

The Modeling of Nitrogen Mass Transport in CoCr Alloys

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Abstract. The kinetics of plasma nitriding of CoCr alloy below temperatures of nitrides formation and mechanisms of nitrogen penetration are analyzed by proposed kinetic modeling in this article. Proposed nitrogen diffusion model is based on the trapping – detrapping (TD) model and developed taking into account the effect of the concentration dependent diffusivity of nitrogen, nitrogen adsorption on the surface of alloy and surface swelling process. The model indicates the influence of chromium atoms to nitrogen atoms diffusivity. The model consists of time and depth dependent diffusion, which is described by a partial differential equation, and it is solved by using Crank – Nicolson finite difference method. By fitting of experimental nitrogen depth profiles, it is shown that nitrogen diffusion coefficient varies with nitrogen concentration according to Einstein-Smoluchowski relation. Nitrogen depth profiles in plasma nitrided medical grade CoCr alloy (ISO 5831 – 12) at $T = 400$ °C for 1, 4 and 20 hours calculated on the basis of this model are in good agreement with experimental nitrogen profiles. Furthermore, the swelling process is showed and analyzed, derived the dependency of swelling rate on nitriding duration – the swelling rate is inversely proportional to the square root of nitriding duration. The obtained diffusion coefficient value and the swelling process rates satisfy the experimental data form Ref. The derived model explains physical processes during plasma nitriding and allows obtaining nitrogen depth profiles for any requisite nitriding duration.

Keywords: Crank – Nicolson method, kinetic modeling, CoCr plasma nitriding.

Introduction

Cobalt chromium alloys are widely used in medicine for the various applications including cardiovascular uses, prosthetic replacements, dentistry implants, because they satisfy the imposed requirements for biomaterials (Lutz & Mändl, 2010). Biomaterials must satisfy the requirements such as biocompatibility and good mechanical properties like strength, durability, hardness, good technological properties, stable structure (Wang, Zhang & Dong, 2010). CoCr alloys are characterized by good yield strength (448-1606 MPa), Young's modulus (210-253 GPa) and low wear rates ($4\text{-}6\cdot 10^{-8}$ mg·(Nm)⁻¹) (Wang, Huang & Zhang, 2012). The biocompatibility of CoCr alloys is related to their good corrosion resistance in the physiological environment because of high chromium concentration (26 ~ 30 at. %). These alloys have thin passive oxide film, mainly composed of Cr₂O₃ with low content of Mo oxides. Oxide film acts as a barrier for corrosion processes (Wang, Huang &

Zhang, 2012). However, CoCr alloys, used as medical implants, have several exploitation problems. The main problem is toxicity by wear debris and deficiency of biocompatibility with surrounding living tissues. The release of toxic ions such as Co, Cr, Al, Ni or nanoparticles as a wear debris from implants to body can cause apoptosis or necrosis (Lutz & Mändl, 2009). The toxic ions and nanoparticles from implants can migrate through the issue and over time by increasing their concentration may cause allergic reactions and osteolysis. On the other hand, the reactive chemical species in physiological environment H₂O₂, O₂⁻, NO can chemically alter the surface of CoCr implant (Çelik *et al.*, 2008). This leads to failure of implant. The increase of the surface hardness and a reduction of the wear rate are still needed to improve biocompatibility and lifetime of the CoCr implants (Öztürk, Türkan & Eroğlu, 2006).

Surface treatment of CoCr alloys by changing the composition, structure, mechanical properties

