Residual stress and strain-free lattice-parameter depth profiles in a γ' -Fe₄N_{1-x} layer on an α -Fe substrate measured by x-ray diffraction stress analysis at constant information depth

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The residual stress and lattice-parameter depth profiles in a γ' -Fe₄N_{1-x} layer (6- μ m thickness) grown on top of an α -Fe substrate were investigated using x-ray diffraction stress analysis at constant penetration depths. Three different reflections (220, 311, and 222) were recorded at six different penetration depths using three different wavelengths. At each penetration depth, x-ray diffraction stress analysis was performed on the basis of the $\sin^2\psi$ method. As a result, the residual-stress depth profile was obtained from the measured lattice strains. The lattice spacings measured in the strain-free direction were used to determine the (strain-free) lattice-parameter depth profile. The nitrogen-concentration depth profile in the layer was calculated by applying a relationship between the (strain-free) γ' lattice parameter and the nitrogen concentration. It was found that the strain-free lattice-parameter depth profile as derived from the 311 reflections is best compatible with nitrogen concentrations at the surface and at the γ'/α interface as predicted on the basis of local thermodynamic equilibrium. It could be shown that the 311 reflection is most suitable for the analysis of lattice-parameter and residual stress depth profiles because the corresponding x-ray elastic constants exhibit the least sensitivity to the type of and changes in grain interaction. The depth-dependence of the grain interaction could be revealed. It was found that the grain interaction changes from Voigt-type near the surface to Reuss-type at the layer/substrate interface.

I. INTRODUCTION

Gas nitriding is a well known thermochemical treatment for workpieces made of iron and iron-based alloys. Depending on time, temperature, and composition of the gas atmosphere, the iron-nitride layer that develops on the surface of the workpiece during this treatment induces favorable properties like high hardness and enhanced resistance to corrosion and wear.¹ In general, such compound layers consist of ϵ -Fe₂N_{1-x} (hexagonally close packed arrangement of iron atoms) and γ' -Fe₄N_{1-x} (face-centered cubic arrangement of iron atoms). The nitrogen atoms in both phases occupy octahedral interstitial sites exhibiting specific long-range ordering.²⁻⁴ For the phase γ' studied in this work, the homogeneity range is rather small, i.e., at 823 K between 19.58 and 19.93 at.% N.^{5,6}

γ' iron nitride has gained growing importance due to its interesting magnetic properties in the form of thin films.⁷⁻¹⁰ In a recent study, it has been shown that γ' possesses an elastic anisotropy which is abnormal for fcc-type materials: its Zener anisotropy ratio is smaller

than 1, yielding $\langle 100 \rangle$ as stiffest and $\langle 111 \rangle$ as most compliant direction.¹¹

In the past, several studies have been conducted to assess the growth kinetics and phase transformations that occur within the γ' iron-nitride layer.^{6,12-14} Furthermore, the formation of γ' thin films has been studied in a number of works, and different production processes as gas-assisted molecular-beam epitaxy, reactive sputtering, laser nitriding of bulk-iron, and gas nitriding of iron thin films have been investigated.^{8,10,15,16}

Previous work identified the nitrogen concentration profile and thermal misfit as stress build-up mechanisms as well as pore development and phase transformations, like the precipitation of α -Fe during slow cooling after nitriding, as stress relaxation mechanisms.^{17,18}

Residual-stress gradients can be measured using several different methods. The typical nondestructive stress measurement technique is (x-ray) diffraction, where lattice strains are measured and related to a residual macrostress (mechanical stress) using suitable elastic constants as x-ray stress factors or, provided the specimen is macroscopically elastically isotropic (quasi-isotropic), x-ray elastic constants (XECs).¹⁹⁻²¹ XECs can be deduced from single-crystal elastic constants by applying a suitable grain-interaction model. A common

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technique to obtain a realistic grain-interaction model is to mix two (or more) extreme grain-interaction models, such as the Voigt and Reuss models.^{21–25}

Traditionally, layer-removal techniques such as grinding and polishing, in combination with x-ray diffraction, have been adopted to determine the depth dependence of the residual stress.^{26,27} Using this approach, it is possible to investigate practically every depth-range, thereby destroying the specimen. A comprehensive description of this approach and its application to a γ' iron-nitride layer is provided in Ref. 17.

For the nondestructive analysis of residual-stress depth profiles, several diffraction methods have been proposed previously.^{28–36} These methods can generally be subdivided into two groups: in one group, it is recognized that the penetration depth varies during one diffraction stress measurement, and the stress-depth dependence is analyzed by using the variation of the penetration depth during the stress measurement; in the other group, the penetration depth is kept constant during one diffraction stress measurement, and information on the stress-depth profile is obtained from several stress measurements at constant penetration depth.

