

## Stress Induced Nitrogen Diffusion in Nitrided Austenitic Stainless Steel

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Received 18 November 2010; accepted 27 February 2011

The nitrogen transport mechanism in plasma nitrided austenitic stainless steel at moderate temperatures (around 400 °C) is explained by non-Fickian diffusion model. The model considers the diffusion of nitrogen in presence of internal stresses gradient induced by penetrating nitrogen as the next driving force of diffusion after concentration gradient. For mathematical description of stress induced diffusion process the equation of barodiffusion is used, which involves concentration dependant barodiffusion coefficient. For calculation of stress gradient it is assumed that stress depth profile linearly relates with the nitrogen concentration depth profile. The calculated nitrogen depth profiles in an austenitic stainless steel are in good agreement with experimental nitrogen profiles. The diffusion coefficient  $D = 1.68 \cdot 10^{-12}$  cm<sup>2</sup>/s for nitrogen in a plasma source ion nitrided 1Cr18Ni9Ti (18-8 type) austenitic stainless steel at 380 °C was found from fitting of experimental data. It is shown that nitrogen penetration depth and nitrogen surface concentration increases with nitriding temperature nonlinearly.

*Keywords:* austenitic stainless steel, nitrogen diffusion, internal stress, modelling.

### 1. INTRODUCTION

The austenitic stainless steels (ASS) are widely used in many industrial branches and also in medicine due to their high corrosion resistance and good mechanical properties. The high corrosion resistance of these steels is associated with their ability to formation of a thin surface layer of a chromium oxide, however primary drawback of this steels is their low hardness and poor frictional wear resistance. The nitriding of ASS at temperatures between 300 °C and 400 °C by nitrogen ion beam implantation [1–2], low-temperature nitriding [3–5], or nitrogen plasma immersion ion implantation (PIII) [6–9] results in formation of a modified layer with outstanding hardness together with high wear resistance, while the excellent corrosion resistance is still preserved. It is well known that nitrogen diffusion in austenitic stainless steel is a complicated process and still not fully understood.

As experimentally observed, the transport of nitrogen in ASS is non-Fickian, so understanding of nitrogen diffusion mechanisms in steel is of great importance. The nitrogen depth profiles in nitrided ASS exhibit plateau-type shapes slowly decreasing from the surface, followed by a rather sharp leading edge, in addition, the nitrogen diffusivity is faster than expected from classical diffusion. Such profiles are not consistent with the standard analytic solution of the diffusion equation (Fick's laws of diffusion). Various earlier publications discuss the calculation of nitrogen depth profiles in nitrided ASS and several models were proposed to explain the shape of nitrogen depth profile and the high diffusivity in ASS: (1) the trapping-detraping model [10] proposed by Parascandola and co-workers; (2) the model based on Fick's laws and nitrogen diffusion coefficient dependence of nitrogen concentration [11] and (3) the model with combination of those two models (1) and (2) [12]; (4) the model proposed by L. Pranevicius and co-workers [13, 14]

based on the study of the stochastic mixing of atoms “ballistically” displaced by incident ions and the flow of atoms into grain boundaries responding to irradiation induced increase in the surface chemical potential.

Nitriding processes are accompanied by changes of stainless steel volume and leads to the formation of expanded austenite, characterized by a high content of interstitially dissolved nitrogen atoms (up to 35 at.%), giving rise to an expansion up to 9 % of the host face centered cubic structure (fcc) ASS lattice [15]. This phenomenon implies the occurrence of local stresses, induced by nitrogen concentration gradients within the solid, and influences nitrogen transport in the steel. Stress is one of the factors determining the chemical potential of components of solid systems. Therefore, self-stress resulting from the gradient of the nitrogen concentration affects the diffusion mechanism of nitrogen in ASS.

### 2. KINETIC MODEL

The mathematical description for the movement of nitrogen in ASS under stress can be formulated by solving the diffusion equation based on gradients of chemical potentials.

Incorporation of nitrogen into austenitic stainless steel causes lattice expansion which induces local internal stresses in matrix. In refs. [16–19], it was analyzed, the chemical potential of hydrogen diffusing in self-stressed isotropic elastic metal matrix. The same expression of chemical potential can be applied for diffusing nitrogen. So, the chemical potential of nitrogen in the steel lattice under a stress depends on the nitrogen concentration ( $C_N$ ) field and on the stress ( $\sigma$ ) field, and can be expressed as:

$$\mu(C_N, \sigma) = \mu_N^0 + RT \ln(f_N \cdot C_N) - V_N \sigma, \quad (1)$$

where  $\mu_N^0$  is the chemical potential in the standard state for reference;  $f_N$  is the activity coefficient of nitrogen;

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term  $\left(\mu_N^0 + RT \ln(f_N \cdot C_N)\right)$  denotes the chemical potential of nitrogen in the stress-free state ( $\sigma = 0$ );  $V_N$  the partial molar volume of nitrogen in the solid matrix;  $T$  is the absolute temperature;  $R = 8.314 \text{ Nm/mol} \cdot \text{K}$  is the gas constant.