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and thickening the native protective oxide layer can increase the wear resistance and reduce the possibility of implant failure (Lutz, Lehmann & Mändl, 2008). Plasma assisted thermochemical surface treatments such as low-temperature plasma nitriding, nitrogen plasma immersion ion implantation, and nitrogen ion beam implantation are used for the purpose to improve wear, corrosion resistance and fatigue strength of CoCr alloys (Wang, Zhang & Shen, 2010). Various experiments of nitriding by plasma immersion ion implantation show an increase of the surface hardness to 15 – 20 GPa with a wear rate reduced by a factor of 10 – 100. These improvements arise because of large (up to 35 at. % N) and deep (up to 10 μm) content of inserted nitrogen into CoCr alloy. Modified surface layer is formed, which consists mainly of a metastable phase, known as supersaturated or expanded austenite γN phase. However, hard and wear resistant surface layer (γN phase) is formed if surface treatments are conducted at temperatures below 400 – 450 $^{\circ}\text{C}$ (Ichiki *et al.*, 2012). At higher temperatures the precipitations of chromium nitrides are formed (Pichon *et al.*, 2010). The formation of nitrides gives a depletion of chromium and lower corrosion resistance of the alloys by suppressing the formation of a Cr_2O_3 surface oxide (Manova *et al.*, 2011; Lutz *et al.*, 2011). The formation of chromium nitrides is a thermally activated process, so the faster formation of CrN at higher temperatures implies the decrease of a mobile nitrogen concentration. It was found that diffusion activation energy differs for low and high process temperatures. At low temperatures, the diffusion activation energy is 1.0 – 1.1 eV, while at temperature above 400 $^{\circ}\text{C}$ the reduced diffusion activation energy of 0.4 – 0.7 eV is observed (Wang, Huang & Zhang, 2012; Çelik *et al.*, 2008). This is explained by different phase transformation depending on temperature: expanded lattice is obtained below 400 $^{\circ}\text{C}$ and CrN formation is obtained above 400 $^{\circ}\text{C}$. For temperature range from 250 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$, diffusion coefficients vary from 10^{-14} to 10^{-10} cm^2s^{-1} (Çelik *et al.*, 2008).

The diffusion coefficients for various CoCr alloys (ISO 5832–12, HS 188, L605) are 10^{-12} – 10^{-11} cm^2s^{-1} at 400 $^{\circ}\text{C}$. Anomalous diffusion process and lattice expansion during nitriding process of CoCr alloys are similar to nitriding of austenitic stainless steels (ASS). Depth profiles of nitrogen both in CoCr and ASS are not coherent with a simple diffusion-limited incorporation (erfc shape). High nitrogen concentration on the surface slowly decreases in the layer and has a sharp decrease and a tail in a bulk. This phenomenon is usually considered by Cr traps and concentration dependent diffusion (Mändl *et al.*, 2013; Öztürk *et al.*, 2011; Okur, 2009).

The purpose of this work is to propose a model, which could quantitatively describe nitriding mechanisms and the nitrogen distribution in CoCr alloys during plasma nitriding process at nitriding temperatures around 400 $^{\circ}\text{C}$.

The model which will be applied for explanation of nitrogen mass transport in nitrided CoCr alloy in this article is named a “trapping – detrapping” model. This model consists of partial differential equations, which were decided to be solved by using Crank – Nicolson method.

Crank – Nicolson method was developed by John Crank and Phyllis Nicolson in 1947 (Crank & Nicolson, 1996). It is a finite difference method used for numerically solving the partial differential equations. This method is widely used in physics for solving diffusion (Tadjan & Meerschaert, 2007; Sweilam, Khader & Mahdy, 2012), heat (Ekolin, 1991) or internal stress equations (Galdikas, Petraitienė & Moskaliuviene, 2015). This article will represent Crank – Nicolson finite difference method application for solving nitrogen transfer processes in CoCr alloy during plasma nitriding. This method is a good choice for solving the diffusion equation as it is unconditionally stable for both 1D and 2D applications. The authors (Crank & Nicolson, 1996) have developed a satisfactory method of evaluating solutions of differential equations in which derivatives with respect to both depth and time are replaced in a particular way by finite difference ratios; the solution is carried out numerically, and the only limitation on the number of intervals is that of time of solution. The time step value should be chosen sufficiently small in order to avoid instabilities or oscillations of the computed results (Harrison, 1996). The ratio of time and depth has to be small (<0.5); otherwise, the code becomes unstable with the occurrence of oscillations (Moskaliuviene & Galdikas, 2012).

