

MODELING OF GAS DIFFUSION INTO METALS ON THE EXAMPLE OF TITANIUM NITRIDING IN GAS DISCHARGE PLASMAS

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In this paper the kinetics of nitriding has been investigated using both computer modeling and analytical solution of the diffusion equation. Mathematical modeling of diffusion processes had been realized with taking into account the formation of new phases and existence of movable boundaries between them. A good agreement between the numerical modeling, analytical modeling and experimental results has been obtained.

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INTRODUCTION

Mathematical modeling of diffusion processes had been realized by solving the basic differential equations of diffusion for relevant boundary and initial conditions. Depending on the nature of the problem, analytical or numerical approaches were used. Analytical solutions are simpler, but they are applicable only for ideal initial and boundary conditions. The most realistic analytical solutions can be obtained by applying the boundary conditions of the third order. