause a stress of -4.1 GPa (more than 10 at%; see Appendix A) which is improbable. Hence it is concluded that the growth stress is mainly caused by about 1 wt% Ti atoms on nitrogen sites. This is compatible with the Ti concentration measured by EPMA (see Fig. 2; section IV.B).

B. Diffraction line broadening
The broadening of a diffraction line is caused by (i) lattice defects present in the investigated specimen and (ii) the so-called instrumental broadening. In the present case the broadenings of the diffraction lines are that large, that the broadening caused by the diffractometer can be neglected: large amounts of lattice defects occur. A wide range of lattice defects exists: grain boundaries (i.e. limited grain size), stacking faults, dislocations, point defects all cause diffraction line broadening.

1. Size broadening
The broadening caused by lattice imperfections is usually separated in broadening caused by the limited size of diffracting crystallites (the so-called size broadening) and broadening induced by the strain fields of the other possible defects (the so-called strain broadening). The separate contributions of size broadening and strain broadening may be assessed by means of a Williamson-Hall plot (see Fig. 5). In the linear version of the Williamson-Hall construction, it is
assumed that the integral breadth of a reflection that is both size and strain broadened is given by sum of the integral breadths of the exclusively size and strain broadened profiles. Then, it can be written [21]:

$$\beta \cos \theta = 2\xi \sin \theta + \lambda / t$$

(16)

where $\lambda$ is the wavelength of the used radiation, $t$ is a mean linear dimension of the crystallites, also called the apparent crystallite size, and $\xi$ is the integral breadth of the strain distribution. In a Williamson-Hall plot, $\beta \cos \theta$ is plotted versus $\sin \theta$ for a number of reflections. From the intercept of the straight line fitted through the data, the apparent crystallite size is obtained; the slope yields $\xi$. It is noted that the cardinal assumption made in the linear Williamson-Hall analysis (notably: the size and strain broadenings are linearly additive) is generally not justified.

From Fig. 5 it is clear that for the present specimens data from different reflections cannot be reconciled with a single straight line in the Williamson-Hall plot. The $\{111\}$ and $\{222\}$ diffraction lines stem from the same crystallites, and therefore a straight line has been drawn through the corresponding data points in the Williamson-Hall plot for each layer thickness. Clearly, the intercepts with the ordinate are negative, which in view of Eq. (16) is impossible ($t$ is always positive). The occurrence of a negative intercept may be caused by the increase of information depth for the diffraction measurement with increase of $2\theta$. The integral breadth increases with increasing penetration depth (section IV.D). The $\{111\}$ reflection has a sampling depth smaller than the $\{222\}$ reflection. Thus, as compared to the integral breadth of the $\{222\}$ reflections, the integral breadth of the $\{111\}$ reflection is relatively small and a negative intercept occurs in the Williamson-Hall plot. Anyhow, recognising the negative part cut from the ordinate, it seems justified to conclude that possible size broadening, if present, can be neglected with respect to strain broadening.

2. Strain broadening

Strain broadening is associated with local variations in the lattice spacing. Localised lattice defects induce microstrains, and therefore line broadening. However, also the (slowly varying within the diffracting volume) strain field associated with a macrostress profile (see section V.A.1) causes line broadening. This last contribution to the broadening is quantified next.

a. Broadening caused by the growth stress depth profile

The peak shapes that would have been measured if the occurring growth stress profiles were the only peak broadening causing mechanism have been calculated in Appendix B. Results for the 1.0 $\mu$m layer are shown Fig. 7. Clearly, the line width decreases with increasing specimen tilt angle. This can be easily understood: because the lattice spacing measured at $\sin^2 \psi = 2/3$ does not depend on the growth stress (cf. section IV.C.3), the stress depth profile (stress increasing with depth; cf. data discussed in section V.A.1) gives rise to diffraction-line breadth decreasing with increasing specimen tilt angle to a minimum at $\sin^2 \psi = 2/3$. This is in correspondence with the experimental results shown in Fig. 6.
Fig. 7: Calculated X-ray diffraction line profiles with the growth stress depth profile as only line broadening mechanism. 1.0 μm TiN layer on the tool steel; CuKα₁ radiation.

The widths of the lines calculated are much smaller than the line widths measured (cf. Fig. 6 and Fig. 7) and also the calculated peak shapes are completely different from the measured ones. Therefore the growth stress depth profile is therefore surely not the only source of peak broadening.

It is possible to estimate quantitatively the extend of the growth stress depth profile broadening with respect to the total diffraction line broadening. The resulting peak shape can be conceived as the convolution of the diffraction lines broadened by the separate diffraction broadening mechanisms. Here the contributions from the stress depth profile to the measured peak profiles have been calculated, by convoluting the peak shapes resulting from the stress depth profiles only (Fig. 7) with split Pseudo Voigt functions, with parameters fitted such that the resulting convoluted peak was as close as possible to the measured peak. It followed that in all cases the influence of the stress depth profile on the measured line broadening could be neglected; i.e. the observed decrease of line width with sin²ψ (Fig. 6) cannot be attributed to the growth stress depth profile.
b. Other strain broadening phenomena

Apparently the strain broadening is caused by localised lattice defects. This picture agrees well with the presence of misfitting particles (see section V.A.2). However, the presence of (many) other localised defects cannot be excluded. In fact, in view of the atomic peening mechanism, a considerable concentration of misfitting atoms is expected. However, the strain fields of such point imperfections are very localised and are unlikely to cause significant peak broadening.

Transmission electron microscopy investigations showed that small angle grain boundaries and dislocations are present within the grains. Quantitative estimates for the line width due to the suggested defects are difficult to make and an unambiguous explanation for the measured large peak widths cannot be given at present.

Because the peak width decreases with increasing specimen tilt angle (Fig. 6), it follows that the lattice imperfections are more 'visible' in the directions perpendicular to the surface than in other directions. Consequently, the varying strain fields associated with the lattice imperfections are mainly present in directions perpendicular to the surface. Further, from the decrease of peak width with increasing layer thickness (see Figs 5 and 6), it is suggested that most of these defects are present near to the substrate.

VI. Conclusions

- The state of stress in magnetron sputtered layers can be derived imaging the layers as a matrix containing misfitting "particles" due to the atomic peening mechanism. The state of stress is composed of a compressive biaxial growth stress component and a tensile hydrostatic growth stress component. In addition, a biaxial thermal stress component can occur.

- In the analysis of such states of stress by X-ray diffraction two cases can be distinguished:
  (i) the misplaced atom experiences a large misfit with the matrix and "particles" (i.e. the misplaced atom + surrounding matrix atoms) diffract independently (incoherently) from the matrix (cf. section II.C.2).
  (ii) the misfitting "particles" experience a small misfit with the matrix and all matrix atoms diffract coherently.

- For magnetron sputtered TiN layers the misfitting particles show large misfit. As a result \( \sin^2 \psi \) plots of layers with different growths stress and equal thermal stress have a point of intersection at \( \sin^2 \psi = 2/3 \) (section II.C.4). The \( \sin^2 \psi \) plots of layers with equal growth stress but different thermal stress intersect at \( \sin^2 \psi = 2\gamma_{1}^{M} / \frac{1}{2} \gamma_{2}^{M} \) (section II.C.4).

- The amount of sputter gas atoms (i.e. Ar) trapped in the layers investigated is insufficient to cause the compressive biaxial growth stresses. It is deduced that about 1 wt% Ti on N sites causes the observed growth stresses.

- Both the size broadening and the broadening caused by the macro stress gradients can be neglected for the layers investigated. The large line widths are caused by localised lattice defects as dislocations, stacking faults or low angle grain-boundaries. The lattice distortions causing the broadening of the peaks are most pronounced in directions parallel to the growth direction and occur especially close to the substrate.

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Appendix A: Evaluation of misfitting volumes and core radii

For the calculation of the stress caused by a given amount of misfitting atoms the misfitting volumes $V_{MIS}$ (section II.A) and the corresponding core radii (section II.C.2) are estimated for the possible misfitting atoms. In this case Ar and Ti on N-sites and N on tetrahedral sites (between Ti atoms) are considered section (V.A.2). The radii of the possibly misfitting Ar, Ti and N atoms in the TiN lattice are taken to be $r_{Ar} = 0.10$ nm, $r_{Ti} = 0.14$ nm and $r_{N} = 0.07$ nm, in accordance with Ref. [23]. Note that the sum of the diameters of the Ti and N atoms approximately equals the lattice parameter: $a_{TiN} = 0.4241$ nm, which in view of the NaCl type lattice structure can be expected.

1. Estimation of $V_{MIS}$

For the calculation of $V_{MIS}$ for the Ar and Ti on N-sites we proceed as follows. Consider a unit cell of TiN, with Ti atoms on the cube corners and at the centres of the cube faces and N atoms in the centre of the cube and at the midpoints of the cube edges. In the centre of the unit cell the misfitting atom (Ar or Ti) is introduced, which is too large for this original N-site. As a result the Ti atoms at the centres of the faces of the TiN unit cell will be displaced outward over a distance $\delta$, where $\delta$ is given by the sum of the radius of the misfitting atom ($r_{MA}$) and the radius of a Ti atom minus half the lattice parameter. The Ti atoms at the corners of the unit cell are not displaced by the misfitting atom. The shape of the dilated unit cell is approximated by a polyhedron, that is built up from the original unit cell cube and six pyramids of height $\delta$ on the faces of the cube (one on each face). The volume of this polyhedron minus the volume of the original unit cell, i.e. the volume of six of these pyramids, equals $V_{MIS}$:

$$V_{MIS} = 6 \cdot \frac{1}{3} a_{TiN}^2 \delta = 2a_{TiN}^2 (r_{Ti} + r_{MA} - \frac{1}{2} a_{TiN})$$

(A1)

For Ar and Ti on N-sites Eq. (A1) yields $V_{MIS}$ values of 0.010 and 0.024 nm$^3$ respectively.

For the determination of $V_{MIS}$ for a N atom on a tetrahedral site a tetrahedron in the TiN lattice, with at each corner a Ti atom, is considered. The volume of a tetrahedron is given by $\frac{1}{3} \sqrt{3} r_{tet} ^3$, where $r_{tet}$ denotes the distance of the corner of a tetrahedron to its center. For a TiN lattice it follows: $r_{tet} = \frac{1}{4} \sqrt{3} a_{TiN}$. Inserting a N atom into the tetrahedral hole dilates the tetrahedron. After insertion the distance from the corner of the tetrahedron to its center is given by the sum of the radius of the inserted N atom and the radius of the Ti atom at the corner. $V_{MIS}$ is given by the difference of the volumes of the tetrahedron with and without the misfitting N atom:
Inserting the above values for the atomic radii it follows that $V_{MIS}$ for a nitrogen atom at a tetrahedral site equals 0.0016 nm$^3$.

It should be noted that the cluster of atoms for which $V_{MIS}$ is calculated is chosen rather arbitrarily. For example for the calculation of the misfit of an Ti atom on an N-site one could also consider the volume encompassed by the nearest Ti neighbours of the misfitting atom. The values found for $V_{MIS}$ in doing so are different from those given above (i.e. 0.007 nm$^3$ for Ar on N-sites and 0.017 nm$^3$ for Ti on N-sites). However, adopting these last values does not affect the main conclusions of this work.

2. Core radii

For the estimation of the core radius (defined as the radial distance from the centre of the misfitting atom where the corresponding misfit equals 10%; cf. section II.C.2.d) of the three point imperfections mentioned it is assumed that the strain field around the misfitting atoms has spherical symmetry. For the strain in the $r$ direction, $e_r$, at a distance $r$ from the center of the strain field it holds [2,3,4]:

$$
e_r = -2 \frac{C^m}{r^3} = -\frac{1}{6\pi} \frac{1 + \nu}{1 - \nu} \frac{V_{MIS}}{r^3}$$  \hspace{1cm} (A3)

For $C^m$ see footnote in section II.A. The core radius $r_c$ corresponding to a maximum strain $e_{\text{max}}$ follows directly from Eq. (A3):

$$r_c = \frac{1}{3} \left( \frac{1 + \nu}{6\pi} \frac{V_{MIS}}{1 - \nu |e_{\text{max}}|} \right)$$  \hspace{1cm} (A4)

Hence for $e_{\text{max}} = 0.1$, it follows for Ar and Ti on N-sites and N on tetrahedral sites that the core radii equal 0.21, 0.28 and 0.11 nm, respectively.

3. Stress

The biaxial stress caused by a given atomic fraction of misfitting atoms in the layer can be estimated from $V_{MIS}$, using Eq. (4). The volume density of misfitting atoms $n$ is related to the atomic and weight percentages of misfitting atoms (at% and wt%) by the following expression:

$$n = \frac{1}{\langle v \rangle} \text{at}.\% = \frac{1}{\langle v \rangle m_{MA}} \text{wt}.\%$$  \hspace{1cm} (A5)

where $\langle m \rangle$ and $\langle v \rangle$ denote the mean mass and the mean volume of an atom in the TiN lattice and $m_{MA}$ is the mass of the misfitting atom. The mean mass of an atom in TiN equals the mean of the
masses of Ti and N; the mean volume is calculated by dividing the volume of the unit cell, $a_{TiN}^3$, by 8, the number of atoms in the cell. The stress can now be related to the amount of misfitting atoms, in at.\% or in wt.\%, using Eq. (4), Eq. (A5) and the above values for $V_{MS}$. It follows, using $E = 470 \text{ GPa}$, $\nu = 0.254$ (Table II) and $\langle \nu \rangle = 9.53 \times 10^{-3} \text{ nm}^3$:

$$\sigma_{Ti} = -5.2 \text{ at.\% (Ti on N-site) GPa}$$
$$\sigma_{Ar} = -2.2 \text{ at.\% (Ar on N-site) GPa}$$
$$\sigma_{N} = -0.3 \text{ at.\% (N on tetrahedral site) GPa}$$

and, using for the atomic masses $m_{Ar} = 39.9$, $m_{Ti} = 47.9$ and $m_{N} = 14.0$ and $\langle m \rangle = 31.0$, it follows:

$$\sigma_{Ti} = -3.4 \text{ wt.\% (Ti on N-site) GPa}$$
$$\sigma_{Ar} = -1.7 \text{ wt.\% (Ar on N-site) GPa}$$
$$\sigma_{N} = -0.7 \text{ wt.\% (N on tetrahedral site) GPa}$$

**Appendix B: Diffraction line broadening due to stress depth profiles**

1. *X-ray averaged lattice spacing*

The growth stress depth profile in the current TiN layers was determined for the present layers in Ref. [22]. That result can be expressed in terms of the spacing $d_{\psi}$ as a function of distance to the layer-substrate interface, $\overline{z}$ (see Eq. (7a-b)); it follows that $d_{\psi}(\overline{z})$ in the layers deposited on the tool steel can be accurately described by:

$$d_{\psi}(\overline{z}) = 8.6941 \cdot 10^{-11} - 0.0832 \cdot 10^{-11} \sin^2 \psi +$$

$$\left[ 0.0630 \cdot 10^{-11} + 0.1120 \cdot 10^{-11} \sin^2 \psi \right] e^{-7.4710^7 \overline{z}}$$

where $\overline{z}$ and $d_{\psi}(\overline{z})$ are in meters.

The X-ray average, i.e. the measured, diffracted intensity weighted average of all the lattice spacings that contribute to the diffraction signal, can be calculated according to [24]:

$$\langle d_{\psi} \rangle = \frac{\mu k}{e^{i\pi D}} \int_{-1}^{1} d_{\psi}(\overline{z}) e^{i\Delta\overline{z}} d\overline{z}$$

where $\mu$ is the linear absorption coefficient (8.26 \times 10^4 \text{ m}^{-1} [25]), $k$ is a geometric factor (for $\omega$-type diffractometers: $k = 2 \sin \theta \cos \omega (\sin^2 \theta - \sin^2 \omega)$ where $\psi$ equals $\omega$) and $D$ is the layer thickness.
2. Peak shape

A diffraction peak from a sample containing a lattice spacing depth profile exhibits broadening because in principle the lattice spacing at each $\bar{z}$ contributes to the diffracted signal. The distribution density function of the diffracted intensity obeys:

$$ f(\bar{z}) \propto e^{-\mu(k(D-\bar{z}))} \tag{B3} $$

Due to absorption of the X-rays the outer regions of the specimen (at relatively large $\bar{z}$) contribute more to the diffracted intensity than the inner regions. Because $d_\psi$ varies monotonically with $\bar{z}$ (see Eq. (B1)), $f(d_\psi)$ can be easily obtained from $f(\bar{z})$ [26]:

$$ f(d_\psi) \propto e^{\mu(k(D-\bar{z}(d_\psi)))} \frac{\partial \bar{z}(d_\psi)}{\partial d_\psi} \tag{B4} $$

Similarly, it holds for the shape of the profile that is exclusively broadened by the $d_\psi$ profile, $f(2\theta)$:

$$ f(2\theta) \propto f(d_\psi(2\theta)) \frac{\partial d_\psi(2\theta)}{\partial 2\theta} \approx f(d_\psi(2\theta)) \tag{B5} $$

since $\partial d_\psi(2\theta) / \partial 2\theta$ can be taken as a constant for a single diffraction profile.

References

Chapter V

Diffraction stress analysis of thin films

Modelling and experimental evaluation of elastic constants and grain interaction

M. van Leeuwen, J.-D. Kamminga, E.J. Mittemeijer

ABSTRACT

Well-known grain interaction models for the description of macroscopic elastic behaviour of polycrystalline specimens, as due to Voigt, Reuss, Neerefeld-Hill and Eshelby-Kröner, may be successfully applied to bulk specimens, but are shown to be less suited for thin films. An elaboration of a proposal due to Vook and Witt for grain interaction is given. It is assumed that the strain parallel to the specimen surface is equal in all crystallites and that the stress perpendicular to the specimen surface is zero in all crystallites. It is shown that these assumptions give rise to elastic anisotropy of the specimen on the macroscopic scale. It is also shown that in this case the dependence of the measured lattice strain (in a diffraction experiment) on the squared sine of the specimen tilt angle $\psi$ (cf. the $\sin^2 \psi$ method), is non-linear, contrary to what is predicted by the bulk grain interaction models. This is the first time that non-linear $\sin^2 \psi$-plots have been calculated using an elastic grain interaction model, in the absence of crystallographic texture. Experimental verification has been achieved by X-ray diffraction strain measurements performed on a vapour deposited nickel film. The experimental results are in good accordance with the Vook-Witt grain interaction model. This is the first experimental evidence of direction dependent grain interaction in thin films.

I. Introduction

X-ray diffraction strain measurements are often used to determine the internal stress in solids. Generally, a specific $(hkl)$-reflection is recorded at several specimen tilt (and possibly rotation) angles [1]. The measured peak positions are used to calculate the lattice spacing and the lattice strain at every tilt (and rotation) angle. The interpretation of the measured lattice strains in terms of macroscopic stress is not straightforward if the single crystallites of the material considered are elastically anisotropic.

A grain interaction model has to be adopted to describe the distribution of stresses and strains over the crystallographically differently oriented crystallites in the specimen. In the past many different grain interaction models have been proposed. The most widely used of these are the
Voigt [2], Reuss [3], Neerfeld-Hill [4,5] and Eshelby-Kröner [6] models. If the specimen is subject to rotationally symmetric plane stress, the calculation of the stress from the lattice strain, using these models, is relatively simple, since then the so-called sin²ψ-method can be applied. The sin²ψ-method relies on the linear dependence of the measured strain on sin²ψ, where ψ is the specimen tilt angle. The stress follows from the slope of the straight line, fitted to the lattice strain data in a sin²ψ-plot, and the values of the elastic constants which are provided by one of the grain interaction models.

All of the grain interaction models mentioned above, were originally devised for the calculation of the macroscopic average elastic constants of bulk materials from the single crystal elastic constants. In a bulk specimen, each crystallite is surrounded by other crystallites in three dimensions. In evaporated films, which have a columnar grain structure [7], each crystallite is surrounded by other crystallites in only two dimensions. Vook and Witt [8] have proposed a set of grain interaction assumptions, that may be applicable to such a microstructure.

In this work various models for grain interaction will be investigated for application to thin films. The classical, Voigt, Reuss, and Neerfeld-Hill models will be compared to the Vook-Witt model, which is investigated detailedy for the first time. In the models due to Voigt, Reuss, and Vook-Witt it is assumed that certain components of the stress and strain tensors in a specimen-fixed frame of reference are equal in all crystallites. For such models a general procedure is given for calculation of the macroscopic elastic constants and the dependence of the lattice strain on the specimen tilt angle (Sec. II).

The results of the calculations for the Vook-Witt model cannot be given in an analytical form. A numerical example is given to illustrate the difference between the results of the current model and the well-known Voigt and Reuss models (Sec. IV.A). A remarkable result is that the calculated sin²ψ-plots are non-linear. To our knowledge, this is the first time that, in the absence of crystallographic texture, non-linear sin²ψ-plots have been calculated as a consequence of only elastic deformation.

For experimental verification, X-ray diffraction measurements have been performed on evaporated nickel layers. It is shown that the Vook-Witt approach leads to better agreement with the experimental data than the Voigt, Reuss, and Neerfeld-Hill models (Sec. IV.B).

II. Theory

In the following sections both the mechanical, i.e. macroscopic, elastic constants for a specimen subjected to a rotationally symmetric plane state of stress and the direction dependent lattice strain as measured by diffraction are calculated. Since both stress and strain are tensorial quantities, the calculations involve some tensor calculus. It is convenient to represent the tensors on coordinate systems which are fixed to either the specimen geometry, the measurement geometry, or the crystallite. Therefore the following three Cartesian coordinate systems are introduced (cf. Figs. 1 and 5):
The $S$ system: the specimen system. This Cartesian coordinate system is fixed to the specimen geometry. The $S_3$-axis is perpendicular to the specimen surface and the $S_1$ and $S_2$ axes are in the surface plane.

The $L$ system: the laboratory system. This Cartesian coordinate system is connected with the measurement: The strain is measured along the $L_3$ axis. For diffraction measurements this is the direction of the diffraction vector.

The $C$ system: the crystal system. For cubic crystal systems, the axes are along the a, b, and c axes in the crystal lattice. For non-cubic crystal structures, a convention, such as the one given in Ref. [9], must be adopted to define the relation between the $C$-system and the a, b, and c directions in the crystal lattice.

![Diagram](image)

*Fig. 1: Definition of the Eulerian angles $\varphi$ and $\psi$, which define the orientation of the measurement direction $L_3$ with respect to the $S$-system. The $S$-system is defined in Appendix A.*

Each tensor is represented in one of the above coordinate systems. The basis of the representation is indicated by a superscript, for example: $s^{C}_{\omega\omega}$ is the representation of the compliance tensor in the crystal ($C$) system. The elements of this representation of the compliance tensor are called the single crystal elastic constants [9]. Values of the single crystal elastic constants for most common materials can be found in the literature [10].