Material and Methods

The modeling

The model, applied in this article, for nitrogen distribution in plasma nitrided CoCr alloy, is named a trapping – detrapping model. This model is based on the theory that diffusion of nitrogen is decelerated by Cr atoms, which associate with N atoms for some time duration (Parascandola, Möler & Williamson, 2000). This model was developed for nitrogen mass transfer in stainless steels (Möller *et al.*, 2001), but according to the similarity of CoCr to stainless steel, the same model can be used for CoCr alloys. After some time duration the nitrogen can be detrapped with detrapping energy and freely diffuse in the bulk. The model also consists of nitrogen adsorption on the surface, concentration dependent diffusion and

$$\frac{\partial N_{dif}(x,t)}{\partial t} = \frac{\partial D(N)}{\partial x} \cdot \frac{\partial N_{dif}(x,t)}{\partial x} + D(N) \frac{\partial^2 N_{dif}(x,t)}{\partial x^2} - S(x,t) + \alpha \cdot j_0(x) \cdot \left(N_o - N_{dif}(x,t) - N_{trap}(x,t) \right) + v_s \frac{\partial N_{dif}(x,t)}{\partial x} \quad (1)$$

$$\frac{\partial N_{trap}(x,t)}{\partial t} = S(x,t) = 4\pi R_l D(N) \cdot \left[N_{dif}(x,t)(H_t - N_{trap}(x,t)) - N_o N_{trap}(x,t) e^{\frac{-E_B}{k_B T}} \right] + v_s \frac{\partial N_{trap}(x,t)}{\partial x} \quad (2)$$

$$\frac{\partial N(x,t)}{\partial t} = \frac{\partial N_{dif}(x,t)}{\partial t} + \frac{\partial N_{trap}(x,t)}{\partial t} \quad (3)$$

$$i_0(x > 0) = 0 \quad (4)$$

where N_{dif} - the amount of nitrogen, which diffuses in the bulk, N_{trap} - the amount of nitrogen, which is in traps. $\alpha \cdot j_0(x) \cdot \left(N_o - N_{dif}(x,t) - N_{trap}(x,t) \right)$ - adsorption term (Moskaliuviene *et al.*, 2011), v_s - swelling rate.

The (2) Eq. describes the nitrogen in the traps. H_t - the concentration of Cr in CoCr alloy, R_l - the lattice constant of Cr, E_B - nitrogen detrapping from Cr activation energy, N_o - the concentration of host atoms. k_B - Boltzmann constant, T - temperature in K. j_0 - flux of the nitrogen, α - the sticking coefficient of nitrogen to the surface atoms. The (4) equation describes the nitrogen adsorption on the surface of nitride alloy. It means that the term of adsorption is involved only on the first monolayer of the surface ($k = 0$). For deeper monolayer ($k > 0$), this term is equal to zero. The adsorption of the nitrogen is on process only on the surface.

swelling process. The final trapping – detrapping model equations are shown below:

According to the general diffusion theory, the diffusion coefficient in a concentration gradient depends on the local concentration of the diffusing element. Furthermore, in previous works (Galdikas & Petraitienė, 2014) it was shown that diffusion coefficient depends on nitrogen concentration according to Einstein-Smoluchowski relation: $D(N) = \frac{RTL}{N}$, where L is the Onsager coefficient, N is the nitrogen concentration, R and T are the universal

gas constant and temperature, respectively. The phenomenological diffusion coefficient $d_{const} = RTL$ is constant parameter in this model and $D(N) = \frac{d_{const}}{N}$ - the diffusion coefficient, dependent on nitrogen concentration.

The partial differential equations (1-3) can be solved by using Crank – Nicolson finite difference method. The nitrogen mass transfer is described by following equations after application of Crank – Nicolson finite difference method:

On the surface (the first monolayer), $k = 0$:

$$\frac{\partial N_{dif}^{(0)}}{\partial t} = -\frac{D(N)^{(0)}}{h^2} (N_{dif}^{(1)} - N_{dif}^{(0)}) + \alpha \cdot j_0 (N_o - N_{dif}^{(0)} - N_{trap}^{(0)}) - S^{(0)} + \frac{D(N)^{(1)} - D(N)^{(0)}}{h^2} \cdot (N_{dif}^{(1)} - N_{dif}^{(0)}) + \frac{v_s}{h} \cdot (N_{dif}^{(1)} - N_{dif}^{(0)}) \quad (5)$$

$$\frac{\partial N_{trap}^{(0)}}{\partial t} = S^{(0)} = 4\pi R_i D(N)^{(0)} \left[N_{dif}^{(0)} (H_t - N_{trap}^{(0)}) - N_0 N_{trap}^{(0)} e^{\frac{-E_B}{k_B T}} \right] + \frac{v_s}{h} \cdot (N_{trap}^{(1)} - N_{trap}^{(0)}) \quad (6)$$

