Thermo-chemical-mechanical simulation of low temperature nitriding of austenitic stainless steel; inverse modelling of surface reaction rates

Küçükyildiz, Ömer C.; Sonne, Mads R.; Thorborg, Jesper; Somers, Marcel A. J.; Hattel, Jesper H.

Published in:
Surface and Coatings Technology

Link to article, DOI:
[10.1016/j.surfcoat.2019.125145](https://doi.org/10.1016/j.surfcoat.2019.125145)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Küçükyildiz, Ö. C., Sonne, M. R., Thorborg, J., Somers, M. A. J., & Hattel, J. H. (2020). Thermo-chemical-mechanical simulation of low temperature nitriding of austenitic stainless steel; inverse modelling of surface reaction rates. *Surface and Coatings Technology*, 381, [125145]. <https://doi.org/10.1016/j.surfcoat.2019.125145>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Thermo-chemical-mechanical simulation of low temperature nitriding of austenitic stainless steel; inverse modelling of surface reaction rates

Ömer C. Kücükyildiz, Mads R. Sonne, Jesper Thorborg, Marcel A.J. Somers, Jesper H. Hattel

PII: S0257-8972(19)31136-3

DOI: <https://doi.org/10.1016/j.surfcoat.2019.125145>

Reference: SCT 125145

To appear in: *Surface & Coatings Technology*

Received date: 26 July 2019

Revised date: 18 October 2019

Accepted date: 6 November 2019

Please cite this article as: Ö.C. Kücükyildiz, M.R. Sonne, J. Thorborg, et al., Thermo-chemical-mechanical simulation of low temperature nitriding of austenitic stainless steel; inverse modelling of surface reaction rates, *Surface & Coatings Technology* (2018), <https://doi.org/10.1016/j.surfcoat.2019.125145>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Thermo-chemical-mechanical simulation of low temperature nitriding of austenitic stainless steel; inverse modelling of surface reaction rates

Ömer C. Kücükıldız^{a*}, Mads R. Sonne^a, Jesper Thorborg^b, Marcel A.J. Somers^a, Jesper H. Hattel^a

^a Technical University of Denmark, Department of Mechanical Engineering

Produktionstorvet b. 425, 2800 Kgs. Lyngby, Denmark

^b Magma GmbH, Aachen, Germany

*corresponding author e-mail: omecak@mek.dtu.dk, phone: 0045 45254819

Abstract

A multi-physics thermo-chemical-mechanical 1-dimensional implicit finite difference model is presented to simulate the evolution of composition and residual stress profiles over the expanded austenite case developing during low temperature nitriding of austenitic stainless steels. The model combines 1-dimensional diffusion of nitrogen in the depth direction with a concentration-dependent diffusivity, elasto-plastic accommodation of the lattice expansion, stress gradient-induced diffusion of nitrogen, solid solution-strengthening by nitrogen and trapping of nitrogen by chromium atoms. The rate of the surface reaction governing the transfer of nitrogen from the gas to the solid is unknown and was evaluated by inverse modelling. The modelling was applied adopting the surface reaction rate as the only fitting parameter and taking mass-uptake curves (thermogravimetry) as the constraint, while all other data were taken from established literature

values. Very good agreement is achieved between the predicted and experimental composition-depth profiles. Further, the applicability of the present model to plasma nitriding was verified by simulating (not fitting) the evolution of composition-depth profiles obtained after plasma nitriding of stainless steel. The good to very good agreement of the present model's predictions with experimental data for gaseous and plasma nitriding, indicates that the essential multi-physics influences and parameters are taken into account, with a minimum of adjustable parameters.

Keywords: gas nitriding, plasma nitriding, austenitic stainless steel, numerical modelling, reaction kinetics, swelling.

1. Introduction

Austenitic stainless steels are industrially applied in a variety of sectors for their corrosion properties, but exhibit poor wear and fatigue properties. Surface engineering by low temperature surface hardening through carburizing, nitriding or nitrocarburizing has the potential to importantly improve the wear and fatigue performance without sacrificing the corrosion performance [1]. The wear performance is enhanced by substantial hardening of the surface zone (up to 1200 HV) and the fatigue performance is improved by compressive residual stresses.

The prediction of composition and stress profiles by numerical simulation, taking the steel composition and process parameters such as gas composition, temperature and treatment time as input, would enable targeted surface engineering of stainless steels. In addition, an adequate numerical model coupled with thermodynamic databases would enable the design of new stainless steel grades that are tailored for optimal performance during low temperature surface hardening, analogous to the well-known nitriding and carburizing steels.

Low-temperature nitriding¹ of austenitic stainless steels is associated with the development of a nitrogen concentration profile over the case depth. Essentially, the interstitial N atoms are dissolved in the austenite lattice and no new phases develop; only short range ordering (SRO) and long range ordering (LRO) in the f.c.c. host lattice of metal atoms [2]. The dissolution of interstitials in austenite leads to a lattice expansion (hence expanded austenite) which is accommodated elasto-plastically, implying that both elastic and plastic strain profiles develop over the case depth. The associated elastic compressive stresses amount to several GPa's (see [3] and references therein). In addition to the residual stresses caused by the composition-induced volume expansion, also thermal stresses develop on cooling from the treatment temperature.

¹ In the sequel only nitriding is considered. Carburizing and nitrocarburizing are analogous, albeit with modifications.

These stresses arise from the composition dependent thermal expansion coefficient, which, for high N containing expanded austenite, changes particularly strongly at Curie temperature (at approx. 550 K) on cooling [3].

At the nitriding temperature an in-depth elastic stress gradient provides an additional driving force for diffusion of nitrogen so that a larger case depth is attained than by concentration-gradient driven diffusion alone. For the extreme case that all lattice expansion is accommodated elastically, the case depth is enhanced by a factor 2 [4]. However, as soon as the elastic limit (yield stress) is reached, further lattice expansion is accommodated by additional plastic straining. Note that the yield stress increases with nitrogen content by solid solution strengthening. If plastic deformation is accomplished by slip along the $\{111\}$ glide planes and the grain orientations are away from out-of-plane orientations $\langle 001 \rangle$ or $\langle 111 \rangle$, the outcome will be lattice rotation [5][6][3]. Near-surface plastic deformation increases the surface roughness and leads to the appearance of slip-lines at the surface [7]. Also grain push-outs can be the result of plastic accommodation of the volume (and thermal) misfit [8][9][10].

Several attempts to model the evolution of composition (and stress) profiles over the expanded austenite case were presented in the literature [11][12][13][14]. Each of these included several aspects and were commented in [15]. Jespersen et al. presented the so-far most comprehensive model, as it was the first to take both elasto-plasticity and solid solution strengthening into account, in addition to the composition-dependent diffusivity of nitrogen [16], stress-gradient induced diffusion (first suggested for this system in [17]) and stress-affected surface concentration [18]. Since then Peng et al. demonstrated that implementing composition dependent mechanical properties as determined from nano-indentation can provide a quantitative prediction of the residual stress profile from the concentration profile [19]. A recent publication attempts to incorporate the hkl dependence of the case depth [20]. However, the multitude of

unknown fit parameters in the model and omitting essential effects as elasto-plasticity, yielded unrealistic results that are not corroborated by the experimental state-of-the-art.

Currently, based on experimental and numerical work, the role of the dissociation of ammonia at the stainless steel surface during nitriding is not fully understood. Particularly, the kinetics of this reaction is uncertain, since large deviations of the surface concentration from local equilibrium are observed. This has been ascribed to huge compressive stresses, which thermodynamically reduce the equilibrium solubility of nitrogen [18].

The objective of this article is to incorporate the effect of surface reaction kinetics to achieve realistic time-dependent concentration profiles during the nitriding treatment, which is essential for achieving accurate (elastic) residual stress and plastic strain profiles. Differently from previous attempts where an explicit iterative approach was used, a fully implicit iterative approach was developed in order to enhance the computational speed by a factor 100. A fast converging numerical model enables inverse modelling to estimate unknown physical inputs, in this case the surface reaction kinetics. The diffusion equation is solved by a mixed control-volume based-/classical finite difference method, where stresses and thermal gradients constitute additional driving forces for diffusion. The stresses are resolved by a plane stress-projected plasticity model, which deviates from the earlier applied J2 flow model [15]. It incorporates the chemical and thermal strains while maintaining the in-plane force equilibrium for integration in the depth direction. The actual surface concentration is determined by the nitriding potential, the surface reaction rate and the compressive surface stresses. In order to be able to simulate the interplay of these parameters effectively, the availability of fundamental parameters as determined experimentally on stress-free homogeneous powders and foils under well-defined conditions is essential. The simulation results are compared to experimental results in terms of

concentration profiles, layer growth and swelling effect. Also, the applicability of the model to expanded austenite cases obtained by plasma nitriding is explored.

2. Methods

A diagram showing the methods used for the one-dimensional finite difference model is shown in Figure 1. The four modules in the figure encompass all the mechanisms in the multi-physics model: heat transfer, diffusion, surface kinetics and mechanics. These modules are shown with different colors and their respective couplings are illustrated with arrows.

Figure 1 – Schematic presentation of the 1D finite difference model consisting of a thermal, a

Figure 2 - The iteration-, inverse model and time-stepping loops.

diffusion, a surface kinetics and a mechanical part. Information paths of the one- and two-way coupled parameters are indicated by single- and double-arrowed drawn lines. The information path for the inverse modelling is represented by a dash-dot line.