Throughout the text, the formulation 'tensor in the ... system' will be used to refer to distinct tensor representations in a certain coordinate system. In some cases it is not necessary to specify a coordinate system, since certain statements are true for every representation of the tensor. For example, the stress tensor is always symmetrical, $\sigma_y = \sigma_{yy}$ [9].
\[
\langle \sigma_0^s \rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{2\pi} \sigma_0^s \, d\alpha \sin \mu \, d\lambda \, d\mu.
\] (6)

The same averaging can be applied to a strain tensor component to calculate its macroscopic average in the \( S \) system. From the obtained values of \( \varepsilon_1^s \), \( \varepsilon_2^s \), and \( \sigma_0^s \) the elastic constants \( A \) and \( B \) can be calculated using Eq. (5).

The elastic constants \( A \) and \( B \) are only sufficient to characterise the macroscopic elastic behaviour of a mechanically transversely isotropic specimen if it is in a rotationally symmetric plane state of stress and if the axes of symmetry of the elastic properties and the state of stress are the same. In states of stress of lower symmetry five constants are needed to characterise the elastic behaviour of a transversely isotropic specimen [9].

On the other hand, for aggregates which are macroscopically elastically isotropic, i.e. of which the mechanical elastic behaviour is isotropic, two elastic constants are sufficient to describe the elastic behaviour in any state of stress. For this purpose, the constants \( S_{1}^{\text{mech}} \) and \( \frac{1}{2} S_{2}^{\text{mech}} \) are generally used. These constants are defined in the principal (\( \mathcal{P} \)) coordinate system, a specimen-fixed coordinate system in which all macroscopic shear stress components are zero, in the following way:

\[
\begin{align*}
\langle \varepsilon_1^s \rangle &= \langle S_{1}^{\text{mech}} + \frac{1}{2} S_{2}^{\text{mech}} \rangle \langle \sigma_{11}^s \rangle + S_{1}^{\text{mech}} \langle \sigma_{22}^s \rangle + S_{1}^{\text{mech}} \langle \sigma_{33}^s \rangle, \\
\langle \varepsilon_2^s \rangle &= S_{1}^{\text{mech}} \langle \sigma_{11}^s \rangle + \langle S_{1}^{\text{mech}} + \frac{1}{2} S_{2}^{\text{mech}} \rangle \langle \sigma_{22}^s \rangle + S_{1}^{\text{mech}} \langle \sigma_{33}^s \rangle, \\
\langle \varepsilon_3^s \rangle &= S_{1}^{\text{mech}} \langle \sigma_{11}^s \rangle + S_{1}^{\text{mech}} \langle \sigma_{22}^s \rangle + \langle S_{1}^{\text{mech}} + \frac{1}{2} S_{2}^{\text{mech}} \rangle \langle \sigma_{33}^s \rangle.
\end{align*}
\] (7)

For the rotationally symmetric plane state of stress (see Eqs. (2) and (3)), the specimen system is a principal system: the \( S \)- and \( \mathcal{P} \)-axes coincide. The following expressions are obtained, using \( \langle \sigma_{33}^s \rangle = \langle \sigma_0^s \rangle = 0 \):

\[
\begin{align*}
\varepsilon_1^s &= \langle \varepsilon_{11}^s \rangle = \langle \varepsilon_{22}^s \rangle = (2 S_{1}^{\text{mech}} + \frac{1}{2} S_{2}^{\text{mech}}) \sigma_{11}^s, \\
\varepsilon_0^s &= \langle \varepsilon_{33}^s \rangle = S_{1}^{\text{mech}} (\sigma_{11}^s + \sigma_{22}^s) = 2 S_{1}^{\text{mech}} \sigma_{11}^s.
\end{align*}
\] (8)

This equation readily provides the relation between the mechanical elastic constants \( A \) and \( B \), as defined in Eq. (5) for a (macroscopically elastically) transversely isotropic specimen in a rotationally symmetric plane state of stress of which the axes of symmetry coincide, and the elastic constants of a (macroscopically elastically) isotropic specimen, \( S_{1}^{\text{mech}} \) and \( \frac{1}{2} S_{2}^{\text{mech}} \). Thus,

---

2 It is also possible to use the constants \( E \) and \( v \) for this purpose. Here \( S_{1}^{\text{mech}} \left( = \frac{E}{1-v} \right) \) and \( \frac{1}{2} S_{2}^{\text{mech}} \left( = \frac{1}{2} \frac{E}{1-v} \right) \) are used because of the analogy of these with the X-ray elastic constants (cf. Sec. II.D).
for a macroscopically elastically isotropic specimen in a rotationally symmetric plane state of stress, the following relations hold:

\[
A = 2S_{1}^{\text{mech}} + \frac{1}{2} S_{2}^{\text{mech}}, \\
B = 2S_{1}^{\text{mech}}.
\]  

(9)

B. Calculation of the mechanical strain in a given direction

The macroscopic average strain tensor on the principal axes (the \(\mathcal{P}\) system) can be used to calculate the average strain tensor in any other coordinate system. In this tensor transformation only the normal strains in the original \(\mathcal{P}\) system contribute, since all other strain components in the \(\mathcal{P}\) system are zero. For example, the strain tensor component \(\varepsilon_{33}'\), the strain along the 3-axis in an arbitrary coordinate system, can be calculated using the direction cosines \(a_{ij}\) between the new system and the principal system (cf. Eq. (A-1)):

\[
\langle \varepsilon_{33}' \rangle = a_{31}a_{31}\langle \varepsilon_{11}^{\varphi} \rangle + a_{32}a_{32}\langle \varepsilon_{22}^{\varphi} \rangle + a_{33}a_{33}\langle \varepsilon_{33}^{\varphi} \rangle. 
\]  

(10)

The strain in a direction which is specified by the Eulerian angles \(\varphi\) and \(\psi\) (see Fig. 1), with respect to the principal axes, can be calculated using Eq. (10) and the expressions for the direction cosines for this transformation, given in Appendix A as \(a^{\mathcal{S}\mathcal{S}}\) (Eq. (A4)). When the state of strain in a specimen is rotationally symmetric, as specified in Eq. (2), the specimen \((\mathcal{S})\) system is a principal \((\mathcal{P})\) system, and the mechanical strain \(\varepsilon_{\psi}^{\text{mech}}\) in a direction which is tilted over \(\psi\) with respect to the surface normal is independent of \(\varphi\) [1],

\[
\varepsilon_{\psi}^{\text{mech}} = \langle \varepsilon_{11}^{\varphi} \rangle \sin^{2} \psi + \langle \varepsilon_{33}^{\varphi} \rangle \cos^{2} \psi = \langle \varepsilon_{33}^{\psi} \rangle + \langle \langle \varepsilon_{11}^{\varphi} \rangle - \langle \varepsilon_{33}^{\varphi} \rangle \rangle \sin^{2} \psi. 
\]  

(11)

For a macroscopically isotropic specimen, the strain values given in Eq. (8) can be used in Eq. (11). This yields the mechanical "\(\sin^{2} \psi\)-formula" (cf. Eq. (14)):

\[
\varepsilon_{\psi}^{\text{mech}} = (2S_{1}^{\text{mech}} + \frac{1}{2} S_{2}^{\text{mech}} \sin^{2} \psi)\sigma_{33}^{\mathcal{S}} 
\]  

(12)

C. Lattice strain; the diffraction strain measurement

In diffraction strain measurements the lattice strain is measured along a direction which is defined with respect to the specimen geometry, by the angles \(\varphi\) and \(\psi\) (see Fig. 1). The expression for \(a^{\mathcal{S}\mathcal{S}}\) as given in Appendix A (Eq. (A4)) is used to calculate the strain in a single crystallite in the measurement direction (the \(\mathcal{L}_{3}\)-direction) from the strain tensor (for that crystallite) in the \(\mathcal{S}\) system:

\[
\varepsilon_{33}^{\mathcal{L}} = a_{31}^{\mathcal{S}\mathcal{S}} a_{33}^{\mathcal{S}\mathcal{S}} \varepsilon_{33}^{\mathcal{S}}. 
\]  

(13)
The calculated strain \( \varepsilon_{ij}^C \) depends on the grain interaction model parameters, the crystallite orientation and the measurement direction.

The diffraction experiment defines a relation between crystallite orientation and measurement direction: the diffracting \( \{hkl\} \)-planes of the crystallites which contribute to the diffraction measurement are perpendicular to the measurement direction. In crystal systems of cubic symmetry, the \( L_3 \)-direction can be chosen along the vector \((h,k,l)\) in the \( C \) system. Since every crystallite which has a set of \( \{hkl\} \)-planes perpendicular to the measurement direction, contributes to the measurement, there is a range of crystallographic orientations contributing to the measurement. Therefore, in Appendix A, the angle \( \alpha \) between the \((0,l,-k)\) vector and the \( L_2 \)-axis is introduced to specify the orientation in the diffracting plane(s). The \((0,l,-k)\) vector is a vector parallel to the diffracting planes, since it is perpendicular to the \((h,k,l)\)-direction. For a non-textured specimen, the average of the strain in all crystallites contributing to the diffraction measurement is given by:

\[
\varepsilon_{\psi,\psi}^{\text{macro}} = \left( \varepsilon_{ij}^C \right)_\alpha = \frac{1}{2\pi} \int_0^{2\pi} \varepsilon_{ij}^C \, d\alpha.
\] (14)

For textured specimens, the crystallographic texture can be incorporated by inserting a distribution function in Eq. (14), giving the appropriate weight (equal to the volume fraction) to each orientation (i.e. value of \( \alpha \)).

D. X-ray elastic constants

For the determination of the stress by diffraction measurements, in a specimen in a rotationally symmetric plane state of stress (Eqs. (2) and (3)), the so-called \( \sin^2 \psi \)-method is often used: the peak position of a certain \( \{hkl\} \)-reflection is measured at different specimen tilt angles \( \psi \). The measured peak positions are used to determine the lattice strain perpendicular to the \( \{hkl\} \)-planes at the different tilt angles \( \psi \). For this case the result of the calculation in Sec. II.C can often be expressed in the form of the so-called \( \sin^2 \psi \)-formula:

\[
\varepsilon_{\psi}^{\text{macro}} = (2S_1^{hkl} + \frac{1}{2} S_2^{hkl} \sin^2 \psi) \sigma_{\parallel}^2.
\] (15)

The constants \( S_1^{hkl} \) and \( \frac{1}{2} S_2^{hkl} \) are independent of \( \psi \) and can be calculated for each reflection \( \{hkl\} \) using a grain interaction model. These constants are called the X-ray elastic constants and were originally introduced by Möller and Martin [11], on grounds of the similarity of Eq. (15) and its mechanical equivalent Eq. (12). Note that there is a difference between the macroscopic strain \( \varepsilon_{\psi}^{\text{mech}} \) (the 'mechanical' strain) in a certain direction \( \psi \) in a stressed specimen and the lattice strain \( \varepsilon_{\psi}^{\text{macro}} \), which is measured in the same direction \( \psi \), by means of a diffraction experiment. The strain \( \varepsilon_{\psi}^{\text{mech}} \) is the average over all crystallites in the specimen, whereas \( \varepsilon_{\psi}^{\text{macro}} \) is the average over the crystallites that contribute in the diffraction experiment.
Decades after the introduction of the X-ray elastic constants, Stickforth [12] has proved that Eq. (15) and the concept of X-ray elastic constants are justified for any (non-textured, polycrystalline) aggregate which is macroscopically elastically isotropic. An evaluation of a number of methods of diffraction analysis based on this concept is given in Ref. [13].

E. The choice of the grain interaction model
In the preceding sections, a general treatment, which is not based on a specific grain interaction model, was given. In this section the choice of a grain interaction model for an evaporated thin film will be dealt with.

The two best known models for grain interaction in bulk materials are the Voigt [2] and Reuss [3] models. The assumption for the grain interaction in the Voigt model is that the strain tensor components in any specimen fixed coordinate system are equal in all crystallites. This assumption implies that the aggregate remains coherent when it is strained, since all crystallites are deformed in exactly the same way. In this case, in any specimen fixed coordinate system, the stress tensor components in each crystallite are different. The resulting discontinuities of the stress at the grain boundaries violate mechanical equilibrium. Alternatively, Reuss has proposed to take the stress tensor components in any specimen fixed coordinate system equal in all crystallites. This assumption, however, leads to discontinuities of the strain at the grain boundaries.

The Reuss and Voigt grain interaction models are extremes for grain interaction assumptions. Hill [5] proved that the values of certain mechanical elastic constants of a macroscopically isotropic aggregate (namely: the bulk modulus $K$, the shear modulus $G$, and the Young's modulus $E$), which are calculated using the Reuss and Voigt models are also the theoretical limits of these elastic constants. Hill therefore proposed to approximate the mechanical elastic constants by taking the average of the Voigt and Reuss values. The use of the average of the Voigt and the Reuss X-ray elastic constants for the interpretation of X-ray diffraction strain measurements had already been proposed earlier by Neerfeld [4], on experimental grounds. The model is therefore referred to as the Neerfeld-Hill model.

The Reuss, Voigt, and Neerfeld-Hill models have originally been proposed to describe the mechanical behaviour of bulk materials, in which each crystallite is surrounded by other crystallites in three dimensions. All three models imply that, in the absence of texture, the aggregate is macroscopically isotropic, since all directions in bulk material are equivalent on a macroscopic scale. Consequently (see end of Sec. II.D), the lattice strain perpendicular to a set of $(hkl)$-planes as a function of the specimen tilt angle $\psi$ satisfies the $\sin^2 \psi$-formula, Eq. (15). Expressions for the mechanical and the X-ray elastic constants in terms of the single crystal elastic constants for the Voigt, Reuss, and Neerfeld-Hill models are given in Appendix B.

---

3 Apart from the well-known crystallographic texture, morphological texture, i.e. the preferred orientation of non-spherical grains in a specimen, can be distinguished. Although morphological texture presents a break of spherical symmetry, a morphologically textured aggregate, which is not crystallographically textured and satisfies the Voigt or Reuss grain interaction models is macroscopically elastically isotropic.
Evaporated thin films have a columnar microstructure [7]. Each crystallite is only surrounded by other crystallites in two dimensions. The interaction between the columns in an evaporated film, in the direction normal to the film surface, is expected to be weak, since there are voids (which may be of atomic size) at the column boundaries [7]. As a result, even in the absence of crystallographic texture, the directions in an evaporated thin film, except for the directions in the plane of the film, are not equivalent on a macroscopic scale. Therefore an evaporated thin film is expected to be only transversely isotropic, the surface normal being the axis of symmetry.

Grain interaction assumptions which reflect transverse isotropy have been proposed by Vook and Witt [8].

F. The Vook-Witt grain interaction model parameters

The Vook-Witt [8] grain interaction model consists of the following assumptions: (i) the strain is rotationally symmetric in the plane of the film and (ii) equal for all crystallites and (iii) the stresses perpendicular to the layer are zero for all crystallites. These assumptions give fixed values to the following stress and strain tensor elements in the $S$ system:

$$
\varepsilon_{11}^S = \varepsilon_{22}^S = \varepsilon_{33}^S = \varepsilon_{ij}^S = 0,
\sigma_{13}^S = \sigma_{33}^S = \sigma_{ij}^S = 0.
$$

In Eq. (16) six independent stress and strain tensor components in the $S$ system ($\varepsilon_{11}^S$, $\varepsilon_{22}^S$, $\varepsilon_{33}^S$, $\sigma_{13}^S$, $\sigma_{33}^S$, and $\sigma_{ij}^S$) are set to a value which is independent of the crystallite orientation. This is indicated by $\varepsilon = \sigma = \varepsilon_{ij}^S = 0$. Due to the symmetry of the stress and strain tensors [9], three more stress and strain tensor components in the $S$ system are fixed. This is indicated by $\varepsilon = \sigma = \varepsilon_{ij}^S = 0$. The remaining stress and strain tensor components depend on the orientation of the crystallite in the $S$ system. The values of these components can be determined for each crystallite using Eq. (1). In this case it is convenient first to solve $\sigma_{11}^S$, $\sigma_{22}^S$, and $\sigma_{12}^S = \sigma_{21}^S$ from the following set of equations (cf. Eq. (1)):

$$
\varepsilon_{12}^S = s_{1211}^S \sigma_{11}^S + s_{1222}^S \sigma_{22}^S + 2s_{1212}^S \sigma_{12}^S = 0,
\varepsilon_{11}^S = s_{1111}^S \sigma_{11}^S + s_{1122}^S \sigma_{22}^S + 2s_{1112}^S \sigma_{12}^S = \varepsilon_{ii}^S,
\varepsilon_{22}^S = s_{2211}^S \sigma_{11}^S + s_{2222}^S \sigma_{22}^S + 2s_{2212}^S \sigma_{12}^S = \varepsilon_{ii}^S.
$$

Then, the stress tensor in the $S$ system $\sigma^S$ is completely known as function of the crystallite orientation, and the strain tensor in the $S$ system $\varepsilon^S$ can be calculated, using again Eq. (1).

The Vook-Witt approach has been used previously only to calculate the lattice strain perpendicular to the specimen surface [8,14]. This is mathematically the most simple case, since the strain in this direction is the same in all crystallites with the same set of \{hkl\}-planes parallel
to the specimen surface, because of the rotationally symmetric state of strain. Consequently, averaging over \( \alpha \) (Eq. (14)) is not necessary. When a direction which is not perpendicular to the specimen surface is considered, the lattice strain in crystallites with a set of \( \{hkl\} \)-planes perpendicular to the considered direction depends on \( \alpha \). Even in the absence of crystallographic texture, the averaging over \( \alpha \) according to the integral in Eq. (14) is very cumbersome when an analytical approach is followed. The results in Sec. IV have therefore been obtained by a numerical computation of this average.

The expected macroscopic elastic anisotropy, arising from the difference between the grain interaction assumptions in the plane of the specimen and perpendicular to the specimen surface (leading to transverse isotropy), is confirmed by the curvature of the calculated \( \sin^2 \psi \)-plots (see Sec. IV.A.2).

Stickforth [12] has shown that, for a transversely isotropic aggregate, there is no general expression, such as the \( \sin^2 \psi \)-formula (Eq. (15)), to calculate the lattice strain in a set of \( \{hkl\} \)-planes as a function of the tilt angle and the single crystal elastic constants.

The mechanical elastic constants \( A \) and \( B \) can be calculated using Eqs. (2)-(6). It should be recognised that the constants \( S_1^{\text{mech}} \) and \( \frac{1}{2} S_2^{\text{mech}} \) can not be used to characterise the elastic behaviour of the aggregate (as in Eq. (7)), since the aggregate is not macroscopically isotropic.

III. Experimental

A. Nickel-layer preparation

Nickel films have been prepared by vapour deposition. The substrates were pieces of single-crystalline silicon wafers with a \(<111>\)-direction perpendicular to the surface. The substrates were cleaned with alcohol before deposition and clamped to a specimen holder which was subsequently mounted in a vacuum vessel. The vessel was pumped down to \( 10^8 \) mbar. Nickel was evaporated by heating pellets of the 99.998% pure metal with an electron beam. The distance between the evaporation source and the substrate was about 1 meter. During evaporation the pressure in the vessel varied as a result of the outgassing of the nickel pellets and 'gettering' by the deposited nickel. The maximum pressure during evaporation was \( 10^{-7} \) mbar. During deposition the layer thickness was measured using a piezo-electrical resonator. Nickel layers of 500 nm thickness were deposited at a rate of 0.25 nm/s.

Two separate runs were performed, using several substrates each run. Before the start of the deposition the substrate was at room temperature, but the substrate temperature rose to approximately 70 °C at the start of the layer deposition.

B. X-ray diffraction measurement

The X-ray diffraction measurements were carried out using a \( \omega \)-differactometer and a \( \psi \)-differactometer. The \( \omega \)-differactometer was a Siemens 500 differactometer which is capable of \( \omega \)-tilting, i.e. tilting around the \( 0-2\theta \)-axis. The differactometer was equipped with a Cu X-ray source and a diffracted beam monochromator set to select the Cu-K\( \alpha \) radiation. For this type of measurement, the angle \( \omega \) corresponds to the tilt angle \( \psi \) as defined in Fig. 1.
The $\psi$-differactometer was a Siemens D5000 diffractometer. The diffractometer was equipped with an Eulerian cradle, for $\psi$-tilting, i.e. tilting of the specimen around the axis which is defined by the intersection of the specimen surface and the plane of diffraction. This diffractometer was provided with a Cu X-ray source and diffracted beam monochromator set to select Cu-K$_{\alpha}$ radiation. The tilt angle $\psi$ for these measurements corresponds to the angle $\psi$ as defined in Fig. 1.

1. Determination of peak position
The measured peak profiles have been fitted with split pseudo-Voigt profiles, using Philips Profit 1.0 software (cf. e.g. Ref. [15]). This program fits a linear background and a peak consisting of identically shaped K$_{\alpha}$ and K$_{\beta}$ peaks with a fixed intensity ratio (0.5) and wavelength difference. The position of the middle at half the height of the K$_{\alpha}$ peak has been determined for asymmetric peak fits as well as symmetric peak fits. The results for both fits were equal to within 0.01°. The peak positions obtained from the symmetric peak fits were converted to values for the lattice spacing using Bragg's law ($K_{\alpha}$ wavelength [19] 1.540562 Å).

2. Strain measurement
For an accurate determination of the stress, the lattice strain (diffraction) measurements should have an accuracy in the $10^{-5}$ to $10^{-4}$ range since the measured strains are usually of the order of $10^{-3}$. X-ray diffraction measurements can be performed reproducibly with this accuracy if the specimen displacement is minimised, sufficiently long counting times are used and the measurement temperature (and the temperature of the cooling water of the X-ray source) are controlled to within a few Kelvin.

The values of $d_{\psi}^{\text{meas}} \sqrt{h^2 + k^2 + l^2}$, determined from the measured lattice spacings $d_{\psi}^{\text{meas}}$ of the {111}-reflection on the $\psi$-differactometer and the {222}-reflection on the $\omega$-differactometer, differ about $3 \times 10^{-3}$ Å. Although this difference seems small, it can bring about a large difference in the calculated lattice strain and a correction is required.

The difference between the $\psi$-differactometer and the $\omega$-differactometer indicates that the measurements on one or both of the diffractometer are subject to systematic errors. Systematic errors may be due to the diffraction measurement itself and/or due to the determination of the average lattice spacing (i.e. peak position) from the measurement. Both types of errors are compensated for by the use of a stress-free reference specimen. Optimum correction is achieved when the stress-free reference specimen is in all aspects, apart from the macroscopic stress, (composition, constitution, thickness, and texture) identical to the specimen on which the strain measurement is carried out.