And for other monolayers, $k > 0$

$$\frac{\partial N_{dif}^{(k)}}{\partial t} = \frac{D(N)^{(k)}}{h^2} (N_{dif}^{(k+1)} - 2N_{dif}^{(k)} + N_{dif}^{(k-1)}) - S^{(k)} + \frac{(D(N)^{(k+1)} - D(N)^{(k)})}{h^2} \cdot (N_{dif}^{(k+1)} - N_{dif}^{(k)}) + \frac{v_s}{h} \cdot (N_{dif}^{(k+1)} - N_{dif}^{(k)}), \quad (7)$$

$$\frac{\partial N_{trap}^{(k)}}{\partial t} = S^{(k)} = 4\pi R_i D(N)^{(k)} \left[N_{dif}^{(k)} (H_t - N_{trap}^{(k)}) - N_0 N_{trap}^{(k)} e^{\frac{-E_B}{k_B T}} \right] + \frac{v_s}{h} \cdot (N_{trap}^{(k+1)} - N_{trap}^{(k)}) \quad (8)$$

where h is the thickness of one monolayer. The eqs. (5) – (8) are integrated over the time interval from t to $t + \Delta t$. The time differences' value is Δt . The limitations of the model are the following: the model can be applied only on the small process temperatures – until 450 °C, because higher temperatures lead to the formation of Cr nitrides (Wang *et. al.*, 2012). The nitriding process duration (more than 20 h) and the relative concentration of nitrogen cannot exceed 40 at. % on the surface of nitrided alloy (Okur, 2009). The model does not involve such processes on the surface which can occur – sputtering on the surface and defect formation due to high energy ion bombardment.

By solving the above equations (Eqs. (5) – (8)) for N_{dif} and N_{trap} one can easily calculate the time evolution of a depth profile.

Materials

To analyze the kinetics of nitriding process and verify modified trapping-detrapping model, the experimental nitrogen depth profiles were fitted by model equations. The experimental results (Figure 1 experimental profiles) are taken from References (Okur, 2009; Öztürk, Fidan & Mändl, 2013) where plasma nitriding of a medical grade wrought low carbon cobalt–chromium–molybdenum (CoCrMo)

alloy (ISO 5832–12) samples were analyzed. The CoCr alloy samples were exposed to the following plasma nitriding conditions (Okur, 2009): (1) a gas composition of 60% N₂ + 40% H₂; (2) a working pressure of ~ 60 mTorr and RF power of 700 W; (3) a substrate temperature of 400°C (to avoid chromium nitride precipitation in the surface treated layer), and the nitriding duration was 1 h, 4 h and 20 h.

Results

The nitrogen depth profiles in CoCr (Figure 1) were calculated by Eqs. (5) – (8). The developer kinetic model equations are solved by using Crank –

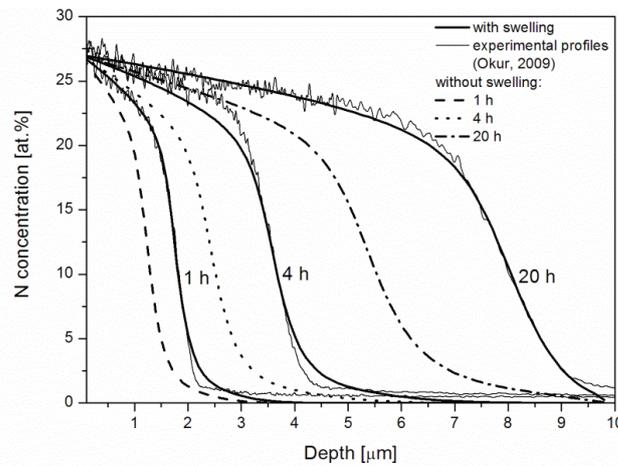


Figure 1. Experimental profiles (Okur, 2009) and calculated (Eqs. (6) – (9)) nitrogen depth profiles (solid lines) in nitrided CoCr alloy at 400 °C for different nitriding durations 1, 4, 20 h. Dash lines – calculations without swelling.