Kumar et al.³⁷ recently proposed such a measurement strategy, where residual-stress depth profiles can be determined nondestructively by (x-ray) diffraction tuned at (several) constant penetration/information depth(s). By adopting this approach, it is possible to determine the residual-stress depth profile within a specimen up to a certain depth, which is determined by the linear absorption coefficient of the material. By a combination of different wavelengths, depending on the wavelengths corresponding to the absorption edges, the possible depth range can be extended.

In this work, the residual-stress depth profile in a γ' -Fe₄N_{1-x} layer grown on an α -Fe substrate has been investigated by x-ray diffraction stress analysis (XRSA) at constant penetration/information depth. It has been shown that the type of grain interaction within the layer changes from Voigt-type to Reuss-type with increasing depth. This finding has been made plausible considering the specimen microstructure. Moreover, the strain-free lattice-parameter depth profile has been deduced from the measured data and related to the variation of nitrogen concentration with depth. It followed that the boundary concentrations of the thus obtained nitrogen-concentration depth profile match well those expected assuming local thermodynamic equilibrium at the layer surface and at the interface of layer and substrate.

II. THEORETICAL BACKGROUND

In the following subsections, the theoretical principles used in this work are described. First, the fundamentals of x-ray residual stress analysis (XRSA) are indicated.

Second, the two basic, isotropic models for elastic grain-interaction, namely the Voigt²² and Reuss²³ models, are explained. Third, the method of XRSA at constant penetration depth and the resulting determination of residual-stress depth profiles are explained.

A. XRSA

In general, the components of the mechanical stress tensor can be determined from x-ray diffraction measurements of lattice strains in several measurement directions (ϕ , ψ), where ϕ is the rotational angle of the diffraction vector around the sample surface normal and ψ is the tilt angle of the diffraction vector with respect to the sample surface normal, according to the $\sin^2\psi$ method.^{19,21} If certain simplifications with respect to the state of stress can be applied, the number of components of the stress tensor and thus the number of lattice strains necessary to determine the stress state is reduced, and the corresponding $\sin^2\psi$ law becomes simplified. In case of a macroscopically elastically isotropic specimen subjected to a planar, rotationally symmetric state of stress, the $\sin^2\psi$ law reads²¹:

$$\varepsilon_{\psi}^{hkl} = \frac{d_{\psi}^{hkl} - d_0^{hkl}}{d_0^{hkl}} = \left(2S_1^{hkl} \sigma_{\parallel} + \frac{1}{2} S_2^{hkl} \sigma_{\parallel} \sin^2\psi \right) \quad , \quad (1)$$

where ε_{ψ}^{hkl} is the strain of the hkl lattice planes, d_{ψ}^{hkl} and d_0^{hkl} are the strained and strain-free lattice spacings of the hkl lattice planes, respectively, S_1^{hkl} and $1/2S_2^{hkl}$ are the XECs, ψ denotes the measurement direction, and $\sigma_{\parallel} = \sigma_{11} = \sigma_{22}$ represents the mechanical in-plane residual stress. Hence, when d_{ψ}^{hkl} is plotted versus $\sin^2\psi$, the stress follows from the division of the slope of the interpolated straight line by d_0^{hkl} and $1/2S_2^{hkl}$.

The strain-free direction $\sin^2\psi_0$ is obtained when Eq. (1) is set equal to zero. It follows:

$$\sin^2\psi_0 = \frac{-2S_1^{hkl}}{1/2S_2^{hkl}} \quad , \quad (2)$$

i.e., the strain-free lattice spacing d_0^{hkl} can be determined by linear interpolation of d_{ψ}^{hkl} versus $\sin^2\psi$ at $\sin^2\psi_0$.

B. Grain-interaction models

In general, the elastic interaction between individual grains in a polycrystalline aggregate is direction-dependent.²⁰ In the present study, the grain interaction can be considered as isotropic (see Sec. IV. B). Then the Voigt and Reuss models represent the two extreme types of grain interaction. In the specimen frame of reference, the Voigt model assumes that all crystallites of a polycrystalline specimen are subjected to an equal state of strain, whereas the Reuss model is based on the postulation that all crystallites have the same state of stress.

Both extremes of grain interaction lead to incompatibilities at the grain boundaries—in the Voigt model a stress mismatch occurs, whereas the Reuss model involves a strain mismatch. Hence, neither the Voigt model nor the Reuss model complies with the real elastic behavior of a polycrystal. Thus, effective grain-interaction models have been proposed to overcome these discrepancies.^{20,21,38–40} An effective grain-interaction model is constructed as the weighted sum of several extreme grain-interaction models. In the present case of isotropic grain interaction, the effective grain-interaction model implies that the actual XECs are given by:

$$S_i^{hkl} = wS_i^V + (1 - w)S_i^{R,hkl}, \quad (3)$$

where S_i^{hkl} ($i = 1, 2$) is the effective XEC, S_i^V and $S_i^{R,hkl}$ are the XECs according to the Voigt model and the Reuss model, respectively, and w is a weighing factor. Note that the XECs after Voigt are isotropic, i.e., they do not depend on hkl , whereas the XECs after Reuss are anisotropic, i.e., they do depend on hkl . A well known effective grain-interaction model that is frequently used is the Neerfeld-Hill model,^{24,25} which uses the arithmetic average of the Voigt and Reuss models (i.e., $w = 0.5$) to describe the effective XECs. However, as shown in previous work,^{38,39,41} w can take any value within $w \in [0,1]$, and in thin films even a depth dependence of these weighing parameters can occur.⁴²

