Cake Resistance in Rotational Dynamic Filtration: Determination and Modeling

Marke, Henrik S.; Breil, Martin P.; Hansen, Ernst Broberg; Pinelo, Manuel; Krühne, Ulrich

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Anisotropy effects on gaseous nitriding of austenitic stainless steel single crystals

Ömer C. Kucukyildiz, Flemming B. Grumsen, Thomas L. Christiansen, Grethe Winther, Marcel A.J. Somers*

Department of Mechanical Engineering, Technical University of Denmark, Productionstorvet b. 425, 2800 Kgs. Lyngby, Denmark

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ABSTRACT

Low temperature nitrided austenitic stainless steel exhibits strong orientation dependent case growth kinetics. Anisotropy effects during low temperature gaseous nitriding of single crystals of austenitic stainless steel with surface-normal orientations (100), (111) and (10 7 2) were investigated with thermogravimetry, X-ray diffractometry (XRD), glow discharge optical emission spectroscopy (GD-OES), nano-indentation and electron back-scatter diffraction (EBSD). Case growth kinetics were fastest for (100) and slowest for (111). Depth-profiling over the case depth was accomplished by successive layer removal combined with X-ray diffraction and nano-indentation. The results indicate that anisotropic case-growth kinetics is related to early nucleation of long-range ordered (LRO) over-stoichiometric \( y'_N - Me_N_x \) (Me-metal atoms) in (100), which is inseparable from short range ordered (SRO) expanded austenite, \( y_N \). Depth ranges of elasto-plastic and purely plastic accommodation of the nitrogen induced lattice expansion were distinguished. In the elasto-plastic region stress-gradient enhanced diffusion of N is observed.

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1. Introduction

Austenitic stainless steels are applied in a variety of industrial sectors for their excellent combination of mechanical properties (strength and ductility) and corrosion performance. Unfortunately, the choice of these materials is inapt for applications where also excellent wear and/or fatigue performance is required. Surface engineering by low temperature carburizing, nitriding or nitrocarburizing can improve the wear and fatigue performance without sacrificing, but rather further improving, the corrosion performance [1–3].

During low-temperature surface hardening of austenitic stainless steel, interstitials are dissolved into the steel at a temperature where no chromium carbides/nitrides develop for the duration of the treatment, so chromium remains in solid solution and corrosion resistance is not jeopardized. As a result, a colossal supersaturation of interstitials in solid solution is obtained in the surface-adjacent region [4]. The depth of this region, the so-called case depth, is determined by the distance bridged by diffusion of the interstitials; substitutional elements are presumed effectively motionless at the maximum process temperatures of 720 K for nitriding and 780 K for carburizing. The zone wherein the austenite is supersaturated with interstitials is generally referred to as expanded austenite. The expanded austenite zone is sometimes referred to as S-phase [2]. Since it is essentially not a phase, with a metal lattice different from f.c.c. austenite and it is not separated from austenite by a phase boundary, this terminology is not considered appropriate and therefore avoided in this article. In the present work only the incorporation of nitrogen is considered. Analogous considerations apply for incorporation of carbon, even though the solubility of carbon is not as colossal as that of nitrogen, because the thermodynamic affinity of Cr for N is higher than for C, which also is the reason why higher carburizing temperatures can be applied (see above) [5]. As a consequence of the establishment of a nitrogen concentration depth profile in austenite and the volume expansion associated with nitrogen dissolution, a composition-induced lattice expansion and associated compressive stress-depth distribution arise [1,6].

Experimental observations for polycrystalline austenitic stainless steel specimens have shown that the case depth achieved during nitriding depends on the grain orientation [7,8,9,40]. In earlier work this has been ascribed to an orientation dependent diffusion coefficient [7], but since expanded austenite is cubic and consequently diffusion is isotropic, this explanation cannot hold [10]. Earlier, the hkl-dependence of the case depth after plasma nitriding of a nickel-base alloy was shown to scale with the anisotropy factor, such that the case depth is deepest for \(<100>\) and shallowest for \(<111>\). Hence, it was suggested that elastic anisotropy is the cause for the variation in layer thickness [8]. However, since the hkl-dependent Young’s modulus, \( E_{hkl} \), increases in the order \( E_{100}>E_{110}>E_{111} \), the opposite dependence would be expected if stress-gradient enhanced diffusion...
would apply. Wu et al. [9] observed a large lattice parameter variation over a small concentration range (16 to 18 at.%) in particular for <100>-oriented grains and to a smaller extent for <111>-orientations. This lattice parameter variation occurs at the depth where the paramagnetic-to-ferromagnetic transition is observed by magnetic force microscopy, consistent with the discontinuous lattice parameter increase explained by Brink et al. [11]. The explanation for the observed hkl-dependent penetration depth given by Wu et al. [9] is that nitrogen solubility at the surface depends on pressure (residual stress), as earlier proposed by Christiansen et al. [12]. Using nanoindentation, Stinville et al. [13] observed a stiffness inversion on comparing un-nitrided and plasma-nitrided stainless steel on the same grains. Later, Tommas et al. [14] showed a gradual transition of the elastic anisotropy inversion over the thickness of the expanded austenite zone. This inversion implies that for expanded austenite the <-111>-orientation is elastically more compliant than the <100>-direction, i.e. opposite to f.c.c. lattices as austenitic stainless steel. Similarly, a hardness inversion was observed in the surface, where the <100>- and <111>-were the stiffest and softest orientations, respectively. It was found that at the depth where the nitrogen content is 25 at.% N, the elastic anisotropy corresponds to that of Fe,N. Recent work by Che et al. [15] shows that expanded austenite with nitrogen contents beyond a stoichiometry of Me:N = 4:1 (Me=metal atoms in the alloy) contains domains with long-range ordering (LRO) of the nitrogen atoms, similar to Fe,N and (FeNi)3,N. This part of the expanded austenite zone was crystallographically identified as γ'N–Me,N1+x with both LRO and SRO of N atoms. The change from ferromagnetic to paramagnetic behavior and the elastic anisotropy inversion appear to be consistent with the development of γ'N insofar as the magnetic transition is accompanied by a change in elastic behavior, as well as a change in the thermal expansion coefficient.