From the diagram, it follows that the concentration profile is obtained internally in the diffusion module using the diffusion

coefficient D_N and the nitrogen trapping threshold K_{CrN} . Externally, the concentration profile depends on the surface flux j_{surf} as a boundary condition, which is calculated in the surface kinetics module and the hydrostatic component of the stress gradient $\Delta\sigma^H$, which is calculated in the mechanics module. Simultaneously, the concentration provides input for the diffusion coefficient and nitrogen trapping capacity, making a two-way coupled problem. At the same time, the concentration provides the one-way coupled input for the yield strength of the material. It is evident that all the variables are directly or in-directly coupled and it is therefore necessary that all solutions converge in each time-step.

The concentration dependent surface reaction rate “constant” k_{rate} is assessed by inverse modelling as follows. For each time-step, the present model makes a trial calculation of the concentration-depth profile of nitrogen, including all the couplings displayed in Figure 1. If the solution converges, then the simulated nitrogen content, which follows from an integration of the calculated concentration profile with respect to depth, is compared to the total experimental nitrogen content incorporated in the sample after a given time. If the difference between these two values is lower than a preset allowable error ε^{tol} (see Figure 2), the solution is accepted and the next time step is initiated. If the difference does not comply with this allowable error, a binary search method adjusts the reaction rate constant and the same time step is recalculated. This is repeated until the total nitriding time is reached (Figure 2).

2.1. Multi Physics Model

2.1.1. Heat transfer

In order to resolve temperature dependent properties, including the consequence of magnetostriction, heat transfer during heating up and cooling down is considered. The heat transfer by conduction follows Fourier's law:

$$\frac{q}{A} = -k(T) \frac{\partial T}{\partial z} \quad (1)$$

which for a non-linear in-depth temperature distribution leads to the transient heat conduction equation (continuity equation):

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(k(T) \frac{\partial T}{\partial z} \right) \quad (2)$$

where ρ is the density, c_p is the heat capacity and $k(T)$ is the temperature dependent conductivity.

2.1.2. Pressure and temperature affected diffusion

Nitriding is a diffusion driven process and can be described as a diffusion problem with one diffusing component, because the nitrogen atoms diffuse rapidly according to an interstitial mechanism, while the substitutional diffusion of metal atoms is negligible. The usual assumption of pressure-independent diffusion cannot be justified, since huge compressive stresses are introduced in the surface.

The diffusive flux, J , under a gradient in the chemical potential of nitrogen, μ_N , is defined as:

$$J = -M_N c_N \frac{\partial \mu_N}{\partial z} \quad \text{where} \quad M_N = \frac{D_N}{R \cdot T} \quad (3)$$

where M_N is the mobility of nitrogen, c_N is the concentration of nitrogen, D_N is the diffusivity of nitrogen and R is the gas constant.

Since pressure and temperature effects cannot be omitted for dissolved nitrogen atoms, the chemical potential becomes:

$$\mu_N(a_N, T) = \mu_{N,0} + RT \cdot \ln(a_N) - V_N \cdot \sigma_H \quad (4)$$

where a_N is the activity of nitrogen in solid solution, V_N is the partial molar volume of nitrogen and σ_H is the hydrostatic stress component (or simply the negative of pressure). Nitrogen activity is defined by the equilibrium constant K_T and the nitriding potential K_N :

$$a_N = K_T \cdot K_N \quad (5)$$

The equilibrium constant K_T is the ratio of reaction rate constants for forward and backward reactions for the dissolution of nitrogen from ammonia and it is a function of temperature and pressure. The nitrogen activity was obtained for thin foils [8] subjected to a range of imposed equilibria between gas and solid state, by varying the nitriding potential $K_N = p_{NH_3}/p_{H_2}^{\frac{3}{2}}$.

Substituting the chemical potential into Fick's 1st law (Eq. 3) and considering mass conservation, a formulation of Fick's 2nd law is obtained, including the first and second order derivative effects of the temperature- and hydrostatic stress gradient with respect to depth:

$$\begin{aligned} \frac{\partial c_N}{\partial t} = & \frac{\partial}{\partial z} \left(D_N(c) \frac{\partial c_N}{\partial z} \right) + D_N(c) \cdot \frac{\partial^2 c_N}{\partial z^2} - \frac{\partial}{\partial z} \left(\frac{D_N(c)}{\frac{\partial K_N}{\partial c_N}} \cdot \frac{K_N}{T} \right) \cdot \frac{V_N}{R} \cdot \frac{\partial \sigma_H}{\partial z} - D_N(c) \cdot \frac{K_N}{\frac{\partial K_N}{\partial c_N}} \cdot \frac{V_N}{R \cdot T} \cdot \frac{\partial^2 \sigma_H}{\partial z^2} + \\ & \frac{\partial}{\partial z} \left(\frac{D_N(c)}{T} \cdot \frac{K_N}{\frac{\partial K_N}{\partial c_N}} \cdot \ln(K_T \cdot K_N) \right) \frac{\partial T}{\partial z} + \frac{D_N(c)}{T} \cdot \frac{K_N}{\frac{\partial K_N}{\partial c_N}} \cdot \ln(K_T \cdot K_N) \cdot \frac{\partial^2 T}{\partial z^2} \end{aligned} \quad (6)$$

The non-linear concentration dependent diffusion coefficient $D_N(c)$ has been determined in [16]. A detailed derivation of the pressure and temperature affected diffusion equation can be found in [15].

2.1.3. Trapping effect

As a consequence of the chromium content in stainless steel, short range ordering of Cr and N takes place. The short range ordering of nitrogen atoms, which can mathematically be conceived as nitrogen trapping, can substantially alter the concentration-depth profile and thus affect the achievable nitriding depth. Generally, the higher the chromium content, the shallower the nitriding depth.

Considering short range ordering, i.e. trapping of nitrogen by chromium atoms, as the “precipitation” of CrN_n nitrides (with n being the number of nitrogen atoms per Cr atom), an equilibrium constant, K_e , of the reaction can be described as:

$$K_e = \frac{1}{[\text{Cr}_\gamma][\text{N}_\gamma]^n} = \frac{1}{K_{\text{CrN}_n}} \quad (7)$$

$$K_{\text{CrN}_n} = [\text{Cr}_\gamma][\text{N}_\gamma]^n \quad (8)$$

where K_{CrN_n} can be conceived as the solubility product of CrN_n , that is the trapping threshold. From the reaction balance (Eq. 8), the amount of trapped and residual nitrogen can be calculated by a simple mass balance. The solubility product is not known, but assuming $n=0.9$ nitrogen atoms per Cr atom, following [18], it is estimated as $K_{\text{CrN}_n} = 4.5 * 10^7$, corresponding to an intermediate trapping threshold.

2.1.4. Surface kinetics and concentration equilibrium

The chemical reaction that takes place at the surface starts with the dissociation of ammonia gas into hydrogen gas and adsorbed nitrogen atoms. The adsorbed nitrogen atoms can either diffuse into the steel or desorb after formation of molecular nitrogen. Thermodynamically the latter is preferred, but at the low temperatures considered here the associated reaction rate is negligibly slow as compared to the dissolution reaction rate. Since the dissociation reaction is not infinitely rapid as compared to diffusion of nitrogen into the solid, the actual nitrogen content at the surface depends on the balance of nitrogen fluxes arriving at the surface (from dissociation) and leaving the surface (by solid-state diffusion and/or desorption). Here it is assumed that the desorption reaction is effectively prevented by the relatively low temperature. Following Grabke [21] the net flux of nitrogen transferred from the gas to the solid, j_{surf} , depends on the balance of ammonia dissociation rate and ammonia formation rate, described by:

and can be written as:

$$j_{surf} = A \cdot k_{rate} \cdot (c_N^{eq} - c_N^s) \quad (9b)$$

with A the effective surface area, k_{rate} the reaction rate constant for the rate controlling step in ammonia dissociation (which for b.c.c. iron depends on the partial pressure of hydrogen gas), c_N^s the actual surface concentration of N, which depends on the balance of fluxes of nitrogen arriving at and departing from the surface, and c_N^{eq} the equilibrium concentration, which is achieved only if the steel has a uniform nitrogen content, i.e. the diffusive flux is nil and no N_2 develops. The

equilibrium concentration of nitrogen in stainless steel can be expressed as a function of the nitrogen activity, using the equilibrium studies between gas and thin stainless steel foils [8].

For b.c.c. Fe, which has a very limited solubility of nitrogen, k_{rate} is independent of the nitrogen content in solid solution. Recognizing that the maximum nitrogen solubility in expanded austenite is more than a hundred times higher than in ferrite, it is anticipated that k_{rate} is a function of the surface concentration, in contrast to assumptions in a previous numerical model [22]. In addition, the surface flux is proportional to the exposed surface area (cf. Eq. 9b), which itself can change as a consequence of swelling and plastic deformation. If a change in surface area is not taken into account, any increase in the surface flux will be interpreted as a change in the reaction rate.

2.2. Mechanics

2.2.1. Mechanical assumptions and force equilibrium

The geometry of the nitrided material in combination with the mechanical consequences of the nitriding itself lead to a number of assumptions, which simplifies the calculation of the stress-depth and strain-depth profiles. A disc with a considerable thickness compared to the nitrided depth and the resulting assumption about its stress and strain state is illustrated in Figure 3.

Figure 3 – Illustration of the modelled geometry and the mechanical assumptions, which follows from an infinitely large plate with parallel, flat surfaces.