C. Determination of real-space depth profiles from XRSA at constant penetration/information depth

A typical XRSA on the basis of the $\sin^2\psi$ method involves the measurement of lattice spacings at various angles ψ using either the ω mode (iso-inclination method) or the χ mode (side-inclination method), where the angle ψ is set via the instrumental angles ω and χ , respectively.²¹ Either of these methods involves a change of x-ray penetration depth during the course of one measurement, i.e., the data points obtained in the $\sin^2\psi$ plot for a particular hkl reflection correspond to different penetration depths. [For (cumbersome) methods for the determination of real-space depth profiles on the basis of such $\sin^2\psi$ -plots, see Refs. 29, 35, and 43.] Thus, if stress gradients are present and their occurrence is not taken into account in the stress evaluation, erroneous results will generally be obtained. Even in the absence of stresses, a lattice-parameter depth profile can result in an apparent stress state (i.e., a $\sin^2\psi$ -plot with a nonzero slope is obtained); this effect is often referred to as “ghost stresses” (see, for example, Ref. 17 and references therein).

The penetration depth τ is the center of gravity of the distribution of measured diffracted intensity versus depth for an infinitely thick, homogenous specimen. Approximately 63% of the diffracted intensity stems

from a volume confined by τ below the sample surface.^{37,44} The penetration depth is given by incidence angle α and exit angle β of incident and diffracted beam, respectively, and by the linear absorption coefficient μ according to^{32,37}:

$$\tau = \frac{\sin\alpha\sin\beta}{\mu(\sin\alpha + \sin\beta)}. \quad (4)$$

The information depth ξ is the center of gravity of the distribution of diffracted intensity versus depth for a particular specimen with finite thickness t . The diffracted intensity originating from each depth z has to be weighted by an absorption factor. This absorption factor accounts for intensity reduction of both the incoming beam and the diffracted beam for the signal originating from depth z . It thus follows⁴⁴:

$$\xi(t) = \langle z \rangle = \frac{\int_0^t z \exp(-z/\tau) dz}{\int_0^t \exp(-z/\tau) dz} = \tau - \frac{t \exp(-t/\tau)}{1 - \exp(-t/\tau)}, \quad (5)$$

where brackets “ $\langle \rangle$ ” indicate averaging. The following limits hold:

$$\lim_{t/\tau \rightarrow 0} \xi(t) = \frac{1}{2} t, \quad (6)$$

and

$$\lim_{t/\tau \rightarrow \infty} \xi(t) = \tau. \quad (7)$$

It follows that the maximum achievable information depth is half of the specimen thickness [see Eq. (6)].

Both the penetration depth and, consequently, the information depth can be kept constant during the course of a residual stress measurement by selection of appropriate incidence and exit angles [i.e., satisfying Eq. (4)] using the so-called combined ω/χ mode proposed in Ref. 37, where the angle ψ is adjusted by a combination of the instrumental angles ω and χ . As a consequence of such measurements, limitations with respect to the accessible ψ -range for a certain hkl reflection, penetration depth, and wavelength occur.³⁷

The result of a diffraction analysis at constant information depth of any parameter, as residual stress, strain-free lattice-parameter, and thus nitrogen concentration, is the Laplace transform of the corresponding real-space depth profile of this parameter [see Eq. (5)]. To determine the real-space depth profiles of this parameter, the following procedure has been used:

A suitable real-space depth profile for the parameter concerned, $\Xi(z)$, is assumed and transformed into Laplace-space by application of:

$$\Xi(\tau) = \frac{\int_0^t \Xi(z) \exp(-z/\tau) dz}{\int_0^t \exp(-z/\tau) dz} \quad (8)$$

To achieve high numerical accuracy, the assumed data points $\Xi(z)$ are interpolated by a cubic spline, and the integration in Eq. (8) is performed over the points returned by the spline function. The number of assumed data points $\Xi(z)$ may only exceed the number of measured points $\Xi(\tau)$, if additional boundary conditions occur, of course; for the purpose of the numerical integration [Eq. (8)], the number of data points returned by the spline interpolation can be much higher.

Next, the resulting calculated Laplace-space depth profile, $\Xi(\tau)$, is compared with the measured Laplace-space depth profile. The assumed points $\Xi(z)$ are then adjusted successively such that the sum of squared differences between calculated and measured Laplace-space depth profile is reduced. This procedure is repeated until agreement of calculated and measured data in Laplace space occurs within a set limit of accuracy.