The stress-free reference specimen has been obtained by removing a nickel layer from its substrate. This was accomplished by first cooling the substrate with the layer to -45 °C in alcohol and subsequently leaving it (in the liquid) to warm up to room temperature. The layer detached itself from the substrate in pieces of approx. 5×5 mm, during the warming up. These pieces were re-attached to a new substrate using a solution of bees wax in alcohol.
For each measured reflection \( \{hkl\} \) and specimen tilt angle \( \psi \), the lattice strain was calculated from the average lattice spacings of the stressed layer \( d_\psi^{\text{meas}} \) and of the stress-free reference specimen \( d_\psi^{\text{sf}} \), according to

\[
\varepsilon_\psi^{\text{meas}} = \frac{d_\psi^{\text{meas}} - d_\psi^{\text{sf}}}{d_{\text{ref}}}. \tag{18}
\]

A reference lattice spacing, \( d_{\text{ref}} \), very close to \( d_\psi^{\text{sf}} \), is used in the denominator of Eq. (18) to calculate the relative change of the lattice spacing, the lattice strain, from the measured absolute change of the lattice spacing. Since the attention is focused on the dependence of the lattice strain on the tilt angle and the reflection, a constant \( d_{\text{ref}} \) is preferred over \( d_\psi^{\text{sf}} \), because \( d_\psi^{\text{sf}} \) may depend slightly on \( \psi \) and the diffraction angle due to instrumental aberrations, as discussed above. Furthermore, an error of a few percent can be tolerated in \( d_{\text{ref}} \), since it will only lead to a systematic change of a few percent of the calculated strain (contrary to errors in \( d_\psi^{\text{sf}} \)). Here, the literature value of the lattice spacing is used for \( d_{\text{ref}} \), which directly follows from the literature value of the lattice constant \( a_{\text{ref}} \) \( a_{\text{ref}} = d_{\text{ref}} \sqrt{h^2 + k^2 + l^2} \). Eq. (18) can now be rearranged to:

\[
\varepsilon_\psi^{\text{meas}} a_{\text{ref}} = (d_\psi^{\text{meas}} - d_\psi^{\text{sf}}) \sqrt{h^2 + k^2 + l^2} = \Delta d \sqrt{h^2 + k^2 + l^2}. \tag{19}
\]

3. Reproducibility of the layer preparation

To check the reproducibility of the nickel layer deposition, two deposition runs have been carried out (see Sec. III.A). During the first run layers were deposited simultaneously onto two substrates; during the second run onto three substrates. The results of the X-ray diffraction measurements of simultaneously deposited layers are identical.

Comparing results of X-ray diffraction measurements of layers deposited during different runs, the same characteristic behaviour, i.e. shape and relative positions of the \( \sin^2 \psi \)-curves, is observed. The macroscopic strain parallel to the specimen surface, however, is different for layers of both runs \( \varepsilon_{\text{run}}^{\psi} \approx 2 \times 10^{-3} \) and \( \varepsilon_{\text{run}}^{\psi} \approx 3 \times 10^{-3} \), respectively).

For practical reasons, the result which are discussed in Sec. IV.0 have been obtained from measurements on layers from the first deposition run, whereas the stress-free reference specimen has been produced using a layer of the second deposition run. The differences in crystallographic texture and microstructure (observed as diffraction line broadening in a diffraction experiment) are so small, if existent at all, that the stress-free reference specimen can be applied in the analysis of measurements on the specimens from the first run.
IV. Results and discussion

A. Numerical illustration

1. Mechanical elastic constants

The macroscopic average elastic constants $A$ and $B$, as defined for a transversely isotropic specimen in a rotationally symmetric plane state of stress in Sec. II.A, have been calculated for the Voek-Witt grain interaction model, using Eqs. (2)-(6). The single crystal elastic constants of nickel [10] were used in the calculation. The results are presented in Table 1. For comparison, the corresponding values for the Voigt and Reuss grain interaction models are also given (these can also be calculated using Eqs. (B1) and (B2)).

The values of the macroscopic elastic constants for the Voek-Witt model are between the Voigt and Reuss values. It should be noted that Hill's proof [4] that the mechanical elastic constants $K$, $G$, and $E$ should be between the values according to the Voigt and Reuss models does not necessarily hold in this case, since the aggregate is not macroscopically isotropic (see Sec. II.E).

Table 1: Macroscopic elastic constants A and B of nickel for the different models. The following values of the single crystal elastic constants of nickel were used [10]: $S_{11}=7.67$ TPa$^{-1}$, $S_{12}=-2.93$ TPa$^{-1}$, and $S_{44}=8.23$ TPa$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>Voigt</th>
<th>Reuss</th>
<th>Vook-Witt</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (TPa$^{-1}$)</td>
<td>3.02</td>
<td>3.45</td>
<td>3.25</td>
</tr>
<tr>
<td>B (TPa$^{-1}$)</td>
<td>-2.42</td>
<td>-3.27</td>
<td>-2.87</td>
</tr>
</tbody>
</table>

2. Comparison of models for lattice strain

To compare the lattice strain values calculated using the three different grain interaction models, sin$^2$ $\psi$-plots (i.e. the lattice strain perpendicular to different \{hkl\} lattice planes as a function of sin$^2$ $\psi$, where $\psi$ is the specimen tilt angle) have been calculated for the Voigt, Reuss and Vook-Witt grain interaction models. The calculations were performed for a specimen in a state of rotationally symmetric plane stress (Eqs. (2) and (3)). For the macroscopic average stress parallel to the specimen surface, a value of 800 MPa was taken:

\[
\left\langle \sigma_{ii}^w \right\rangle = \left\langle \sigma_{11}^w \right\rangle = \sigma_{11}^v = 800 \text{ MPa},
\]

\[
\left\langle \sigma_{ij}^w \right\rangle = \left\langle \sigma_{12}^w \right\rangle = 0,
\]

\[
\left\langle \sigma_{ii}^{\perp} \right\rangle = \left\langle \sigma_{11}^{\perp} \right\rangle = 0.
\]

The average strains $\epsilon_{ii}^w$ parallel to and $\epsilon_{ii}^{\perp}$ perpendicular to the specimen surface have been calculated using Eq. (5) and the values of $A$ and $B$ in Table 1, for each model. The results are presented in Table 2.
Table 2: Average strains parallel to and perpendicular to the specimen surface calculated using three different grain interaction models, for a rotationally symmetric plane state of stress ($\sigma_{ij}^5=800$ MPa).

<table>
<thead>
<tr>
<th></th>
<th>Voigt</th>
<th>Reuss</th>
<th>Vook-Witt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{ii}^5 \times 10^3$</td>
<td>2.42</td>
<td>2.76</td>
<td>2.60</td>
</tr>
<tr>
<td>$\varepsilon_{ij}^5 \times 10^3$</td>
<td>-1.94</td>
<td>-2.62</td>
<td>-2.30</td>
</tr>
</tbody>
</table>

To calculate the lattice strain as a function of $\psi$, using the Vook-Witt grain interaction model parameters, the value of $\varepsilon_{ii}^5$ as given in Table 2 is substituted in Eq. (16) and the calculation as outlined in Sec. II.C is applied to calculate the $\sin^2 \psi$-plots.

The $\sin^2 \psi$-plots for the Voigt and Reuss grain interaction models are most conveniently calculated by substituting the values of the X-ray elastic constants $S_{1}^{ML}$ and $\frac{1}{2} S_{2}^{ML}$, given by Eqs. (B1) and (B3), in the $\sin^2 \psi$-formula, Eq. (15). It is also possible to use Eq. (14) to calculate the lattice strain from the strain tensor in the $\delta$ system in each crystallite. The strain tensor in the $\delta$ system is given for the Voigt model in Table 2. For the Reuss model it can be calculated for each crystallite, using Eq. (1) and the stress tensor values given in Eq. (20).

The results of the calculations are depicted in Fig. 2. The Voigt model yields a single straight line (dotted in Fig. 2) independent of $\{hkl\}$, because the strain tensor in any specimen-fixed coordinate system is the same in all crystallites. The Reuss model also yields straight lines, each

![Image of Fig. 2](image-url)

Fig. 2: The $\sin^2 \psi$-plots calculated according to the Voigt, Reuss, and Vook-Witt grain interaction models for a rotationally symmetric plane state of stress in an evaporated nickel film. The macroscopic average stress parallel to the specimen surface is 800 MPa. The Voigt-$\sin^2 \psi$-plot is given by the dotted line. All Reuss-$\sin^2 \psi$-plots fall within the lightly shaded area bounded by the $\{h00\}$- and $\{hkh\}$-plots (dashed lines). For the Vook-Witt model only the $\{h00\}$- and $\{hkh\}$-$\sin^2 \psi$-plots have been drawn.

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corresponding to a different reflection \{hkl\}. All Reuss-lines fall within the lightly shaded area in Fig. 2. The intersection point of the Reuss-lines is at exactly \(\sin^2 \psi = 2/3\), as can be easily verified using Eqs. (B3) and (15). The steepest \(\sin^2 \psi\)-plot is the \{h00\}-plot and the \{hhh\}-plot is the least steep plot. This reflects that the [111]- and the [100]-directions are the stiffest and most compliant directions in a nickel crystal, respectively.

The \{hhh\}- and \{h00\}-\(\sin^2 \psi\)-plots for the Vook-Witt model are also shown in Fig. 2. The \(\sin^2 \psi\)-plots as calculated for the Vook-Witt model are distinctly curved (see Sec. II.E).

The \{hhh\}- and \{h00\}-\(\sin^2 \psi\)-plots for the Vook-Witt model intersect at \(\sin^2 \psi = 0.52\). There is no single intersection point for all \{hkl\}-plots (see also Fig. 3).

For values of \(\sin^2 \psi\) below approximately 0.56, the values of the lattice strain perpendicular to the \{h00\}- and \{hhh\}-planes, which have been calculated using the Vook-Witt model, are in-between the results for the Voigt and the Reuss models. For larger values of \(\sin^2 \psi\), the lattice strain according to the Vook-Witt model can be outside the Voigt and Reuss bounds. Clearly, although the mechanical elastic constants for the Vook-Witt model are in-between the values according to the Voigt and Reuss models, the lattice strain is not always in-between the values according to the Voigt and Reuss models. This is possible, because the mechanical elastic constants are the result of averaging over all crystallite orientations whereas the direction

### Figure 3: Fit of the Vook-Witt model to the lattice spacings measured from the evaporated nickel film (dotted lines). To indicate which lines belong to which experimental data, the (smaller) markers on the fitted lines correspond to the (larger) markers of the experimental data of the same (type of) reflection. The measurements on the \(\psi\)-diffractometer are marked with closed symbols. The experimental scatter in the strain data is estimated at few times the size of the (larger) markers, recognising that the relative uncertainty in the determination of a peak position is \(10^{-1}-10^{4}\) (see Sec.III.B.2).
dependent lattice strain is only averaged over the diffracting crystallites.

B. Experiments

The results of the measurements on both the $\psi$- and the $\omega$-diffractometers have been combined in one graph, which is shown in Fig. 3. The good agreement between the measurements of the \{111\}- and \{200\}-reflections on the $\psi$-diffractometer and the \{222\}- and \{400\}-reflections on the $\omega$-diffractometer, is due to the elimination of the systematic errors by using the stress-free reference specimen (cf. Sec. III.B.2).

The nickel layers revealed a slight $<111>$ fibre texture: the integrated intensity of the \{111\} reflection at $\psi = 0$, corrected for absorption in a thin layer (according to Ref. [17]), is four times the intensity as recorded for larger $\psi$, since the diffracting volume for a random specimen is normally much less than 1% of the irradiated volume (cf. Ref. [17]), the texture in the specimen considered is very weak.

The measurements were fitted using the Voek-Witt grain interaction model. To calculate the strain, the literature value of the lattice constant [17] $a_{\text{ref}} = 3.5238 \ \text{Å}$, was used in Eq. (19).

It is clear that the Voigt model, which predicts one single $\sin^2 \psi$-plot for all reflections, is not

![Graph](image)

**Fig. 4:** Fit of the Neerfeld-Hill model to the lattice spacings measured from the evaporated nickel film (dotted lines). To indicate which lines belong to which experimental data, the (smaller) markers on the fitted lines correspond to the (larger) markers of the experimental data of the same (type of) reflection. The fitted lines for the \{311\}- and \{420\}-reflections practically coincide. The measurements on the $\psi$-diffractometer are marked with closed symbols. The experimental scatter in the strain data is estimated at a few times the size of the (larger) markers, recognising that the relative uncertainty in the determination of a peak position is $10^2$-$10^4$ (see Sec. III.B.2).
applicable to this specimen. As for the other two models (Neerfeld-Hill and Reuss), the Neerfeld-Hill model yields the best fit to the measurements (see Fig. 4).

Comparison of Fig. 3 and Fig. 4 shows that the Vook-Witt model yields the best fit of the experimental results of the evaporated nickel layer. Especially the predicted curvature of the \(\{hhh\}\), \(\{331\}\), and \(\{h00\}\) -plots is confirmed by the experiment.

The value of the strain parallel to the specimen surface \(\varepsilon^S_{hh}=1.81\times10^{-3}\) which has been determined from the fit of the Vook-Witt model, shown in Fig. 3, has been used to calculate the stress parallel to the specimen surface, using Eq. (5) and the appropriate value of \(A\) (Table 1).

The stress parallel to the specimen surface is 557 MPa. This stress consists of a thermal and a growth component. It can be readily calculated that the thermal strain, i.e. the strain generated during the cooling down from the deposition temperature (approx. 70 °C) to room temperature, is approximately \(4\times10^{-4}\) (data for the thermal expansion coefficients of layer and substrate can be found in Ref. [10]), corresponding to a thermal stress of approx. 120 MPa.

The stress exceeding the thermal stress is called growth stress. It is often suggested that growth stress in evaporated films originates from the microstructure of columnar grains separated by void networks [7]. The interatomic forces acting over the voids between the columns are thought to be the main cause of tensile stress. Both simulations [18,19] and experiments [20] indicate that the interatomic forces acting over the grain boundaries can indeed bring about macroscopic tensile stress.

This view on the origin of growth stress is compatible with the Vook-Witt grain interaction model assumptions: in the direction perpendicular to the film surface, the columns can expand or shrink rather freely, whereas in the plane of the film, the columns are tightly connected to each other by the interatomic forces.

The present work provides experimental evidence for direction dependent grain interaction in evaporated thin films.

V. Conclusion

The grain interaction models due to Voigt, Reuss, Neerfeld-Hill, and Eshelby-Kröner are, strictly speaking, inappropriate for the analysis of macroscopic stress in thin films, because the microstructure of thin films is not compatible with the inherently assumed macroscopic elastic isotropy.

The Vook-Witt grain interaction model, i.e. equal strain parallel to the specimen surface and zero stress perpendicular to the specimen surface, may be more appropriate for the analysis of macroscopic stress in thin films. A remarkable feature of the Vook-Witt grain interaction model is that, even in the absence of crystallographic texture, the \(\sin^2\psi\)-plots are curved; an aggregate which satisfies the Vook-Witt assumptions is not macroscopically elastically isotropic.

The Vook-Witt model provides a better fit to the experimentally observed lattice strain in an evaporated nickel film than the Voigt, Reuss and Neerfeld-Hill models. The experimentally observed curvature of the \(\sin^2\psi\)-plots is the first experimental evidence for direction dependent grain interaction in stressed films.
X-ray diffraction strain measurements can be used to examine direction dependent grain interaction.

Acknowledgments
We are indebted to Dr. J. Verhoeven (FOM-AMOLF, Amsterdam) for providing the evaporation facilities and to Ms. N. Rutte for technical assistance during layer preparation. We would also like to thank Dr. Ir. Th. H. de Keijser, Dr. Ir. R. Delhez and Dott. Ing. Ph.D. M. Leoni (MPI Stuttgart) for careful reading of the early versions of the manuscript and fruitful discussions.

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Appendix A: Calculation of the direction cosines

The representation of a tensor in a certain coordinate system can be transformed to another coordinate system, using the appropriate direction cosines. For example the representation of a vector (a first-rank tensor) in the \( S \) system \( V^S \) can be transformed to the representation of the vector in the \( L \) system \( V^L \), according to the following formula [9]:

\[
V_i^L = a_{ij}^S V_j^S,
\]

(A1)

where the coefficients \( a_{ij}^S \) are the direction cosines between the \( L \) and the \( S \) systems. The direction cosine \( a_{ij}^S \) is the cosine of the angle between unit vector \( j \) in the \( S \) system and unit vector \( i \) in the \( L \) system.

In the following the direction cosines \( a_{ij} \) are given in the form of a direction cosine matrix \( a \). The direction cosine \( a_{ij} \) is the \( j \)th element of the \( i \)th row of the matrix \( a \).

In the calculations as outlined in Sec. II, the following direction cosines are used: \( a_{ij}^{SC} \) and \( a_{ij}^{LS} \).

First an expression for \( a_{ij}^{LS} \), explicit in terms of the angles \( \varphi \) and \( \psi \), which define the measurement direction with respect to the specimen system, will be given. The direction cosines can be calculated in two steps since the Eulerian angles \( \varphi \) and \( \psi \) are the angles of rotation of two subsequent rotations (see Fig. 1). The first step is the rotation over \( \varphi \), around the \( S_1 \)-axis. The new coordinate system is referred to as \( S' \). The direction cosine matrix \( a_{ijs}^{SS} \), for the transformation from the \( S \) to the \( S' \) is given by (see Fig. 1)

\[
a_{ijs} = \begin{pmatrix}
\cos \varphi & \sin \varphi & 0 \\
-\sin \varphi & \cos \varphi & 0 \\
0 & 0 & 1
\end{pmatrix}.
\]

(A2)

The second step is the rotation over \( \psi \) around the \( S'_2 \) axis, to transform the \( S' \) system into the \( L \) system. The direction cosine matrix \( a_{ij}^{LS} \), for this transformation is:
\[
a^{CS} = \begin{pmatrix}
\cos \psi & 0 & -\sin \psi \\
0 & 1 & 0 \\
\sin \psi & 0 & \cos \psi 
\end{pmatrix}.
\]

The tensor transformation matrix \(a^{CS}\), for the combination of both subsequent rotations, i.e. the transformation from the \(S\) system to the \(L\) system, satisfies

\[
a^{CS} = a^{LC} a^{SS}. \tag{A4}
\]

Next, to obtain an expression for \(a^{LC}\) explicit in terms of the indices \(h, k, l\) of the diffracting planes, use is made of the relation between the measurement direction, the \(L_3\)-axis, and the orientation of the crystallite (the \(C\) system), which is imposed by the diffraction experiment. Here only the case of cubic crystal symmetry is considered: the crystal axes are the \(a\), \(b\) and \(c\) lattice directions and the \([hkl]\)-direction is perpendicular to the \((hkl)\)-plane.

It is convenient to introduce an intermediate coordinate system, the \(L'\) system which has a fixed orientation with respect to the \(C\) system. The \(L'_3\) axis is along the diffraction vector of the experiment, along the \((h,k,l)\) vector in the crystal \((C)\) system. The other two axes are chosen along \((l^2+k^2,-kh,-lh)\) and \((0,l,-k)\), i.e. perpendicular to the \(L'_3\) axis and to each other. The matrix \(a^{LC}\) can now be obtained by noting that the multiplication of each of the basis vectors \((1,0,0), (0,1,0), (0,0,1)\) in the \(L'\) system with \(a^{LC}\) yields the vectors in the \(C\) system (i.e. the normalised vectors along \((l^2+k^2,-kh,-lh)\), \((0,l,-k)\), and \((h,k,l)\) respectively, see also Eq. (A1)):

\[
a^{LC} = \begin{pmatrix}
\frac{l^2+k^2}{\sqrt{l^2+k^2}\sqrt{h^2+k^2+l^2}} & 0 & \frac{h}{\sqrt{h^2+k^2+l^2}} \\
\frac{-kh}{\sqrt{l^2+k^2}\sqrt{h^2+k^2+l^2}} & \frac{l}{\sqrt{l^2+k^2}} & \frac{k}{\sqrt{l^2+k^2}} \\
\frac{-lh}{\sqrt{l^2+k^2}\sqrt{h^2+k^2+l^2}} & \frac{k}{\sqrt{h^2+k^2+l^2}} & \frac{l}{\sqrt{h^2+k^2+l^2}} 
\end{pmatrix}. \tag{A5}
\]

The orientations of the \(C\) system with respect to the \(L'\) system which have the \((h,k,l)\) vector in the \(C\) system along the \(L'_3\) axis are obtained by rotation of the \(L'\) system around the \(L'_3\) axis. The angle of rotation is denoted by \(\alpha\) (see Fig. 5). The corresponding direction cosine matrix \(a^{LC}\) is given by:

\[
a^{LC} = \begin{pmatrix}
\cos \alpha & -\sin \alpha & 0 \\
\sin \alpha & \cos \alpha & 0 \\
0 & 0 & 1
\end{pmatrix}. \tag{A6}
\]

The following relation now expresses \(a^{LC}\), as function of \(h, k, l,\) and \(\alpha\):

\[
71
\]
Fig. 5: The conversion of the $L'$ system to the $L$ system, by a rotation over $\alpha$ around the $L_3/L'_3$ axis.

$$a^{cc} = a^{cc'} a^{c'c}.$$  \hfill (A7)

It is also possible to define the $L_3$-direction using the spherical polar coordinates $\mu$ and $\lambda$ instead of the indices $h$, $k$, and $l$. The expression for $a^{cc'}$ in terms of the spherical polar coordinates $\mu$ and $\lambda$ is obtained by the following substitutions in Eq. (A5):

$$h = \sin \mu \sin \lambda,$$
$$k = \sin \mu \cos \lambda,$$
$$l = \cos \mu.$$  \hfill (A8)

Calculation of $a^{cc'}$ using Eq. (A7) provides an expression in terms of $\lambda$, $\mu$, and $\alpha$.

Finally, $a^{x'}$ is obtained from:

$$a^{x'} = (a^{cs})^{-1} = (a^{cc'} a^{co})^{-1}.$$  \hfill (A9)

---

$^4$ Since all matrices $a$ are orthonormal, the inverse $a^{-1}$ of the matrix $a$ is equal to the transposed matrix $a^T$. This markedly simplifies the calculation of the inverse matrices.
Appendix B: Mechanical and X-ray elastic constants for bulk grain interaction models

A. The Voigt model

The grain interaction assumption which has been proposed by Voigt [2] is that, in any specimen fixed coordinate system, the strain tensor components are equal in all crystallites.

The values of the X-ray elastic constants are equal to the values of the mechanical elastic constants. The elastic constants for the Voigt model can be directly calculated from the single crystal elastic constants, according to the following equations [1,2]:

\[
S_{1}^{hkl} = S_{1}^{mech} = \frac{(s_{1111}^{c} - s_{1122}^{c} - 2s_{1212}^{c}) (s_{1111}^{c} + 2s_{1212}^{c}) + 10s_{1122}^{c}s_{1212}^{c}}{3s_{1111}^{c} - 3s_{1122}^{c} + 4s_{1212}^{c}}.
\]

\[
\frac{1}{2} S_{2}^{hkl} = \frac{1}{2} S_{2}^{mech} = \frac{10s_{1122}^{c}(s_{1111}^{c} - 2s_{1212}^{c})}{3s_{1111}^{c} - 3s_{1122}^{c} + 4s_{1212}^{c}}.
\] (B1)

B. The Reuss model

The grain interaction assumption which has been proposed by Reuss [3] is that, in any specimen fixed coordinate system, the stress tensor components are equal in all crystallites.