Most likely, also the plastic anisotropy plays a role in affecting the case depth. In particular, plastic deformation in f.c.c. affects the strong elastic anisotropy in deformed expanded austenite, leading to anomalous peak shifts of particularly the 200 reflection in X-ray diffractograms [16]. Templier et al. [17] observed crystallographic lattice rotations caused by plastic accommodation of the volume expansion induced by nitrogen dissolution, such that <111>- and <100>-textured components were amplified, while <110>-was reduced. With regard to lattice rotation, a rotationally symmetric biaxial state of stress parallel to the surface, as introduced upon nitriding, should be identical to the rotation corresponding to uniaxial tension applied in the direction perpendicular to the surface; the only difference being a hydrostatic component of stress. Only those grains with an orientation in the zone rotating towards <-111>- exhibit significant rotations upon prolonged nitriding. Lattice rotations over the expanded austenite zone of up to 13° towards the <-111>-orientation have been reported [17,18].

Clearly, nitrided austenitic stainless steel shows strong anisotropic behavior which changes with the nitrogen content. The interplay of solid-state diffusion of nitrogen, relatively slow kinetics of nitrogen transfer from a gaseous environment to the solid, mechanics affecting both the thermodynamics (equilibrium solubility) and diffusion of nitrogen, as well as changing elastic and plastic anisotropy, lattice rotation, solid solution strengthening (and work-hardening) and a magnetic transition makes this a most complicated system to describe numerically [10,19]. Another complicating factor is that most investigations were done on polycrystalline stainless steel, which adds to the complexity as also lateral diffusion fluxes, grain-to-grain mechanical interaction and different surface conditions play a role. Therefore, in the present work, single crystals were investigated to obtain a better understanding of the nitrogen-concentration dependent anisotropy effects, in particular elastic and plastic anisotropy. Three single crystals of austenitic stainless steel AISI 316 with the surface-normal orientations (100), (111) and (10 7 2) were gaseously nitrided to form a zone of expanded austenite. The motivation for choosing these three orientations is that (100) and (111) are the extremes seen from an elastic anisotropy and a Taylor factor (plasticity) point of view. These crystal orientations are not expected to experience lattice rotation upon the induced plastic deformation. On the other hand, (10 7 2) has an intermediate elastic behavior and Taylor factor; for this orientation lattice rotation is expected.

2. Experimental

Single crystal discs (Ø 15 × 3 mm) of AISI 316 with composition 16 wt% Cr, 14 wt% Ni, 2 wt% Mo, 2 wt% Mn and 0.15 wt% C1 and surface-normal orientations (100), (111) and (10 7 2) were cut from the same crystal, ground and polished to a final state with Struers’ OP-S to minimize the surface deformation. X-ray diffraction (XRD) confirmed that deformation-free surfaces were obtained. Both sides of the discs were gaseously nitrided at 693 K (420 °C) for 14 h in a Netzsch STA 449 C Jupiter thermal analyzer (TGA) in a gas mixture containing 80 vol.% NH3 and 20 vol.% H2. A long time in-situ activation of the samples in a strongly reducing gas removed the passivating oxide layer prior to nitriding.2

For depth profiling with XRD and nano-indentation, sub-layers of 0.5–1.0 μm were consecutively removed by 1 μm diamond polishing, with OP-S as the final stage. The removed sublayer thickness was quantified from the weight loss of the sample and from the change in the diagonal lengths of Vickers indentations.

A Bruker Discovery D8 equipped with Cr Kα radiation was used to determine the evolution of the X-ray line profiles and the texture with depth. For the (111) crystal, the 111 line profile (2θ: 58–70°) was measured, while for the (100) and (10 7 2) crystals the 200 line profiles (2θ: 62–84° and 68–83.2°, respectively) were measured. The step-size was 0.03°/step and the counting time per step was 0.2 s. For the (10 7 2) specimen the maximum intensity of the 200 reflection was mapped for the χ-angle 32–38° by optimizing ϕ rotation and 2θ for maximum diffraction intensity; accordingly, pole plots in the vicinity of 200 are obtained.