The assumptions follow the procedure originally put forward by Boley and Weiner [23] for analyzing thermal stresses in a free plate with temperature variation through the thickness only. This has been used previously in literature for the analysis of stresses in-depth near the surface by Hattel and Hansen [24][25] and later by Jespersen et al. [15]:

- The surface is free to deform and is therefore stress-free in the direction perpendicular to it: $\sigma_{33} = 0$ (σ_{33} being parallel to the surface normal).
- The stress state in the surface is described by rotational symmetry and consequently the normal stresses parallel to the surface are equal: $\sigma_{11} = \sigma_{22} = \sigma(z)$.
- A consequence of no bending is the uniform expansion throughout the depth: $\epsilon_{11}^{tot} = \epsilon_{22}^{tot} = \epsilon^{tot}$.
- Another consequence of no bending in combination with the assumption of isotropic elasticity is that the elastic shear strain (and thereof stress) components are zero: $\epsilon_{12}^{el} = \epsilon_{13}^{el} = \epsilon_{23}^{el} = 0$ and $\sigma_{12} = \sigma_{13} = \sigma_{23} = 0$.

The total strain is expressed as the sum of all contributing strains:

$$\epsilon^{tot} = \epsilon^{el} + \epsilon^{pl} + \epsilon^{ch} + \epsilon^{th} \quad (10)$$

where ε^{pl} is the plastic strain, ε^{ch} is the chemical strain and ε^{th} is the thermal strain.

An important consequence of the no-bending assumption above is the formulation of an in-depth force equilibrium in terms of the in-plane stress distribution, which is expressed in an integral manner, i.e.:

$$F = \int_0^d \sigma(z) * dz = \int_0^d \frac{E(z)}{1-\nu} * \varepsilon^{el}(z) * dz = 0 \quad (11)$$

where $d=L/2$ is half of the total depth (thickness) of the domain. From Eq. 10 we obtain the elastic strain as:

$$\varepsilon^{el}(z) = \varepsilon^{tot} - (\varepsilon^{pl}(z) + \varepsilon^{ch}(z) + \varepsilon^{th}(z)) \quad (12)$$

By substitution, a single point evaluation of the force equilibrium in terms of the average total strain, ε^{tot} , which is valid for the whole depth, can be obtained:

$$F = \int_0^d \frac{E(z)}{1-\nu} * (\varepsilon^{tot} - \varepsilon^{pl}(z) - \varepsilon^{ch}(z) - \varepsilon^{th}(z)) * dz = 0 \quad (13a)$$

$$\int_0^d \frac{E(z)}{1-\nu} * \varepsilon^{tot} * dz = \int_0^d \frac{E(z)}{1-\nu} * (\varepsilon^{pl}(z) + \varepsilon^{ch}(z) + \varepsilon^{th}(z)) * dz \quad (13b)$$

$$\varepsilon^{tot} = \frac{\int_0^d \frac{dE(z)}{1-\nu} * (\varepsilon^{pl}(z) + \varepsilon^{ch}(z) + \varepsilon^{th}(z)) * dz}{\int_0^d \frac{dE(z)}{1-\nu} * dz} \quad (13c)$$

2.2.2. Plane-stress elasto-plasticity

The plane stress elasto-plasticity model is a projection of the generalized three-dimensional model with a von Mises yield surface and isotropic strain hardening [26]. The modified model is obtained by applying expressions relating the elastic and plastic strain components in the third direction, which is perpendicular to the plane of the surface, to those in the first and second in-

plane directions. Thereby only the in-plane stress and strain components are involved in determining the yield surface and strain hardening coefficient, while the out of plane components are obtained subsequently.

Considering the general stress and strain relations for a plane-stress state, the elastic strain in the direction normal to the surface follows from setting $\sigma_{13} = \sigma_{23} = \sigma_{33}$ equal to zero, following the previous assumption of the surface being able to freely move perpendicular to the plane. For a homogeneous isotropic linear elastic material, the third stress component can be expressed in terms of the bulk modulus (K) and shear modulus (G):

$$\sigma_{33} = K(\varepsilon_{11}^{el} + \varepsilon_{22}^{el} + \varepsilon_{33}^{el}) + 2G\left(\varepsilon_{33}^{el} - \frac{1}{3}(\varepsilon_{11}^{el} + \varepsilon_{22}^{el} + \varepsilon_{33}^{el})\right) = 0 \quad (14)$$

The *elastic* strain normal to the surface then becomes:

$$\varepsilon_{33}^{el} = \frac{\nu(\varepsilon_{11}^{el} + \varepsilon_{22}^{el})}{(\nu - 1)} \quad (15)$$

In the case of *plastic* strain, the relation comes from plastic incompressibility:

$$\varepsilon_{33}^{pl} = -(\varepsilon_{11}^{pl} + \varepsilon_{22}^{pl}) \quad (16)$$

Using the two equations defining the elastic and plastic strain relations (Eqs. 15 and 16), a set of new equations can be formulated, where the third (out of plane) direction is omitted, since it is ‘projected’ onto the in-plane directions. Eqs. 15 and 16 constitute the set of equations representing plane stress.

Expanded austenite is not linear elastic, neither is it elastic- and plastically isotropic. However due to the restriction of a one-dimensional model to resolve anisotropic behavior, the following plasticity model is assumed to approximate an averaged elastic and plastic isotropic behavior.

Thereby the set of equations for the von Mises model with isotropic strain hardening becomes:

$$\Phi = \sqrt{\frac{3}{2} \left[\sigma_{\alpha\beta} \sigma_{\alpha\beta} - \frac{1}{3} (\sigma_{\alpha\alpha})^2 \right]} - \sigma_y(c_N, T, \bar{\epsilon}^{pl}) \quad (17)$$

$$\dot{\epsilon}_{\alpha\beta}^{pl} = \dot{\gamma} \sqrt{\frac{3}{2} \frac{s_{\alpha\beta}}{\sqrt{\sigma_{\gamma\delta} \sigma_{\gamma\delta} - \frac{1}{3} (\sigma_{\gamma\gamma})^2}}} \quad (18)$$

where $\alpha, \beta, \gamma, \delta = (1, 2)$ and Φ is the yield function. The yield strength $\sigma_y(c_N, T, \bar{\epsilon}^{pl})$ is a function of the concentration, temperature and equivalent plastic strain. The concentration-dependent strengthening was determined from cross-sectional hardness profiles for low temperature nitrided 316L [27] and the temperature and strain hardening were determined for the untreated 316L using a Gleeble 1500 thermal-cycle simulation instrument. After calculating an initial elastic predictor state, in case of a pure *elastic* state, the state variables are updated with the trial *elastic* state variables. However, if the yield function is not satisfied ($\Phi \not\leq 0$), a return-mapping algorithm [28] is applied and the equations are iteratively solved by the Newton-Raphson method and thereby the equilibrium equations and the plane stress assumption is solved to a pre-determined level of accuracy.

2.2.3. Chemically induced strains

The volumetric expansion due to the interstitial nitrogen atoms is described with a composition-induced chemical strain in one of three principal directions. Assuming isotropic chemical strain, it is then simply the volumetric expansion with respect to the reference volume for which no nitrogen atoms are interstitially occupied:

$$\epsilon_{ij}^{ch} = \frac{V(y_N)^{1/3} - V_{ref}^{1/3}}{V_{ref}^{1/3}} \quad \text{for} \quad i=j \quad (19)$$

where the concentration-dependent volume of the metal lattice $V(y_N)$, with y_N the number of N atoms per metal atom, is described by the following polynomial fit to experimental lattice parameter data [8], [15]:

$$V(y_N) = 2.8147 \cdot 10^{-29} * y_N + 4.7134 * 10^{-29} \quad (20)$$

and the reference volume V_{ref} is obtained from the nitrogen-free lattice.

2.2.4. Thermally induced strains

The thermal strain is of little effect in the case of a uniform coefficient of thermal expansion (CTE) combined with a small temperature gradient. However, for a given range of interstitial nitrogen contents, the CTE in the paramagnetic expanded austenite changes considerably [29] [3]. Furthermore, the CTE is lower below the Curie temperature in ferromagnetic expanded austenite than in paramagnetic expanded austenite above the Curie temperature, due to positive volume magnetostriction. The difference in CTE makes thermal expansion and associated strains significant upon cooling after nitriding.

The thermal strain is given by the product of the CTE, α , and the temperature change from a non-strained reference temperature, ΔT :

$$\varepsilon_{ij}^{th} = \alpha \Delta T \quad \text{for} \quad i=j \quad (21)$$

Below the Curie temperature, α is simply a weighted mixture of the two magnetic states:

$$\alpha_v = w * \alpha^{ferro} + (1 - w) * \alpha^{para} \quad (22)$$

and α^{ferro} and α^{para} are functions of the interstitial nitrogen content in the ferromagnetic and paramagnetic states, determined in [29].

2.3. Computational Procedure

2.3.1. Control volume based formulation of the heat conduction equation

A control-volume based finite difference discretization of the heat transfer equation (Eq. 2), is obtained by the use of resistance terms $r = \frac{\Delta z}{2 \cdot k}$, where the temperature at the new time-step is the sum of the solution at the old time-step and the accumulated incremental contributions $T_i^{t+\Delta t} = T_i^t + \Delta T$. Here $\Delta T = \sum_{j=1}^{n_{iter}} \delta T$ is the sum of the incremental solutions of all iterations for a given time-step. The heat transfer problem is solved directly with a tri-diagonal matrix algorithm (TDMA), where the material properties are updated iteratively until the solution has converged. The discretized implicit resistance approach is then expressed as:

$$\rho c_p \frac{\Delta z}{\Delta t} (T_i^{t+\Delta t} - T_i^t) = \frac{(T_{i-1}^{t+\Delta t} - T_i^{t+\Delta t})}{\frac{\Delta z_{i-1}}{2k_{i-1}^{t+\Delta t}} + \frac{\Delta z_i}{2k_i^{t+\Delta t}}} + \frac{(T_{i+1}^{t+\Delta t} - T_i^{t+\Delta t})}{\frac{\Delta z_{i+1}}{2k_{i+1}^{t+\Delta t}} + \frac{\Delta z_i}{2k_i^{t+\Delta t}}} \quad (23)$$

where i is the spatial index.