III. EXPERIMENTAL

A. Specimen preparation

The specimen was prepared from a cold rolled α -Fe (Alpha Aesar 99.98 wt%) cast rod in the form of a rectangular sheet with an area of $18 \times 25 \text{ mm}^2$ and a thickness of 1 mm. Before the nitriding treatment, the specimen was recrystallized for 2 h at 973 K in a hydrogen atmosphere, mechanically polished up to 1- μm diamond paste, and ultrasonically cleaned in ethanol.

The nitriding treatment was performed in a vertical quartz-tube furnace at a temperature of 823 K using a gas mixture of NH_3 (99.999 vol%) and H_2 (99.999 vol%). The composition of the nitriding gas atmosphere was chosen as 43 vol% NH_3 /57 vol% H_2 , and the nitriding time was 5 h. Thus, a γ' -Fe₄N_{1-x} compound layer with a thickness of approximately 6 μm on top of the ferrite substrate was obtained.⁶ After the nitriding process, the specimen was quenched by dropping it into cold water flushed with nitrogen gas.

B. Metallography

A cross-section of the specimen was obtained by cutting using an Accutom-50 (Struers GmbH, Willich, Germany). The cut piece was galvanized with a protective nickel layer,⁴⁵ embedded in Polyfast (Buehler GmbH, Düsseldorf, Germany), ground, polished down to 1- μm diamond paste, and etched in 1 vol% Nital containing 0.1 vol% HCl.^{46,47} Optical microscopy was performed using a Zeiss Axiophot microscope (Carl Zeiss MicroImaging GmbH, Jena, Germany). Several micrographs of the

specimen cross-section were taken close to both faces of the specimen, and the surface-layer thickness was determined as arithmetic average of multiple measurements using conventional image-analysis software.

C. X-ray diffractometry

Qualitative x-ray diffraction (XRD) phase analysis was performed using a Philips (now PANalytical, Almelo, The Netherlands) materials research diffractometer (MRD) equipped with an Eulerian cradle. Co K α radiation ($\mu_{\text{Fe4N, Co K}\alpha} = 0.039 \text{ }\mu\text{m}^{-1}$; as calculated from data for Fe and N in Refs. 48 and 49) emerging from the point focus of a sealed tube operating at 40 kV and 40 mA was converted into a quasiparallel beam by an x-ray lens. The size of the incident beam was set to $4 \times 4 \text{ mm}$ by crossed slits. The residual divergence of the incident beam as conditioned by the x-ray lens was approximately 0.3° . The diffracted beam passed a parallel-plate collimator (acceptance angle 0.18°) before being detected by a gas proportional counter.

Near-surface XRD stress analysis was conducted using a Bruker AXS D8 Discover diffractometer (Karlsruhe, Germany) equipped with an Eulerian cradle. Cu K α radiation ($\mu_{\text{Fe4N, Cu K}\alpha} = 0.207 \text{ }\mu\text{m}^{-1}$; as calculated from data for Fe and N in Refs. 48 and 49), emerging from the point focus of a rotating anode source (Bruker TXS) operating at 50 kV and 20 mA, was converted into a quasi-parallel beam by a single-reflection collimating x-ray mirror (XENOCS FOX2D CU 12_INF, Sassenage, France).⁵⁰ The incident beam diameter was set to 0.8 mm by a circular pinhole collimator which, in addition, reduced the residual divergence of the beam as conditioned by the mirror (0.06°). The diffracted beam passed a parallel plate collimator (acceptance angle 0.23°) before being detected by an energy-dispersive detector (Bruker Sol-X).

XRD stress analysis at larger penetration depths was carried out at the synchrotron beamline B2 of HASY-LAB (Hamburg, Germany), equipped with an Eulerian cradle. The beamline was used in direct, unmirrored beam configuration⁵¹ (parallel-beam setup), the wavelength λ was adjusted to 0.8 Å ($\mu_{\text{Fe4N, 0.8 Å}} = 0.034 \text{ }\mu\text{m}^{-1}$; as calculated from data for Fe and N in Refs. 48 and 49), and the incident beam was size to $5 \times 1 \text{ mm}$. The diffracted beam passed a Ge (111) analyzer crystal before being detected by a NaI scintillation counter.

During all measurements, the specimen was rotated around its surface normal (approximately 2 rev./s) to attain better crystallite statistics. The rotational symmetry of the stress state was confirmed by additional stress measurements at different, constant, rotation angles φ around the specimen surface normal. The stress measurements were carried out in the combined ω/χ mode to keep the x-ray penetration depth τ constant during the stress measurement^{21,37}; due to the rotational symmetry of the stress state, only the angle ψ was controlled.