The as-measured XRD line profiles were corrected for background and spurious CrKα radiation. The surface topography of the as-nitrided specimens was investigated using a Phenom Pro-X table-top scanning electron microscope to reveal the slip patterns that were introduced by plastic accommodation.

A CMS nano-indentor equipped with a Berkovich indenter was applied to determine the nano-hardness and the indentation moduli. After each XRD investigation, and prior to sublayer removal, nine areas were measured with a constant information depth of 350–400 nm, while varying the force applied by the indenter from 9 to maximally 40 mN. In each of the areas 9 measurements were taken, to obtain a reliable statistical average. For the substrate, indentations were made for each 15° rotation about the surface normal, to assess the in-plane anisotropy. The values presented are the average of this in-plane anisotropy.

The nitrogen concentration-depth profiles for each crystal were determined with glow discharge optical emission spectroscopy (GD-OES) on a Horiba Jobin Yvon GDProfiler 2. For this purpose, the oppositely polished sides of the discs were used. The RF plasma for sputtering was realized at a pressure of 1000 Pa and a power of 40 W. Calibration curves for quantitative analysis of the various elements were based on austenitic steels with certified compositions and, for quantitative N assessment, custom-made nitrided pure iron.

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1 The carbon content is beyond the limit of 0.08 wt.% as applying for AISI 316. According to the manufacturer, MaTeck GmbH this is a consequence of segregation during the single crystal manufacturing procedure. Further, the nickel content is at the maximum content for AISI 316.

2 The research team involved has 20 years of experience with gaseous nitriding of stainless steel. Over the years several entirely different activation procedures have been developed, all with the same expanded austenite zone as a result.
samples with a γ′-Fe$_3$N (20 at.% N) or a ζ-Fe$_3$N (33 at.% N) layer at the surface. For calibration of the depth range, the total depth removed by sputtering during GD-OES measurements was measured with a Taylor Hobson Talysurf 50 surface profiler.

Electron back-scatter diffraction (EBSD) was applied on a cross section of the (10 7 2) single crystal to investigate lattice rotations associated with plastic accommodation of the lattice expansion. In order to prevent rounding off at the surface, the crystal was sheathed with a nickel electrolydeposit. Standard metallographic preparation finishing with OP-U (1:5 H$_2$O) for 12 min was applied to obtain a deformation-free cross section for investigation. EBSD analysis was performed on a Zeiss Supra 35 FEGSEM with 15 keV electrons at 50 nm resolution.

3. Results and interpretation

3.1. Thermogravimetry, composition-depth profiles and surface topography

Mass-uptake curves reflecting the uptake of nitrogen atoms per unit area as a function of time are given in Fig. 1. For the calculation of the surface area both the flat parallel surfaces and the rim of the crystals were taken into account. Clearly, the amount of nitrogen taken up by the (100) crystal is significantly higher than for the (111) crystal. In the early stage of nitriding the uptake of nitrogen is modest and identical for the different crystal orientations, indicating that surface activation is equally effective for the different crystal orientations. The nitrogen uptake accelerates after about 3 ks for (100) and, much later, after 12 ks for (111). On the basis of numerical modelling the nitriding kinetics for polycrystalline AISI 316, the cause for this acceleration was found to coincide with the onset of plastic deformation in expanded austenite [19,20]. Conceiving an equi-biaxial state of compressive stress as a hydrostatic state of stress combined with a uniaxial tensile stress along the surface normal, i.e. parallel to (hkl), plastic deformation is indeed expected to be introduced earlier for (100) than for (111) oriented crystals, because the (111) (0 1T) slip systems have the highest Schmid factor for (100) and the lowest for (111).

The (10 7 2) crystal firstly follows the curve as measured for the (100) crystal and later runs more or less parallel with the (111) curve, implying equal mass-uptake rates for (111) and (10 7 2). The Schmid factor for (10 7 2) is in-between the extrema for (100) and (111).

For comparison, the mass uptake is also given for polycrystalline AISI 316 L with composition 17 wt% Cr, 11 wt% Ni, 2 wt% Mo, 1 wt% Mn, which was activated and nitrided under identical conditions as the single crystals. Evidently, the behaviour of polycrystalline material is consistent with the single crystals in that the (100) and (111) single crystals mark the boundaries wherein the other crystal orientations lie.