2.3.2. Mixed implicit control-volume based-/classical finite difference formulation of the modified Fick's 2nd law

The hydrostatic stress (pressure) and temperature gradient dependent diffusion was previously discretized in [15] by using the classical finite difference method combined with explicit time integration. A similar approach is used for the pressure and temperature terms here; however the concentration gradients are determined by an implicit control volume-based finite difference method [24], which has higher stability. Thereby, the numerical method applied becomes an implicit mixed control-volume based-/classical finite difference formulation. In addition, since the diffusion problem is non-linear due to the concentration dependent diffusion coefficient as well as additional driving forces from the thermal and mechanical gradients, the diffusion solver

is used in an iterative scheme, such that the concentration is in equilibrium with the diffusion coefficient and the gradients of temperature and stress. The control-volume based finite difference discretization of the extended Fick's 2nd law in Eq. 6, is solved by the use of resistance terms, following a similar method as for the heat transfer equation discretized above and solved by using the tridiagonal matrix algorithm. The discretized implicit mixed resistance/classical finite difference approach is then expressed as:

$$\begin{aligned}
 \frac{\Delta z}{\Delta t} (c_i^{t+\Delta t} - c_i^t) &= \frac{(c_{i-1}^{t+\Delta t} - c_i^{t+\Delta t})}{\frac{\Delta z_{i-1}}{2D_{i-1}^{t+\Delta t}} + \frac{\Delta z_i}{2D_i^{t+\Delta t}}} + \frac{(c_{i+1}^{t+\Delta t} - c_i^{t+\Delta t})}{\frac{\Delta z_{i+1}}{2D_{i+1}^{t+\Delta t}} + \frac{\Delta z_i}{2D_i^{t+\Delta t}}} \\
 - \frac{\left(\frac{D_{N_{i+1}}^{t+\Delta t}}{T_{i+1}^{t+\Delta t}} \cdot \frac{K_N^{i+1}}{\frac{\partial K_N}{\partial c_N}} - \frac{D_{N_{i-1}}^{t+\Delta t}}{T_{i-1}^{t+\Delta t}} \cdot \frac{K_N^{i-1}}{\frac{\partial K_N}{\partial c_N}} \right)}{2} \cdot \frac{V_N}{R} \cdot \frac{(\sigma_{H_{i+1}}^{t+\Delta t} - \sigma_{H_{i-1}}^{t+\Delta t})}{2\Delta z} - D_{N_i}^{t+\Delta t} \cdot \frac{K_N}{\frac{\partial K_N}{\partial c_N}} \cdot \frac{V_N}{R \cdot T_i^{t+\Delta t}} \\
 \cdot \frac{(\sigma_{H_{i+1}}^{t+\Delta t} - 2\sigma_{H_i}^{t+\Delta t} + \sigma_{H_{i-1}}^{t+\Delta t})}{\Delta z} \\
 + \frac{\left(\frac{D_{N_{i+1}}^{t+\Delta t}}{T_{i+1}^{t+\Delta t}} \cdot \frac{K_N^{i+1}}{\frac{\partial K_N}{\partial c_N}} \ln(K_T^{t+\Delta t} \cdot K_N^{i+1}) - \frac{D_{N_{i-1}}^{t+\Delta t}}{T_{i-1}^{t+\Delta t}} \cdot \frac{K_N^{i-1}}{\frac{\partial K_N}{\partial c_N}} \ln(K_T^{t+\Delta t} \cdot K_N^{i-1}) \right)}{2} \cdot \frac{(T_{i+1}^{t+\Delta t} - T_{i-1}^{t+\Delta t})}{2\Delta z} + \frac{D_{N_i}^{t+\Delta t}}{\frac{\partial K_N}{\partial c_N}} \cdot \frac{K_N^i}{T_i^{t+\Delta t}} \cdot \\
 \ln(K_T \cdot K_N^i) \cdot \frac{(T_{i+1}^{t+\Delta t} - 2T_i^{t+\Delta t} + T_{i-1}^{t+\Delta t})}{\Delta z} \quad (24)
 \end{aligned}$$

The full diffusion problem is solved with material properties prescribed at the new time level.

3.1. Mechanics

3.1.1. Force equilibrium

Considering non-constant element length in the depth, a node index is introduced to Eq. 13c. The elastic strain is temperature dependent and depends on the element's distance from the surface. However, the Poisson ratio is assumed constant, by which it is omitted from the force equilibrium equation. Furthermore, the force equilibrium has to hold for the whole depth. Hence, the numerical discretization of Eq. 13c is simply obtained by introducing a numerical summation over all elements:

$$\bar{\varepsilon}^{tot} = \frac{\sum_{i=1}^n E(T)_i (\varepsilon_i^{pl} + \varepsilon_i^{ch} + \varepsilon_i^{th}) \cdot dz_i}{\sum_{i=1}^n E(T)_i dz_i} \quad (25)$$

where n is the total number of elements. Thus, a single-point evaluation that ensures force equilibrium for the whole system considering the contribution from the thermal-, chemical- and plastic strains and temperature dependent elastic modulus is obtained.

3.1.2. The elastic predictor and the Newton-Raphson solution to the return-mapping algorithm for plasticity

An initial guess is made assuming purely elastic strain and defining a trial state:

$$\varepsilon_{n+1}^{el,trial} = \varepsilon_n^{el} + \Delta \varepsilon^{el} \quad (26)$$

where the elastic strain increment is found from the sum of all strains $\Delta \varepsilon^{el} = \Delta \varepsilon^{tot} - \Delta \varepsilon^{ch} - \Delta \varepsilon^{th}$ and

$$\sigma_{n+1}^{trial} = \mathbf{D}^e \varepsilon_{n+1}^{el,trial} \quad (27)$$

$$\bar{\varepsilon}_{n+1}^{pl} = \bar{\varepsilon}_n^{pl} \quad (28)$$

where $\mathbf{D}$ is the plane stress elasticity matrix. The assumed elastic stress state is tested by the trial yield function Φ^{trial} , which is essentially the squared form of the yield function in Eq. 17:

$$\Phi^{trial} = \frac{1}{2}\xi^{trial} - \frac{1}{3}\sigma_y^2(c_{N_{n+1}}, T_{n+1}, \bar{\epsilon}_{n+1}^{pl}) \quad (29)$$

$$\xi^{trial} = \frac{1}{6}(\sigma_{11}^{trial} + \sigma_{22}^{trial})^2 + \frac{1}{2}(\sigma_{22}^{trial} - \sigma_{11}^{trial})^2 \quad (30)$$

If $\Phi^{trial} \leq 0$ then the current variables are updated with trial values. However, if the yield criterion is not satisfied, the nonlinear equation $\tilde{\Phi}(\Delta\gamma) = 0$ is solved by the Newton-Raphson algorithm in combination with the return-mapping algorithm. An initial guess for the plastic multiplier $\Delta\gamma = 0$ is applied for the residual $\tilde{\Phi}$ in Eqs. 29 and 30. Newton-Raphson is then performed on the following set of equations that express the hardening modulus H , the residual derivative $\tilde{\Phi}'$ and the new guess for the plastic multiplier $\Delta\gamma$:

$$H = \frac{d\sigma_y}{d\bar{\epsilon}^{pl}} \quad (31)$$

$$\xi' = -\frac{(\sigma_{11}^{trial} + \sigma_{22}^{trial})^2}{9\left[1 + \frac{E\Delta\gamma}{3(1-\nu)}\right]^3} \frac{E}{(1-\nu)} - 2G \frac{(\sigma_{22}^{trial} - \sigma_{11}^{trial})^2}{(1+2G\Delta\gamma)^3} \quad (32)$$

$$\bar{H} = 2\sigma_y \left(c_{N_{n+1}}, T_{n+1}, \bar{\epsilon}_n^{pl} + \Delta\gamma \sqrt{\frac{2}{3}\xi} \right) H \sqrt{\frac{2}{3}} \left(\sqrt{\xi} + \frac{\Delta\gamma \xi'}{2\sqrt{\xi}} \right) \quad (33)$$

$$\tilde{\Phi}' = \frac{1}{2}\xi' - \frac{1}{3}\bar{H} \quad (34)$$

$$\Delta\gamma = \Delta\gamma - \frac{\tilde{\Phi}}{\tilde{\Phi}'} \quad (35)$$

The convergence is evaluated by checking if the residual is below a preset tolerance $|\tilde{\Phi}| \leq \epsilon$:

$$\xi = \frac{(\sigma_{11}^{trial} + \sigma_{22}^{trial})^2}{6\left[1 + \frac{E\Delta\gamma}{3(1-\nu)}\right]^2} + \frac{\frac{1}{2}(\sigma_{22}^{trial} - \sigma_{11}^{trial})^2}{(1+2G\Delta\gamma)^2} \quad (36)$$

$$\tilde{\Phi} = \frac{1}{2}\xi - \frac{1}{3}\sigma_y^2 \left(c_{N_{n+1}}, T_{n+1}, \bar{\epsilon}_n^{pl} + \Delta\gamma \sqrt{\frac{2}{3}\xi} \right) \quad (37)$$

Finally, the stress, elastic- and equivalent plastic strains are updated:

$$\boldsymbol{\sigma}_{n+1} = \mathbf{A}(\Delta\gamma)\boldsymbol{\sigma}_{n+1}^{trial} \quad (38)$$

$$\boldsymbol{\varepsilon}_{n+1}^{el,trial} = \mathbf{C}\boldsymbol{\sigma}_{n+1} \quad (39)$$

$$\bar{\varepsilon}_{n+1}^{pl} = \bar{\varepsilon}_n^{pl} + \Delta\gamma \sqrt{\frac{2}{3}\xi(\Delta\gamma)} \quad (40)$$

where $\mathbf{C}$ is the inverse of the plane stress elastic matrix $\mathbf{C} \equiv (\mathbf{D}^e)^{-1}$, $\mathbf{A}$ is a matrix relating the trial stresses to the updated stress tensor $\mathbf{A}(\Delta\gamma) \equiv [\mathbf{C} + \Delta\gamma\mathbf{P}]^{-1}\mathbf{C}$, where $\mathbf{P}$ is a matrix relating the stresses σ to the array of plane deviator components s .