The mechanical elastic constants for the Reuss model in terms of the single crystal elastic constants are [11]

\[
S_{1}^{mech} = s_{1122}^{c} + \frac{1}{2} (s_{1111}^{c} - s_{1122}^{c} - 2s_{1212}^{c}),
\]

\[
\frac{1}{2} S_{2}^{mech} = s_{1111}^{c} - s_{1122}^{c} - \frac{1}{2} (s_{1111}^{c} - s_{1122}^{c} - 2s_{1212}^{c}).
\] (B2)

The X-ray elastic constants are {hkl}-dependent, according to [11]

\[
S_{1}^{hkl} = s_{1122}^{c} + (s_{1111}^{c} - s_{1122}^{c} - 2s_{1212}^{c}) \Gamma,
\]

\[
\frac{1}{2} S_{2}^{hkl} = s_{1111}^{c} - s_{1122}^{c} - 3(s_{1111}^{c} - s_{1122}^{c} - 2s_{1212}^{c}) \Gamma,
\] (B3)

where: \( \Gamma = \frac{h^{2}k^{2}l^{2} + k^{2}l^{2} + l^{2}h^{2}}{(h^{2} + k^{2} + l^{2})^{2}} \).

C. The Neerfeld-Hill model

The Neerfeld-Hill model is often used in practice to determine internal stress from \( \sin^{2} \psi \) measurements. Both the mechanical and the X-ray elastic constants for the Neerfeld-Hill model are the arithmetic mean values of the values for the elastic constants according to Voigt and Reuss. The experimentally observed values of the mechanical elastic constants of any macroscopically elastically isotropic specimen are always in-between the values according to the Voigt and Reuss models. This is not necessarily so for the X-ray elastic constants.

The equations presented in Secs. II.A and II.C cannot be used for the calculation of the elastic constants for the Neerfeld-Hill model, since there are no grain interaction model parameters for
the Neerfeld-Hill model. The Neerfeld-Hill elastic constants are directly calculated using the values of these constants according to the Voigt and Reuss models.

References

Chapter VI

New methods for diffraction stress measurement

A critical evaluation of new and existing methods

J.-D. Kamminga, Th.H. de Keijser, R. Delhez, E.J. Mittemeijer

ABSTRACT

New methods of diffraction stress analysis of polycrystalline materials, consisting of cubic, elastically anisotropic crystallites, are proposed and compared with existing methods. Whereas for the existing methods knowledge of the diffraction elastic constants is presupposed, three new methods are presented that require only knowledge of the (macroscopic) mechanical elastic constants. The stress values obtained with these new methods on the basis of the mechanical elastic constants are more reliable than those obtained with the methods on the basis of the diffraction elastic constants. New and existing methods are illustrated by means of X-ray diffraction measurements from a magnetron sputtered TiN layer.

I. Introduction

Diffraction can be used to measure strains with very high precision and accuracy [1,2]. However, for the calculation of the stress from the measured strains elastic constants are needed and the accuracy of these constants is a decisive factor for the accuracy of the values obtained for the stress. It is necessary to distinguish between mechanical elastic constants and the elastic constants that are generally used to interpret diffraction strain measurements: the so-called diffraction elastic constants. For polycrystalline specimens that consist of elastically anisotropic crystallites the mechanical elastic constants and the diffraction elastic constants differ. In a diffraction experiment the data obtained stem from a selection of crystallites that have defined orientations with respect to the diffraction geometry, whereas the mechanical elastic constants concern averages over all crystallites.

The values of both mechanical and diffraction elastic constants not only depend on the substance of the specimen considered but also on the grain interaction in the specimen, i.e. how the stresses and strains are distributed over the various grains. Thus, these elastic constants can be different for specimens that consist of the same substance, but have different microstructures (published values for mechanical and diffraction elastic constants of materials should therefore be handled with care).

Values for both the mechanical and the diffraction elastic constants can be obtained in two ways. It is best to measure these constants for each specimen considered. This can be done with a
tensile testing device, that for the measurement of diffraction elastic constants should be designed such, that it can be mounted on a diffractometer [1,2]. Unfortunately, such experimental assessment of elastic constants is not always possible. Then, for homogeneous polycrystalline specimens, mechanical and diffraction elastic constants have to be calculated from the single crystal elastic constants. Several models exist to calculate these constants, all making different assumptions for the grain interactions in the specimen. The values obtained differ considerably for the different grain interaction models and there exists no generally valid criterion to decide which model should be used for a given specimen.

The calculated values for the mechanical elastic constants depend less on the used grain interaction model than the corresponding values for the diffraction elastic constants. Moreover, theoretical upper and lower bounds can be given for mechanical elastic constants, which is not the case for diffraction elastic constants. Consequently, whether the elastic constants are obtained from measurement or from model calculations, in the interpretation of diffraction stress measurements the use of mechanical elastic constants is to be preferred.

The present paper provides new methods of diffraction stress analysis in which stress values are derived from the measured diffraction strain data employing mechanical elastic constants. The results of six different methods of diffraction stress analysis, of which three are based on diffraction elastic constants and three are based on mechanical elastic constants, are compared and discussed for the case of a magnetron sputtered TiN layer.

II. Background

If a polycrystalline specimen that is elastically isotropic on a macroscopic scale is subjected to a rotationally symmetric biaxial state of stress parallel to the specimen surface \((\sigma_{\varphi}^{\text{mech}} = \sigma_1^{\text{mech}} = \sigma_2^{\text{mech}})\) the stress is connected to the strain by the following equation (cf. Refs [1,2]):

\[
\varepsilon_\varphi^{\text{mech}} = \left(2S_1^{\text{mech}} + \frac{1}{2} S_2^{\text{mech}} \sin^2 \psi\right) \sigma_{\varphi}^{\text{mech}} \tag{1a}
\]

A treatment for \(\sigma_1^{\text{mech}} \neq \sigma_2^{\text{mech}}\) is given in Appendix A. In the above equation the superscript \(\text{mech}\) has been used to denote macroscopic entities, \(\psi\) is the angle between the specimen surface normal and the direction in which the strain \(\varepsilon_\varphi^{\text{mech}}\) is measured, and \(S_1^{\text{mech}}\) and \(\frac{1}{2} S_2^{\text{mech}}\) are mechanical elastic constants of the (elastically isotropic) aggregate. The mechanical elastic constants \(S_1^{\text{mech}}\) and \(\frac{1}{2} S_2^{\text{mech}}\) can be written in terms of Young's modulus \(E\) and Poisson's ratio \(\nu\). It holds [1,2,3]:

\[
S_1^{\text{mech}} = -\frac{\nu}{E} \tag{1b}
\]

\[
\frac{1}{2} S_2^{\text{mech}} = \frac{1 + \nu}{E} \tag{1c}
\]
Note that the (mechanical) strain $\varepsilon_{\psi}^{\text{mech}}$ is an average of the strains in all crystallites (contrary to the strains measured with diffraction, see below). When the strain $\varepsilon_{\psi}^{\text{mech}}$ is measured at a given angle $\psi$ and the mechanical elastic constants are known, the stress can be obtained from Eq. (1a).

Lattice strains can be measured using diffraction. The lattice spacing $d_{\psi}^{\text{hkl}}$, determined from the position of an $hkl$ reflection recorded at a specimen tilt angle $\psi$ is then used as an internal strain gauge. Diffraction stress analysis for a biaxially loaded homogeneous specimen with $\sigma_{\psi}^{\text{mech}} = \sigma_1^{\text{mech}} = \sigma_2^{\text{mech}}$ of a cubic substance and using diffraction elastic constants is based on the following equation (cf. Refs [1,2]):

$$\varepsilon_{\psi}^{\text{hkl}} = \frac{d_{\psi}^{\text{hkl}} \sqrt{h^2 + k^2 + l^2} - a_0}{a_{\text{ref}}} = \left(2S_1^{\text{hkl}} + \frac{1}{2} S_2^{\text{hkl}} \sin^2 \psi\right)\sigma_{\psi}^{\text{mech}}$$  \hspace{1cm} (2)

where $\varepsilon_{\psi}^{\text{hkl}}$ is the strain for the $(hkl)$ lattice planes at angle $\psi$, $a_0$ denotes the lattice parameter of the strain free material, $a_{\text{ref}}$ is a reference spacing, which has been introduced for convenience (see section III) and is chosen very close to $a_0$, and $S_1^{\text{hkl}}$ and $\frac{1}{2} S_2^{\text{hkl}}$ are the diffraction elastic constants for the reflection $(hkl)$. Generally, the diffraction elastic constants depend on $hkl$. Note that in an $\varepsilon_{\psi}^{\text{hkl}}$ measurement only a (small) part of the crystallites of the aggregate contribute, namely only those having $(hkl)$ lattice planes perpendicular to the diffraction vector.

For a specimen consisting of elastically anisotropic crystallites, it was demonstrated by Stickforth [4] that Eq. (2) can only be used with $\psi$ independent $S_1^{\text{hkl}}$ and $\frac{1}{2} S_2^{\text{hkl}}$ if the specimen is macroscopically isotropic, i.e. the specimen exhibits neither crystallographic texture nor morphologic anisotropy. For example, a specimen with parallel columnar grains is morphologically anisotropic. It should be realised that morphologic anisotropy is also associated with the outer dimensions of a specimen. It is thus always present if the outer dimensions of the specimen are non-spherical.

If a specimen is macroscopically isotropic, the diffraction elastic constants of a cubic material can always be written as [4]:

$$S_1^{\text{hkl}} = K_1 + K_3 \Gamma$$ \hspace{1cm} (3a)
$$\frac{1}{2} S_2^{\text{hkl}} = K_1 - 3K_2 \Gamma$$ \hspace{1cm} (3b)

where $\Gamma$ is given by

$$\Gamma = \frac{h^2k^2 + k^2l^2 + h^2l^2}{(h^2 + k^2 + l^2)^2}$$ \hspace{1cm} (3c)

The constants $K_1$, $K_2$ and $K_3$ depend on both the single crystal elastic constants and the microstructure of the macroscopically isotropic specimen, but are in any case $hkl$ independent. The mechanical elastic constants $S_1^{\text{mech}}$ and $\frac{1}{2} S_2^{\text{mech}}$ follow from Eqs (3a) and (3b) setting $\Gamma = 1/5$ [3,4,5], i.e.
\[ S_i^{\text{mech}} = S_i^{\text{hkl}} (\Gamma = \frac{1}{2}) \quad i = 1, 2 \tag{3d} \]

Consequently, the diffraction elastic constants can be expressed in terms of the mechanical elastic constants (cf. Eqs (3a) and (3b)):

\[ S_1^{\text{hkl}} = S_1^{\text{mech}} + K_2 (\Gamma - \frac{1}{2}) \tag{4a} \]
\[ \frac{1}{2} S_2^{\text{hkl}} = \frac{1}{2} S_2^{\text{mech}} - 3 K_2 (\Gamma - \frac{1}{2}) \tag{4b} \]

From Eqs (2) and (1a) one can now write down an expression that provides the relation between the mechanical strain and the ‘diffraction’ strain, using Eqs (4a) and (4b):

\[ \varepsilon_\psi^{\text{hkl}} - \varepsilon_\psi^{\text{mech}} = (2 K_2 (\Gamma - \frac{1}{2}) - 3 K_2 (\Gamma - \frac{1}{2}) \sin^2 \psi) \sigma_{\parallel}^{\text{mech}} \tag{5} \]

III. Methods of diffraction stress analysis

In this section new and existing methods for diffraction stress analysis are treated that can be used to measure rotationally symmetric biaxial stresses in homogeneous specimens that consist of a cubic material and that are macroscopically isotropic. The pros and cons of the various methods are discussed in section IV.

If the elastic constants are known, the stress can be determined from a single \( \varepsilon_\psi^{\text{mech}} \) or \( \varepsilon_\psi^{\text{hkl}} \) measurement using Eq. (1a) or Eq. (2). For the assessment of the strain \( \varepsilon_\psi^{\text{hkl}} \) from a measured lattice spacing, an accurate value of \( a_0 \) should be available (cf. Eq. (2)). Due to the small difference between the measured values of \( d_\psi^{\text{hkl}} \sqrt{h^2 + k^2 + l^2} \) and \( a_0 \), small errors in \( a_0 \) introduce large errors in \( \sigma_{\parallel}^{\text{mech}} \). Even if a literature value of \( a_0 \) is available, one still has to consider the errors in the \( d_\psi^{\text{hkl}} \) values originating from the instrumental aberrations. On the other hand, a small error in \( a_{\text{ref}} \) is of minor importance and any value close to \( a_0 \) can be used for \( a_{\text{ref}} \). Consequently, \( a_{\text{ref}} \) can be considered as a known constant. All methods for diffraction stress analysis discussed below allow determination of the stress without a precise knowledge of \( a_0 \).

A. Stress analysis on the basis of diffraction elastic constants

1. \( \sin^2 \psi \) method; the ‘classical’ method

Most often, the so-called \( \sin^2 \psi \) method is used for diffraction stress measurements. Then a set of \( d_\psi^{\text{hkl}} \) values is measured at different \( \psi \) angles using a certain reflection \( \{hkl\} \). A plot of \( d_\psi^{\text{hkl}} \) versus \( \sin^2 \psi \) (the so-called \( \sin^2 \psi \) plot) yields a straight line and from its slope the stress \( \sigma_{\parallel}^{\text{mech}} \) can be obtained when \( \frac{1}{2} S_2^{\text{hkl}} \) is known (see Eq. (2)).
2. \( f(\psi) \) method

A second method, which can be used for a series of \( d_{\psi}^{\text{bl}} \) values measured for different \( \psi \) and/or, in particular, different \( hkl \), will be referred to as the 'f(\psi) method'. If the diffraction elastic constants are known, the stress can be solved on the basis of a plot of \( d_{\psi}^{\text{bl}} \sqrt{h^2 + k^2 + l^2} \) versus \( f(\psi) \), where \( f(\psi) = a_{\text{ref}}(2S_1^{\text{bl}} + \frac{1}{2}S_2^{\text{bl}} \sin^2 \psi) \), which yields a straight line whose slope equals the stress (cf. Eq. (2)). This method is also appropriate for crystallographically textured specimens where \( d_{\psi}^{\text{bl}} \) values for a given \( hkl \) can only be measured at specific angles \( \psi \). For that case this method has been called the crystallite group method [1].

3. \( \Gamma \) method

A third method, also based on Eq. (2), is presented here for the first time and will be called the '\( \Gamma \) method'. From Eqs (2), (3a) and (3b) it follows:

\[
\frac{d_{\psi}^{\text{bl}} \sqrt{h^2 + k^2 + l^2} - a_0}{a_{\text{ref}}} = K_3 \left( 2 - K_4 \right) \sin^2 \psi \sigma_{\mu}^{\text{mech}} + 3K_2 \left( \frac{2}{3} - \sin^2 \psi \right) \sigma_{\mu}^{\text{mech}} \Gamma
\]  

(6)

If a set of \( d_{\psi}^{\text{bl}} \sqrt{h^2 + k^2 + l^2} \) values for various \( hkl \) reflections measured at one given \( \psi \) is plotted versus \( \Gamma \) (the so-called \( \Gamma \) plot), a straight line is obtained. From the slope the stress \( \sigma_{\mu}^{\text{mech}} \) can be obtained if \( K_2 \) is known. For \( K_2 = 0 \) (the Voigt-case, see below) and for \( \sin^2 \psi = 2/3 \), the slope of the \( \Gamma \) plot is zero and then \( \sigma_{\mu}^{\text{mech}} \) cannot be determined with the \( \Gamma \) method.

B. Stress analysis on the basis of mechanical elastic constants

Three methods of diffraction stress analysis on the basis of the mechanical elastic constants \( S_1^{\text{mech}} \) and/or \( \frac{1}{2}S_2^{\text{mech}} \) are proposed.

1. Direct solution method

Substituting Eqs (4a) and (4b) in Eq. (2) yields:

\[
\varepsilon_{\psi}^{\text{bl}} = \frac{d_{\psi}^{\text{bl}} \sqrt{h^2 + k^2 + l^2} - a_0}{a_{\text{ref}}}
= \left( 2S_1^{\text{mech}} + 2K_2(\Gamma - \frac{1}{3}) + \left( \frac{1}{2}S_2^{\text{mech}} - 3K_2(\Gamma - \frac{1}{3}) \right) \sin^2 \psi \right) \sigma_{\mu}^{\text{mech}}
\]  

(7)

From at least 3 values of \( d_{\psi}^{\text{bl}} \sqrt{h^2 + k^2 + l^2} \) the unknowns in Eq. (7), i.e. \( a_0, K_2 \) and \( \sigma_{\mu}^{\text{mech}} \), can be obtained by fitting. To judge the results, they can be visualised in classical \( \sin^2 \psi \) plots, calculated using the values for \( a_0, K_2 \) and \( \sigma_{\mu}^{\text{mech}} \) obtained from the fit, and plotting these together with the measured data.
2. Modified \( \sin^2 \psi \) method

In this method a \( \sin^2 \psi \) plot is constructed, that can be interpreted using mechanical elastic constants. Therefore an expression for the macroscopic strain \( \varepsilon_{\psi}^{\text{mech}} \) should be acquired (cf. Eq. (1a)) in terms of the measured lattice spacings. The macroscopic strain is the (volume weighted) average of the strains in the direction \( \psi \) in all crystallites and can be written as:

\[
\varepsilon_{\psi}^{\text{mech}} = \frac{a_{\psi}^{\text{mech}} - a_0}{a_{\text{ref}}} \tag{8a}
\]

where \( a_{\psi}^{\text{mech}} \) is a ‘formal’ (volume weighted) average lattice parameter of all crystallites and taken in the direction \( \psi \). It thus holds:

\[
a_{\psi}^{\text{mech}} = <d_{\psi}^{\text{hkl}} \sqrt{h^2 + k^2 + l^2}> \tag{8b}
\]

It is obtained from Eq. (5) by expressing \( \varepsilon_{\psi}^{\text{hkl}} \) in terms of \( d_{\psi}^{\text{hkl}} \) (Eq. (2)) and \( \varepsilon_{\psi}^{\text{mech}} \) in terms of \( a_{\psi}^{\text{mech}} \) (Eq. (8a)):

\[
d_{\psi}^{\text{hkl}} \sqrt{h^2 + k^2 + l^2} = a_{\psi}^{\text{mech}} + a_{\text{ref}} \left( 2K_2(\Gamma - \frac{1}{2}) - 3K_2(\Gamma - \frac{1}{2}) \sin^2 \psi \right) \sigma_{\text{ref}}^{\text{mech}} \tag{9}
\]

When at least two \( d_{\psi}^{\text{hkl}} \) values at a given \( \psi \) are available, a plot of \( d_{\psi}^{\text{hkl}} \sqrt{h^2 + k^2 + l^2} \) versus \( a_{\text{ref}} \left( 2(\Gamma - \frac{1}{2}) - 3(\Gamma - \frac{1}{2}) \sin^2 \psi \right) \) yields a straight line whose intercept with the \( d_{\psi}^{\text{hkl}} \sqrt{h^2 + k^2 + l^2} \) axis equals\(^1\) \( a_{\psi}^{\text{mech}} \).

The above procedure should be repeated for at least one more value of \( \psi \). Then, a plot of the obtained \( a_{\psi}^{\text{mech}} \) values versus \( \sin^2 \psi \) yields a straight line and from its slope the stress can be obtained when a value for \( \frac{1}{2} S_2^{\text{mech}} \) is available (see Eqs (1a) and (8a)).

3. Modified \( \Gamma \) method

In this case, a \( \Gamma \) plot’ is constructed that can be interpreted using mechanical elastic constants. The slope \( \zeta \) of a classical \( \sin^2 \psi \) plot can be written as (cf. Eqs (2) and (4b)):

\[
\zeta = a_{\text{ref}} \sigma_{\text{ref}} \frac{1}{2} S_2^{\text{hkl}} = a_{\text{ref}} \left( \frac{1}{2} S_2^{\text{mech}} - 3K_2(\Gamma - \frac{1}{2}) \right) \sigma_{\text{ref}}^{\text{mech}} \tag{10}
\]

From a set of \( \sin^2 \psi \) plots, each pertaining to a specific \( \{hkl\} \) reflection, a plot can be made of the slope of the \( \sin^2 \psi \) plot versus \( (\Gamma - 1/5) \). This plot yields a straight line (cf. Eq. (10)) whose intercept with the \( \zeta \) axis equals \( a_{\text{ref}} \frac{1}{2} S_2^{\text{mech}} \sigma_{\text{ref}}^{\text{mech}} \), from which the stress can be obtained when a value for \( \frac{1}{2} S_2^{\text{mech}} \) is available.

\(^1\) Note that for \( \Gamma = 1/5 \) or for \( \sin^2 \psi = 2/3 \): \( a_{\psi}^{\text{mech}} = d_{\psi}^{\text{hkl}} \sqrt{h^2 + k^2 + l^2} \).
C. Assessment of the elastic constants
In the above methods for diffraction stress analysis it was presupposed that the diffraction elastic constants or mechanical elastic constants of the specimen considered are known. This is rarely the case, recognizing that the elastic constants mentioned depend on the microstructure of the specimen. Therefore it is best to measure the elastic constants of the specimen separately. If this is impracticable, the diffraction elastic constants or mechanical elastic constants have to be calculated from the single crystal elastic constants. Several models exist for the calculation of the diffraction elastic constants and the mechanical elastic constants from the single crystal elastic constants, all making different assumptions about the grain interaction in the specimen. Commonly used are the Voigt, Reuss, Neerfeld-Hill and Eshelby-Kröner models [3,5,6], which all have been developed for macroscopically isotropic specimens and their resulting elastic constants for cubic materials thus obey Eqs (3a-d). For the Voigt model, and for elastically isotropic (cubic) materials, $K_2 = 0$ and the diffraction elastic constants then are $hkl$ independent.

The diffraction elastic constants (and thus $K_1$, $K_2$ and $K_3$) can differ significantly for the different grain-interaction models and there is no generally valid criterion to determine which of the models should be used in a particular case.

However, the various grain interaction models yield mechanical elastic constants that are relatively close to each other. Moreover, it was shown by Hill [7] that the mechanical elastic constant $\frac{1}{2}S_{2}^{\text{mech}}$ of a macroscopically isotropic aggregate is between the results of the Voigt and Reuss models, which can thus be considered as the theoretical limits of $\frac{1}{2}S_{2}^{\text{mech}}$. For cubic materials it is easily shown that also $S_{1}^{\text{mech}}$ is between the Voigt and Reuss limits (see Appendix B).

IV. A critical evaluation of the various methods of stress analysis
For all treated methods of diffraction stress analysis it holds that the presuppositions associated with Eqs (1) and (2) should be fulfilled: i.e. presence of a biaxial rotational symmetric state of stress and macroscopic isotropy. The presuppositions will be considered first. Next, the various methods of diffraction stress analysis are compared with respect to the accuracy and the model uncertainties in the resulting stress. Also, specific experimental (dis)advantages of the various methods are discussed.

A. Check on presuppositions

1. State of stress
Macroscopic stress components normal to any free surface are zero. Therefore, near a free surface the state of (macro)stress is always biaxial. This state of stress does not necessarily show
rotational symmetry, i.e. $\sigma_1^{\text{mech}}$ may differ from $\sigma_2^{\text{mech}}$ (where $\sigma_1^{\text{mech}}$ and $\sigma_2^{\text{mech}}$ are principal stresses; the '3' axis is normal to the free surface).

Then, in the absence of crystallographic texture, Eqs (1a) and (2) can still be used with

$$\sigma_{\parallel}^{\text{mech}} = \frac{1}{2}(\sigma_1^{\text{mech}} + \sigma_2^{\text{mech}})$$

if the specimen is rotated around the surface normal during the measurements (see Appendix A).