Quantitative composition-depth profiles as determined with GD-OES are given in Fig. 2. Evidently, the case of expanded austenite obtained during nitriding is deepest for the (100) crystal and shallow-est for the (111) crystal, while the case depth for the (10 7 2) crystal is in-between these extremes. The nitrogen contents at the surface are comparable for the (100) and (10 7 2) crystals, while the (111) crystal has a higher nitrogen content at the surface. The profiles for (100) and (111) are in excellent qualitative agreement with earlier presented composition profiles for gaseously nitrided single crystals of the same orientation, albeit for another steel batch, a different surface activation and a higher nitriding temperature [21]. For the above-mentioned polycrystalline specimen a gradual case-core transition is observed, which is caused by the averaging (during GD-OES measurement) over various grain orientations, each with a distinct, but different, nitrogen-depth profile. At the case-core transitions of the nitrogen profiles, local maxima in carbon content are observed for all three crystals, as well as for the polycrystalline specimen. These maxima are explained from carbon originally present in the alloy, that has been pushed ahead of the advancing nitrogen front [22]. For the polycrystalline specimen a very low carbon content is observed and the accumulation is very broad as compared to those for the single crystal orientations. The low intensity reflects the very low carbon content in the polycrystalline specimen, while the broad depth range

Fig. 1. Thermogravimetric evolution of the overall nitrogen uptake in AISI 316 during nitriding at 693 K in a gas mixture of 80 vol.% NH$_3$ and 20 vol.% H$_2$ for single crystals with indicated surface-normal orientation (hkl) and a polycrystalline (poly) specimen.

Fig. 2. Nitrogen (top) and carbon (bottom) occupancy-depth profiles for nitrided single crystals with out of plane orientation (hkl) and polycrystalline (PC) stainless steel, as determined with GD-OES. The occupancy refers to the fraction of occupied octahedral interstices by the respective interstitial elements. For an f.c.c. lattice this corresponds to the number of interstitials per metal atom.
of the carbon “accumulation” is again a consequence of averaging over various grain orientations during measurement (see above for the nitrogen profiles).

The surface topographies of the three single crystals show slip patterns, indicating that the lattice expansion is, at least close to the surface, accommodated plastically. The slip patterns are the intersection lines between the activated {111} slip planes and the surface plane. The quadratic and triangular patterns on the (100) and (111) surface planes, respectively (Fig. 3) are in agreement with the expected equal activities on 4 and 3 slip planes in the (100) and (111) oriented crystals; as a net result no lattice rotation occurs. For the (10 7 2) crystal single slip was expected for an equi-biaxial compressive stress state, but two sets of slip lines are observed, implying that more than one slip system was activated.

3.2. X-ray diffraction and EBSD investigation

X-ray diffractograms for the nitrided (111) and (100) crystals measured after repeated sub-layer removals are given in Fig. 4. In order to show the changes in the X-ray line profile as clearly as possible, the diffractograms are scaled such that the intensity of the substrate reflection is kept constant (note the square root intensity scale). The line profile measured deepest in the crystal is representative for the line profile before nitriding. The intensity distribution at a range of lower scattering angles than the substrate reflection is the line profile reflecting the nitrided case. Clearly, for the nitrided case of the (100) crystal more diffracted intensity is measured than for the nitrided case of the (111) crystal (cf. the intensity distributions as compared to the substrate reflection measured through the case for both crystals). This is in agreement with the deeper case for (100) than for (111) (cf. Figs. 1 and 2 in Section 3.1). Moreover, for both crystals it appears that close to the surface a separate peak is present, which disappears after polishing off 2 μm for the (111) crystal and 5–6 μm for the (100) crystal. These observations resemble those in recent work by Che et al. [15], wherein it was shown that close to the surface the nitrided case consists of small domains with long-range order of nitrogen atoms similar to the ordering in Fe4N, which, as austenite, has an f.c.c. iron sub-lattice. The locations of the 111 and 200 peaks for stoichiometric Fe4N [25] are indicated in Fig. 4. It is concluded that also in the present work γ'N−Me₄Nₓ⁺ is present, where Me reflects the metallic composition of the AISI 316 alloy. The over-stoichiometry with respect to Me:N = 4:1 leads to a shift to lower Bragg angles as compared to the positions for Fe₄N and is a consequence of Cr-N short-range order (SRO) in addition to long-range order (LRO) among the nitrogen atoms [23].

Deeper below the surface the “expanded austenite” loses its LRO and only contains SRO, hence this part is essentially expanded austenite, γN. The shift of the f.c.c. peak with respect to the substrate...
peak is a consequence of the lattice expansion associated with the dissolution of nitrogen, and the associated compressive residual stresses within the plane of the crystal surface. In this respect, deeper in the case, the shape of the 200 line profile for the (100) crystal differs significantly from the shape of the 11 line profile for the (111) crystal: the former has a plateau appearance, whereas the latter appears (distorted) Gaussian. This phenomenon appears typical for the 200 line profile of expanded austenite relatively close to the substrate and has been attributed to the large variation in elastic strain after plastic deformation, because the (100) direction is elastically more compliant and plastically softer [25]. The shoulder to the low-angle side of the 200 line profile is attributed to the carbon accumulation (cf. Fig. 2). A similar shoulder is not observed for 111, because this reflection is less sensitive for small composition variations.