3.2. Properties, boundary conditions and domain

The yield strength of the 316L material was determined from its temperature and work hardening for the un-nitrided austenite and the concentration dependent strengthening, in such a way that the individual yield stress contributions were additively summed:

$$\sigma_y = \sigma_0(c_N, T) + H * \bar{\varepsilon}^{pl} \quad (41)$$

The non-linear diffusion coefficient of nitrogen is following a Lorentzian distribution with a simple Arrhenius type temperature dependence. The temperature dependence is experimentally validated in the temperature range 693-718K.

Table I: Material properties and simulation parameters for low temperature gas nitriding of 316L.

Young's Modulus, $E(T)$	Poisson's ratio, ν	Yield strength, $\sigma_y(c, T, \bar{\varepsilon}^{pl})$	Diffusion coefficient, $D(c)$	Thermal diffusivity, $\alpha_v(T)$	Thermal expansion coefficient, $\alpha_v(T)$	Heat transfer coefficient, h
160-193 GPa	0.3	180-4100 MPa	$0.3 - 5.9 * 10^{-15} \text{ m}^2/\text{s}$	$5.4 * 10^{-6} \text{ m}^2/\text{s}$	$8.9 - 10.3 * 10^{-6}$	30 W/m ² K

The boundary conditions are applied at the surface and at the symmetry line. These are illustrated in Figure 4 for the thermal and diffusion problem. The selected heat transfer coefficient corresponds to the case of forced convection of a gas [30]. It is remarked that the diffusion problem is insensitive to the actual value chosen for the heat transfer coefficient, since the time scale of heating and cooling is very short compared to the time scale of diffusion. For the diffusion, the flux through the surface is controlled by the reaction rate, which is the proportionality constant between flux through the surface, j_{surf} , and the concentration difference between equilibrium (as imposed by the gas composition, i.e. K_N) and the actual surface concentration, Δc .

Figure 4 - Illustration of mesh size and boundary conditions for the solution variables concentration and temperature. The boundary conditions for the diffusion problem are governed by the equilibrium concentration C_N^{eq} , surface concentration C_N^{surf} and the reaction rate coefficient k_{rate} . The boundary conditions for the heat transfer problem are governed by the furnace temperature T^{furnace} , the surface temperature T^{surf} and the heat transfer coefficient h .

The equilibrium concentration is implemented via a ghost cell and the surface concentration at the surface. At the symmetry line, a Neumann boundary condition with zero flux is enforced.

Analogously, for the temperature, a heat transfer coefficient between the furnace temperature and

surface temperature is employed, assuming convective flow in the furnace (see Table). The symmetry boundary condition is similar to that of the diffusion problem. The domain consists of two mesh sizes: a fine mesh for the surface adjacent region resolving the full concentration depth with 60 elements of $0.5\mu\text{m}$ length and a coarse mesh for the substrate region of no nitrogen content with 30 elements of $44\mu\text{m}$ length. The domain has a line symmetry at the center of the disc and the total thickness of $L = 2 \cdot d = 2.7 \text{ mm}$. It should be noted that all elements obviously contribute to the force equilibrium expression in Eq. 27.

4. Results

Experimentally, the evolution of the total nitrogen content absorbed was determined with thermogravimetric analysis (TGA) in a Netzsch STA 449 F3 simultaneous thermal analyzer on $\varnothing 16 \times 2.7 \text{ mm}$ AISI 316 discs at 693 K. The nitriding potentials (K_N) imposed by $\text{NH}_3\text{-H}_2$ gas mixtures were 2.49 (60-40% $\text{NH}_3\text{-H}_2$), 9.38 (80-20% $\text{NH}_3\text{-H}_2$) and infinity (100% NH_3) and the nitriding time was 14h. Prior to nitriding the specimens were stripped from their protective chromium oxide layer by a proprietary in-situ activation step. After nitriding, the concentration profiles were determined by glow discharge optical emission spectroscopy (GD-OES) in a Horiba Jobin Yvon GD Profiler 2.

Numerical simulation of the evolution of composition profiles for the three experimentally applied nitriding conditions were done under the assumption that a moderate amount of trapping of nitrogen by chromium atoms takes place. A crude estimation from the retractable and non-retractable nitrogen gives a solubility product of $K_{CrN_n} = 4.5 \cdot 10^7$. However, a better correspondence with experimental results was achieved with a similar, but slightly lower threshold of $K_{CrN_n} = 1.5 \cdot 10^7$. Initially, the surface reaction (Eq. 9b) is assumed to be infinitely rapid, implying that the mass uptake is entirely controlled by solid state diffusion, which provides

the theoretical maximum uptake. A comparison of the experimental results from thermogravimetry and GD-OES and the simulated mass uptake curves as a function of time is given in Figure 5.

Figure 5 - Comparison of experimental (drawn lines and symbols) and simulated (dashed lines) mass-uptake as a function of nitriding time for the indicated nitriding potentials K_N . The simulated profiles were obtained under the assumption that the surface reaction is infinitely rapid, so that nitrogen uptake is governed by solid state diffusion only.

Figure 6(a) Evolution of the effective k -rate as a function of the surface concentration and (b) evolution of the surface concentration and the concentration that would be obtained if equilibrium between gas and solid is achieved with time.

Evidently, the simulated nitrogen uptake for the case that the surface reaction (Eq. 9a) is assumed to be infinitely rapid is appreciably faster in the initial stage than the experimental nitrogen uptake. The discrepancy is assumed to be caused by the slow kinetics of the ammonia dissociation at the stainless steel surface. The comparison in Figure 5 also shows that there is a potential for much faster nitriding, provided that the rate of the surface reaction can be accelerated. A good agreement is found between the uptake measured by TGA, considering the additional uptake from the area represented by the disc wall thickness, and the final uptake calculated from GD-OES profiles (symbols in Figure 5). Next, the evolution of the nitrogen uptake was simulated by inverse modelling with the effective k_{rate} as a fit parameter and taking the experimental nitrogen uptake in Figure 5 as a constraint. The simulated reaction rate is the effective rate, since a change in surface area is not taken into account. From inverse modelling, the evolution of k_{rate} with the surface concentration and the evolution of the surface concentration with time are obtained (Figure 6a-b).

Initially, the surface concentrations evolve non-linearly because of the relatively slow, but accelerating, rate of ammonia dissociation at the surface (cf. Eq. 9b). The equilibrium

concentrations, i.e. the nitrogen concentrations imposed by the gas mixture and obtained in the solid under a (local) equilibrium condition (that includes the state of stress), decreases as a consequence of the hydrostatic stress that builds up in the solid upon dissolving nitrogen. The time to reach leveling off of the surface concentration and reaching a more or less constant value for the equilibrium concentration, is approximately $t=0.5, 2.5$ and 5 hours for potentials $K_N = \infty, 9.38$ and 2.49 , respectively. Obviously, under the experimental conditions applied here, no local equilibrium is achieved within the 14 h treatment time, but rather a steady state appears to have developed for all conditions, as reflected by the more or less constant difference between equilibrium and actual surface concentrations (Figure 6b). The obtained evolutions of k_{rate} with the surface concentration appear to be consistent for the two lowest nitriding potentials (Figure 6b), where a relatively steep increase is observed for surface concentrations in the range 18×10^3 to $23 \times 10^3 \text{ mol.m}^{-3}$. For the highest nitriding potential an appreciably higher k_{rate} is observed for the lower surface concentration range ($< 18 \times 10^3 \text{ mol.m}^{-3}$). The concentration-depth profiles after 14 h nitriding as obtained by the abovementioned inverse modelling, are given in Figure 7a. The strain profiles induced by the composition-depth profile (ϵ^{ch}) and the cooling from 693 K to 298 K (ϵ^{th}) are presented in Figure 7b. Obviously, the composition-induced strain dominates (by far) over the thermal strain. The elastic and plastic strains in the direction perpendicular to the surface are shown in Figure 7c. Evidently, the plastic strains are up to $6-7$ times as high as the elastic strains. Figure 7c explains the origin of the kinks in the concentration (and ϵ^{ch}) profiles at approximately $15 \times 10^3 \text{ mol.m}^{-3}$. Above this concentration the elastic strain remains constant, implying that only for lower concentrations does an elastic stress gradient contribute to the driving force for diffusion. Thus, the kinks mark the depth below which a stress gradient-induced diffusive flux has contributed to the concentration profile. Apparently, for concentrations beyond $15 \times 10^3 \text{ mol.m}^{-3}$ additional chemical strain is entirely accommodated plastically, which leads to

the important notion that, within the assumptions of the present model, the increase in k_{rate} as observed in Figure 6b is a consequence of plastic deformation.