2. Macroscopic isotropy

The two conditions for macroscopic isotropic specimens are crystallographic and morphologic isotropy. In practice, macroscopic isotropy does not occur for a specimen subject to diffraction stress analysis, because a flat free surface is usually present. The implications of the associated macroscopic anisotropy on the stress analysis methods discussed here cannot be estimated easily. It is believed that the above methods of stress analysis are of value as long as the measured data obey the equations of the different methods of stress analysis. For example, a specimen having a slight crystallographic texture can be considered as 'almost' macroscopically isotropic as long as straight sin$^2\psi$ and $\Gamma$ plots are measured. If these plots are curved, the discussed methods of stress analysis become unreliable.

The methods for diffraction stress analysis treated in this paper cannot be applied to heavily textured specimens in general. However, for specimens with the often encountered $<111>$ type fibre texture, diffraction stress analysis can be accurately performed. This case is dealt with in Appendix C.

B. Accuracy

The accuracy of a diffraction stress measurement, i.e. the liability of the result with respect to systematic errors, is determined by systematic deviations in the measured values for the spacings $d_{hkl}^{\text{bkl}} \sqrt{h^2 + k^2 + l^2}$ caused by instrumental aberrations (i.e. instrumental peak-shift) and deficiencies in the data evaluation. Systematic instrumental errors can be corrected for, using corresponding measurements from a strain free specimen. If such correction is performed, all methods of stress analysis have in principle the same accuracy (inaccuracies in the obtained values of the stress caused by the uncertainties in the elastic constants will be considered in section IV.3). The magnitude of systematic deviations that occur as a result of systematic errors made in the peak fitting procedure is difficult to estimate. However, when diffraction peak shapes are more or less symmetric, the deviations will generally be small.
C. Uncertainty in the stress due to the choice of the grain interaction model

Uncertainty in the resulting stress is caused by the choice of the grain interaction model to calculate the elastic constants from the single crystal elastic constants. Of course, if the diffraction elastic constants or mechanical elastic constants are measured independently, these uncertainties are absent. The susceptibility of a method of diffraction stress analysis for such uncertainties may be assessed by a comparison of the stress values obtained in applying (all) different grain interaction models. It will be presupposed that $S_{1}^{hl}$ and $\frac{1}{2} S_{2}^{hl}$ are between the values obtained by applying the Voigt and Reuss models. It should be noted that there is, to our knowledge, no theoretical evidence for this, whereas this has been proven to hold for $S_{1}^{mech}$ and $\frac{1}{2} S_{2}^{mech}$ (see Appendix B).

The stress obtained by the $\Gamma$ method is most sensitive to uncertainty in the elastic constants, because of its sensitivity for the value of $K_2$, that can vary considerably for the different models of grain interaction (between zero, pertaining to the Voigt model, and the Reuss value; see Table 1). The large uncertainty in $K_2$ corresponds to a large uncertainty in the value of $\sigma_{ii}^{mech}$ (cf. Eq. (6)). On the other hand, if one is interested in the grain interaction in a given specimen, the application of Eq. (6) may be beneficial.

The $f(\psi)$ method is less sensitive to the value of $K_2$ as also the values of $K_1$ and $K_3$ are used for calculation of the diffraction elastic constants (see Eqs (3a-c)) and $K_1$ and $K_3$ depend less than $K_2$ on the grain interaction model used (see Table 1).

The uncertainty in the stress obtained with the classical $\sin^2 \psi$ method as caused by the uncertainties in the diffraction elastic constants calculated, depends on the reflection that is applied. The uncertainty is very low when the value of $\Gamma$ corresponding to the used reflection is near to 1/5. Then $d_h^{hl} \sqrt{h^2 + k^2 + l^2}$ approaches $a_{ii}^{mech}$ (see Eq. (9)). The range in values of $S_{1}^{hl}$ and $\frac{1}{2} S_{2}^{hl}$, as resulting from application of the various grain interaction models to calculate the diffraction elastic constants, then is relatively small and the associated uncertainties in the results from the $\sin^2 \psi$ method and those from the methods on the basis of mechanical elastic constants approach each other.

Table 1: Values of $K_1$, $K_2$ and $K_3$ (cf. Eqs (3a-b)) for various grain-interaction models for TiN. Values of the mechanical elastic constants as obtained from the $K$-values (see Eq. (3d)) have also been given. Single crystal elastic constants given in ref. [9] have been used (i.e. $s_{11} = 1.80$ TPa$^{-1}$, $s_{12} = -0.38$ TPa$^{-1}$ and $s_{44} = 6.13$ TPa$^{-1}$).

<table>
<thead>
<tr>
<th>Model</th>
<th>Reuss</th>
<th>Voigt</th>
<th>Neerfeld-Hill</th>
<th>Eshelby-Kröner</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$ (TPa$^{-1}$)</td>
<td>-0.38</td>
<td>-0.53</td>
<td>-0.45</td>
<td>-0.45</td>
</tr>
<tr>
<td>$K_2$ (TPa$^{-1}$)</td>
<td>-0.89</td>
<td>0</td>
<td>-0.45</td>
<td>-0.45</td>
</tr>
<tr>
<td>$K_3$ (TPa$^{-1}$)</td>
<td>2.17</td>
<td>2.63</td>
<td>2.40</td>
<td>2.40</td>
</tr>
<tr>
<td>$S_{1}^{mech}$ (TPa$^{-1}$)</td>
<td>-0.55</td>
<td>-0.53</td>
<td>-0.54</td>
<td>-0.54</td>
</tr>
<tr>
<td>$\frac{1}{2} S_{2}^{mech}$ (TPa$^{-1}$)</td>
<td>2.71</td>
<td>2.63</td>
<td>2.67</td>
<td>2.67</td>
</tr>
</tbody>
</table>

83
The uncertainties in the resulting stress for the methods based on the mechanical elastic constants are smaller than those for the methods based on the diffraction elastic constants, because the mechanical elastic constants are relatively insensitive to the model used for their calculation. Moreover, as indicated in section II.C, the values of the mechanical elastic constant $S_{1\text{mech}}$ and $\frac{1}{2} S_{2\text{mech}}$ obtained with the Voigt and the Reuss models can be considered as the theoretical limits for these mechanical elastic constants. Therefore, the methods in which the mechanical elastic constants are used, deliver theoretical limits for the resulting stress by applying the values for $S_{1\text{mech}}$ and $\frac{1}{2} S_{2\text{mech}}$ as calculated from the Voigt model and from the Reuss model.

**D. Practical considerations of the various methods of diffraction stress analysis**

In view of the above discussion it is best to use methods of diffraction stress analysis on the basis of mechanical elastic constants. However, the methods based on the mechanical elastic constants have the disadvantage that generally a relatively large number of diffraction peaks (different in $hkl$ and/or at different $\psi$) need to be measured. This can be a problem. For example, in the case of a thin layer where there is much overlap of diffraction peaks from substrate and layer. Then one has to apply the methods using diffraction elastic constants.

From an experimental point of view, the classical $\sin^2 \psi$ method and the modified $\Gamma$ method have an advantage over the other methods. Because with the nowadays used diffractometers the $\psi$ dependence of the diffractometer error can be neglected, these two methods can be employed, without performing a correction for the instrumental peak shift, because only slopes of $\sin^2 \psi$ plots are used, in which 20 dependent errors play no role.

The main importance of the $f(\psi)$ and $\Gamma$ methods concerns situations where one is forced to use simple diffraction set-ups, e.g. if one has to cope with specimens that do not fit in a standard diffractometer. Clearly, if it is impossible to apply different $\psi$ tilts, the $\Gamma$ method and the $f(\psi)$ method can be used because only measurements at a single $\psi$ are needed. In cases where a fixed position of the source of radiation or the counter with respect to the specimen has to be used the $f(\psi)$ method is still applicable. The $f(\psi)$ method is also valuable when stress analyses of very thin layers have to be performed. Then, the incident or diffracted beam can be chosen at a grazing angle with the specimen surface: problems of overlap with substrate peaks are minimised and higher intensities are realised. When data measured for various $\psi$ and $hkl$ are available the $f(\psi)$ method can be used to select the best model for the calculation of the diffraction elastic constants (see section VI.B.2). Lastly, the $f(\psi)$ method is used in the stress analysis of heavily textured samples, where reflections can only be measured at well defined specimen tilt angles [1]. However, note that heavily textured specimens are by no means macroscopically isotropic.

Of the methods of diffraction stress analysis on the basis of mechanical elastic constants, the modified $\Gamma$ method is preferred for the currently used diffractometers, because it is not necessary to apply correction for the diffractometer error (see above). Secondly, it is only necessary to use...
a value for $\frac{1}{2}S_{2}^{\text{mech}}$, whereas in the direct solution method, also knowledge of $S_{1}^{\text{mech}}$ is presupposed.

If one also needs a value for $a_0$, correction for instrumental errors is always necessary. The direct solution method straightforwardly yields values for $a_0$, $K_2$ and the stress. Using the direct solution method, the correspondence of all data with the theoretically expected behaviour can be easily verified (see section VI.C.1).

V. Experimental

The above methods for diffraction stress analysis are illustrated for the case of a magnetron sputtered TiN layer deposited on a tool steel substrate (deposition parameters of the 2.0 $\mu$m thick layer considered here are given elsewhere [8]).

X-ray diffraction measurements were performed with a Siemens D-500 $\omega$-type diffractometer, equipped with a diffracted-beam monochromator set to select Cu K$\alpha$ radiation. Because of the small TiN layer thickness, the observed diffraction patterns consist of overlapping reflections of layer and substrate.

For the diffraction stress analysis, specimen tilt angles were applied corresponding to $\sin^2 \psi = 0, 0.05, 0.10, 0.15$ and 0.20. In all scans at fixed $\psi$, always the \{222\}, \{400\}, \{331\}, \{420\} and \{422\} reflections were measured. If possible, also the \{111\}, \{200\}, \{220\} and \{311\} reflections were recorded (on an $\omega$-type diffractometer low angle reflections cannot be measured at high specimen tilt angles, i.e. $\psi$ must be smaller than $\theta$). The counting times of the scans were such that at the peak maximum of most diffraction peaks at least 1000 counts were collected. A step size of 0.1 °/2θ was used.

For obtaining peak positions, the 20 scans employed in the experiments were subdivided into a small number of groups in which a set of (severely overlapping) diffraction peaks could be fitted simultaneously using a linear background. Because of the overlap reliable peak positions could only be obtained by fitting profile-shape functions to the measured diffractograms. Fits were obtained by using profile shapes consisting of two symmetric Pseudo Voigt functions for each diffraction peak composed of an $\alpha_1$ and an $\alpha_2$ component. An $\alpha_2/\alpha_1$ intensity ratio of 0.5 was used. The thus obtained $\alpha_1$ peak positions were used for the determination of the lattice spacings $d_{\omega}^{\text{fit}}$.

Peak shifts due to diffractometer aberrations were investigated by means of a strain free molybdenum powder. It was obtained that the instrumental peak shift could be neglected with respect to the peak shifts induced by the strain in the TiN layer, for reflections recorded at 2θ angles larger than 60 °. TiN lattice spacings from reflections recorded below 60 ° were corrected using results from measurements at the strain free molybdenum powder.
Fig. 1: ‘Classical’ $\sin^2 \psi$ plots, for several reflections \{hkl\}, obtained for the investigated TiN layer. Dotted lines denote a linear least square fit to data of a given reflection \{hkl\}.

VI. Results

A. Elastic constants

The values of $K_1$, $K_2$ and $K_3$ in Eqs (3a) and (3b), as calculated for TiN from its single crystal elastic constants [9] have been given in Table 1 for the Reuss, Voigt, Neerfeld-Hill and Eshelby-Kröner models (for the expressions used see Refs. [1,2,5]$^2$. From these values the diffraction elastic and mechanical elastic constants can be easily obtained for each model using Eqs. (3a) and (3b). Indeed, the mechanical elastic constants $S_{\text{mech}}$ and $\frac{1}{2} S_{2\text{mech}}$ as calculated for the different models are relatively close to each other (see Table 1 and discussion in section III.C).

B. Diffraction stress analysis on the basis of diffraction elastic constants

1. $\sin^2 \psi$ method

The $a_{\psi} \sqrt{h^2 + k^2 + l^2}$ values have been plotted versus $\sin^2 \psi$ for several reflections \{hkl\} in Fig. 1. The straight lines shown are least squares fits to the data. Most reflections satisfy well the

\footnote{It should be noted that it cannot be excluded that in the present case the single crystal elastic constants used for the calculation of $K_1$, $K_2$ and $K_3$ may not be appropriate (i.e. elastic constants of TiN are known to depend on the composition [10].}
Fig 2: Plot of $d_{\psi}^{\text{R}} \sqrt{h^2 + k^2 + l^2}$ values obtained for the investigated TiN layer versus $f(\psi)$ for the Reuss and Voigt grain interaction models. The dotted lines denote linear least squares fits to all data.

straight lines shown. The stresses, obtained from the slopes of the fitted straight lines for each reflection, have been gathered in Table 2 for each of the mentioned grain-interaction models\(^3\).

2. $f(\psi)$ method
For each of the grain-interaction models all $d_{\psi}^{\text{R}} \sqrt{h^2 + k^2 + l^2}$ values (variable $hkl$ and $\psi$) can be plotted versus $f(\psi)$. This has been done for the Reuss and the Voigt grain-interaction models in Fig. 2. Clearly, the data satisfy the expected straight line (cf. Eq. (2)) better for the Reuss model than for the Voigt model. Note that this procedure allows selection of the most appropriate grain interaction model for the specimen investigated. The stresses deduced have been given in Table 2.

3. $\Gamma$ method
For each of the applied $\sin^2 \psi$ values the $d_{\psi}^{\text{R}} \sqrt{h^2 + k^2 + l^2}$ values have been plotted versus $\Gamma$ in Fig. 3. Except for the data measured at $\sin^2 \psi = 0$, the data fall more or less on straight lines (cf. Eq. (6)). From the linear least squares fits through the data the stresses have been obtained for each model adopted for the calculation of the diffraction elastic constants (see Table 2). In this case the Voigt model cannot be applied (see section III.A.3).

\(^3\) For $a_{eq}$ a literature value for the lattice parameter of TiN has been used in all methods of stress analysis, i.e. 4.241 Å [11].
Fig. 3: $\Gamma$ plots for the investigated TiN layer for several values of $\sin^2 \psi$. Dotted lines denote linear least square fits to the data measured at a specific $\sin^2 \psi$.

Table 2: Stresses (in GPa) in the TiN layer investigated, as derived from the classical $\sin^2 \psi$ method (section III.A.1) and the $f(\psi)$ method (section III.A.2) and the $\Gamma$ method (section III.A.3). These methods are all based on the diffraction elastic constants. Error margins indicated correspond to the deviations observed after performing the linear least squares fits to the measured data.

<table>
<thead>
<tr>
<th>Classical $\sin^2 \psi$ method</th>
<th>Reuss</th>
<th>Voigt</th>
<th>Neerfield-Hill</th>
<th>Eshelby-Kröener</th>
</tr>
</thead>
<tbody>
<tr>
<td>{311} $\Gamma = 0.16$</td>
<td>-6.1 ± 0.6</td>
<td>-6.0 ± 0.5</td>
<td>-6.1 ± 0.5</td>
<td>-6.1 ± 0.5</td>
</tr>
<tr>
<td>{222} $\Gamma = 0.33$</td>
<td>-6.3 ± 0.2</td>
<td>-7.3 ± 0.2</td>
<td>-6.8 ± 0.2</td>
<td>-6.8 ± 0.2</td>
</tr>
<tr>
<td>{400} $\Gamma = 0.00$</td>
<td>-4.3 ± 0.8</td>
<td>-3.6 ± 0.6</td>
<td>-3.9 ± 0.7</td>
<td>-3.9 ± 0.7</td>
</tr>
<tr>
<td>{331} $\Gamma = 0.27$</td>
<td>-5.6 ± 0.4</td>
<td>-6.2 ± 0.5</td>
<td>-5.9 ± 0.5</td>
<td>-5.9 ± 0.5</td>
</tr>
<tr>
<td>{420} $\Gamma = 0.16$</td>
<td>-3.9 ± 1.0</td>
<td>-3.9 ± 1.0</td>
<td>-3.9 ± 1.0</td>
<td>-3.9 ± 1.0</td>
</tr>
<tr>
<td>{422} $\Gamma = 0.25$</td>
<td>-5.8 ± 0.3</td>
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$\Gamma$ method

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<td>0.20</td>
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Fig. 4: Plot of all $d_{\psi}^{hl} \sqrt{h^2 + k^2 + l^2}$ values obtained for the investigated TiN layer versus $\sin^2 \psi$. Dotted lines denote the results, for the indicated reflection, obtained from the direct solution method fit.

C. Diffraction stress analysis on the basis of mechanical elastic constants

1. Direct solution method

Using all measured data (variable $hkl$ and $\psi$) and values for the mechanical elastic constants (Table 1), the values of $a_0$, $K_2$ and $\sigma_{ij}^{mech}$ have been determined by fitting on the basis of Eq. (7), such that the square root of the sum of the squared differences between the measured $d_{\psi}^{hl} \sqrt{h^2 + k^2 + l^2}$ values and the fitted ones was minimised. The values obtained for $a_0$, $K_2$ and $\sigma_{ij}^{mech}$ are given in Table 3. The results of the fit have been visualised in Fig. 4 by means of $\sin^2 \psi$ plots as calculated from the fitted parameters.

2. Modified $\sin^2 \psi$ method

The measured $d_{\psi}^{hl} \sqrt{h^2 + k^2 + l^2}$ values have been plotted versus $a_{nl} (2(\Gamma - \frac{1}{3}) - 3(\Gamma - \frac{1}{3}) \sin^2 \psi)$ for each $\sin^2 \psi$ applied (cf. section III.C.2) in Fig. 5. Straight lines were fitted to the data using a single value for $K_2 \sigma_{ij}^{mech}$ for all lines. Then the $\sigma_{ij}^{mech}$ values obtained from this fitting are plotted versus $\sin^2 \psi$ in Fig. 6. Values for the stress have been obtained from the slope of the straight line
fitted to the data in Fig. 6 and the values for $\frac{1}{2}S_2^\text{mech}$ according to the different grain interaction models (Table 1) are given in Table 3.

$$\sin^2 \psi$$

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Fig. 5: Plot to determine the values of $a_\psi^\text{mech}$ at various values for $\sin^2 \psi$ (see section VI.C.2). The linear least squares fits (dotted lines) were forced to have equal slopes.

3. Modified $\Gamma$ method

The slopes $\zeta$ of the classical $\sin^2 \psi$ plots for the reflections $\{hkl\}$ measured (see section VI.B.1

Fig. 6: 'Modified' $\sin^2 \psi$ plot: $a_\psi^\text{mech}$ (see Fig. 5) versus $\sin^2 \psi$. In this way the stress can be determined using (only) the mechanical elastic constant $\frac{1}{2}S_2^\text{mech}$ (see section VI.C.2). The dotted line denotes a linear least squares fit to the data.
Fig. 7: 'Modified' Γ plot. The dotted line represents a weighted least squares fit through the data using the inverse of the errors in the slopes ζ as weighting factor. The errors in the slopes correspond to the deviations observed for the linear least squares fits of the classical sin²ψ plots (see Fig. 1) as indicated by the error margins in the current plot.

and Fig. 1) have been plotted versus (Γ-1/5) in Fig. 7. From a straight line fitted through the data the value of the intercept with the ζ axis is obtained (cf. Eq. (10)). Values for the stress have been deduced from the intercept using the values of $\frac{1}{2}S_2^{\text{mech}}$ according to each of the grain interaction models (see Table 3).

VII. Discussion

The good correspondence of most data with the theoretically expected behaviour (see e.g. Fig. 4, showing the result for the direct solution method) shows that the investigated TiN layer can be analysed on the basis of Eqs (1a) and (2). Clearly, the values of the stresses obtained depend on the grain interaction model adopted (see Tables 2 and 3). Also, for each grain interaction model, the obtained stresses are distinctly different for the methods of stress analysis on the basis of diffraction elastic constants (e.g. considerable hkl dependence is present in the results of the classical sin²ψ method (see Table 2)). This implies that none of the treated grain interaction models is compatible with the specimen investigated.

Yet, the upper and lower margins of the mechanical elastic constants $S_1^{\text{mech}}$ and $\frac{1}{2}S_2^{\text{mech}}$, as given by the values calculated using the Voigt and Reuss models, are known and close to each other (see Table 1). An accurate determination of the stress is therefore still possible, using the
Table 3: Stress in the TiN layer investigated, as derived from the direct solution method (section III.B.1), the modified $\sin^2 \psi$ method (section III.B.2) and the modified $\Gamma$ method (section III.B.3). These methods are all based on the mechanical elastic constants. Error margins indicated were obtained from an educated guess (direct solution method) and from the deviations between fit and data observed for the linear least squares fits in the modified $\sin^2 \psi$ method and in the modified $\Gamma$ method (see text). With the direct solution method, the lattice parameter $a_0$ and the value for $K_2$ have been determined simultaneously with the stress.

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<th>Direct solution method</th>
<th>Reuss</th>
<th>Voigt</th>
<th>Neerfeld-Hill</th>
<th>Eshelby-Kröner</th>
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<td></td>
<td>$a_0$ (Å ± 0.0003)</td>
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<td>4.2472</td>
<td>4.2471</td>
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<tr>
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<td>$K_2$ (TPa$^{-1}$ ± 0.15)</td>
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<td>-1.36</td>
<td>-1.38</td>
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</tr>
<tr>
<td>$\sigma_{\text{mech}}^{m}$ (GPa ± 0.2)</td>
<td>-5.7</td>
<td>-5.8</td>
<td>-5.8</td>
<td>-5.8</td>
<td>-5.8</td>
</tr>
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</table>

|                  | Modified $\sin^2 \psi$ method | $\sigma_{\text{mech}}^{m}$ (GPa ± 0.2) | -5.6 | -5.8 | -5.7 | -5.7 |
|                  | Modified $\Gamma$ method      | $\sigma_{\text{mech}}^{m}$ (GPa ± 0.2)  | -5.6 | -5.8 | -5.7 | -5.7 |

proposed methods for diffraction stress analysis on the basis of mechanical elastic constants. Even though the appropriate grain interaction model is unknown.

Indeed, the stress values obtained by application of the methods that are based on mechanical elastic constants agree very well, in contrast with what is observed for the methods based on diffraction elastic constants (cf. Tables 2 and 3). From the results of the methods of diffraction stress analysis based on the mechanical elastic constants it follows that the stress in the specimen is $-5.7 \pm 0.4$ GPa (see Table 3). Note that the error margin includes the uncertainty caused by the choice of the grain interaction model.

The values found for $a_0$ (see Table 3) are significantly higher than the literature value of $a_0$ (4.241 Å, see Ref. [11]), which, as explained elsewhere [8,12], is attributed to a large concentration of point defects in the layer, caused by the magnetron sputter deposition.