Pole figures around the 100 pole for the (10 7 2) crystal are given as a function of rotation angle $\phi$ and tilt angle $\chi$ in Fig. 5a. In these pole figures, the position of the substrate peak remains at the same $\chi$, while its $\phi$ can vary from case to case, depending on the accuracy of re-mounting the nitried single crystal in the diffractometer after sub-layer removal. For this reason the as-measured $\phi$-scale is not given in Fig. 5a and the $\phi$-position of the substrate peak is taken as a reference. Evidently, the largest change occurs in the first few microns, where the diffracted intensity from the nitried case, which is initially separated, approaches the substrate reflection with depth. From the 29 positions for the measured 200 line profile (not shown) it follows that the $\gamma'_{N-Me_{11}Ni_{1-x}}$ phase is only included for the intensity distribution at $z = 0 \mu$m. Evidently, this phase has been polished off already in the first polishing step. The $\chi$-rotation between the substrate peak and the expanded austenite peak proves that lattice rotation does occur, as anticipated. The observed activation of both the primary and the conjugate slip planes at the surface in Fig. 3 indicates that the conjugate slip plane is activated at a higher plastic strain, while the primary plane dominates deeper in the case, i.e. for smaller strains. The total misorientation in $\gamma'_{N-Me_{11}Ni_{1-x}}$ obtained from the intensity plot in Fig. 5a is provided in Fig. 5b and reaches about 4° at the surface. The observation of a change in the decline of the misorientation beyond about 4 $\mu$m hints at a change in plastic accommodation of the lattice expansion induced by nitrogen dissolution and coincides with the separation between the region with two activated slip planes (larger misorientation) and one activated slip plane (deeper in the nitried zone). The results of the EBSD investigation of the (10 7 2) single crystal are analogous to those obtained with XRD (Fig. 5b). Quantitatively, the XRD results show a larger lattice rotation than the EBSD results and misorientation appears to reach deeper; the change in the decline of the misorientation with depth is observed at 2.5 $\mu$m for EBSD as compared to 4 $\mu$m for XRD. The quantitatively larger misorientations could be explained from minor shape changes caused by relaxation of elastic strains in the direction perpendicular to the plane of the cross section. It is suggested that such elastic relaxation can lead to an “additional” lattice rotation that counteracts the lattice rotation induced by plasticity. The larger depth reached for the XRD results may indicate that the sublayer thickness polished off for XRD (and nano-indentation; see below) is slightly overestimated 4. It is noted that the EBSD results cover the same depth range as the nitrogen-depth profile (see inset in Fig. 5b) and have a change in slope at the same depth of 2.5 $\mu$m. The observed features show a striking resemblance to misorientation plots obtained from EBSD and plastic strain predicted by a 1-dimensional model [10,18,20]. Such behavior marks the depth where elasto-plastic accommodation of the compositionally induced strain at larger depth is replaced by only additional plastic straining (at practically constant elastic strain) in the surface-adjacent region.

3.3. Nano-indentation

The hardness and indentation modulus were evaluated from the force-displacement curves applying the reverse analysis algorithm by Dao et al. [26]. The method relies on dimensionless functions relating various parameters extracted from the experimental force-displacement curve to the materials parameters. In contrast to the widely applied Oliver-Pharr method [27], the method by Dao et al. [26] accounts for the sink-in and pile-up effect [28]. Work-hardening of the material was assumed to follow a power law, which provided good fits to a tensile curve of AISI 316 up to 20% strain. Regardless of the nitrogen content, a constant work hardening exponent, $n$, of 0.3, reflecting un-nitried AISI 316, was assumed. It is anticipated that $n$ depends on the interstitial content, as was demonstrated for carburized stainless steel [29]. Nevertheless in the present data analysis $n$ was assumed constant in order to obtain convergence towards a unique solution.

The obtained hardness from the Dao et al. evaluation procedure is a Vickers hardness value ($HV$) [26]. The hardness and the indentation modulus ($E'$) are given as a function of depth in Fig. 6. Because of the slip lines at the surface (see Fig. 3) and associated surface roughness the indentation data measured at the surface of the as-treated single crystals should be interpreted cautiously and are therefore not included in Fig. 6. Both (111) and (100) exhibit a hardness of more than 17 GPa close to the surface. The (10 7 2) crystal has a hardness slightly below this value. The large difference in case depth among the crystal orientations is evident from the depth ranges of the hardness profiles, with (111) shallowest and (100) reaching deeper than 9 $\mu$m, and is analogous to the nitrogen concentration profiles in Fig. 2. The grey markers in Fig. 6 indicate the depths for which $\gamma'_{N-Me_{11}Ni_{1-x}}$ was identified with XRD (see Section 3.2). Beyond the depth where $\gamma'_{N}$ is present (2 $\mu$m for (111) and 5 $\mu$m for <100>), the hardness profile declines steeply. All hardness profiles appear to change their slope around 10 GPa, i.e. at 3, 4 and 7 $\mu$m for (111), (10 7 2) and (100), respectively. Interestingly, for (10 7 2) this depth corresponds to the depth where the misorientation changes slope (Fig. 5b) and separates the depth in the expanded austenite zone where the accommodation of the lattice expansion changes from elasto-plastic (at larger depth) to pure plastic (closer to the surface). In the depth range where the elastic strain changes, stress-gradient-induced diffusion of nitrogen is expected to contribute to the evolution of the composition profile and hence, affects the hardness profile, such that it does not decline as fast as in the preceding depth range, where the elastic strain remained constant. The profile tails for hardness values below 10 GPa are compared in Fig. 7 after removing the part of the depth range where only plastic accommodation occurs. The reduced depth in Fig. 7 is obtained by a shift of the profiles with respect to each other, such that an intersection of the hardness profiles occurs at 9.3 GPa at a “reduced” depth of 0.34 $\mu$m. 4 Evidently, the profile tails for (100) and (111) reach shallowest and deepest, respectively, which is opposite to the difference in case depths. This observation is in excellent agreement with the anticipated effect of stress-gradient induced diffusion for (100) and (111). The (111) direction is roughly three times as stiff as the (100) direction (Young's moduli, $E_{111}$, are 308 GPa and 100 GPa, respectively). This implies that, assuming a constant Poisson ratio, the stress gradient corresponding to a composition-induced strain gradient is three times as steep for (111) as for (100) and thus the contribution of stress-gradient induced diffusion is much more pronounced for (111)