According to the Onsager theory [20] the diffusion flux of nitrogen  $J_N$  is proportional to the gradient of chemical potential  $\mu(C_N, T, p)$ :

$$J = -L \nabla \mu(C_N, T, p), \quad (2)$$

where  $L$  is the Onsager coefficient. Chemical potential in general case is the function of concentration  $C_N$ , temperature  $T$  and pressure  $p$ . The pressure  $p$  for solids is related with stress as  $p = -\sigma$ , where  $\sigma$  represents 'stress', which is the trace of the stress tensor induced by the presence of nitrogen in the steel. So,  $\sigma$  is the hydrostatic part of this tensor, and is analogue of hydrostatic pressure [16].

The relationship between diffusion coefficient  $D$  and the Onsager coefficient  $L$  describes the Einstein-Smoluchowski relation [21]:

$$D = \frac{RT}{C_N} L. \quad (3)$$

Hence, by introducing eq. (3) in terms of eqs. (1)–(2) and assuming that (1) the temperature gradient does not exist, (2) the activity of nitrogen in the steel matrix is equal to one  $f_N = 1$  (ideal solution), and (3) the transport of nitrogen is one-dimensional, the diffusion flux of nitrogen in the stressed steel can be expressed as:

$$J_N = -D \nabla C_N + \frac{D C_N V_N}{RT} \nabla \sigma. \quad (4)$$

The diffusion equation in presence of internal stresses as driving force of diffusion is obtained by

$$\frac{\partial C_N(x, t)}{\partial t} = -\nabla J = D \nabla^2 C_N(x, t) - \frac{D \cdot V_N}{RT} \left( \nabla C_N(x, t) \nabla \sigma(x, t) + C_N(x, t) \nabla^2 \sigma(x, t) \right). \quad (5)$$

The boundary conditions including incoming nitrogen flux to the surface can be written as

$$\frac{\partial C(0, t)}{\partial t} = \frac{\alpha j}{q N_{surface}} (N_0 - C(0, t)) + D \nabla \left( \nabla C(0, t) - \frac{V_N C(0, t)}{RT} \nabla \sigma(0, t) \right), \quad (6)$$

where  $j$  is average nitrogen ion current density;  $\alpha$  is the sticking coefficients of nitrogen to the corresponding components;  $q = 1.602 \cdot 10^{-19} \text{ C}$  is the elementary charge;  $N_0$  is the host atoms atomic density and  $N_{surface}$  is the surface concentration of host atoms. The first term

$\left( \frac{\alpha j}{q N_{surface}} (N_0 - C_N(0, t)) \right)$  is the adsorption term, which describes the process of nitrogen adsorption on the surface.

In order to solve equations (5) and (6) the stress profile  $\sigma(x)$  has to be defined. In ref. [22] it was shown that for nitriding or carburizing of stainless steel the linear dependence of compositionally induced compressive stress on concentration (eq. (15) in ref. [22]) can be expressed as:

$$\sigma(x) = \frac{\beta E}{1-\nu} (\bar{C}_N - C_N(x)) \quad (7)$$

where  $\beta$  is Vegard's constant for nitrogen dissolved in austenite,  $E$  the Young's modulus of austenite,  $\nu$  the Poisson's constant and  $\bar{C}_N$  is the average nitrogen content in the sample.

The compositionally induced compressive stress values of several GPa's have been reported [23, 24], therefore T. Christiansen et al. [22] show that eq. (7) can be rewritten in the following form, which we will use for our calculations:

$$\sigma(x, t) = -X_{stress} \cdot C_N(x, t) \quad (8)$$

where  $X_{stress}$  is the proportionality constant. In ref. [22] the value of  $X_{stress}$  was taken as  $X_{stress} = 200 \text{ MPa} \cdot (\text{at.}\%)^{-1}$ .

The equations (5) and (6) were solved numerically by using the finite difference method (according to the Crank-Nicholson approach).