The absolute value found for $K_2$ (see Table 3) is larger than predicted by any of the models for the elastic constants (cf. Tables 1 and 3) which, once more, illustrates that the Reuss, Voigt, Neerfeld-Hill and Eshelby-Kröner models are inappropriate for the specimen investigated.
VIII. Conclusions

Diffraction stress analysis should preferably be based on mechanical elastic constants, instead of so-called diffraction elastic constants, because

(i) the mechanical elastic constants depend less on the grain interaction in the specimen, than the diffraction elastic constants. This is especially favourable if the elastic constants to be used have to be calculated from the single crystal elastic constants;

(ii) the mechanical elastic constants can be measured easily and reliably.

Diffraction stress analysis on the basis of mechanical elastic constants is possible using three methods, proposed here, all having their specific merits; i.e.

(i) the direct solution method (section III.B.1)

(ii) the modified $\sin^2 \psi$ method (section III.B.2)

(iii) the modified $\Gamma$ method (section III.B.3).

Experimentally, the proposed methods of diffraction stress analysis that use mechanical elastic constants have been shown to be superior as compared to the existing methods of diffraction stress analysis that use diffraction elastic constants.

Application of the diffraction stress analysis methods based on the mechanical elastic constants, as proposed here, allows determination of the grain interaction model best suited to the specimen under investigation.

Acknowledgements
This work was sponsored by the Programme for Innovative Research, surface technology (IOP Oppervlaktechnologie). The authors would like to thank Ir. M. van Leeuwen for many fruitful discussions. We are grateful to Ir. D. Tran (Eindhoven University of Technology) for deposition of the TiN layer.

Appendix A: Biaxial state of stress with $\sigma_1 \neq \sigma_2$

For biaxially loaded, macroscopically isotropic, specimens with $\sigma_1^{\text{mech}} \neq \sigma_2^{\text{mech}}$, where the '1' and '2' axis correspond to the principal axes, the mechanical strain is connected to the stress according to (cf. Eq. (1a)):

$$\varepsilon_\psi^{\text{mech}} = S_1^{\text{mech}} (\sigma_1^{\text{mech}} + \sigma_2^{\text{mech}}) + \frac{1}{2} S_2^{\text{mech}} \sigma_\psi^{\text{mech}} \sin^2 \psi$$  \hspace{1cm} (11)

with:
\[ \sigma^\text{mech} = \sigma_1^\text{mech} \cos^2 \varphi + \sigma_2^\text{mech} \sin^2 \varphi \]

(12)

where \( \varphi \) denotes the angle in the specimen-surface plane between the \( \sigma_1^\text{mech} \) direction and the measurement direction. A derivation similar to the one leading to Eq. (9) yields:

\[ d_{\text{wp}} \sqrt{h^2 + k^2 + l^2} = a_{\text{wp}}^\text{mech} + a_{\text{ref}} \left( (\Gamma - \frac{1}{3})(\sigma_1^\text{mech} + \sigma_2^\text{mech}) - 3(\Gamma - \frac{1}{3})\sigma_\varphi^\text{mech} \sin^2 \varphi \right) K_2 \]

(13)

Methods for stress analysis on the basis of the mechanical elastic constants analogous to the ones given in section III can be performed on the basis of Eq. (13). It follows from Eq. (13) that at \( \Gamma = 1/5 \) or \( \sin^2 \varphi = \frac{1}{3}(\sigma_1^\text{mech} + \sigma_2^\text{mech})/\sigma_\varphi^\text{mech} \) it holds \( a_{\text{wp}}^\text{mech} = d_{\text{wp}} \sqrt{h^2 + k^2 + l^2} \). Consequently, in \( \sin^2 \varphi \) plots of reflections with different \( \Gamma \) values lines should intersect at \( \sin^2 \varphi = \frac{1}{3}(\sigma_1^\text{mech} + \sigma_2^\text{mech})/\sigma_\varphi^\text{mech} \). For \( \sigma_1^\text{mech} = \sigma_2^\text{mech} \) a point of intersection at \( \sin^2 \varphi = 2/3 \) is obtained.

If a specimen without texture (or with a fibre texture) is rotated around the specimen surface normal, during the diffraction measurement, the measured value of the lattice spacing is given by:

\[ \frac{1}{2\pi} \int_0^{2\pi} d\varphi \cdot \]

Integration of Eq. (13) over \( \varphi \) yields Eq. (9), with \( c_{\text{II}}^\text{mech} = \frac{1}{2}(\sigma_1^\text{mech} + \sigma_2^\text{mech}) \).

Appendix B: Theoretical limits for \( S_1^\text{mech} \) and \( \frac{1}{2} S_2^\text{mech} \)

Diffraction elastic constants can always be written as a linear combination of the results for the Reuss and the Voigt models, i.e.:

\[ S_1^{\text{hkl}} = \eta_1^{\text{hkl}} \left[ S_1^{\text{Reuss}} \right] + (1 - \eta_1^{\text{hkl}}) \left[ S_1^{\text{Voigt}} \right] \]

\[ \frac{1}{2} S_2^{\text{hkl}} = \eta_2^{\text{hkl}} \left[ \frac{1}{2} S_2^{\text{Reuss}} \right] + (1 - \eta_2^{\text{hkl}}) \left[ \frac{1}{2} S_2^{\text{Voigt}} \right] \]

(14)

where \( \eta_1^{\text{hkl}} \) and \( \eta_2^{\text{hkl}} \) are the Reuss fractions for \( S_1^{\text{hkl}} \) and \( \frac{1}{2} S_2^{\text{hkl}} \) respectively, that are not necessarily in between 0 and 1 and may be different for each \( hkl \) considered.

For cubic materials it follows from Eqs. (3a) and (3b):

\[ 3 S_1^{\text{hkl}} + \frac{1}{2} S_2^{\text{hkl}} = 3 K_1 + K_3, \]

(15)

i.e. \( 3 S_1^{\text{hkl}} + \frac{1}{2} S_2^{\text{hkl}} \) is \( \Gamma \) independent. Consequently, writing down \( 3 S_1^{\text{hkl}} + \frac{1}{2} S_2^{\text{hkl}} \) using Eq. (14) and applying Eqs. (3a) and (3b), it holds that the \( \Gamma \) dependent terms must cancel. It then follows straightforwardly:

\[ \eta_1^{\text{hkl}} = \eta_2^{\text{hkl}} = \eta^{\text{hkl}}. \]

(16)
Hill [7] showed that upper and lower boundaries for the shear modulus (= 1/S²_mech), of a macroscopically isotropic specimen are formed by the results of the Voigt and the Reuss models respectively. Thus for the mechanical elastic constant 1/2 S²_mech (i.e. 1/2 S²_kkl (Γ = 1/3)), η_kkl is in-between 0 and 1. Consequently, for cubic materials also S¹_mech is between the results from the Voigt and the Reuss models.

Appendix C: Strongly textured specimens

Generally, mechanical or diffraction elastic constants of crystallographically textured specimens cannot easily be derived from the single crystal elastic constants. However, when a specimen of cubic material exhibits a 111 texture such that all crystallites are oriented with the corresponding direction <111> perpendicular to the specimen surface, the elastic constants can be obtained analytically. Because such specimens are elastically isotropic for directions in the surface plane, the same biaxial state of stress occurs in each crystallite if the specimen is subjected to a macroscopically biaxial state of stress. Then, if a rotational symmetric biaxial state of stress is applied to the specimen, all shear strains are zero in each crystallite. In this case, to determine the strain from the stress, an orthogonal coordinate system is defined with the ‘1’ and ‘2’ axes in the plane of the specimen surface and the ‘3’ axis normal to the surface. Then it holds for each crystallite:

\[
\begin{align*}
\varepsilon_{11} &= \varepsilon_{22} = \varepsilon_{\text{mech}} = (s'_1 + s'_{12})\sigma_{\text{mech}} \\
\varepsilon_{33} &= \varepsilon_{\text{mech}} = 2s'_{13}\sigma_{\text{mech}}
\end{align*}
\] (17)

Where s'_{ij} denote the elements of the compliance tensor in the matrix notation [13] for a coordinate system with the 3-axis parallel to the <111> direction. The prime has been added to the elements of the compliance tensor to indicate the difference with the compliance tensor elements in the representation on the crystal axes. For the macroscopic strain at a specimen tilt angle ψ, it can be written:

\[
\varepsilon_{\psi \text{mech}} = \varepsilon_{33} + (\varepsilon_{11} - \varepsilon_{33})\sin^2 \psi
\] (18)

From Eqs (17) and (18) and comparing with Eq. (1a), it is easily seen that in the present case Eq. (1a) can be used with S¹_mech = s'_{33} and 1/2 S²_mech = s'_{11} + s'_{12} - 2s'_{13}. Expressions for the tensor elements s'_{ij} have been given by Vook and Witt [14]. For the 111 type texture it follows:

\[
S_{1\text{mech}} = \frac{1}{3}s_{11} + \frac{2}{3}s_{12} - \frac{1}{6}s_{44} \quad \text{and} \quad \frac{1}{2} S_{2\text{mech}} = \frac{1}{2}s_{44}, \quad \text{where} \quad s_{11}, s_{12} \quad \text{and} \quad s_{44}\] denote the single crystal elastic constants.
Because the crystallites are all oriented with the <111> direction perpendicular to the surface only 111 reflections can be measured at well defined specimen tilt angles (i.e. $\psi = 0$, 70.5). Similarly, other reflections can only be measured at well defined specimen tilt angles. Because, all possible diffraction peaks stem from <111> oriented crystallites, the diffraction elastic constants equal the mechanical elastic constants for each reflection in this special case. Therefore, the stress analysis can be applied on the basis of Eqs (1a), (8a-b) and (9) using $K_2 = 0$ and the above values for the mechanical elastic constants. The result is the same as the one given by Korhonen & Paszkiet [15].

For textures with another direction perpendicular to the specimen surface the elastic constants cannot be that easily obtained because then the material is not elastically isotropic in the plane. Consequently the biaxial state of stress may vary from crystallite to crystallite. In that case tedious averaging procedures should be used (see e.g. Ref. [16]).

References

Chapter VII

Determination of Young’s modulus and stress in TiN layers from a combination of two methods of stress analysis

J.-D. Kamminga, R. Delhez, E.J. Mittemeijer

ABSTRACT
Both a curvature method for stress analysis and a new diffraction method for stress analysis have been applied to a set of magnetron sputtered TiN layers deposited on stainless steel foils. The combination of the two methods allows the determination of Young’s modulus of the TiN layers. The dependence of Young’s modulus of magnetron sputtered TiN layers on the deposition parameters has been revealed. Also the stress and the average elastic anisotropy of a crystallite in the layer are shown to depend on the deposition parameters.

1. Introduction

Stresses in thin layers can be of paramount importance for practical applications of layer-substrate systems: for example they can lead to cracking or peeling off of the layer. Much is still unknown about the origins of stress and the stress-property relations for layer-substrate systems.

Stress in thin layers can be investigated using diffraction techniques. Diffraction methods for stress analysis allow the determination of the whole stress tensor, which can be of large value in investigations on the origins of the stress (e.g. Refs. [1] and [2]). Furthermore, they can be utilised to determine the separate stresses in the different phases constituting the specimen investigated, which is of great importance for e.g. analysis of stresses in multilayers. In fact lattice strains are measured in diffraction stress measurements and the stress values derived thereof are very sensitive to the, to that end, used so-called diffraction elastic constants (see e.g. Refs [3,4]) of the layer. Unfortunately these elastic constants are often not precisely known. Recently new methods for diffraction stress analysis were proposed for cubic materials which relieve this problem by performing stress analysis on the basis of the mechanical elastic constants [5]. The mechanical elastic constants can be measured in general more easily or calculated more precisely than the diffraction elastic constants. However, especially for thin layers, also the mechanical elastic constants can differ from specimen to specimen [6,7]. Therefore, whether diffraction stress analysis is performed on the basis of diffraction elastic constants or mechanical elastic constants, there is a need to measure the specific elastic constants of the layer investigated.

In curvature stress measurements, the curvature of the free standing specimen induced by the force that the stressed layer exerts on the (ideally initially flat) substrate is used as a measure for the stress [8-11]. The stress obtained using a curvature measurement is practically insensitive to
the mechanical elastic constants of the layer, but is sensitive to the mechanical elastic constants of the substrate. Only the overall biaxial stress can be obtained from curvature stress measurements.

The combination of diffraction stress measurements and curvature stress measurements can be used to investigate the (mechanical) elastic constants of the layer. Because the stress obtained in a diffraction stress measurement is especially sensitive to the value used for the Young's modulus of the layer (whereas the value used for the Poisson's ratio is less important (see section IV.A)), it is of particular interest to determine Young's modulus of the layer considered by this combination of methods.

In the present paper the 'bending foil method' for curvature stress analysis [9] is combined with the 'direct solution method' for diffraction stress analysis [5] for a set of TiN layers deposited on stainless steel foils using different deposition parameters. Thus the dependence of the stress and Young's modulus on the deposition parameters is revealed. Also data on the average elastic anisotropy of a crystallite in the polycrystalline layer are obtained.

II. Essentials of stress measurement

For all stress measurements it is assumed that the state of stress in the layers is biaxial (i.e. the stress perpendicular to the specimen surface is zero) and rotationally symmetric. The substrates and layers are supposed to be elastically isotropic on a macroscopic scale; i.e. single crystal elastic anisotropy can occur.

A. Stress analysis from diffraction measurements of lattice strain

In a diffraction stress measurement the lattice spacing \( d^{hkl}_\psi \) measured for a reflection \( \{hkl\} \) at a specimen tilt angle \( \psi \) is used as an internal strain gauge. For the calculation of the stress from the measured lattice spacings the (\( \psi \) independent) diffraction elastic constants \( S_1^{hkl} \) and \( \frac{1}{2} S_2^{hkl} \) are mostly used. For materials consisting of elastically anisotropic single crystallites, the values of \( S_1^{hkl} \) and \( \frac{1}{2} S_2^{hkl} \) depend on the reflection selected in the diffraction experiment [3,4].

New methods for performing diffraction stress analysis on the basis of the mechanical elastic constants \( S_1^{\text{mech}} \) and \( \frac{1}{2} S_2^{\text{mech}} \) were proposed in Ref. [5]. The mechanical constants \( S_1^{\text{mech}} \) and \( \frac{1}{2} S_2^{\text{mech}} \) are related to Young's modulus \( E \) and Poisson's ratio \( \nu \) by:

\[
\begin{align*}
S_1^{\text{mech}} &= -\frac{\nu}{E} \quad (1a) \\
\frac{1}{2} S_2^{\text{mech}} &= \frac{1 + \nu}{E} \quad (1b)
\end{align*}
\]

The use of mechanical elastic constants for diffraction stress measurements has several advantages. First, the mechanical elastic constants are more conveniently measured. Secondly, if elastic constants must be calculated from the single crystal elastic constants, the obtained mechanical elastic constants are generally less sensitive to the model used for the calculation than the diffraction elastic constants [5].
**Direct solution method**

In this work the so-called 'direct solution method' will be used for the diffraction stress analysis. For macroscopically isotropic specimens of cubic material subject to a rotationally symmetric biaxial state of stress it holds [5]:

$$
\varepsilon_{\nu}^{hkl} = \frac{d^{hkl}_{\nu}}{a_{ref}} \sqrt{h^2 + k^2 + l^2 - a_0} \\
= \left(2S_1^{\text{mech}} + 2K_2(\Gamma - \frac{1}{3}) + \left(\frac{1}{3}S_2^{\text{mech}} - 3K_2(\Gamma - \frac{1}{3})\right)\sin^2 \psi\right)\sigma_{\nu}^{\text{mech}}
$$

(2a)

with:

$$
\Gamma = \frac{h^2k^2 + k^2l^2 + h^2l^2}{(h^2 + k^2 + l^2)^2}
$$

(2b)

where $\varepsilon_{\nu}^{hkl}$ and $d^{hkl}_{\nu}$ are the strain and the measured lattice spacing pertaining to that reflection $\{hkl\}$ that is recorded at specimen tilt angle $\psi$, $a_0$ is the lattice parameter of the strain free material, $a_{ref}$ is a reference spacing very close to $a_0$, and $\sigma_{\nu}^{\text{mech}}$ is the stress in the layer. Distinction between $a_{ref}$ and $a_0$ is made in recognition of their different effects on the precision of the stress obtained: whereas an error in $a_{ref}$ of several percent leads to an equally small relative error in the obtained stress, the error induced by a similar error in $a_0$ is much larger. Consequently, $a_{ref}$ can be considered as a known constant, contrary to $a_0$. $K_2$ is a measure for the elastic anisotropy of the crystallites in the layer. It is proportional to the maximum difference for the measured strains of diffracting crystallites (in dependence on $\{hkl\}$) from the mechanical average strain (see Ref. [5] and appendix A). For materials that consist of elastically isotropic crystallites $K_2 = 0$.

From at least three measured $d^{hkl}_{\nu}$ values (of variable $\psi$ and $\{hkl\}$), $K_2$, $a_0$ and $\sigma_{\nu}^{\text{mech}}$ can be obtained straightforwardly from Eq. (2a).

**B. Stress analysis from curvature measurements**

Introduction of stress in a layer on an initially flat macroscopically isotropic substrate will cause the free standing layer-substrate system to bend. If the layer is macroscopically isotropic and subjected to a rotationally symmetric biaxial state of stress, the surface shape of the curved specimen will be spherical as long as the surface deflection is small. Then the stress $\sigma_{\nu}^{\text{curv}}$ in the layer, if it were present on an infinitely rigid substrate, is related to the curvature (radius of curvature $r$) of the free standing specimen (layer on not infinitely rigid substrate) according to the so-called Stoney equation [12]:

$$
\sigma_{\nu}^{\text{curv}} = \frac{E_{\text{sub}}}{1 - \nu_{\text{sub}}} \frac{d^2}{6rt}
$$

(3)
where $E_{\text{sub}}$ and $\nu_{\text{sub}}$ denote the Young’s modulus and Poisson’s ratio of the substrate respectively, $t$ is the layer thickness and $d$ is the substrate thickness. For layers in a uniaxial state of stress (parallel to the surface) Eq. (3) can be applied replacing $E_{\text{sub}}/(1-\nu_{\text{sub}})$ by $E_{\text{sub}}$. Then the expression given in Ref. [8] is obtained. If the surface deflection becomes too large, shape bifurcation occurs [11]. Then the shape of the surface of the specimen is characterised by unequal curvatures along different directions in the plane of the specimen surface and the Stoney equation cannot be used straightforwardly. In that case the so-called bending foil stress measurement may be applied.

**Bending foil stress measurement**

For a planar, stressed layer substrate system of which the length is much larger than the width, the stress $\sigma_{ij}^{\text{curv}}$ in the layer, if it were present on an infinitely rigid substrate, is related to the curvature according to [9] (see also Ref. [11]):

$$\sigma_{ij}^{\text{curv}} = \frac{E_{\text{sub}}}{1-\nu_{\text{sub}}} \left( \frac{d + E_{\text{lay}}}{E_{\text{sub}} (1-\nu_{\text{sub}})} \right)^3 \frac{1}{6rdt}$$  (4)

where $E_{\text{lay}}$ and $\nu_{\text{lay}}$ denote the Young’s modulus and Poisson’s ratio of the layer respectively. For layers in a uniaxial state of stress Eq. (4) can be applied replacing the $E/(1-\nu)$ terms by $E$. Then the expression given in Ref. [10] is obtained. For specimens with $E_{\text{sub}} \gg E_{\text{lay}}$ and/or $d \gg t$ Eq. (4) reduces to Eq. (3).

In this work, from the highly (bifurcated) curved circular specimens, thin strips are cut which are then used for the curvature stress measurement (see section III.A). This method for curvature stress analysis is referred to as bending foil stress measurement [9].

It is emphasised that Eqs. (3) and (4) relate the curvature of the specimen to the so-called true stress in the layer, i.e. the stress that would be present in the layer if it were attached to an infinitely rigid substrate, as deduced from the radius of curvature from a layer-substrate system of which the substrate is *not* infinitely rigid [10].

**C. Comparison of the stress values obtained from both methods**

The stress values obtained from the diffraction and curvature measurements cannot be compared directly. The stress $\sigma_{ij}^{\text{mech}}$ measured by diffraction is the stress in the layer on top of the not infinitely rigid substrate at the moment of the stress measurement. In the substrate holder used for the diffraction experiments (see section III.B), the specimens are prevented to bend, but they are unconstrained in in-plane directions. This implies that $\sigma_{ij}^{\text{mech}}$ is the stress that is present in the layer when mechanical equilibrium exists between the (forced to be) flat substrate and the layer. On the other hand, the stress $\sigma_{ij}^{\text{curv}}$ obtained using Eqs. (3) or (4) is the stress present in the layer as if attached to an infinitely rigid substrate. Thus $\sigma_{ij}^{\text{curv}}$ is obtained from $\sigma_{ij}^{\text{mech}}$ by adding to
\( \sigma_{ij}^{\text{mech}} \) the stress in the layer corresponding to the strain necessary to annihilate hypothetically the strain in the not infinitely rigid substrate.

For the layer and the not infinitely rigid, flat substrate in mechanical equilibrium (i.e. the diffraction experiment case), the stress \( \sigma_{ij}^{\text{sub}} \) in the substrate can be expressed in terms of the stress in the layer \( \sigma_{ij}^{\text{mech}} \), the thickness of the substrate \( d \), and the layer thickness \( t \) according to the force balance:

\[
\sigma_{ij}^{\text{sub}} \cdot d + \sigma_{ij}^{\text{mech}} \cdot t = 0
\]

Rotational symmetric biaxial states of stress, indicated by the stress \( \sigma_{ij} \), are connected to in-plane strains \( \varepsilon_{ij} \), \( E \) and \( \nu \), according to [3,4]:

\[
\sigma_{ij} = \frac{E}{1 - \nu} \varepsilon_{ij}
\]

It follows from Eqs (5) and (6) for the biaxial strain in the substrate:

\[
\varepsilon_{ij}^{\text{sub}} = -\sigma_{ij}^{\text{mech}} \frac{t}{d} \frac{1 - \nu_{\text{sub}}}{E_{\text{sub}}}
\]

Hence, a strain \( -\varepsilon_{ij}^{\text{sub}} \) imposed on the entire specimen annihilates the strain in the substrate.

The stress \( \sigma_{ij}^{\text{curv}} \) in the layer is obtained by adding to the stress \( \sigma_{ij}^{\text{mech}} \) in the layer, the stress in the layer that corresponds to the strain \( -\varepsilon_{ij}^{\text{sub}} \):

\[
\sigma_{ij}^{\text{curv}} = \sigma_{ij}^{\text{mech}} - \frac{E_{\text{lay}}}{1 - \nu_{\text{lay}}} \varepsilon_{ij}^{\text{sub}} = \sigma_{ij}^{\text{mech}} \left( 1 + \frac{t}{E_{\text{lay}}} \frac{1 - \nu_{\text{sub}}}{d} \frac{1 - \nu_{\text{lay}}}{E_{\text{sub}}} \right)
\]

Of course, for an in reality 'almost' infinitely rigid substrate \( \sigma_{ij}^{\text{mech}} \) approaches \( \sigma_{ij}^{\text{curv}} \).

