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Whole powder pattern decomposition - An application for the evaluation of residual stress states in consideration of steep stress gradients

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ABSTRACT

The whole powder pattern decomposition procedure is an established tool for the analysis of diffraction patterns with overlapping reflections. Its adapted application to data obtained in asymmetric diffraction geometry was shown to yield depth-resolved results of biaxial residual stress states, e.g. of thin film materials. Yet, with increasing coating thickness and in presence of pronounced stress gradients, this approach overestimates the magnitudes of the residual stresses present. The current work aims at overcoming this by including the variations in X-ray penetration depth encountered during the experiment into the applied refinement strategy. A proof of concept is obtained by measuring stress states in molybdenum thin films as a model material using the proposed approach in comparison to classical X-ray residual stress evaluation techniques.

1. Introduction

In the last decades, the range of applications and use of thin films and coatings significantly changed from mere protection of material surfaces to adding distinct functional properties to the surface and/or the underlying substrate. For most applications of thin films reliability and failure tolerance of the systems play a major role. The presence of residual stresses in the coatings governs the long-term behavior. Industrial design and production of thin film material thus requires means to analyze stresses and stress gradients with high precision and in reasonable amounts of time. In the case of crystalline coatings, X-ray diffraction methods are widely employed.

Often, only limited experimental facilities are available to this end. Nevertheless, even with a θ-2θ-type standard diffractometer without a Eulerian cradle, these analyses can be performed. With the ω-tilt, isoinclination mode, a classical approach can readily be employed by measuring the peak-shifts for single hkl reflections at large 2θ values. As will be shown in more detail in Section 3.1.1, some drawbacks with respect to the aforementioned goals are then encountered. On the one hand the attainable $\sin^2\psi$-range is limited in comparison to χ-mode measurements with Eulerian cradle equipment due to geometrical reasons. On the other hand, depth resolved residual stress analysis is often not possible, since X-ray penetration exceeds the film thickness in almost the whole tilt range. Both cases contribute to insensitivity for stress gradient determination. Moreover, in case of peak overlaps due to the presence of other phases, the peak deconvolution is not always unambiguous, leading to errors in calculating interplanar spacings.

As an alternative, residual stress measurements in asymmetric diffraction geometries can be performed. There, the whole diffraction pattern of the thin film specimen is recorded and the subsequent residual stress analysis is performed using all reflections of an individual phase [1]. To this end, the whole powder pattern decomposition procedure (wppd) can be employed. In its framework, the effects of elastic anisotropy can be directly implemented. This is based both on the connected unit cell parameters and the hkl indexing as obtained during the refinement process. Consequently, the analysis of diffraction patterns with superimposing reflections stemming from the thin film specimen with multiple phases is possible. By stepwise variation of the fixed X-ray beam incidence angle α and recording the resulting diffraction pattern, depth resolved results for biaxial stress states even in the presence of stress gradients can be obtained. As a prerequisite, the layers need to be sufficiently thin for the X-ray beam either to penetrate the whole sample at each reflection hkl or to remain within a constant depth, the latter holds for small incidence angles α (see Section 3.3). Then, each individual reflection of the diffractogram contains the integral information of the film as a whole or of a distinct depth interval.

With increasing sample thickness and pronounced stress gradients problems due to the X-ray penetration depth arise. For incidence angles $\alpha > 6°$, it varies within the applied diffraction angle 2θ [2,3]. Thus, a single measurement may contain information on possible stress gradients present which lead to a distortion of the whole diffraction pattern. In turn, asymmetric peak shifts arise, leading to erroneous refinement results due to difficulties in the minimization of the lattice parameter a_0. The present work aims at introducing an adapted refinement and

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decomposition strategy capable of circumventing this drawback. Using a sputter-deposited molybdenum coating as a model material the approach is tested and compared to classical residual stress evaluation techniques.

2. Theoretical background

2.1. X-ray residual stress measurements on a single reflection

At present, several classical X-ray diffraction techniques are well established for the determination of residual stress states on a single hkl in the high 2θ-range. The most prominent methods using laboratory equipment shall briefly be summarized here.

In ω-mode the sample is rotated (tilted) about the ω-axis being the normal to the diffraction plane located at the sample surface. Hence, both, ω and 2θ are in the same plane. To achieve the diffraction condition, the values of tilt ψ are added for positive ψ, or subtracted for negative ψ, to the Bragg angle θ. Most conventional powder diffractometers with decoupled ω-drive (i.e. independent movement of ω- and 2θ-axes respectively) are able to perform measurements using this method. Due to the small incidence angles of the X-ray beam at negative tilts and the correlated defocusing effect, peaks measured under these conditions are generally less intense compared to those from positive ψ-offsets. Using parallel beam diffraction geometries, this can be circumvented.

In contrast, the χ- or side-inclination method has the sample rotate about the χ-axis, which is located in a plane normal to the diffraction plane. From a hardware standpoint, the χ-method is more complex due to the necessity to use a Eulerian cradle enabling χ- and ϕ-rotations. For further details concerning the geometrical setups the reader is referred to literature such as [4].