Figure 7(a) Simulated nitrogen concentration-depth profiles obtained by inverse modelling for a nitriding time of 14 h at 693 K in the nitriding potentials indicated in the legend; (b) profiles of chemical and thermal strains associated with the concentration profiles in (a); (c) elastic and plastic strains in the direction perpendicular to the surface corresponding to (a).

Figure 8(a) Stresses within the plane of the surface as a function of depth for a temperature of 693K and (b) an illustration of the symmetric in-plane stress-depth distribution. The inset in Figure 8(a) shows the stress levels in the core of the 2.7mm thick disc.

The maximum compressive stress at 293K for the principal in-plane directions, σ_{11} and σ_{22} , is approximately 4.1 GPa for all potentials Figure 8(a). The symmetric stress distribution with a centerline at half thickness is schematically shown in Figure 8(b). Approaching from the surface towards the substrate, the following is observed. The small differences in the stress value at the surface and the slight decline in compressive stress within the plateau are caused by the assumption that limited work hardening occurs in expanded austenite. The steep decrease of the compressive stress value indicates the region where the solid solution strengthening effect is strongly concentration dependent. On reaching the unaffected stainless steel the stress level changes from compressive to modest tensile stress of 17, 23 and 26 MPa for the lowest, intermediate and highest nitriding potential, respectively. This is an immediate consequence of the assumption of force equilibrium in combination with the shallow case depth as compared to a relatively thick specimen.

The swelling thickness, i.e. the additional thickness of the nitrided surface compared to the unnitrided surface, is estimated from the total strain in the direction of the surface normal. The plastic deformation depth is determined by the last element with plastic strain. The case depth of expanded austenite is here taken as the depth where the concentration has reached 1 at% nitrogen. These parameters are given in the following table for 3, 8 and 14 hours nitriding treatment.

Table II - Simulated swelling thickness, plastic deformation depth and case depth at $t=3, 8$ and 14 h. gas nitriding treatment.

	K_N	3 h.	8 h.	14 h.
Swelling thickness [μm]	2.49	0.02	0.19	0.36
	9.38	0.10	0.39	0.60
	∞	0.24	0.50	0.78
Plastic deformation depth [μm]	2.49	0.7	3.4	5.9
	9.38	2.6	5.8	8.6
	∞	3.4	6.3	9.0
Case depth for 1 at% [μm]	2.49	1.3	4.1	6.8
	9.38	2.6	5.8	8.6
	∞	3.8	7.0	9.8

5. Discussion

5.1. The rate of the surface reaction during gas nitriding

The importance of the rate of the surface reaction on nitriding in ammonia/hydrogen gas mixtures has been a subject of study for many years. The seminal work by Grabke in the sixties on the

nitriding kinetics of very thin foils, demonstrated that ammonia dissociation does not proceed infinitely rapidly and that for temperatures above about 723 K the surface concentration on pure iron foils depends on the competition between ammonia

Figure 9 – the reaction rate at the surface of 316L during nitriding with potentials $K_N=2.49$, 9.38 and ∞ at $T=693K$ estimated from the inverse model and estimated rates during de-nitriding from Grabke [21] for iron at $T=693K$ in varying H₂/Argon gas mixture.

dissociation and the desorption of molecular nitrogen [21]. Rozendaal, et al. demonstrated that the competition between ammonia dissociation rate at the surface and nitrogen diffusion into the solid state can explain the gradual increase of the surface concentration and the occurrence of an incubation time for iron-nitride development [31]. Later, also the role of the molecular nitrogen desorption on the incubation time for iron nitride formation was included [32]. For the present case of low temperature nitriding of austenitic stainless steel, the desorption of N₂ can be omitted,

because of the low nitriding temperature of 693 K. The minimum and maximum values for k_{rate} for AISI 316 at 693 K as determined by inverse modelling (cf. Figure 6a) are compared to the values for k_{rate} applying for de-nitriding of *pure iron* at 693 K in diss. The data from Grabke [21] apply for the de-nitriding of nitrided ferrite foils, with very low nitrogen contents, in various partial pressures of hydrogen in Ar-H₂ gas mixtures, while the data from the present work apply to nitriding in NH₃/H₂ gas mixtures and pertain to high nitrogen contents. The reaction rates assessed in the present work, are a factor 100 lower than those found experimentally for iron. As a side note, the oscillations observed for the reaction rates for high surface concentrations are a direct consequence of the experimental nitrogen uptake curves from TGA. Assuming a linear nitrogen uptake as a function of time, similar reaction rates are obtained for the higher nitrogen contents but without the oscillations, which is caused by the ill-posed nature of the inverse problem. On comparing the reaction rates obtained experimentally by Grabke for iron (b.c.c.) and those obtained in the present work by inverse modelling for expanded austenite (f.c.c.), the following important differences have to be considered. Firstly, the crystal structures for the two phases are different. Secondly, the solubility of nitrogen in b.c.c. iron is very low for the applied temperatures (max. 0.075 N atoms per 100 metal atoms at 773K), while it is max. 61 N atoms per 100 metal atoms for expanded austenite, i.e. approx. 800 times as high!). The narrow solubility range for N in b.c.c. Fe justifies Grabke's assumption that k_{rate} is independent of the nitrogen content in solid solution. A similar assumption is not justified for the case of expanded austenite, because the dissolution of nitrogen in f.c.c. leads to a volume expansion of the austenite lattice by about 36% for the highest nitrogen content, which will affect the adsorption and desorption kinetics. Moreover, the onset of plastic deformation leads to slip lines and associated enlargement of the surface area, thus providing more lattice sites for ammonia adsorption and subsequent

decomposition [9]. As a consequence the value for k_{rate} changes with the surface concentration of nitrogen in expanded austenite, which explains the range of values shown in Figure 6a.

5.2. Comparison of simulated to experimental concentration profiles

The simulated nitrogen concentration-depth profiles are compared to experimental profiles determined by glow discharge optical emission spectroscopy in Figure 10. The experimental profiles were measured on the thermogravimetry specimens nitrided for 14 h under the conditions mentioned earlier and used for inverse modelling of the evolution of the nitrogen uptake. Note that these profiles were not used in the inverse modelling. This could have been done, provided that additional parameters in the model, for example the concentration-dependent diffusion coefficient were adopted as fitting parameters. Obtaining a perfect fit is not the prime purpose of this research. Rather, the purpose is to verify the influence of essential physical parameters, taking the fundamental data obtained on homogenous thin foils as input parameters. Still, a comparison between the simulated and experimental profiles shows a surprisingly good match. Of course this is partly due to the good agreement between the TGA and GD-OES measurements in terms of total nitrogen uptake per area. However, the shape of the experimental and simulated profiles are concave and deviate markedly from the complementary error function profiles obtained for constant diffusion coefficients. Furthermore, the treatment depth matches quite closely for the intermediate and high potential, whereas the low potential deviates slightly, partly due to having the largest deviation between TGA and GD-OES uptake. Comparing the surface-near region, the inverse model slightly and consistently underestimates the surface concentration. Whether this is related to a measurement artifact from GD-OES, the predicted equilibrium concentration in the surface or due to differences in concentration profiles of different grain orientations is not known. Both the nitrogen intensity and the sputter rate depend non-linearly on the nitrogen concentration, leading to non-linearity along both axes for the experimental profiles

in Figure 10. Furthermore, from literature investigations on polycrystalline material and our own investigations on single crystals [33], it is known that the depth of expanded austenite is (strongly) hkl dependent. Consequently, during GD-OES an average is obtained over many grain orientations, which will smear out the effect of details in individual grains. For this reason, GD-OES will not be able to demonstrate the kinks indicating a contribution of stress-gradient induced diffusion, which will occur at different depths for different hkl. Lastly, preferential and forward sputtering effects occurring during GD-OES will lead to a general smearing of concentration profiles. Seen in this light, the agreement between the simulated and the measured profiles is convincing.

Figure 10 - Comparison of simulated and experimental glow discharge optical emission spectroscopy nitrogen-concentration profiles for the nitriding conditions indicated.

5.3. Applicability of the model description to plasma nitriding of stainless steel

The present model was developed for the numerical multi-physics simulation of composition and residual stress profiles in expanded austenite during low temperature nitriding. In the present work in particular the role of the surface reaction during gaseous nitriding was considered and led to a satisfactory agreement. The first nitriding of stainless steels at low temperature leading to expanded austenite was achieved in a plasma; also the majority of the literature on expanded austenite formation on austenitic stainless steels in fact deals with plasma nitriding. The main reason for this is that surface activation, implying stripping of the passive layer, is an inherent sputtering step in plasma processing. Here, the comprehensive data published by Templier, et al. [34] and Stinville, et al. [9] are used to verify the qualitative and quantitative applicability of the present model description. The evolution of nitrogen concentration-depth profiles during plasma nitriding at 400 °C is shown in [34], where in Figure 1a it is observed that for nitriding times up to 3h the surface concentration increases up to 33 at.%, whereafter it remains constant. This observation indicates that also plasma nitriding could be considered to be characterized by an effective surface reaction, albeit much faster for the current plasma nitriding conditions than for the gaseous nitriding experiments described in the results section of this article. The nitrogen content of 33 at% suggests that ϵ -phase has developed here. For treatment times longer than 1 h, the composition profiles as determined with GD-OES show an initial steep decrease in nitrogen content. At the case-core transition a tail develops, which becomes more pronounced with nitriding time. This tail penetrates deeper with increasing treatment time. The reason for its emergence is two-fold. Firstly, it is this depth region where a gradient in the residual stress contributes to a nitrogen diffusion flux (see above). Secondly, the depth range of expanded austenite is hkl dependent, implying that averaging over many grain orientations, as during profiling with GD-OES, provides an average of various hkl dependent N-profiles. In addition, it was commented that the samples did not have the same texture [5].