Assuming that  $\sigma^{(k)} = -X_{stress} \cdot C_N^{(k)}$  (by eq.(8)) the eqs. (5)–(6) will have the following form: for  $k = 0$

$$\frac{\partial C_N^{(k)}}{\partial t} = \frac{\alpha j}{q N_{surface}} (N_0 - C_N^{(k)}) + \frac{D}{h^2} \left[ \left( C_N^{(k+1)} - C_N^{(k)} \right) + B \left[ \left( C_N^{(k+1)} \right)^2 - \left( -C_N^{(k+1)} C_N^{(k)} \right) \right] \right] \quad (9)$$

for  $k > 0$

$$\frac{\partial C_N^{(k)}}{\partial t} = \frac{D}{h^2} \left[ \left( C_N^{(k+1)} + C_N^{(k-1)} - 2C_N^{(k)} \right) + B \left[ \left( C_N^{(k+1)} \right)^2 - C_N^{(k)} \cdot \left( C_N^{(k+1)} - C_N^{(k-1)} \right) \right] \right], \quad (10)$$

where  $B = \frac{V_N X_{stress}}{RT}$ .

It must be noted that Eqs. (9) and (10) are non linear. So, the diffusion on nitrogen in internal stress field goes on under nonlinear effects.

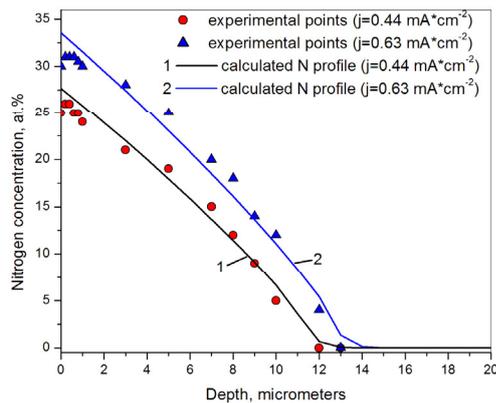
**The limitations of the model:** (1) The proposed model can be used to describe the nitrogen distribution in austenitic stainless steel during nitriding process at temperatures till chromium nitride formation ( $\sim 400^\circ \text{C}$ ); (2) The nitriding time and nitrogen flux cannot exceed the values for which the nitrogen surface concentration becomes higher than about 35 at.% (higher concentrations may promote nitride formation which is not included in the model); (3) In addition, the proposed stress induced

diffusion model cannot be used for high current density values because the effects due to sputtering rate and to the occurrence of defects induced by high energy ion bombardment were not evaluated in this model.

### 3. RESULTS AND DISCUSSION

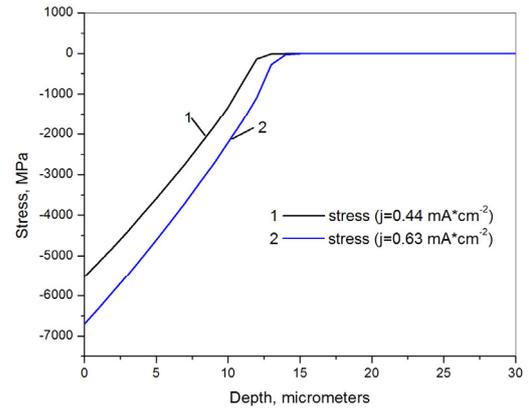
The experimental results from refs. [25] were fitted by using proposed stress-induced diffusion model for the purpose of validation of the model. The experimental conditions are the following: commercial ASS 1Cr18Ni9Ti (0.1 wt.% C, 1.5 wt.% Mn, 0.8 wt.% Si, 18 wt.% Cr, 9 wt.% Ni, 0.8 wt.% Ti,  $P \leq 0.035$  wt.%,  $S \leq 0.03$  wt.% and Fe as the balance) was nitrided using plasma nitriding method. Nitriding was done for 4 h at temperature  $T = 653$  K and at two different nitrogen ion current densities  $0.44 \text{ mA}\cdot\text{cm}^{-2}$  and  $0.63 \text{ mA}\cdot\text{cm}^{-2}$ .