The γ' 220, 311, and 222 reflections were measured with a detector step size in 2θ varying between 0.002 and 0.04° depending on the instrument applied and on the hkl reflection investigated. A sufficient 2θ range was collected for each reflection to accurately describe peak tails and background. The diffraction-line positions were obtained by fitting Pearson-VII functions⁵² to the measured data points. The γ' reflections were measured at constant penetration depths: $\tau = 400, 700$, and 1000 nm in the laboratory diffractometer and at $\tau = 1000, 2000, 3000$, and 4000 nm at the synchrotron beamline. The coverable ψ range for XRSA at constant penetration depth varies with photon energy, diffraction angle, and penetration depth.³⁷ For the measurements conducted in this work, the width of the coverable ψ range varied between 16 and 42°. The absence of crystallographic texture could be verified by the analysis of reflection intensities as a function of ψ .

IV. RESULTS AND DISCUSSION

A. Microstructure and phase analysis

A cross-sectional bright-field optical micrograph of the specimen investigated is shown in Fig. 1. The microstructure of the γ' layer consists of predominantly columnar grains with a considerable amount of twins. The average grain size in the direction of the surface normal and laterally is of the order of the layer thickness. Due to the substrate preparation procedure (see Sec. III. A) and because the layer grows inwardly the specimen surface is smooth, whereas the γ'/α interface exhibits a considerable roughness.

Qualitative phase analysis of the nitrated specimen was performed by x-ray diffraction. The resulting diffraction pattern is shown in Fig. 2. It is evident that the compound layer is composed exclusively of γ' -Fe₄N_{1-x}, as expected, on the basis of the nitriding gas composition, pressure, and temperature.⁶ Due to the relatively low absorption of the x-ray radiation used (Co K α radiation was used), additional reflections from the α -Fe substrate are visible.

FIG. 1. Optical micrograph of a cross-section of the nitrated α -Fe specimen.

B. Diffraction analysis at constant penetration depth

Due to the ψ -dependent asymmetry of the measured diffraction lines, which is indicative for the presence of a stress- and/or strain-free lattice-parameter gradient, the centroid has been used for the determination of the diffraction-line position.⁵³ It is worth noting that the obtained $\sin^2\psi$ plots (for an exemplary plot, see Fig. 3) exhibit low scatter and no curvature, so that the measured data could be well fitted by a straight line [see Eq. (1)].

The linearity of the obtained $\sin^2\psi$ plots, on the one hand, and the equiaxed nature of the specimen's microstructure (see Fig. 1) are both consistent with an isotropic nature of the grain interaction (see beginning of Sec. II. B).

FIG. 2. Diffraction pattern collected from the surface of the nitrated α -Fe specimen using the Philips MRD (Co K α radiation). Only reflections stemming from γ' -Fe₄N_{1-x} and α -Fe (originating from the substrate; indicated by " α ") were detected.

FIG. 3. Measured $\sin^2\psi$ plot; 220 lattice plane spacing d_{ψ}^{220} of γ' -Fe₄N_{1-x} versus $\sin^2\psi$ at penetration depth $\tau = 2000$ nm (Beamline B2, HASYLAB, $\lambda = 0.8$ Å). The dots denote the measured data points, and the straight line shows the linear fit to these data.

TABLE I. XECs used in this work for the determination of depth profiles of lattice parameter and residual stress.¹¹

hkl	S_1^{hkl} [TPa ⁻¹]	$1/2S_2^{hkl}$ [TPa ⁻¹]
220	-2.18	8.26
311	-2.11	8.05
222	-2.24	8.45

The XECs of γ' used in the calculation of lattice parameters (and thus of nitrogen concentration) and residual stresses (see Secs. IV. B. 1 and IV. B. 2) have been listed in Table I. These XECs have been adopted from a previous work, where single-crystal elastic constants of γ' were determined by first-principles calculations and an effective grain interaction parameter $w = 0.85$ (see Sec. II. B) was determined experimentally for the same specimen investigated in this work.¹¹

1. Lattice-parameter and nitrogen-concentration depth profiles

The lattice-parameter depth profile was obtained from data for the strain-free lattice spacing, d_0^{hkl} , as derived from the $\sin^2\psi$ analysis at various constant penetration depths along the strain-free direction, $\sin^2\psi_0$ [see Eqs. (1) and (2)]. Major instrumental aberrations in parallel-beam geometry as instrumental offsets in diffraction angle and photon energy (for the synchrotron measurements) were quantified by measuring a standard specimen. Thus, it was possible to correct the obtained diffraction-line positions for these offsets in the synchrotron measurements. The offset of the diffraction-angle scale in the laboratory diffractometer measurements was determined such that the lattice-parameter values determined in the laboratory and at the synchrotron at the same information depth coincide; for the laboratory diffractometer, a standard measurement was not available.

Thus, the determined strain-free lattice-parameter depth profiles in Laplace space, as derived from the strain-free directions of the 110, 311, and 111 lattice planes (220, 311, and 222 reflections), are shown in Fig. 4.