Nicholson finite difference method. For the calculations, a computer program was written by using Borland Delphi 7 software package.

The d_{const} , E_B and v_s are undefined model parameters and in this work were extracted by fitting the experimental curves of nitrogen depth profiles. The other model parameters were defined either by the experiment (Öztürk *et al.*, 2011) or from literature data: $E_A = 1,1$ eV (Lutz, Lehmann & Mändl, 2008); $R_t = 0,38 \times 10^{-9}$ m (Martinavičius *et al.*, 2009); $N_0 = 8,8 \times 10^{16}$ m⁻³ (Mishler, Munoz, 2013); $H_t = 2,64 \times 10^{16}$ m⁻³. The calculations were performed by varying free model parameters v_s , d_{const} and E_B values in order to get the best fit. According to the similarity of the CoCr alloys to stainless steels, the varying free model parameters were chosen similar to the ones for stainless steel from References (Abrasonis

et al., 2005, Moskaliuviene *et al.*, 2011, Stinville *et al.*, 2011). The detrapping energy varied from 0,3 eV to 0,4 eV by step of 0,1 eV, the phenomenological diffusion coefficient varied from 1 to 3×10^{-15} m²s⁻¹ by step of $0,1 \times 10^{-15}$ m²s⁻¹ and the swelling rate changed in the interval from 0,05 to 0,03 μm·h⁻¹ by step of 0,001 μm·h⁻¹. The best fit was chosen by visual equivalent of experimental distribution of nitrogen depth profile.

Fitting results are presented in Figure 1 together with the experimental nitrogen depth profiles. All three nitrogen depth profiles (for 1 h, 4 h and 20 h of nitriding) were calculated with the same $d_{const} = 2,0 \times 10^{-15}$ m²/s and $E_B = 0,35$ eV values. The concentration dependent diffusion coefficient $D(N)$ values, which were used to calculate nitrogen profiles (Figure 1) are plotted in Figure 2.

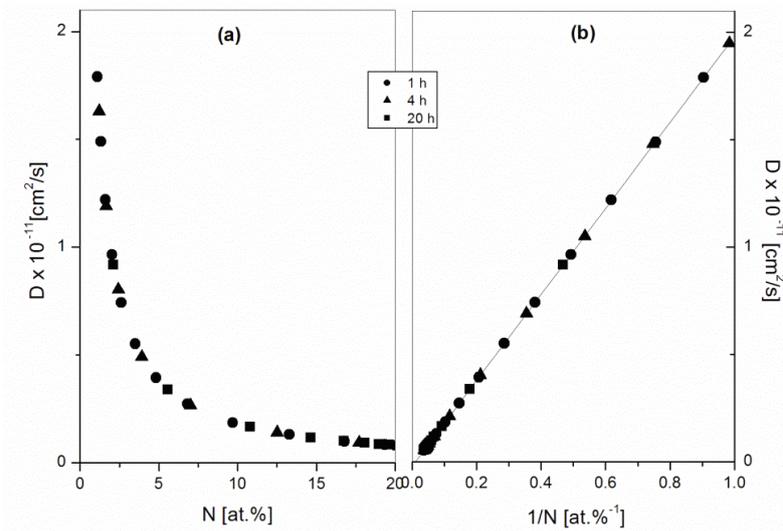


Figure 2. The diffusion coefficient values plotted as functions of (a) N and (b) $1/N$.