To calculate nitrogen profiles in 1Cr18Ni9Ti steel, equations (9) and (10) were solved numerically. The diffusion coefficient ( $D$ ) is undefined parameter and in this work was extracted by fitting the experimental curves of nitrogen depth profiles. All other parameters were defined either by the experiment (see experimental conditions) or from literature data:  $X_{stress} = 200 \text{ MPa}\cdot(\text{at}\cdot\%)^{-1}$  [22];  $V_N = 4 \cdot 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$  [26];  $N_0 = 0.8 \cdot 10^{23} \text{ cm}^{-3}$ . The calculations were performed by changing  $D$  value in order to get the best fit. The best fit was obtained at  $D = 1.68 \cdot 10^{-12} \text{ cm}^2 \cdot \text{s}^{-1}$ . Fitting results are presented in Fig. 1 together with the experimental points [25]. The both calculated curves show a good agreement with experimental depth profiles using the same values of  $D$  at experimental values of  $j$ . Comparison between the numerical prediction and experimental results agrees with each other very well, which shows that proposed diffusion model based on influence of internal stresses as a driving force for diffusion is valid and can be used to explain nitriding process in ASS.



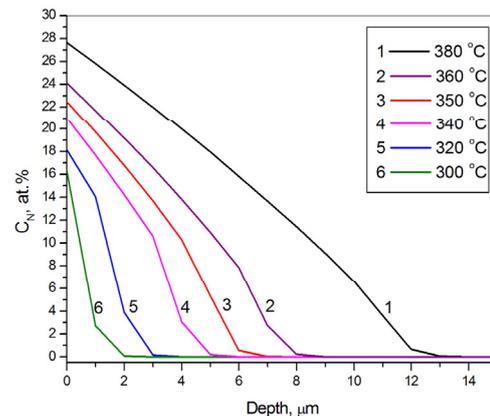
**Fig. 1.** Experimental (points) [25] and calculated depth profiles of nitrogen after nitridation of austenitic stainless steel 1Cr18Ni9Ti at different ion current densities. Calculated curves obtained from eqs. (9) and (10) with  $D = 1.68 \cdot 10^{-12} \text{ cm}^2 \cdot \text{s}^{-1}$ ,  $X_{stress} = 200 \text{ MPa}\cdot(\text{at}\cdot\%)^{-1}$

Calculated stress profiles extracted from fitted data are presented in Fig. 2. It is seen that the increasing the nitrogen ion implantation dose rate, the internal stresses increases.



**Fig. 2.** Calculated (eqs. (9) and (10)) stress profiles in nitrided 1Cr18Ni9Ti austenitic stainless steel at  $380^\circ\text{C}$  for 4 hours, calculated at  $D = 1.68 \cdot 10^{-12} \text{ cm}^2 \cdot \text{s}^{-1}$ ,  $X_{stress} = 200 \text{ MPa}\cdot(\text{at}\cdot\%)^{-1}$  and different ion implantation dose rates ( $0.44 \text{ mA}\cdot\text{cm}^{-2}$  and  $0.63 \text{ mA}\cdot\text{cm}^{-2}$ ) values

The influence of the nitriding temperature on the nitrogen depth profiles is shown in Fig. 3. The nitrogen depth profiles are calculated by eqs. (9) and (10) with  $j = 0.44 \text{ mA}\cdot\text{cm}^{-2}$ ,  $X_{stress} = 200 \text{ MPa}\cdot(\text{at}\cdot\%)^{-1}$  and with value of  $D$  obtained from fitting of experimental results (Fig. 1). It is seen that with the increase of nitriding temperature the penetration depth and the surface concentration of nitrogen increases. The influence of the nitriding temperature to the stress distribution across the thickness of the ASS sample is shown in Fig. 4. The stress profiles are calculated with the same values of parameters as for curves of Fig. 3. The results show that with the increase of the nitriding temperature the internal stresses and thickness of stressed layer increase.



**Fig. 3.** The influence of nitriding temperature on the nitrogen temperature depth profiles

The influence of the nitriding temperature to the surface concentration of nitrogen and to the penetration depth is shown in Fig. 5. As a penetration depth we are assuming distance from the surface until layer with nitrogen relative concentration equal to 0.1 at.%. The surface concentration of nitrogen and the penetration depth were calculated by eqs. (9) and (10) with the values of parameters obtained from fitting of experimental results (Fig. 1). It can be seen (Fig. 5) that the surface

concentration and the penetration depth of nitrogen vary exponentially with the nitriding temperature. The main influence of the nitriding temperature to the calculations results is defined by the adsorption term  $\left(\frac{\alpha j}{qN_{surface}} \cdot (N_0 - C_N^{(k)})\right)$  in eq. (9), where the sticking coefficients increases with treatment temperature by exponential law  $\left(\alpha = f\left(e^{\left(\frac{1}{T}\right)}\right)\right)$  and by the terms which describes diffusion process, where  $D = f\left(e^{\left(\frac{1}{T}\right)}\right)$ .