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4 Alternatively, the slight deviation may be a consequence of a slight difference in zone thickness on the two flat surfaces of the crystal, because XRD/nano-indentation and EBSD/GD-OES were measured on opposite sites of the single crystal.
than for \langle100\rangle. The effect of a stress-gradient on the profile for \langle10\ 7\ 2\rangle is in-between those for \langle111\rangle and \langle100\rangle, recognizing that $E_{10\ 7\ 2} = 191$ GPa.

For the indentation modulus, $E^*$, the following is observed. The error bars are relatively large because of the variation in $E^*$ with the rotation angle within the plane of indentation. A steep decrease in
the expanded austenite zone appears to fade out or slightly increase along the depth axis, referred to a
Comparison of the tails of the hardness pro
Fig. 7. 

decreases strongly and can thus be associated with the disappearance of $\gamma_N'$-Me$_4$N$_{1+x}$. The continuous decrease in modulus with depth in the expanded austenite zone appears to fade out or slightly increase again on approaching the substrate. In the region close to the surface the $E^*$ values for the three investigated crystal are about equal in value, while for the region close to the substrate it is observed $E_{100} < E_{1072} < E_{111}$ which reflects the order of corresponding Young's moduli in austenite. The abovementioned variation in $E^*$ with the rotation angle within the indentation plane is smallest close to the surface and largest in the substrate, which is in good agreement with the expected difference in rotational anisotropy between $\gamma_N'$-Me$_4$N$_{1+x}$ and the AISI 316 alloy.

4. Discussion

4.1. Model description of the nitrided case on stainless steel

From the experimental results the following picture emerges for the graded microstructure in the case developing on austenitic stainless steel AISI 316 during low temperature nitriding. The surface-adjacent region consists of $\gamma_N'$-Me$_4$N$_{1+x}$ with a nitrogen content exceeding the solubility in Me$_4$N. Recent work for a wide range of steels with various Cr and Ni contents demonstrated that $\gamma_N'$-Me$_4$N$_{1+x}$ develops on all alloys during nitriding [15]. This phase is isomorphous with expanded austenite, $\gamma_N$, the only difference being the long-range order (LRO) of nitrogen atoms in $\gamma_N'$-Me$_4$N$_{1+x}$ while over-stoichiometry implies more nitrogen on disorder sites [23]. Applying XRD, the occurrence of LRO among the nitrogen atoms remains undetected, because of the limited size of the ordered domains. A striking observation is that the $\gamma_N'$ phase reaches significantly deeper in the nitried case on the (100) crystal than on the (10 7 2) and (111) crystals. This difference in depth for $\gamma_N'$ can largely explain the difference in nitrogen uptake (Fig. 1) and the observed difference in case depth (Figs. 2 and 6). The acceleration of the nitrogen uptake as observed in Fig. 1 is initiated by plastic deformation [19,20]. Earlier plastic deformation for (100) than for (111) is anticipated because the Schmid factor for (100) is highest and thus a smaller lattice expansion is necessary to exceed the hkl-dependent yield strength. Evidently, plastic deformation, also, has an influence on $\gamma_N'$ formation. The reason for an earlier development of $\gamma_N'$ on the (100) crystal as compared to the (111) crystal is most likely associated with the lattice expansion in the (100) direction, which has repeatedly been concluded to be anomalous as compared to other crystallographic directions for as nitrided surfaces [30,31,32] as well as for homogeneously nitried powders [16]. Recently, it was demonstrated that this anomaly is related to the combined influence of elastic and plastic anisotropy [16]. Here, it is suggested that the anomaly in lattice expansion in the (100) direction, that is introduced upon plastic deformation, allows the development of $\gamma_N'$ because this is associated with an additional (discontinuous) increase in lattice parameter as a consequence of a transition from para- to ferro-magnetism (see Fig. 7 in [11]). Also, the XRD lattice parameter data in Fig. 8 of [15] showed that the merge of $\gamma'$ and $\gamma_N'$ line profiles firstly occurs for 200, consistent with the above interpretation.