From thermodynamic data of the system Fe-N,⁶ it follows for the specimen-preparation conditions applied (see Sec. III. A) that the nitrogen concentration varies between 19.93 at.% at the surface (γ' in equilibrium with the gas atmosphere) and 19.58 at.% at the layer/substrate interface (γ' in equilibrium with α -Fe). As a consequence of this concentration gradient, a (strain-free) lattice-parameter gradient also exists. A relatively small change of nitrogen concentration, c_N , results in a relatively large change of lattice parameter, a_0 , for γ' -Fe₄N_{1-x}; see the relation given between a_0 and c_N given in Ref. 54. Because the layer grows by inward diffusion of nitrogen,¹⁴ a decreasing nitrogen concentration and thus lattice parameter with increasing information depth is expected. Such behavior is observed

FIG. 4. Strain-free lattice parameter, a_0 , and nitrogen concentration, c_N , versus information depth as derived from lattice-parameter measurements along the strain-free direction of the 110, 311, and 111 lattice planes (220, 311, and 222 reflections) obtained in the laboratory (Bruker AXS D8, Cu K α radiation) and at the synchrotron ($\lambda = 0.8$ Å).

for the data derived from the 311 and 222 reflections. However, the gradient deduced from the 220 reflection is more or less zero. To explain this discrepancy, the XECs used for the calculation of the strain-free directions for the three sets of lattice planes are considered detailed.

The XECs calculated according to the Voigt and Reuss models have been plotted in Fig. 5 versus the orientation parameter for cubic materials,³⁴

$$\Gamma_{hkl} = \frac{h^2k^2 + h^2l^2 + k^2l^2}{(h^2 + k^2 + l^2)^2} \quad (9)$$

It is evident from Figs. 5(a) and 5(b) that among all XECs, those pertaining to the 311 planes ($\Gamma_{311} = 0.157$) remain nearly unchanged upon a variation in grain interaction between the two extremes given by the Voigt and Reuss models. Hence, among the investigated

FIG. 5. (a, b) Calculated values of the XECs, S_1^{hkl} and $1/2 S_2^{hkl}$, according to the Voigt and Reuss models versus $3\Gamma_{hkl}$. (c) Strain-free direction versus grain-interaction parameter for the 220, 311, and 222 reflections.

FIG. 6. Real-space lattice-parameter and nitrogen-concentration depth profile (left) including indications for the thermodynamically calculated local equilibrium nitrogen concentrations at the surface and at the γ'/α interface (arrows),⁶ and measured and calculated Laplace-space depth profiles (right) for the 311 reflection.

reflections, the strain-free direction as derived from the 311 reflection proves to be the least sensitive to a variation of grain interaction [see Fig. 5(c)]. Therefore, because the type of grain interaction can change with depth, the lattice-parameter gradient as derived from the 311 reflection is considered the most reliable one. In a previous study,¹⁷ the 420 reflection was used. It follows that in this case ($\Gamma = 0.160$), the XECs are also insensitive to the type of grain interaction. For a detailed discussion on the elastic anisotropy of γ' -Fe₄N, see Ref. 11.

To extract the lattice-parameter depth profile in real space [Fig. 6 (left)] from the one in Laplace space [Fig. 6 (right)], the procedure described in Sec. II. C has been adopted. For the reasons stated above, the lattice-parameter depth profile derived from the 311 planes has been selected for determination of the real-space lattice-parameter depth profile. Thus, the obtained real-space profile and the comparison of calculated and measured Laplace-space profile are illustrated in Fig. 6. It follows that the Laplace-space profile calculated from the real-space profile fits well with the measured Laplace-space profile. The nitrogen concentrations near the surface and at the γ'/α interface were calculated assuming local thermodynamic equilibrium, and the corresponding lattice-parameter values were treated as fixed values in the assessment of the real-space lattice-parameter depth profile [see arrows in Fig. 6 (left)].⁶ Hence, the number of variables in the real-space profile does not exceed the

number of measured data points in the Laplace-space profile (see Sec. II. C). The slight decrease in nitrogen concentration in the surface-adjacent region is due to the formation of pores at the surface (see Ref. 17).

2. Residual stress-depth profile

Here, only the results derived from the 311 reflection will be discussed: it has been shown in Sec. IV. B. 1 that the data derived from the 220 and 222 reflections are unreliable because of incorrect values for the XECs used. The residual stress values as derived in $\sin^2\psi$ evaluations [see Eq. (1)] of the 311 reflection has been plotted in Fig. 7 (right) versus the penetration depth (i.e., in Laplace space). By applying a procedure analogous to the one used for the strain-free lattice-parameter depth profiles (Sec. IV. B. 1 and Sec. II. C), the real-space residual stress-depth profile has been derived from the Laplace-space residual stress-depth profile. The result is shown in Fig. 7.