III. Experimental

A. Specimen preparation

TiN layers were reactivity sputtered on circular stainless steel foils (AISI 316) with a diameter of 60 mm and a thickness of 75 \( \mu \text{m} \). Prior to deposition the substrates were ultrasonically cleaned in 96\% ethanol.

The layers were deposited in a Teer UDP 350 4-RF system [13]. The apparatus consists of a cylindrical sputter chamber (height and diameter approximately 0.5 m) in which a cylindrical specimen mill is placed such that the axes of both cylinders coincide. The mill was rotated at about 5 rpm around its cylinder axis. The foils were clamped on the mill by means of a steel ring with an outer diameter of 60 mm and an inner diameter of 40 mm. Thus the layer was deposited on a central area of the foil of 40 mm diameter. One titanium sputter target (Teer, 99.5 wt.% Ti),
of lateral dimensions 130x240 mm, was placed along the cylindrical chamber wall. When the foils on the rotating specimen mill were in front of the target, the foil-target distance was approximately 130 mm. The glow in front of the sputter targets was monitored using an optical emission unit tuned such that the intensity of the 502 nm Ti line was recorded.

Prior to the deposition of TiN the chamber was evacuated to a pressure below 0.001 Pa, followed by inlet of argon to a pressure of 0.3 Pa. A so-called bias voltage of -750 V (DC) was applied to the substrates and a plasma was initiated between the negatively charged substrates and the chamber wall.

First a titanium (inter)layer (thickness about 100 nm) was sputtered on the substrates. This was done for 4 min, i.e. until a stable Ti signal was acquired with the optical emission unit. Subsequently the bias voltage was set at -65 V, nitrogen was led into the chamber and upon sputtering continuously the Ti targets, a TiN layer was deposited on the substrate.

The nitrogen inlet was controlled by means of the optical emission unit and a rapidly responding piezo valve. Because the presence of nitrogen in the sputter chamber leads to TiN formation on the target (which decreases the titanium sputter yield), the intensity of the recorded titanium line decreases with increasing nitrogen pressure. Hence, the ratio of the intensity of the titanium line recorded during TiN deposition and the intensity of the titanium line recorded during deposition of the titanium interlayer can be used as a measure for the nitrogen pressure in the sputter chamber. The piezo valve was controlled such that the so-called ‘relative intensity’ of the titanium line was kept at a value that could be tuned accurately between 20% and 100%.

A series of TiN layers was deposited using a deposition time of 30 minutes and relative titanium line intensities of 20%, 40%, 55% and 60%. The thicknesses of the layers, measured from specimen cross sections with a scanning electron microscope (JEOL 6400 F) whose magnification was calibrated before the measurements, were 1.09, 1.54, 2.12 and 2.06 ± 0.05 μm respectively.

B. X-ray diffraction measurements

X-ray diffraction measurements were performed with an AXS D5005 θ-θ type diffractometer, equipped with a diffracted-beam monochromator set to select Cu Kα radiation.

The specimen holder used in the diffraction experiments consists of a hollow, brass box of 51x50x10 mm. In the topside about 30 holes (diameter 0.5 mm) were drilled. The (curved) foils were kept flat in the diffractometer during measurements by placing them on the topside of the specimen holder and by continuously pumping the pressure inside of the specimen holder down to about 1 Pa.

For verification of the specimen flatness and the position of the specimen in the diffractometer, some Si standard powder was put on the surface of one of the specimens. It was found that peak shifts induced by deficiencies in the flatness and specimen displacement could be neglected.

For the diffraction stress analysis, specimen tilt angles were applied corresponding to \( \sin^2 \psi = 0, 0.05, 0.10, 0.15 \) and 0.20. Because of the small TiN layer thickness, the observed diffraction patterns consist of overlapping reflections of layer and substrate which hinders the evaluation of some of the TiN diffraction peaks. In all scans at fixed \( \psi \), always the \{331\}, \{420\}
and (422) reflections could be measured. If possible, also the (200) and (220) reflections were recorded (on an θ-θ type diffractometer low angle reflections cannot be measured at high specimen tilt angles, i.e. ψ must be smaller than θ). The counting times of the scans were such that at the peak maximum of most diffraction peaks at least 1000 counts were collected. A step size of 0.1° was used.

For obtaining peak positions, the 2θ scans employed in the experiments were subdivided into 2θ ranges in which a set of (severely overlapping) diffraction peaks could be fitted simultaneously using a linear background. Because of the overlap reliable peak positions could only be obtained by fitting profile-shape functions to the measured diffraction patterns. Fits were obtained by using profile shapes consisting of two symmetric Pseudo Voigt functions for each diffraction peak composed of an α₁ and an α₂ component. An α₂/α₁ intensity ratio of 0.5 was used. The thus obtained α₁ peak positions were used for the determination of the lattice spacings \( d^{hkl}_\psi \) by applying Bragg's law.

C. Bending foil stress measurements

Strips were cut from the foils as close as possible through the centre of the foil. Thus strips of about 60 x 0.7 mm were obtained. The curvature that was present near the centre of the strips was measured by putting them on a calibration graph in which circles of various diameters had been drawn.

IV. Results and discussion

A. Stress analysis using literature values for the elastic constants

The mechanical elastic constants \( S_{1}^{\text{mech}} \) and \( \frac{1}{2} S_{2}^{\text{mech}} \) of the TiN were calculated from the single crystal elastic constants using the Neerfeld-Hill model, which takes the arithmetic average of the constants obtained with the Voigt and the Reuss models [3,4,14]. The obtained elastic constants and the corresponding values of \( E \) and \( \nu \) (cf. Eqs (1a-b)) are presented in Table 1. Also \( E \) and \( \nu \) of the steel foils have been indicated.

The stress \( \sigma_{\psi}^{\text{mech}} \), the strain free lattice parameter \( a_0 \) and the 'elastic anisotropy' parameter \( K_2 \) (cf. Eq. (2a)) were obtained from the positions of all measured reflections for each specimen (least squares fitting). The results have been gathered in Table 2.

| Table 1: Mechanical elastic constants of TiN calculated from the single crystal elastic constants \( (s_{11} = 1.80 \text{ TPa}^{-1}, s_{12} = -0.38 \text{ TPa}^{-1}, s_{44} = 6.13 \text{ TPa}^{-1} [15]) \) using the Neerfeld-Hill model. \( E \) and \( \nu \) of the stainless steel substrate were measured in a tensile tester [11]. |
|-------------------------------|-------------------------------|----------------|----------------|-------------------------------|-------------------------------|
| \( S_{1}^{\text{mech}} \) (TPa⁻¹) | \( \frac{1}{2} S_{2}^{\text{mech}} \) (TPa⁻¹) | \( E \) (GPa) | \( \nu \) | \( E \) (GPa) | \( \nu \) |
| 0.54 | 2.67 | 470 | 0.254 | 170 | 0.3 |
Table 2: Stress values determined by X-ray diffraction for TiN layers deposited at different relative titanium-line intensities, using the values for $2S_1^{\text{mech}}$ and $\frac{1}{2}S_2^{\text{mech}}$ given in Table 1. Also the values obtained for $a_0$ and $K_2$ have been given.

<table>
<thead>
<tr>
<th>Rel. Int.</th>
<th>$a_0$ (Å)</th>
<th>$K_2$ (TPa$^{-1}$)</th>
<th>$\sigma_{II}^{\text{mech}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>4.2493 ± 0.0010</td>
<td>-3.0 ± 0.5</td>
<td>-4.5 ± 0.3</td>
</tr>
<tr>
<td>40%</td>
<td>4.2494 ± 0.0010</td>
<td>-2.6 ± 0.3</td>
<td>-4.5 ± 0.2</td>
</tr>
<tr>
<td>55%</td>
<td>4.2431 ± 0.0010</td>
<td>-1.2 ± 0.3</td>
<td>-5.6 ± 0.2</td>
</tr>
<tr>
<td>60%</td>
<td>4.2455 ± 0.0010</td>
<td>-1.6 ± 0.4</td>
<td>-5.3 ± 0.3</td>
</tr>
</tbody>
</table>

The values of the stress $\sigma_{II}^{\text{curv}}$, determined from the measured layer thicknesses and radii of curvature using the bending foil method (Eq. (3)), have been given in Table 3. Also, the values for $\sigma_{II}^{\text{mech}}$ derived from the values of $\sigma_{II}^{\text{curv}}$ using Eq. (8) have been given in Table 3.

Table 3: Layer thickness $t$, radius of curvature $r$ and stress $\sigma_{II}^{\text{curv}}$ measured with the bending foil method for TiN layers deposited at different relative titanium-line intensities using the values for $E$ and $v$ given in Table 1. Values of $\sigma_{II}^{\text{mech}}$ were calculated from the corresponding values of $\sigma_{II}^{\text{curv}}$ using Eq. (8).

<table>
<thead>
<tr>
<th>Rel. Int.</th>
<th>$t$ (µm)</th>
<th>$r$ (mm)</th>
<th>$\sigma_{II}^{\text{curv}}$ (GPa)</th>
<th>$\sigma_{II}^{\text{mech}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>1.09 ± 0.05</td>
<td>30.0 ± 1.0</td>
<td>-7.9 ± 0.4</td>
<td>-7.6 ± 0.4</td>
</tr>
<tr>
<td>40%</td>
<td>1.54 ± 0.05</td>
<td>26.7 ± 1.0</td>
<td>-6.5 ± 0.3</td>
<td>-6.2 ± 0.3</td>
</tr>
<tr>
<td>55%</td>
<td>2.12 ± 0.05</td>
<td>20.7 ± 1.0</td>
<td>-6.5 ± 0.3</td>
<td>-6.0 ± 0.3</td>
</tr>
<tr>
<td>60%</td>
<td>2.06 ± 0.05</td>
<td>21.7 ± 1.0</td>
<td>-6.3 ± 0.3</td>
<td>-5.9 ± 0.3</td>
</tr>
</tbody>
</table>

Clearly, the corresponding values for the stress $\sigma_{II}^{\text{mech}}$ obtained with the two different methods do not coincide (see Fig. 1, data indicated with open symbols '□' and '○'). Especially for the layers deposited at low relative titanium-line intensities (cf. section III.A), the stresses $\sigma_{II}^{\text{mech}}$ measured with the bending foil method are distinctly larger than the stresses $\sigma_{II}^{\text{mech}}$ measured using X-ray diffraction. These discrepancies are attributed to marked deviations of the actual elastic constants of the TiN layers from those calculated from the literature data for the single crystal elastic constants. Indeed, significant differences between values of elastic constants reported in the literature exist. This holds especially for TiNx in dependence on its composition $x$ [6,7]. For layers deposited at different relative titanium-line intensities and thus at different nitrogen pressure (see section III.A), the composition is likely to be different. Consequently, the elastic constants of the investigated layers will be different as well.

For the diffraction stress measurements, the sensitivity of $\sigma_{II}^{\text{mech}}$ and $K_2$ for the value of $E$ used in the data evaluation is clarified by rewriting Eq. (2a) by means of Eqs (1a-b). Thus it follows:
Fig. 1: The stresses $\sigma_{\text{mech}}$ in the TiN layers deposited with various relative titanium-line intensities (cf. section III.A) (i) as determined with the 'bending foil method' for curvature stress analysis (□) and (ii) as determined with the 'direct solution method' for diffraction stress analysis (○), using in both cases the elastic constants based on literature data given in Table 1. Also, the stress values in the TiN layers have been indicated as determined by combining both sets of data (diffraction and curvature data) leading to determination of Young's modulus (see Table 5 and the filled symbols ◆ in the figure).

\[
\varepsilon_{\psi}^{\text{hkl}} = \frac{d_{\psi}^{\text{hkl}} \sqrt{h^2 + k^2 + l^2} - a_0}{a_{\text{ref}}} \\
= \left( -2\nu + 2K_2E(\Gamma - \frac{1}{2}) + \left( \frac{1}{2} (1 + \nu) - 3K_2E(\Gamma - \frac{1}{2}) \right) \sin^2 \psi \right) \frac{\sigma_{\text{mech}}^{\text{mech}}}{E}
\]  

(9)

For a varying value of $E$ and a constant value of $\nu$, the stress $\sigma_{\text{mech}}$ varies linearly with $E$ and $K_2$ varies linearly with $I/E$. The strain free lattice parameter $a_0$ however is not affected.

The values of $\sigma_{\text{mech}}$ and $K_2$ are not very sensitive to the value for $\nu$ used in the data evaluation. This is illustrated by the data shown in Table 4, where $\sigma_{\text{mech}}$ and $K_2$ for the layer deposited using a relative titanium-line intensity of 20% have been calculated for various values of $\nu$ at constant $E$. However, as compared to the dependence of $a_0$ on composition [16], the value of $a_0$ varies considerably with $\nu$ and therefore, in view of the uncertainty in $\nu$, the values obtained for $a_0$ (Table 2) must be considered as unreliable for determination of layer composition.

Because stress values from curvature measurements are insensitive for both $E$ and $\nu$ of the thin layer (as long as $t << d$; see section II.B), and stress values from diffraction measurements are
Table 4: Values of $a_0$, $K_2$ and $\sigma_{\|}^{\text{mech}}$, calculated from X-ray diffraction measurements, using various values of $v$ and $E = 470$ GPa (cf. Table 1), for the specimen sputtered with a relative titanium-line intensity of 20%.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$a_0$ (Å)</th>
<th>$K_2$ (TPa$^{-1}$)</th>
<th>$\sigma_{|}^{\text{mech}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>4.2530</td>
<td>-2.9</td>
<td>-4.7</td>
</tr>
<tr>
<td>0.245</td>
<td>4.2493</td>
<td>-3.0</td>
<td>-4.5</td>
</tr>
<tr>
<td>0.3</td>
<td>4.2464</td>
<td>-3.1</td>
<td>-4.4</td>
</tr>
</tbody>
</table>

*cf. Table 1

relatively insensitive for $v$ but very sensitive for $E$, a combination of the two methods for stress analysis can be used to determine a reliable value for $E$.

B. Determination of Young's modulus $E$

Using the value for $v$ given for TiN in Table 1, the value of $E$ can be determined by fitting to the diffraction and curvature data such that equal values are obtained for the corresponding stresses $\sigma_{\|}^{\text{mech}}$ as derived from both methods for stress analysis. The thus obtained values for $E$ and $\sigma_{\|}^{\text{mech}}$, are shown in Table 5.

Large values for $E$ have been observed before (cf. Refs. [6,7]), which well agrees with the present results. The values observed for $E$ in this work reveal a strong dependence of $E$ on the relative titanium-line intensity prevailing during layer deposition. Because the nitrogen pressure during layer deposition corresponding to a low relative titanium-line intensity is relatively high (see section III.A), the corresponding layers will have a relatively high nitrogen content. An increase of $E$ with nitrogen content, as observed here, has been reported before in Refs [6,7]. The presently obtained values for $E$ are relatively large as compared to the earlier data [6,7], which may be ascribed to microstructural differences due to different values for the layer-deposition parameters.

The present results demonstrate that large errors in stress values can occur when literature data are used for the elastic constants in order to arrive at measured stress values (cf. Tables 2,3, and 5 and see Fig. 1). Especially for the diffraction stress measurements, the corresponding

Table 5: Values for $E$ and $\sigma_{\|}^{\text{mech}}$ obtained by combining the curvature and the diffraction data for TiN layers deposited at different relative titanium-line intensities. Also the corresponding values of $K_2$ and $-K_2 / \frac{1}{2} S_{\|}^{\text{mech}}$ (cf. Eq. (A3)) have been given.

<table>
<thead>
<tr>
<th>Rel. Int.</th>
<th>$E$ (GPa)</th>
<th>$\sigma_{|}^{\text{mech}}$ (GPa)</th>
<th>$K_2$ (TPa$^{-1}$)</th>
<th>$-K_2 / \frac{1}{2} S_{|}^{\text{mech}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>828 ± 72</td>
<td>-8.0 ± 0.5</td>
<td>-1.7 ± 0.3</td>
<td>1.12 ± 0.21</td>
</tr>
<tr>
<td>40%</td>
<td>684 ± 46</td>
<td>-6.5 ± 0.3</td>
<td>-1.8 ± 0.2</td>
<td>0.98 ± 0.13</td>
</tr>
<tr>
<td>55%</td>
<td>507 ± 33</td>
<td>-6.1 ± 0.3</td>
<td>-1.2 ± 0.3</td>
<td>0.49 ± 0.13</td>
</tr>
<tr>
<td>60%</td>
<td>531 ± 41</td>
<td>-6.0 ± 0.3</td>
<td>-1.4 ± 0.4</td>
<td>0.59 ± 0.16</td>
</tr>
</tbody>
</table>
differences in stress values can be drastic. The use of the present literature values of the elastic constants for the evaluation of stress in TiN layers from measured strain data is therefore dissuaded.

C. Stress versus microstructure of the TiN layers
The larger stresses are measured for the thinner layers (e.g. see Table 5); i.e. for the layers produced with the lower growth rates. This can be qualitatively understood. Compressive stresses in sputtered thin layers are believed to be caused by atomic peening [17]; bombarding ions and atoms which hit the surface of the thin layer during deposition knock surface atoms deeper into the growing layer or they get themselves trapped in the layer. The associated introduction of additional volume in the layer induces compressive stress due to the constraining substrate. A layer that grows more slowly will be subjected to a more intense atomic bombardment. Thus a higher stress occurs in layers that have been grown at lower growth rate.

The results obtained for $K_2$ and $- K_2 / \frac{1}{3} S_2^{mech}$ (see Appendix A and Table 5) suggest that the crystallites in the TiN layers exhibit more elastic anisotropy if their nitrogen concentration is smaller. This need not be a direct consequence of corresponding changes in the single crystal elastic constants: a variation in the microstructure of the layers can induce a change in the elastic behaviour as well.

V. Conclusions

-A direct comparison of stress values, for thin layers on a substrate, derived from lattice-strain (diffraction) measurements and from curvature measurements requires that these stress values pertain to a common basis: e.g. a thin layer on an infinitely rigid substrate (cf. Eq. (8)).
-
The determination of stress in thin layers derived from lattice-strain (diffraction) data requires a distinctly higher accuracy of the elastic constants of the layer than holds for the determination of stress in thin layers from specimen curvature data.
-
A combination of the results of lattice-strain (diffraction) measurements and curvature measurements allows determination of Young’s modulus.
-
Higher values of stress and Young’s modulus of a sputtered TiN layer correspond with lower layer-growth rate and higher nitrogen content.
-
The average elastic anisotropy of the crystallites of TiN layers is the larger, the lower the titanium-line intensity and thus the growth rate (i.e. the smaller the thickness of the layer).

Acknowledgements
The present work was sponsored by the Programme for Innovate Research, Surface Technology (IOP oppervlaktetechnologie). We are grateful to Ir. M. van der Meer for deposition of the TiN layers and performing the bending foil measurements. Mr. J. Helmig is thanked for the layer thickness measurements and Ing. N.M. van der Pers for his assistance with the diffraction experiments.
Appendix A: Elastic anisotropy

It was shown in Ref. [18] that for a specimen that consists of a cubic material and that is macroscopically isotropic the diffraction elastic constants can always be written as (see also Ref. [5]):

\[ S_{1}^{hl} = K_{1} + \Gamma K_{2} \]  
\[ \frac{1}{2} S_{2}^{hl} = K_{3} - 3\Gamma K_{2} \quad (A1a) \]

\[ \frac{1}{2} S_{2}^{mech} \quad (A1b) \]

The mechanical elastic constants \( S_{1}^{mech} \) and \( \frac{1}{2} S_{2}^{mech} \) are obtained by substituting \( \Gamma = 1/5 \) in Eqs (A1a-b). Then it is easily seen that Eq. (2a) is identical to the more familiar expression [3,4]:

\[ \varepsilon_{\psi}^{hl} = \frac{a_{ref}}{d_{\psi}^{hl} \sqrt{h^2 + k^2 + l^2 - a_{0}}} \left( 2S_{1}^{hl} + \frac{1}{2} S_{2}^{hl} \sin^2 \psi \right) \sigma_{\psi}^{mech} \quad (A2) \]

A measure for the average elastic anisotropy of the crystallites in the specimen can be obtained by relating the maximum possible difference in the \( \frac{1}{2} S_{2}^{hl} \) values (i.e. the difference in \( \frac{1}{2} S_{2}^{hl} \) values for \( \Gamma = 0 \) and \( \Gamma = 1/3 \) [14,18]) to \( \frac{1}{2} S_{2}^{mech} \). It holds (cf. Eq. (A1b)):

\[ \frac{\frac{1}{2} S_{2}^{hl} (\Gamma = 1/3) - \frac{1}{2} S_{2}^{hl} (\Gamma = 0)}{\frac{1}{2} S_{2}^{mech}} = -\frac{K_{2}}{\frac{1}{2} S_{2}^{mech}} \quad (A3) \]

References

Chapter VIII

A tool for X-ray diffraction analysis of thin layers on substrates

Substrate Peak Removal Method

J.-D. Kamminga, R. Delhez, Th.H. de Keijser, E.J. Mittemeijer

ABSTRACT
A method is proposed that removes from a diffraction pattern, recorded from a substrate covered with a thin layer and in which overlapping peaks of the layer and the substrate are present, the substrate peaks, using a separate measurement of the uncovered substrate. The obtained diffractogram without substrate peaks can then be used for the characterisation of the microstructure of the thin layer. As an example, the method is shown to yield good results for a TiN layer deposited on a tool steel substrate.

I. Introduction

Upon subjecting thin layers on substrates to X-ray diffraction analysis, problems may arise because the recorded diffraction pattern comprises diffraction peaks and background contributions from both the thin layer and the substrate. The associated overlap of layer and substrate peaks hinders the characterisation of the microstructure of the layer. It is therefore desirable to remove the substrate diffraction peaks from the measured diffraction pattern. As will be shown here, elimination of the substrate peaks can be straightforwardly performed if a separate diffractogram of the uncovered substrate is recorded. This ‘substrate’ diffraction pattern can be scaled to correct for the absorption of X-rays in the thin layer and it can then be subtracted from the ‘layer + substrate’ diffraction pattern. The substrate peaks are thus removed. Several problems, e.g. those associated with minor imperfections in the reproducibility of the diffraction angle, 2θ, scale for two separate measurements on the same diffractometer, for which the analysis is very sensitive, must be solved in such a procedure.

An important application of the substrate peak removal method is in the diffraction analysis of stress (‘sin²ψ method’) in thin layers, where the specimen is subjected to various angles of tilt in the diffractometer, implying variable contribution of the substrate diffraction to the measured total diffraction pattern.

The proposed method is illustrated by means of measurements from a 2.0 μm TiN layer deposited on a tool steel substrate. An θ-2θ type diffractometer is employed, but the proposed method is by no means restricted to the used diffraction geometry.
II. Basis

For the intensity $I^A$ measured from an uncovered substrate in a diffraction experiment $A$ it can be written:

$$I^A = I^A_{\text{SUB}} + I^A_{\text{IN}}$$  (1)

where $I^A_{\text{SUB}}$ concerns all intensity stemming from X-rays scattered by the substrate; i.e. including the contributions of the substrate to the background. All other (background) intensities, as air scatter and instrumental noise, are included in $I^A_{\text{IN}}$.