This leads to an explanation why the $\gamma_N'$ phase is much more pronounced for (100) than for (111) and (10 7 2). Firstly, the early appearance of $\gamma_N'$ on (100) provides more time for the growth of this phase. Secondly, the diffusivity of nitrogen is strongly dependent on the dissolved nitrogen content; especially in the composition range where $\gamma_N$ becomes stable a strong increase in diffusivity with nitrogen content occurs [33]. Thirdly, the diffusivity of nitrogen in expanded austenite is influenced by the presence of (elastic) residual stress, both by the pressure effect (the hydrostatic stress component) and the stress gradient (stress-gradient induced diffusion), as first suggested for the case of expanded austenite in [34]. Stress-gradient induced diffusion plays a role of importance in the region of the expanded austenite zone where a compressive stress gradient is present, i.e. the transition from case to core (see below). The pressure effect is anticipated to play a role in the region where plastic

![Fig. 6. Hardness (top) and indentation modulus (bottom) as derived from nano-inden- tation at the specimen surface after repeated sub-layer removal. Grey-filled markers in the hardness profile indicate the depths where $\gamma_N'$ phase was identified with XRD.](image1)

![Fig. 7. Comparison of the tails of the hardness profiles. The profiles are translated along the depth axis, referred to a “reduced depth” such that a hardness of 9.3 GPa is reached at 0.36 μm.](image2)
deformation and γ_{ii} are present. The earlier onset of plasticity for (100) implies that the elastic residual stress for which plastic deformation initiates is lower than for (111). Moreover, on continued plastic deformation on increasing the strain (by dissolution of nitrogen and the associated volume expansion) the true (elastic) stress increases most for (111) and least for (100) [35,36]. Consequently, the pressure (hydrostatic compression) effect on the diffusivity, which corresponds to a reduction of the diffusivity, will be most severe for (111). All abovementioned influences, i.e. earlier formation of γ_{ii}, higher nitrogen diffusivity and less severe pressure effect, imply that within a certain time span γ_{ii} can grow deeper into (100) than into (111).

In Fig. 1 the accelerated nitrogen uptake for (10 7 2) coincides with that for (100), indicating that γ_{ii} develops at the same instance. However, on continued nitriding γ_{ii} on (10 7 2) does not grow to the same extent as on (100), which may be a consequence of the lattice rotation (towards <111>) introduced by the underlying γ_{ii}.

An earlier explanation for a difference in hkl-dependent case depth was based on different nitrogen contents at the surface as a consequence of elastic anisotropy [9]. This explanation is contradicted by the present results, which demonstrate that the nitrogen content at the surface of nitried (111) is slightly higher than on nitried (100), despite the deeper case on (100), i.e. opposite to the explanation in [9].

4.2. Mechanical anisotropy

In the region immediately underneath the surface-adjacent γ_{ii}, the nitrogen content decreases steeply for all investigated crystals. Fig. 8 shows that a linear relation applies between the indentation modulus, E′, and the hardness, HV. For the <111> and <10 7 2> crystals the data overlaps on the same line while for the <100> crystal the linear relation lies at lower E′ values. Clearly, the combinations of HV and E′ in the γ_{ii} phase (grey markers in Fig. 8) deviate from the linear relations for γ_{ii}, confirming that this phase has different mechanical properties.

Earlier work by Stinvil et al. [13] and Tommas et al. [14], indicated a reversal in the anisotropy of the elastic behavior close to the surface as compared to the unnitried substrate, such that at the nitried surface E_{100} > E_{111} and in the substrate E_{100} < E_{111}. Such a reversal would be consistent with the presence of γ_{ii} phase at the surface, because γ_{ii} phase is stiffest in the <100> direction [37], while austenite is stiffest in the <111> direction. The observations in [13,14] were done on polycrystalline AISI 316 L and probing in differently oriented grains. Quantitatively, the present values for E_{ii} are identical with those in [13,14], indicating that the Oliver-Pharr method, as applied in [13,14] and the Dao et al. method yield the same results (this was also verified for our data set). Consistent with the observations in [13,14], the present investigation showed E_{100} < E_{111} for the substrate and for the values at about 1 μm it appears that E_{100} > E_{111} (Fig. 6). No clear reversal of the anisotropy was observed for the current single crystals because in the present experiments the nitriding time was shorter than in [13,14], with the consequence that the depth range of the γ_{ii} phase for the <111> crystal is limited to 2 μm.

Within the γ_{ii} region the hardness decreases from about 15 to 2.5 GPa. In this region the lattice expansion as compared to the substrate is accommodated elasto-plastically for a hardness of up to about 9 GPa. Beyond this value the lattice expansion is almost entirely accommodated plastically and the elastic strain remains virtually constant. In the elasto-plastic region the (elastic) compressive stress and the yield stress increase with nitrogen content to a value of up to 5–6 GPa in excellent correspondence with earlier experimental assessments of compressive residual stress [18]. The (elastic) stress-gradient provides a driving force for nitrogen diffusion (cf. [10]). As a consequence, the inward nitrogen flux in this region is enhanced, leading to a deeper penetration of the concentration profile. The stiffer the diffusion direction the more pronounced this effect is. Hence, the tail of the hardness profile for (111) penetrates appreciably deeper than for (100), while for (10 7 2) an intermediate stress-induced diffusive flux has contributed to the profile.