It is evident that a good agreement between measured and calculated Laplace-space stress-depth profiles has been achieved. Thus, the extracted real-space depth profile [Fig. 7 (left)] shows an increase in absolute value of compressive stress with increasing depth due to stress relaxation near the surface; the layer exhibits a compressive stress maximum at half the layer thickness; and finally, decrease in compressive stress towards the α/γ' interface is observed. This stress-depth behavior can be discussed as follows.

FIG. 7. Real-space residual-stress depth profile (left) and measured and calculated Laplace-space stress depth profiles (right); results are derived from 311-reflection measurement.

The compressive nature of the residual stress in the γ' layer has two different origins¹⁷: (i) thermal compressive stress, constant over the layer thickness, is built up in the layer during cooling from the nitriding temperature (823 K) to room temperature as a consequence of the difference of the coefficients of thermal expansion α of layer ($\alpha_{\gamma'-\text{Fe}_4\text{N}_{1-x}} = 7.62 \times 10^{-6} \text{ K}^{-1}$)⁵⁴ and substrate ($\alpha_{\alpha-\text{Fe}} = 11.8 \times 10^{-6} \text{ K}^{-1}$ at 293 K, $14.8 \times 10^{-6} \text{ K}^{-1}$ at 823 K)⁵⁵; and (ii) compressive stress varying over the layer thickness due to elastic accommodation of the nitrogen concentration-depth profile. The magnitude of the compressive stress is expected to decrease with increasing depth as the nitrogen concentration (and thus, the strain-free γ' lattice parameter) decreases with increasing depth (see Fig. 6). Superimposed on this behavior is a stress relaxation close to the specimen surface due to pore and (by coalescence of pores) channel formation along grain boundaries. [Such pore/channel formation is a consequence of the thermodynamic instability of γ' iron nitride with respect to the decomposition in Fe and N₂ gas (especially at grain boundaries).¹⁷] As a result, the magnitude of residual compressive stress in real space should first increase, then pass through a maximum, and subsequently decrease with increasing depth.

3. Thermal and compositionally induced strains

The thermal strain in the γ' layer parallel to the surface (constant over the layer thickness), $\varepsilon_{||}^{\text{th}}$, follows from the thermal misfit of layer and substrate, due to the difference of the coefficients of thermal expansion of layer, $\alpha_{\gamma'}$, and substrate, α_{Fe} , induced upon cooling down from temperature, T' , to room temperature, T_0 (293 K), according to the following:

$$\varepsilon_{||}^{\text{th}} = \int_{T_0}^{T'} (\alpha_{\gamma'} - \alpha_{\text{Fe}}) dT \quad (10)$$

Using literature data for $\alpha_{\gamma'}$ ⁵⁴ and α_{Fe} ,⁵⁵ and taking T' as the nitriding temperature T_n (823 K), a thermal strain $\varepsilon_{||}^{\text{th}} = -3.7 \times 10^{-3}$ follows.

Assuming that the growth (specific volume) misfit between γ' and α -Fe is completely accommodated plastically (for details see Ref. 17), the thermal strain should be equal to the difference of the average macrostrain parallel to the surface, $\varepsilon_{||}$, and the compositionally induced strain parallel to the surface $\varepsilon_{||}^c$. The average, mechanical macrostrain parallel to the surface is given by:

$$\varepsilon_{||} = \frac{1 - \nu}{E} \sigma_{||} \quad (11)$$

where ν is the Poisson ratio, E is Young's modulus, and $\sigma_{||}$ follows from the $\sin^2\psi$ plot of the reflection considered [see Eq. (1)]. The compositional strain parallel to the surface is assessed by the strain model given in Ref. 17. In this model, the layer is imagined to be separated from the substrate and sectioned parallel to the surface into slices. Because the nitrogen concentration decreases towards the γ'/α interface, the unconstrained surface area of each slice also decreases towards the interface, provided that each slice contains the same number of iron atoms. As in reality all slices must have the same surface area as the slice adjacent to the interface, their cohesion leads to a compressive strain that is varying over the layer thickness and equals:

$$\varepsilon_{||}^c = \frac{a_{\text{int}} - a}{a} \quad (12)$$

where a is the strain-free lattice parameter of the slice considered and a_{int} is the strain-free lattice parameter of the interface-adjacent slice.

The variation of $\varepsilon_{||}$ and $(\varepsilon_{||} - \varepsilon_{||}^c)$ with depth for the interface-adjacent region is shown in Fig. 8. It follows that the strain corrected for compositionally induced strain near the interface $(\varepsilon_{||} - \varepsilon_{||}^c) \approx -2.8 \times 10^{-3}$. The magnitude of this value is distinctly lower than the magnitude of the strain calculated if the thermal misfit induced by cooling from T_n to T_0 would be accommodated fully elastically ($\varepsilon_{||}^{\text{th}} = -3.7 \times 10^{-3}$, see above). If the strain $(\varepsilon_{||} - \varepsilon_{||}^c)$ fully corresponds to thermal strain,