The increase of the nitriding temperature gives higher surface concentration of nitrogen until all the adsorption centers  $\left(N_0 - C_N^{(k)}\right)$  are occupied and higher penetration depth of nitrogen.

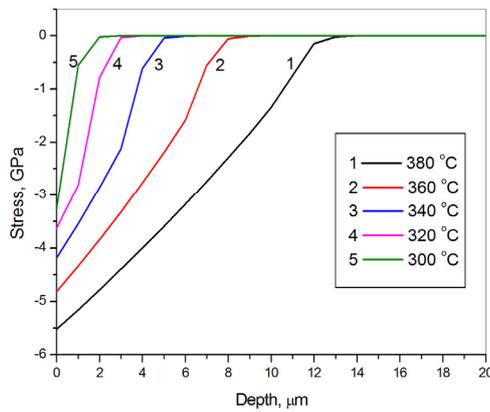


Fig. 4. The influence of the nitriding temperature on the stress profiles

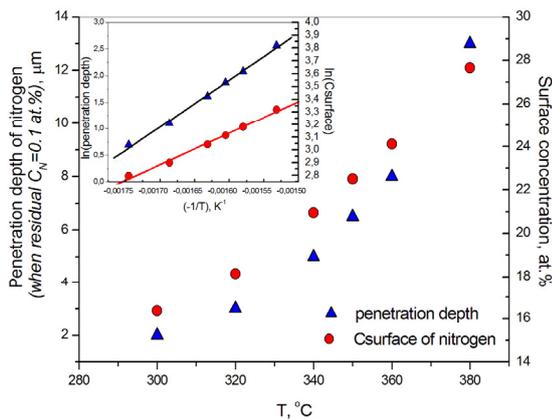


Fig. 5. The dependencies of nitrogen penetration depth and nitrogen surface concentration on the nitriding

In the proposed stress-induced diffusion model important parameter is  $X_{stress}$  (eq. (8)). The values  $X_{stress} = 200 \text{ MPa} \cdot (\text{at.}\%)^{-1}$  was proposed in ref. [22] which we used in our calculations. The influence of parameter  $X_{stress}$  to the nitrogen diffusion coefficient  $D$  is shown in Fig. 6. The calculations were conducted by changing  $D$  and

$X_{stress}$  values in order to get the best fit of experimental data [25].

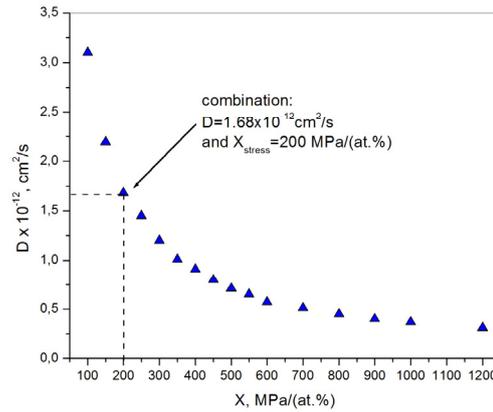


Fig. 6. The influence of parameter  $X_{stress}$  on the nitrogen diffusion coefficient  $D$

Fig. 6 shows that there are different combinations of  $D$  and  $X_{stress}$ , which give good agreement of theoretical and experimental results. From Fig. 6 results it follows that increase of coefficient  $X_{stress}$  the diffusion coefficient  $D$  decreases, i.e. increase of stress-induced diffusion influence on nitrogen transport in ASS the Fickian diffusion influence decreases.

#### 4. CONCLUSIONS

The stress-induced diffusion model is developed to account for stress-diffusion interaction in the nitriding of an austenitic stainless steel. Nitrogen depth profiles fitted on the basis of non-Fickian diffusion model, which considers the diffusion of nitrogen in presence of internal stresses as a driving force of diffusion, are in good agreement with experimental nitrogen depth profiles. The diffusion coefficient for nitrogen in plasma source ion nitrided 1Cr18Ni9Ti (18-8 type) austenitic stainless steel at 380 °C was found  $D = 1.68 \cdot 10^{-12} \text{ cm}^2/\text{s}$  from fitting of experimental data. The nitrogen penetration depth and nitrogen surface concentration increases with nitriding temperature nonlinearly.

#### Acknowledgement

This research was funded by a grant (No. TAP-46/2010) from the Research Council of Lithuania.

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Presented at the National Conference "Materials Engineering'2010" (Kaunas, Lithuania, November 19, 2010)