To mimic plasma nitriding and the associated fast surface reaction, a constant and high effective reaction rate of $k_{rate} = 2 * 10^{-9}$ and an effective nitriding potential $K_N = 100$ were assumed in order to reflect the efficiency of plasma processing in transferring nitrogen to the solid state. The concentration dependent diffusion coefficient was extrapolated to 400 °C.

Figure 11 – concentration profiles from prediction of plasma nitriding.

Comparing the concentration profiles in Figure 11 to the GD-OES profiles in [34], an excellent agreement is observed for 1, 3 and 8 hours of nitriding. The predicted concentration is slightly lower in the surface, which is in line with the results for the gaseous nitriding experiments. For 20

Figure 12(a) the simulated layer thickness and (b) swelling thickness calculated from the sum of strains perpendicular to the surface compared to those measured by Stinville et al. [9] for plasma nitrided stainless steel.

and 33 hours, the simulated profiles show a higher nitrogen uptake but a similar case depth. The experimental and simulated evolutions of case depth and swelling during plasma nitriding are compared in Figure 12(a) and (b) and show a satisfactory agreement.

The layer thickness predicted by the isotropic 1D model is expected to follow that of $\langle 100 \rangle$ grains, since this corresponds to the depth at which 1 at. % nitrogen remains. The model slightly overestimates the case depth at 20 and 33h. The higher uptake and slightly larger case depth predicted for 20 and 33 hours as compared to the experiments, is thought to be caused by the formation of new phases (ϵ phase) in the surface and the hkl dependence of the concentration profile as described above. The predicted swelling thickness profile from the plane-stress elasto-plasticity model is centered between those measured for $\langle 100 \rangle$ and $\langle 111 \rangle$ grains. This indicates a correct description of the mechanical response due to the volumetric expansion from the interstitial nitrogen.

Evidently, the model provided in the present work also allows simulation of the evolution of nitrogen-depth profiles during plasma nitriding and thus includes the essential multi-physics parameters concerning the nitrogen profile developing in the solid. For obvious reasons the interaction of the plasma with the solid surface is not included, but can effectively be taken into account by a surface reaction as for gaseous nitriding. Sputtering however is omitted, so case depth reduction by sputtering is not accounted for.

5.4. Limitations of the current model

The current model couples thermal, chemical and mechanical influences during the nitriding of stainless steel in a gaseous environment. The model includes important influences as the finite rate of the surface reaction, stress gradient-induced nitrogen diffusion, trapping of nitrogen by chromium, chemical and thermal strains as well as elastic and plastic accommodation of the

strains accounting for solid solution strengthening. Nevertheless, the model cannot account for the hkl dependence of the expanded austenite case depth, as reported in the literature for single crystals as well as well for polycrystals [35][36]. The main reason for this limitation of the present model is that it relies on input from polycrystalline experiments, averaging over several grain orientations and that it departs from multiaxial stress state and assumes isotropic elasto-plasticity and therefore only considers one direction, i.e. the diffusion direction. It is well-known that austenitic stainless steel is strongly mechanically anisotropic, both elastically and plastically. Incorporation of such anisotropy is the topic of future investigation.

6. Conclusion

Inverse multi-physics modelling of low temperature gaseous nitriding of stainless steels results in a very good agreement between simulated and experimental nitrogen concentration-depth profiles. The agreement is obtained on the basis of thermogravimetry experiment taking the total nitrogen uptake (as provided by thermogravimetry) as a constraint and adopting the surface reaction as the only fit parameter. All other thermodynamics, diffusion kinetics, volume and thermal expansion data was obtained for homogeneously nitrated powders or foils. The one-dimensional thermo-chemical-mechanical finite-difference model provides the following main findings:

- Considerable plastic deformation of up to 9% takes place in expanded austenite during nitriding.
- The surface reaction rate is not constant and probably scales with nitrogen and the amount of plastic deformation in the surface, increasing the lattice parameter and the effective surface area.

- The surface reaction rate for f.c.c. expanded austenite is about two orders of magnitude smaller than for nitriding of b.c.c. iron.
- Assuming a high, constant reaction rate the evolution of composition-depth profiles (and most likely also the associated residual stress profiles) during plasma nitriding can effectively be predicted. Satisfactory agreement is obtained between predicted and experimental case depths and excellent agreement results for the swelling thickness after plasma nitriding.

The good to very good agreement of the present model's predictions with experimental data for gaseous and plasma nitriding, demonstrates that the essential multi-physics parameters governing the evolution of nitrogen concentration-depth profiles (and associated stress profiles) are taken into account, while choosing a minimum of adjustable parameters. This proves that the model is robust and can even be applied for inverse modelling. The main limitation of the model is that it is 1-dimensional and that it assumes elastic and plastic isotropy.

Acknowledgement

Part of this work was supported by the Strategic Research Center "REWIND – Knowledge based engineering for improved reliability of critical wind turbine components," Danish Research Council for Strategic Research, grant no. 10-093966.

References

- [1] T. L. Christiansen and M. A. J. Somers, “Low-temperature gaseous surface hardening of stainless steel: the current status,” *Int. J. Mater. Res.*, vol. 100, no. 10, pp. 1361–1377, Oct. 2009.
- [2] H. L. Che, S. Tong, K. S. Wang, M. K. Lei, and M. A. J. Somers, “Co-existence of γ' N phase and γ N phase on nitrided austenitic Fe–Cr–Ni alloys- I. experiment,” *Acta Mater.*, vol. 177, pp. 35–45, 2019.
- [3] M. A. J. Somers, Ö. C. Küçükyildiz, C. A. Ormstrup, H. Alimadadi, J. H. Hattel, T. L. Christiansen, and G. Winther, “Residual Stress in Expanded Austenite on Stainless Steel; Origin, Measurement, and Prediction,” *Mater. Perform. Charact.*, vol. 7, no. 4, pp. 693–716, Jun. 2018.
- [4] T. L. Christiansen and M. A. J. Somers, “The Influence of Stress on Interstitial Diffusion - Carbon Diffusion Data in The Influence of Stress on Interstitial Diffusion - Carbon Diffusion Data in Austenite Revisited,” *Defect Diffus. Forum*, vol. 297–301, no. April, pp. 1408–1413, 2010.
- [5] J. C. Stinville, P. Villechaise, C. Templier, J. P. Rivière, and M. Drouet, “Lattice rotation induced by plasma nitriding in a 316L polycrystalline stainless steel,” *Acta Mater.*, vol. 58, no. 8, pp. 2814–2821, 2010.
- [6] C. Templier, J. C. Stinville, P. Villechaise, P. O. Renault, G. Abrasonis, J. P. Rivière, A. Martinavičius, and M. Drouet, “On lattice plane rotation and crystallographic structure of the expanded austenite in plasma nitrided AISI 316L steel,” *Surf. Coatings Technol.*, vol. 204, no. 16–17, pp. 2551–2558, 2010.
- [7] Ö. C. Küçükyildiz, F. B. Grumsen, T. L. Christiansen, G. Winther, and M. A. J. Somers, “Submitted work,” 2019.
- [8] T. Christiansen and M. A. J. Somers, “Controlled dissolution of colossal quantities of nitrogen in stainless steel,” *Metall. Mater. Trans. A*, vol. 37, no. 3, pp. 675–682, 2006.
- [9] J. C. Stinville, C. Templier, P. Villechaise, and L. Pichon, “Swelling of 316L austenitic stainless steel induced by plasma nitriding,” *J. Mater. Sci.*, vol. 46, no. 16, pp. 5503–5511, 2011.
- [10] F. Borgioli, A. Fossati, E. Galvanetto, and T. Bacci, “Glow-discharge nitriding of AISI 316L austenitic stainless steel: Influence of treatment temperature,” *Surf. Coatings Technol.*, vol. 200, no. 7, pp. 2474–2480, 2005.
- [11] S. Parascandola, “The nitrogen transport in austenitic stainless steel at moderate temperatures,” *Appl. Phys. Lett.*, vol. 76, no. 16, pp. 2194–2196, 2000.
- [12] A. Galdikas and T. Moskaliuviene, “Stress induced nitrogen diffusion during nitriding of austenitic stainless steel,” *Comput. Mater. Sci.*, vol. 50, no. 2, pp. 796–799, 2010.
- [13] A. Martinavičius, G. Abrasonis, and W. Möller, “Influence of crystal orientation and ion bombardment on the nitrogen diffusivity in single-crystalline austenitic stainless steel,” *J. Appl. Phys.*, vol. 110, no. 7, 2011.