FIG. 8. Macroscopic strain, $\varepsilon_{||}$, as a function of real depth, z , for the interface-adjacent region of the γ' -layer. After subtracting the compositionally induced strain, $\varepsilon_{||}^c$, the (thermal) strain ($\varepsilon_{||} - \varepsilon_{||}^c$) remains. For the calculation of $\varepsilon_{||}$ at various depths, the stress values derived in the real-space residual-stress profile [Fig. 7 (left)] have been used; for $z = 4000$ nm, the stress value has been derived by linear interpolation of the stresses at $z = 3000$ and $z = 5000$ nm. $E = 166.3$ GPa was taken from literature¹¹ using $w = 0.85$ (see Sec. IV. B), and for ν a value of 0.3 was adopted.

then, according to Eq. (10), the thermal strain build-up upon cooling to room temperature would have started at a temperature of approximately 720 K, whereas the nitriding temperature was 823 K. The plastic accommodation (relaxation) of thermal misfit in temperature ranging from 823 to 720 K can be ascribed to precipitation of α -Fe in the substrate-adjacent part of the γ' layer, which occurs at temperatures above 600 K.¹⁸

4. Assessment of grain-interaction depth profile

It follows from Fig. 5 (see the considerations made in Sec. IV. B. 1) that correct values for the strain-free directions, $\sin^2\psi_0$, of the 110 and 111 lattice planes can be obtained by varying the XECs of the 220 and 222 reflections, i.e., by varying the grain-interaction parameter w [see Eq. (3)], such that the strain-free lattice-parameter data determined from the 220 and 222 reflections fit the strain-free lattice-parameter value deduced from the 311 reflection. By performing this procedure for every penetration/information depth, the dependence of w on depth is revealed. Thus, the obtained strain-free directions and values of w are shown in Fig. 9 for the synchrotron measurements.

It follows that the type of grain interaction changes from the Voigt ($w = 1$) to Reuss type ($w = 0$) with increasing depth. This finding is remarkable, because it represents the opposite of what is found for thin films, which are deposited onto a substrate, e.g., by sputtering. The result may be understood as follows. The γ' layer has grown into the α -Fe substrate, and the interface between γ' and α shows a considerable roughness (see

FIG. 9. Strain-free directions obtained for coincidence of the measured lattice-parameter depth profiles, derived from the 220, 311, and 222 reflections as described in the text. The corresponding values for w for the 222 (near top) and 220 (near bottom) reflections are shown for each penetration depth. The solid, dashed, and dotted lines indicate the strain-free directions corresponding to the 220, 311, and 222 reflections for $w = 0.85$, as initially used for the calculation of the XECs (see Table I).

Sec. IV. A), whereas the layer surface is relatively smooth. The considerable interface roughness can be associated with a relatively independent deformation mechanism of the different γ' crystallites during the nitriding treatment, provided that α -Fe (the substrate) is more compliant than γ' iron nitride (the layer). Then, due to the growth (specific volume) misfit of γ' and α , an equal in-plane stress (Reuss-type interaction; as a consequence of establishing mechanical equilibrium at the interface for each γ' grain individually; no laterally continuous layer) rather than an equal in-plane strain [Voigt-type interaction; as expected for accommodation of laterally imposed strain (as thermal strain), on a laterally continuous layer⁵⁶] is conceivable at the interface. Near the layer surface, the nitrogen concentration, and thus the compositional strain, obtains a maximum value. Thus, it is suggested that the Voigt-type grain interaction in the surface region, i.e., in the laterally continuous part of the nitride layer, results from an equal in-plane compositional strain due to the nitrogen-concentration depth profile. As the layer grows into the substrate, independent, separate deformation of grains can only occur at the layer/substrate interface.

V. CONCLUSIONS

(1) For the first time, a nondestructive x-ray diffraction method to simultaneously determine both the composition depth profile and the residual-stress depth profile, by measurements at constant penetration/information depths, has been successfully applied to a γ' -Fe₄N_{1-x} layer on top of an α -Fe substrate.

(2) The 311 reflection has been used to determine the depth profiles of the strain-free lattice parameter (and thus the nitrogen concentration) and the residual stress, because this reflection has been shown to be insensitive to the type and variation of grain interaction. By tuning the strain-free direction of the 220 and 222 reflection such that they yield the same strain-free lattice parameter as the 311 reflection, the depth dependence of the grain interaction has been determined.

(3) The grain interaction changes from Voigt type near the surface to Reuss type at the layer/substrate interface. This finding could be ascribed to the morphology of the layer and the development of lateral compositional strain.

(4) The thus obtained nitrogen-concentration depth profile satisfies the thermodynamic, local equilibrium boundary conditions at the layer surface and at the γ'/α interface.

(5) The residual-stress depth profile as derived from the 311 reflection can be interpreted as the result of stress build-up by thermal misfit and the nitrogen concentration increasing with decreasing depth and stress relaxation in the surface-adjacent region due to pore/channel formation.

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