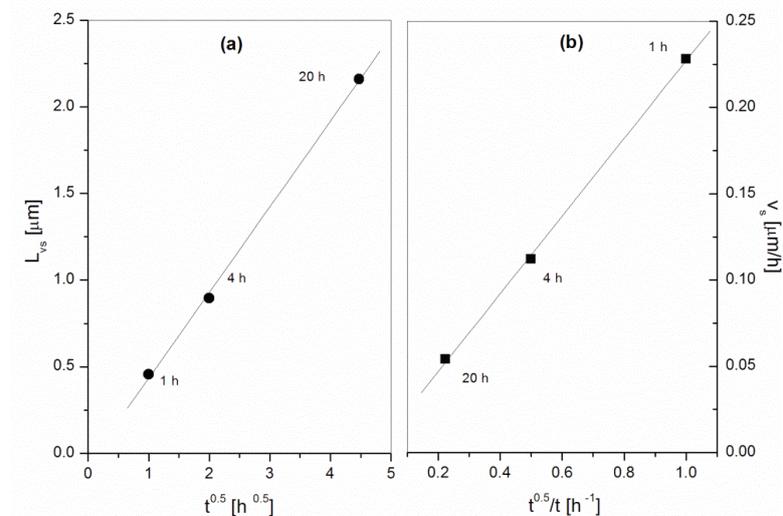


Figure 3. The dependencies of swelling thickness (a) and swelling rate (b) on nitriding time.

During nitriding the process of swelling takes place (Stinville, *et. al.*, 2011). In order to keep d_{const} coefficient as a constant and to get best fit for experimental results, it was necessary to take account of the swelling process. The calculated profiles without swelling (by Eqs. (5) – (8) with $v_s = 0$) are plotted in Figure 1. It is seen that the calculated results disagree with the experiment. According to the literature (Stinville *et. al.*, 2011; Chollet *et. al.*, 2013), the swelling rate v_s is not constant, it is dependent on the nitriding time as a function $v_s \approx f(1/\sqrt{t})$. Obtained from the fitting v_s values (0,228 $\mu\text{m}\cdot\text{h}^{-1}$, 0,122 $\mu\text{m}\cdot\text{h}^{-1}$ and 0,054 $\mu\text{m}\cdot\text{h}^{-1}$ for 1, 4 and 20 h nitriding durations, respectively) are different for different nitriding durations and are plotted in Figure 3 a.

Discussion

The concentration of nitrogen in the alloy is dependent on the nitriding duration – with the increase of nitriding time the concentration of nitrogen increases (Figure 1), and it means that diffusion coefficient $D(N)$ decreases with the increase of nitrogen concentration (Figure 2a). According to the Einstein – Smoluchowski, the diffusion coefficient is inversely proportional to the nitrogen concentration (Figure 2b). Further, it is seen (Figure 2) that all values of diffusion coefficient for different nitriding time samples (1 h, 4 h and 20 h) lie in one line as function of $D \sim (1/N)$. It is important to note that obtained from fitting d_{const} value is the same for different samples with different nitriding duration and correlates with diffusion coefficient values for similar CoCr alloys which were reported in Ref. (Okur, 2009). The extracting of value d_{const} from experimental fitting of this model allows calculating nitrogen concentration depth profiles for any nitriding duration.

The values of swelling thickness obtained by fitting show linear increase with the square root of the nitriding time (Figure 3 b). The same linear dependency on square root nitriding time is experimentally obtained for stainless steels (Stinville, *et. al.*, 2011; Chollet, *et. al.*, 2013). From the above analysis follows that the main processes which occur during plasma nitriding of CoCr alloys below temperatures of nitrides formation are the trapping – detrapping, concentration dependent diffusion and also swelling. Including those processes into kinetic differential equations gives a good comparison between the numerical prediction and experimental results.

Conclusion

The “trapping - detrapping” model was applied for analysis of nitrogen mass transfer in CoCr alloys. The partial differential equations of this model were solved by using Crank – Nicolson finite difference method. During experiments with this model, a conclusion to involve nitrogen concentration dependent diffusion coefficient of nitrogen and alloy’s swelling processes was made. These changes let us reduce the number of variable parameters of model dependent on nitriding duration and leave only one variable parameter swelling rate, which depends on the nitriding duration $v_s = f(\sqrt{t})$. During experiment it was found that nitrogen detrapping energy for ISO 5831 - 12 alloy is 0,35 eV. Phenomenological diffusion coefficient for ISO 5831 - 12 alloy is $2 \cdot 10^{-15} \text{ m}^2\text{s}^{-1}$ at 400 °C temperature and the swelling rates: $v_{s,1h} = 0,2286 \mu\text{m}\cdot\text{h}^{-1}$, $v_{s,4h} = 0,1249 \mu\text{m}\cdot\text{h}^{-1}$ and $v_{s,20h} = 0,0624 \mu\text{m}\cdot\text{h}^{-1}$.

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