For hardness values below about 5 GPa, E′ appears to increase with depth, albeit within experimental accuracy as suggested by the error bars. GD-OES investigation showed that the carbon accumulation occurs in this depth range (cf. Figs. 2 and 6). In solid solutions of interstitials in iron-based f.c.c. SRO occurs for interstitial nitrogen, promoted by metallic bonds, whilst clustering occurs for interstitial carbon, promoted by covalent bonds [38]. The two types of bonds will have different effects on the Young’s modulus. Hence, it is suggested that co-existence of N and C, and thus both types of bonds, at the case-core transition affects the local variation in E′.

4.3. Implications for polycrystalline materials

The results presented above for single crystals show a very clear effect of the grain orientation on the nitrogen uptake and the case depth achieved during nitriding. The observations are consistent with other publications on nitriding of single crystals of austenitic stainless steel [7,21], confirming that the present observations are representative for the actual dependence of the nitriding kinetics on crystal orientation. In polycrystalline materials this will manifest as uneven grain-orientation dependent case depths, as has been reported by several research groups [7,9,10]. The nitrogen uptake curves (Fig. 1) and the nitrogen-depth profiles (Fig. 2), convincingly demonstrate that for polycrystalline material a behaviour intermediate between the extrema <100> and <111> is obtained. The correlation found by He et al. [8] for Ni-base alloys showing that the case depth decreases with increasing anisotropy factor, i.e. (100) is thickest and (111) is thinnest, is also observed here. This dependence implies that the variation in case depth is not a consequence of stress-enhanced diffusion over the entire case depth, as this would result in the opposite effect [39]. Neither can it be a consequence of a lower surface concentration for (111) than for (100), as suggested by Wu et al. [9], because the opposite is observed for the present single crystals and other independent investigations [21]. The notion that the development of the γ_{ii} phase depends on the onset of plastic
deformation and that the depth range of γ′ₙ phase correlates with case depth appears to provide a consistent explanation. It is recognized that the investigated AISI 316 single crystals have a relatively high nickel content as compared to commercial AISI 316. It can be excluded that this relatively high nickel content is the reason for the occurrence of γ′ₙ. A systematic investigation of Fe-Cr-Ni alloys with Ni contents ranging from 8.2 wt% (in AISI 304) to a model Fe-Cr-Ni alloy with 27 wt% Ni convincingly demonstrated that γ′ₙ phase was present irrespective of the Ni content. Rather, the development of the γ′ₙ out of γₙ is a consequence of LRO among the abundant nitrogen atoms, which dissolve due to the high chromium content.

Even though crystal orientations away from (100) and (111) can develop γₙ in a relatively early stage of nitriding (see Fig. 1 for |10 7 2|), the occurrence of lattice rotation on continued growth of the γₙ/γ′ₙ case is accompanied by a reduction of the growth rate. It is suggested that the above interpretation also applies for the Ni-base alloy investigated by He et al. [8].

5. Conclusions

Single crystals of AISI 316 L show strongly hkl-dependent behaviour during gaseous nitriding, which is manifested as an hkl-dependent acceleration of the nitrogen uptake rate and a strong variation of the achieved case depth. The crystal orientations (100) and (111) mark the extremes, with (100) as the earliest acceleration and the deepest nitrogen diffusion depth. The earlier acceleration and deeper nitrogen diffusion for the (100) crystal coincide with the presence of the γ′ₙ phase over a larger depth range than for (111).

Plastic deformation appears to promote this development of γ′ₙ. This is related to the elastic and plastic anisotropy of the f.c.c. lattice, where the lattice expansion on (100) reaches the lattice spacing range of γ′ₙ earlier than for (111). The earlier plastic deformation and the associated earlier development of γₙ the higher nitrogen diffusivity and the less severe pressure effect (by the hydrostatic stress component) can explain the deepest penetration of the expanded austenite zone into on the (100) crystal and, analogously, the shallower in (111).

In the depth region where elasto-plastic accommodation of the lattice expansion occurs, hkl-dependent hardness profiles consistent with stress-gradient assisted diffusion of nitrogen atoms are observed. This entails that the tail of the hardness profile, as a measure for the nitrogen concentration, at the case-core transition extends deeper for (111) than for (100), because the stress-gradient induced diffusion is more pronounced for (111) than the latter, as a consequence of a difference in Young’s modulus by a factor 3.

For (10 7 2) and (111) crystals the indentation modulus depends linearly on the hardness in the γₙ region, while for (100) a lower indentation modulus was observed, consistent with the expected elastic anisotropy of γₙ phase. For compositions in the γₙ phase region the relation between indentation modulus and hardness is different, indicating a change in the elastic constants. For low interstitial contents the indentation modulus appears to increase with decreasing hardness. Probably this is related to the presence of carbon.

The composition profiles for a polycrystalline specimen and a (10 7 2) single crystal that were nitrided under the same conditions as (111) and (100), lie in-between the extremes of (100) and (111).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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