- [14] X. Gu, G. M. Michal, F. Ernst, H. Kahn, and A. H. Heuer, "Numerical Simulations of Carbon and Nitrogen Composition-Depth Profiles in Nitrocarburized Austenitic Stainless Steels," *Metall. Mater. Trans. A*, vol. 45, no. 10, pp. 4268–4279, 2014.
- [15] F. N. Jespersen, J. H. Hattel, and M. A. J. Somers, "Modelling the evolution of composition-and stress-depth profiles in austenitic stainless steels during low-temperature nitriding," *Model. Simul. Mater. Sci. Eng.*, vol. 24, no. 2, p. 31, Feb. 2016.
- [16] T. L. Christiansen and M. A. J. Somers, "Determination of the concentration dependent diffusion coefficient of nitrogen in expanded austenite," *Int. J. Mater. Res.*, vol. 99, no. 9, pp. 999–1005, Sep. 2008.
- [17] M. A. J. Somers and T. L. Christiansen, "Kinetics of Microstructure Evolution during Gaseous Thermochemical Surface Treatment," *J. Phase Equilibria Diffus.*, vol. 26, no. 5, pp. 520–528, 2005.
- [18] T. Christiansen, K. V. Dahl, and M. A. J. Somers, "Nitrogen diffusion and nitrogen depth profiles in expanded austenite: experimental assessment, numerical simulation and role of stress," *Mater. Sci. Technol.*, vol. 24, no. 2, pp. 159–167, 2008.
- [19] Y. Peng, Z. Liu, Y. Jiang, B. Wang, J. Gong, and M. A. J. Somers, "Experimental and numerical analysis of residual stress in carbon-stabilized expanded austenite," *Scr. Mater.*, vol. 157, pp. 106–109, Dec. 2018.
- [20] T. Moskalioviene and A. Galdikas, "Kinetic model of anisotropic stress assisted diffusion of nitrogen in nitrided austenitic stainless steel," *Surf. Coatings Technol.*, vol. 366, no. March, pp. 277–285, 2019.
- [21] H. J. Grabke, "Reaktionen von Ammoniak, Stickstoff und Wasserstoff an der Oberfläche von Eisen," *Berichte der Bunsengesellschaft für Phys. Chemie*, vol. 72, no. 4, pp. 533–541, 1968.
- [22] A. Galdikas and T. Moskalioviene, "Modeling of stress induced nitrogen diffusion in nitrided stainless steel," *Surf. Coatings Technol.*, vol. 205, no. 12, pp. 3742–3746, 2011.
- [23] B. A. Boley and J. H. Weiner, *Theory of Thermal Stresses*. Wiley, New York, 1960.
- [24] J. H. Hattel, *Fundamentals of Numerical Modelling of Casting Processes*. Polyteknisk Forlag, 2005.
- [25] J. H. Hattel and P. N. Hansen, "A 1-D analytical model for the thermally induced stresses in the mold surface during die casting," *Appl. Math. Model.*, vol. 18, no. 10, pp. 550–559, 1994.
- [26] E. de Souza Neto, D. Peric, and D. R. J. Owen, *Computational Methods for Plasticity*, vol. 55. 2008.
- [27] F. N. Jespersen, "Interaction of stress and phase transformation during thermochemical surface engineering, PhD thesis," Technical University of Denmark, 2015.
- [28] "Computational inelasticity," *Comput. Math. with Appl.*, vol. 37, no. 6, p. 134, Mar. 1999.
- [29] B. K. Brink, K. Ståhl, T. L. Christiansen, C. Frandsen, M. F. Hansen, and M. A. J. Somers, "Composition-dependent variation of magnetic properties and interstitial ordering in homogeneous expanded austenite," *Acta Mater.*, vol. 106, pp. 32–39, 2016.

- [30] F. P. Incropera, D. P. DeWitt, T. L. Bergman, and A. S. Lavine, *Fundamentals of Heat and Mass Transfer 6th Edition*. 2007.
- [31] H. Rozendaal, E. Mittemeijer, P. Colijn, and P. Van Der Schaaf, "The development of nitrogen concentration profiles on nitriding iron," *Metall. Mater. Trans. A*, vol. 14, no. 2, pp. 395–399, 1983.
- [32] P. B. Friehling, F. W. Poulsen, and M. A. J. Somers, "Nucleation of iron nitrides during gaseous nitriding of iron; effect of a preoxidation treatment," *Zeitschrift für Met.*, vol. 92, no. 6, pp. 589–595, 2001.
- [33] E. J. Mittemeijer and M. A. J. Somers, *Thermochemical surface engineering of steels : improving materials performance*. Woodhead Publishing, 2015.
- [34] C. Templier, J. C. Stinville, P. Villechaise, P. O. Renault, G. Abrasonis, J. P. Rivière, A. Martinavičius, and M. Drouet, "On lattice plane rotation and crystallographic structure of the expanded austenite in plasma nitrided AISI 316L steel," *Surf. Coatings Technol.*, vol. 204, no. 16–17, pp. 2551–2558, 2010.
- [35] G. Abrasonis, J. P. Riviere, C. Templier, A. Declémy, S. Muzard, and L. Pranevicius, "A comparative study of ion beam nitriding of single-crystalline and polycrystalline 316L austenitic stainless steel," *Surf. Coatings Technol.*, vol. 196, no. 1–3, pp. 262–266, 2005.
- [36] A. Martinavičius, G. Abrasonis, W. Möller, C. Templier, J. P. Rivière, A. Declémy, and Y. Chumlyakov, "Anisotropic ion-enhanced diffusion during ion nitriding of single crystalline austenitic stainless steel," *J. Appl. Phys.*, vol. 105, no. 9, 2009.

Tables

Table I: Material properties and simulation parameters for low temperature gas nitriding of 316L.

Young's Modulus, $E(T)$	Poisson's ratio, ν	Yield strength, $\sigma_y(c, T, \bar{\epsilon}^{pl})$	Diffusion coefficient, $D(c)$	Thermal diffusivity, $\alpha_v(T)$	Thermal expansion coefficient, $\alpha_v(T)$	Heat transfer coefficient, h
160-193 GPa	0.3	180-4100 MPa	$0.3 - 5.9 * 10^{-15} \text{ m}^2/\text{s}$	$5.4 * 10^{-6} \text{ m}^2/\text{s}$	$8.9 - 10.3 * 10^{-6}$	30 W/m ² K

Table II - Simulated swelling thickness, plastic deformation depth and case depth at $t=3, 8$ and 14 h. gas nitriding treatment.

	K_N	3 h.	8 h.	14 h.
Swelling thickness [μm]	2.49	0.02	0.19	0.36
	9.38	0.10	0.39	0.60
	∞	0.24	0.50	0.78
Plastic deformation depth [μm]	2.49	0.7	3.4	5.9
	9.38	2.6	5.8	8.6
	∞	3.4	6.3	9.0
Case depth for 1 at% [μm]	2.49	1.3	4.1	6.8
	9.38	2.6	5.8	8.6
	∞	3.8	7.0	9.8

List of figure captions

Figure 1 - information path of the one- and two-way coupled parameters and the information path for the inverse modelling.

Figure 2 - the iteration-, inverse model and time-stepping loops.

Figure 3 – illustration of the modelled geometry and the mechanical assumptions, which follows from an infinitely large plate with parallel, flat surfaces.

Figure 4 - illustration of mesh size and boundary conditions for the solution variables concentration and temperature. The boundary conditions for the diffusion problem are governed by the equilibrium concentration c_N^{eq} , surface concentration c_N^{surf} and the reaction rate coefficient k_{rate} . The boundary conditions for the heat transfer problem are governed by the furnace temperature $T^{furnace}$, the surface temperature T^{surf} and the heat transfer coefficient h .

Figure 5 - Comparison of experimental (drawn lines and symbols) and simulated (dashed lines) mass-uptake as a function of nitriding time for the indicated nitriding potentials K_N . The simulated profiles were obtained under the assumption that the surface reaction is infinitely rapid, so that nitrogen uptake is governed by solid state diffusion only.

Figure 6(a) Evolution of the k_{rate} as a function of the surface concentration and (b) evolution of the surface concentration and the concentration that would be obtained if equilibrium between gas and solid is achieved with time.

Figure 7(a) Simulated nitrogen concentration-depth profiles obtained by inverse modelling for a nitriding time of 14 h at 693 K in the nitriding potentials indicated in the legend; (b) profiles of chemical and thermal strains associated with the concentration profiles in (a); (c) elastic and plastic strains in the direction perpendicular to the surface corresponding to (a).

Figure 8(a) Stresses within the plane of the surface as a function of depth for a temperature of 693K and (b) an illustration of the symmetric in-plane stress-depth distribution. The inset in Figure 8(a) shows the stress levels in the core of the 2.7mm thick disc.

Figure 9 – the reaction rate at the surface of 316L during nitriding with potentials $KN=2.49$, 9.38 and ∞ at $T=693K$ estimated from the inverse model and estimated rates during de-nitriding from Grabke [21] for iron at $T=693K$ in varying $H_2/Argon$ gas mixture.

Figure 10 - Comparison of simulated and experimental glow discharge optical emission spectroscopy nitrogen-concentration profiles for the nitriding conditions indicated.

Figure 11 – concentration profiles from prediction of plasma nitriding.

Figure 12(a) the simulated layer thickness and (b) swelling thickness calculated from the sum of strains perpendicular to the surface compared to those measured by Stinville et al. [9] for plasma nitrided stainless steel.

Figures

1

2

3

4

5

6

8

9

10

11

12

Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Considerable plastic deformation of up to 9% takes place during nitriding.
- The reaction rate is not constant and probably scales with nitrogen and plasticity.
- The reaction rate for FCC austenite is two orders of magnitude smaller than BCC iron.
- Assuming a high, constant reaction rate can effectively predict plasma nitriding.
- Satisfactory predicted swelling thickness and case depth during plasma nitriding.