2.2. Asymmetric diffraction experiments and Pawley refinement analysis

The evaluation of residual stresses from the whole diffraction pattern is based on the multiple hkl-method [1,5] and can be realized employing a wppd-method according to Pawley [6]. To this end, a complete diffraction pattern of the thin film specimen is recorded under asymmetric parallel beam diffraction conditions (grazing incidence). The incidence angle α between the X-ray beam and the sample surface is kept constant throughout the individual measurement.

The general technique of obtaining unit cell and crystallographic structural parameters by applying a least-square fitting procedure to the entire diffraction pattern was first published by Rietveld [7]. The formal definition of this process is the minimization of the function $S_y = \sum_i w_i(y_i(obs)-y_i(calc))^2$, where $y_i(obs)$ is the measured intensity at point i in the pattern, $w_i = {}^1/_{y_i(obs)}$ and $y_i(calc)$ represents a calculated intensity output of the introduced crystallographic structure. Originally, its application was limited to patterns derived from untextured powder samples. In addition it requires à priori information with regard to the possible crystalline structures present.

Apart from these idealized boundary conditions, engineering reality has to deal with more complicated influences on the measured diffraction patterns such as the presence of multiple phases and their respective anisotropy, texture and stress states. The differences in response to mechanical forces of variously oriented hkl planes within individual grains are caused by two distinct effects: firstly, by the anisotropy of the elastic stiffness of individual grains (elastic anisotropy) and secondly by the anisotropy of the relaxation mechanism on a granular level, as slip occurs preferentially on certain slip systems (plastic anisotropy). Pawley [6] introduced a modification to the Rietveld method. Here, the peak intensities can vary freely during the refinement while the peak positions are determined in the usual way from the unit cell parameters. The diffraction community already employs both methods for the analysis of residual stress states [8–11]. In more detail, Pawley suggested that diffraction profiles could be fitted using only the following parameters:

1. I(hkl) - Intensity of each reflection hkl;
2. A, B, C, D, E, F - Unit-cell metric tensor parameters;
3. U,V,W - Peak-width parameters;
4. Other peak-shape parameters and instrumental zero error.

The advantage of fitting multiple diffraction peaks simultaneously leads to an increase in accuracy of the determined lattice parameter because more data points are available in the fitting process.

However the use of this technique in its original construction raises a complication due to the non-uniform effect of stresses on individual reflections. To account for this within the framework of the Pawley refinement Eqs. (1a) and (1b) [12,13] were introduced:

$$\Delta 2\theta = -2\tan\theta\left\{\frac{1}{2}S_2\left[\sigma_{11}\cos^2\varphi + \sigma_{12}\sin(2\varphi) + \sigma_{22}\sin^2\varphi\right]\sin^2\psi + \frac{1}{2}S_2\left[\sigma_{13}\cos\varphi\sin(2\psi) + \sigma_{23}\sin\varphi\sin(2\psi) + \sigma_{33}\cos^2\psi\right] + S_1(\sigma_{11+22} + \sigma_{33})\right\} \quad (1a)$$

$$\psi = (\theta - \alpha) \text{ for asymmetric diffraction} \quad (1b)$$

To correct for sample displacement Eq.(2) [14] has been implemented and for refraction correction [2] Eqs. (3a) and (3b) can be applied:

$$\Delta 2\theta = -z\sin(2\theta)/(R\sin\alpha) \quad (2)$$

$$\Delta 2\theta = \delta[\cot\alpha + \cot(2\theta - \alpha) + 2\tan\theta] \quad (3a)$$

$$\cos\alpha_c = 1 - \delta \quad (3b)$$

with

α Incidence angle of the primary X-ray beam (°)
α_c Critical angle of the total external reflection (°)
δ Material specific property representing the dispersion for X-rays
σ_{ii}, σ_{ij} Normal and shear stresses (MPa)
Φ Azimuthal angle (angle between the projected diffracting planes normal to the sample's surface with respect to the x-axis of the sample) (°)
Ψ Tilt angle between the normal of the diffracting plane and the normal of the sample's surface (°)
R Goniometer-radius (mm)
θ Bragg angle (°)
$S_1, \frac{1}{2}S_2$ Diffraction elastic constants (MPa^{-1})
z Displacement (mm):

As biaxial stress states (σ_{11}, σ_{22}) without shear components ($\sigma_{ij} = 0$) are characteristic for sputtered coatings, the boundary conditions of the refinement were set accordingly. Further, the stress component σ_{33} (normal to the surface) was assumed to be zero for the calculation of the in plane stress components.

3. Experimental details

3.1. X-ray diffraction setups

All X-ray diffraction experiments were carried out on a Bruker D4 Endeavor diffractometer, equipped with a Goebel mirror, θ-2θ goniometer, Sol-X energy dispersive detector and auto-sampler using Cu radiation ($\lambda_{K\alpha} = 1.5406$ Å, X-ray tube Siemens KFL Cu 2 K, long fine focus). The diffractometer was aligned with high accuracy to determine the lattice constant of LaB_6 (NIST SRM 660a, line position and line profile standard) with a relative precision of ± 0.0001. The determination of the