For the intensity $I^B$ measured from a substrate covered with a thin layer in a diffraction experiment $B$ it holds:

$$I^B = I^B_{\text{LAY}} + I^B_{\text{IN}} + I^B_{\text{SUB}}$$  (2)

where $I^B_{\text{LAY}}$ denotes all intensity that originates from X-rays scattered by the layer, including the background caused by the layer.

With equal incident beam intensities it holds for the experiment $A$ and $B$ that at equal $2\theta$ and specimen tilt angles:

$$I^B_{\text{SUB}} = I^A_{\text{SUB}} e^{-\mu l}$$  (3a)

where $\mu$ is the linear absorption coefficient of the layer and $l$ is the length of the path of the X-ray beam through the layer for the given diffraction and specimen tilt angles. For an $\omega$-type diffractometer, $l$ is related to the layer thickness $D$, specimen tilt angle $\omega$ and diffraction angle $2\theta$ according to [1]:

$$l = \frac{2 \sin \theta \cos \omega}{\sin^2 \theta - \sin^2 \omega} \cdot D$$  (3b)

For a $\psi$ diffractometer (specimen tilt angle $\psi$) it holds [1]:

$$l = \frac{2}{\sin \theta \cos \psi} \cdot D$$  (3c)

It follows from Eqs (1) and (2), using Eq. (3a):

$$I^B - I^A e^{-\mu l} = I^B_{\text{LAY}} + I^B_{\text{IN}} - I^A_{\text{IN}} e^{-\mu l}$$  (4)

So from the measured diffractograms $I^A$ and $I^B$, a diffractogram $I^B - I^A e^{-\mu l}$ can be constructed in which there are no contributions from the substrate whatsoever and which
contains the diffractogram of the layer, $I_{\text{L}}^B$ on top of a 'constructed' instrumental background $I_{\text{in}}^B - I_n^A e^{-\mu t}$. This instrumental background will be small and will vary slowly and continuously with $2\theta$ and can thus be removed, together with the background stemming from the layer (which is included in $I_{\text{L}}^B$) by 'normal' procedures used for diffractograms.

III. Practical considerations

Although the principle of substrate peak removal is very simple, experimental problems hinder straightforward application.

A. Scaling of the substrate diffraction pattern
Firstly, the two measurements, $A$ and $B$, must be performed using equal incident beam intensities. Therefore, measurements $A$ and $B$ must be performed as shortly as possible after each other (thereby assuring equal X-ray source intensity and air pressure). If the intensities of the incident beams of both diffraction experiments are not equal, the measured intensities must be normalised (see section V).

Secondly, $I_{\text{SU}}^A$ needs to be scaled for absorption in the layer (Eq. (3a)). In general, the linear absorption coefficient $\mu$ and the thickness $D$ of the thin layer are not precisely known. The linear absorption coefficient depends on the wavelength of the X-rays and the chemical constitution and density of the layer. The wavelength of the X-rays for the measured intensities can be tuned by applying a diffracted beam monochromator\(^1\). However, the chemical constitution and/or density of the thin layer are often not sufficiently well known for a determination of $\mu$ that is precise enough for the subtraction procedure. Also the value of $D$ can be a problem. Therefore, and because $\mu$ and $D$ only appear jointly as the product $\mu D$ in the equations (cf. Eqs (3a-c)), the value of $\mu D$ is used as a fit parameter in the procedure.

B. Specimen surface displacement and irreproducibility of the diffraction experiment
Specimen surface displacement is the diffractometer error occurring when the surface of the diffracting specimen is not at the reference plane of the diffractometer. Specimen surface displacement of the substrate is invariably present when the substrate on which a layer is deposited is mounted in the diffractometer such that the top of the specimen (and thus of the layer) is at the reference plane. Specimen surface displacement leads to shifts $\Delta 2\theta$ in the diffractogram that depend on the diffraction angle. For the above case, \textit{i.e.} a substrate surface at depth $D$ below the specimen surface, it holds for the shift $\Delta 2\theta$ (in degrees) of the substrate diffractogram, using an $\omega$ diffractometer (cf. Ref. [2]):

\[\Delta 2\theta = \frac{2 \pi D}{\lambda} \sin \theta.\]

\(^1\) The use of a monochromator is not strictly necessary, as long as the background of the diffraction pattern varies slowly. Then the resulting layer peaks obtained after the substrate peak removal, will still lie on a 'constructed' slowly varying background, that can be removed by 'normal' procedures for diffractograms.
\[ \Delta 2\theta = \frac{360 \sin \theta \cos \theta}{\pi R \sin(\theta + \omega)} D \] \hspace{1cm} (5a)

where \( R \) is the radius of the diffractometer. For a \( \psi \) diffractometer it holds (cf. Ref. [2]):

\[ \Delta 2\theta = \frac{360 \cos \theta}{\pi R \cos \psi} D \] \hspace{1cm} (5b)

In both cases \( \Delta 2\theta \) indicates a shift to lower \( 2\theta \) (for \( D > 0 \)).

A diffractometer does not perfectly reproduce the values of the diffraction angles in different diffraction experiments. For the currently used diffractometer (see section V) the reproduction is better than 0.001 \( ^\circ \)2\( \theta \). Although the corresponding shifts in the diffraction patterns are very small, problems yet arise in the subtraction procedure when the diffraction peaks are relatively sharp.

To solve \( 2\theta \) position problems, shifting of the diffraction pattern \( I^A \) is necessary. The procedure to be used is discussed next.

**Shifting diffraction patterns**

Two different types of shifts in \( 2\theta \) have to be considered: shifts caused by specimen surface displacement (that in principle depend on \( 2\theta \), see Eqs (5a-b)), and shifts caused by irreproducibility of the diffractometer that are assumed not to depend on \( 2\theta \).

If \( D \) is unknown, a \( 2\theta \) independent shift in \( 2\theta \) of the diffraction pattern \( I^A \) may yet applied here. This requires that the investigated range in \( 2\theta \) is not too large, in order that the \( 2\theta \) dependence of the shift due to this specimen surface displacement effect can be neglected (cf. Eqs (5a) and (5b)). Then, the constant shift in \( 2\theta \) applied can be conceived as incorporating both the \( 2\theta \) shift due to the specimen surface displacement effect and the \( 2\theta \) shift caused by the irreproducibility of \( 2\theta \) scale of the diffractometer. This \( 2\theta \) independent shift is denoted by \( x \) in what follows. Because in any case the (contribution to) \( x \) caused by the irreproducibility of the \( 2\theta \) scale of the diffractometer is unknown, the shift \( x \) is considered as a fitting parameter.

After shifting diffractogram \( I^A \), as described above, the \( 2\theta \) positions of the intensity data in \( I^A \) and \( I^B \) are in general not the same. To enable subtraction, according to Eq. (4), interpolation is necessary. This can be done by fitting e.g. a spline function [3] to the diffractogram obtained in measurement \( A \).

**C. Fit criterion**

Thus, two parameters remain to be fitted: \( \mu D \) (cf. Eqs (3) and (4) and section III.A) and \( x \) (cf. section III.B). A criterion should be used to judge the quality of the diffraction pattern obtained after the subtraction \( I^B - I^A e^{-\omega} \) (Eq. (4)). The best resulting diffraction pattern is that pattern where the substrate peaks have totally disappeared. In practice this will be a diffraction pattern with a minimum amount of peaks and wiggles. It is suggested that the length of a line through all data points after the subtraction is a measure for the number and extent of peaks and wiggles. Counting statistical noise on the data would lead to a significant contribution to the length of this
line and affect the sensitivity of the fit criterion. Therefore, the data are first smoothed and then the length of the line through the smoothed data points is calculated and used to judge the quality of the subtraction as determined in a fit procedure leading to values for $\mu D$ and $x$. The smoothing can be done by e.g. using orthogonal polynomial weighting functions [4].

IV. Computation programme

The above considerations have led to the following procedure for the substrate peak removal method:

1. If necessary, normalise $I^A$ such that measurements $A$ and $B$ can be treated as being recorded using equal incident beam intensities (see section III.A and for a practical method section V).
2. If a value for $D$ is available, adjust the $2\theta$ values of $I^A$ for the effect of specimen surface displacement in $I^B$ using Eqs (5a) or (5b). This step may be omitted (see section III.B).
3. Fit a spline function to the uncovered substrate diffraction pattern (possibly modified according to steps 1 and 2).
4. Choose starting values for $\mu D$ and $x$.
5. Scale the spline obtained in 3, by multiplying it with $e^{\mu D}$ (for each data point) and shift over $x$. Then determine the values of the scaled spline at each $2\theta$ value used in measurement $B$.
6. Subtract the splined, scaled, and shifted uncovered substrate diffraction pattern from the layer + substrate diffraction pattern (see Eq. (4)) and calculate the length of the line connecting the data points after smoothing the thus obtained layer diffraction pattern.
7. Fit $\mu D$ and $x$ by repeating steps 5 and 6 until the ‘length’ of the smoothed layer diffraction pattern obtained in step 6 is minimal.

V. Example

Measurements were performed on a magnetron sputtered TiN layer, deposited on a tool steel. For practical reasons, it was not possible to use the same substrate in measurements $A$ and $B$. However, the substrate used for measurement $A$ was from the same batch of material and was subjected to the same preparation procedure as held for measurement $B$.

The deposition of the TiN layer was performed as follows. First the substrate was sputter cleaned. Then a Ti interlayer, of about 200 nm was sputtered, and finally a TiN layer of $(2.0 \pm 0.1) \mu m$ was deposited on top of the Ti interlayer. The specimen without the TiN layer, used for measurement $A$, was subjected to the same procedure, including deposition of the Ti interlayer, except for the deposition of the TiN layer.

The diffraction measurements were performed on a Siemens 500 $\alpha$-type diffractometer equipped with a diffracted beam monochromator set to select Cu K$\alpha$ radiation. Equal slits were used in both experiments. For measurement $A$ and measurement $B$, $2\theta$ scans were recorded using a measurement range from 113 to 149 $^\circ 2\theta$ and a step size of 0.05 $^\circ 2\theta$. The specimens were rotated during the measurements and a specimen tilt angle $\alpha$ of $26.56^\circ$ was used.
Fig. 1: Substrate \( I^A \) and layer+substrate \( I^B \) diffractograms and the layer diffractogram obtained after substrate peak removal. Diffractograms from the TiN layer and/or the tool steel substrate were recorded using a diffractometer equipped with a diffracted beam monochromator set to select the CuK\(\alpha\) radiation (see section V) and have been shifted vertically in the figure.

For the diffractometer used, the incident beam intensity was gauged as a function of time by, now and then, measuring the integral intensity of the \{211\} reflection of a quartz specimen. Normalised intensities \( I^A \) were obtained from the measured \( I^A \) by multiplying with an interpolated value for the \{211\}quartz intensity at about the time of measurement \( B \) and dividing with an interpolated value for the \{211\}quartz intensity at about the time of measurement \( A \).

The spline algorithm given in Ref. [3] was applied. For the smoothing of \( I^B - I^A e^{-\mu d} \) (step 6 in section IV), orthogonal polynomial weighting functions were used (see Ref. [4]).

The substrate measurement \( A \), after normalisation and adaptation for specimen surface displacement (see steps 1 and 2 in section IV), is shown together with the fitted spline function in Fig. 1. Also, the layer + substrate measurement \( B \) and the layer diffraction pattern, obtained after the procedure for removal of the substrate peaks given in section IV, are presented.

Clearly, the substrate peaks have been removed successfully from measurement \( B \) and thereby the layer peaks at \( 2\theta = 124^\circ \) and \( 2\theta = 140^\circ \) can now be interpreted reliably.

The values obtained for \( x \) and \( \mu D \) were \(-0.0635 \, \text{rad}\) and \(0.2216\) respectively. Additional measurements performed in this work showed that the shift \( x \) is mainly due to a difference in stress in the two substrates.

Using a value of \(8.26 \times 10^4 \, \text{m}^{-1}\) for \( \mu \) (cf. Ref. [5]) and a value of \(2.0 \, \mu \text{m}\) for \( D \) one attains \(\mu D = 0.17\), which is smaller than the value obtained by the fit. This can be due to the uncertainties in \( \mu \) and \( D \), but may also stem from differences in the air pressure during measurements \( A \) and \( B \) and/or between the two different substrates.
In practice, often different substrates must be used for measurements A and B. The present results show that as long as similar substrates are used, the proposed substrate peak removal procedure even then can be performed satisfactorily.

VI. Conclusions

-The diffraction pattern of a layer can be isolated from the measured diffraction pattern of a layer-substrate system by subtracting an appropriately scaled, separately measured, diffraction pattern of an uncovered substrate.
- The product of the linear absorption coefficient and the layer thickness, \( \mu D \), and a systematic diffraction angle error, angular shift \( x \), can be determined by fitting.
- An effective fit criterion is the ‘length’ of the diffraction pattern from which the substrate peaks have been removed.

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References

Summary

Thin layers can be used to improve the surface properties of materials. The residual stress that is often present in thin layers, can largely influence the properties of the layer/substrate system. Therefore it is important to understand these stresses in a fundamental way. Residual stresses in thin layers are the primary subject of this thesis. Following some ideas in the literature concerning the origins of the stress, the state of stress in various types of layers has been modelled. These models have been verified experimentally by means of X-ray diffraction. The measurement of stresses using X-ray diffraction is not without complications. How stresses can be extracted from diffraction data in a reliable way is the second topic of this thesis.

The state of stress in a series of sputtered TiN layers of different thicknesses has been investigated in detail in Chapters 2, 3 and 4. By depositing each layer simultaneously on two different substrate materials it was possible to separate the thermal stresses (i.e. stresses induced by the cooling down from deposition temperature to room temperature due the different thermal expansion coefficients of layer and substrate) satisfactorily from the other stresses and to determine Poisson’s ratio of the layers. The resulting stresses in the layers, the so-called growth stresses, have been investigated in view of the atomic peening model. According to this model, fast particles that knock on the layer during growth shoot surface atoms deeper into the growing layer, or get themselves trapped in the layer. The extra volume introduced causes compressive stress. The state of stress in the layer caused by atomic peening has been modelled. Good correspondence of the predictions from the model with experimental X-ray diffraction data has been found. The model developed has been used for a quantitative assessment of the type and amount of "misfitting particles" shot in the layer. It has been concluded that the growth stresses in the layers can be attributed to about 1 wt.% Ti interstitials in the TiN. The layer thickness dependence of the stresses has also been investigated. It has been found that the thermal stresses in the layers depend on the substrate material but not on the layer thickness. The growth stress in all layers can be described with a single growth stress profile in which the compressive stress reduces with increasing distance to the layer-substrate interface.

In evaporated thin layers, tensile stresses often occur. In the literature, these stresses are attributed to the atomic interaction acting across the grain-boundaries. In view of the columnar microstructure that is often present in such layers, this mechanism leads to a strong direction dependence of the grain interaction: whereas the interaction of grains in in-plane directions, i.e. perpendicular to the columns, will be large (leading to the tensile stress), the grain interaction in directions parallel to the columns will be small due to the free space between the columns. In general, conventional methods for diffraction stress analysis are not suitable for specimens that exhibit such direction dependence in the grain interaction. Therefore, in Chapter 5, the diffraction results for such layers have been calculated directly, assuming that the strain in each columnar shaped crystallite was equal in directions parallel to the surface and that all stress components normal to the surface were zero for each crystallite. The experimental diffraction results from an evaporated Ni layer are in good correspondence with the calculated results.
Even if a strong direction dependence in the elastic interaction between the grains is absent, the translation of the lattice strains measured with X-ray diffraction into a state of stress is complicated. New methods for diffraction analysis have been proposed in Chapter 6 that, contrary to conventional methods for diffraction stress analysis, are not based on the diffraction elastic constants, but that are based on the mechanical elastic constants. Methods for diffraction stress analysis on the basis of mechanical elastic constants are preferred for several reasons. In the first place the mechanical elastic constants are more easily measured than the diffraction elastic constants. Secondly, the mechanical elastic constants depend in general less on the choice of grain interaction model than the diffraction elastic constants, which is of advantage if experimental assessment of the elastic constants is not possible, so that they must be calculated from the single crystal elastic constants using some grain interaction model. The conventional and the new methods of diffraction stress analysis have been illustrated in Chapter 6 using diffraction data from a sputtered TiN layer.

One of the new methods for diffraction stress analysis on the basis of mechanical elastic constants has been used in Chapter 7 to determine Young's modulus for a series sputtered TiN layers with different Ti/N ratios. Young's modulus has been determined by a combination of the results of diffraction stress with the results of curvature stress measurements, where the stress in the layer is calculated from the curvature of the layer/substrate system. The values of the stress and Young's modulus depend strongly on the Ti/N ratio.

A problem that often occurs in X-ray diffraction measurements from thin layers on substrates is the overlap of substrate and layer reflections. This is investigated in Chapter 8. A method has been developed that removes from a measured layer+substrate diffraction pattern the substrate peaks, using a separate diffraction pattern of the uncovered substrate. The method yields good results for a sputtered TiN layer deposited on a tool steel.
Samenvatting

Dunne lagen kunnen worden gebruikt om de oppervlakte-eigenschappen van materialen te verbeteren. Vaak zijn in dunne lagen restspanningen aanwezig, die grote invloed kunnen hebben op de eigenschappen van het laag-substraat systeem. Het is daarom van belang deze spanningen op fundamenteel niveau te begrijpen. In dit proefschrift worden de restspanningen in dunne lagen onderzocht. Uitgaande van ideeën die er in de literatuur bestaan over de oorzaken van spanningen is de spanningstoestand in diverse typen dunne lagen gemodelleerd. Deze modellen zijn experimenteel geverifieerd met behulp van Röntgendiffractie. Het meten van spanningen met behulp van Röntgendiffractie is niet zonder complicaties. Om die reden is ook onderzocht hoe uit diffractiedata zo betrouwbaar mogelijk spanningen kunnen worden bepaald.

De spanningstoestand in een verzameling gesputterde TiN lagen met verschillende laagdikten is in detail onderzocht in hoofdstukken 2, 3 en 4. Het gebruik van twee verschillende substraatmaterialen maakte het mogelijk de thermische spanningen in de lagen (veroorzaakt tijdens het afkoelen van depositietemperatuur naar kamertemperatuur door de verschillende thermische expansiecoëfficiënten van substraat en laag) op bevredigende wijze te scheiden van de overige spanningen. Bovendien kon de dwarscontractiecoëfficiënt (Poisson ratio) van de TiN lagen bepaald worden. De resterende spanningen de lagen, de zogenaamde groeispanningen, zijn geïnterpreteerd in het licht van het atomic peening model. Volgens dit model schieten snelle deeltjes, die tijdens de groei op het oppervlak van de groeiende laag botsen, oppervlakteatomen dieper in de laag, of worden zelf in de laag gevangen. Het daardoor geïntroduceerde extra volume in de laag veroorzaakt drukspanning. De door dit proces geïnduceerde spanningstoestand in de laag is gemodelleerd. Er is goede overeenstemming gevonden tussen experimentele Röntgendiffractieresultaten en de voorspellingen uit het model. Het model is gebruikt om tot een kwantitatieve afschatting van de hoeveelheid en het type van de ingeschoten "mispassende deeltjes" te komen. De spanningen in de beschouwde TiN worden toegeschreven aan ongeveer 1 gewichtsprocent Ti interstitiën in het TiN. Ook is de laagdikte-afhankelijkheid van de spanning in de lagen onderzocht. Gevonden is dat thermische spanning in de lagen afhangt van het gebruikte substraat, maar onafhankelijk is van de laagdikte. De groeispanning in alle lagen kan worden beschreven met een (substraat-onafhankelijk) enkel spanningssprofiel, waarin de drukspanning afneemt met toenemende afstand tot het substraat-laag grensvlak.

In opgedampte lagen worden vaak trekspanningen gemeten. In de literatuur worden deze trekspanningen toegeschreven aan de aantrekkingskracht tussen atomen aan verschillende zijden van de korrelgrenzen. Gezien de kolonnaire microstructuur van dergelijke lagen leidt dit mechanisme tot een sterke richtingsafhankelijkheid van de korrelwisselwerking: waar de wisselwerking tussen de korrels in de richtingen in het vlak (loodrecht op de kolommen) groot is, leidend tot de trekspanningen in de laag, is wisselwerking in richtingen parallel aan de kolommen klein, gezien de open ruimte tussen de korrels. In het algemeen zijn de gebruikelijke methoden van diffractie spanningsanalyse voor preparaten met een richtingsafhankelijke korrelwisselwerking ongeschikt. Daarom zijn in hoofdstuk 5 de diffractieresultaten voor dergelijke lagen direct berekend, waarbij aangenomen is dat de rek in richtingen parallel aan het
oppervlak in ieder kristal identiek is, en dat alle spanningscomponenten loodrecht op het oppervlak voor elk kristal nul zijn. De experimentele resultaten van diffractiemetingen verricht aan opgedampte Ni lagen zijn in goede overeenstemming met de berekende resultaten.

Ook als een richtingsafhankelijkheid in de elastische wisselwerking tussen korrels in een preparaat niet aanwezig is, is het vertalen van de met Röntgediffraeactie gemeten roosterspaties naar een spanningstoestand niet zonder complicaties. In hoofdstuk 6 worden nieuwe methoden voor diffractie spanningsanalyse aangereikt die, in tegenstelling tot wat gebruikelijk is, niet uitgaan van diffractie elastische constanten, maar die gebaseerd zijn op de mechanische elastische constanten. Methoden van diffractie spanningsanalyse op basis van mechanische elastische constanten zijn te prefereren om diverse redenen. Ten eerste zijn de mechanische elastische constanten in het algemeen eenvoudiger experimenteel te bepalen dan de diffractie elastische constanten. Daarnaast zijn de mechanische elastische constanten minder gevoelig voor de keuze van het korrelwisselwerkingsmodel dan de diffractie elastische constanten, wat een voordeel is als de elastische constanten niet experimenteel bepaald kunnen worden, maar uit de eencristal elastische constanten bepaald moeten worden met een zeker korrelwisselwerkingmodel. Aan de hand van diffractiedata van een gesputterde TiN laag zijn de nieuwe en de conventionele methoden van diffractie spanningsanalyse geïllustreerd in hoofdstuk 6.

Een van de nieuwe methoden van diffractie spanningsanalyse op basis van mechanische elastische constanten is in hoofdstuk 7 gebruikt om de Young's modulus E te meten in een serie gesputterde TiN lagen met verschillende Ti/N verhoudingen. Dit is gedaan door de resultaten van diffractie spanningsmetingen te combineren met de resultaten van krommings spanningsmetingen, waarin uit de kromming van het substraat-laag systeem de spanning in de laag wordt berekend. De waarden van de spanning en Young's modulus bleken in hoge mate afhankelijk te zijn van de Ti/N verhouding.

Een vaak optredend probleem in Röntgediffraeactiemetingen aan dunne lagen op substraten, de overlap van dunne laag en substraatrelecties, is onderzocht in hoofdstuk 8. Een methode is ontwikkeld waarmee de substraatpieken uit het gemeten substraat-laag diffractiepatroon verwijderd kunnen worden met behulp van een diffractiepatroon van uitsluitend het substraat. De methode geeft goede resultaten voor een gesputterde TiN laag gedeporteerd op een gereedschapstaal.
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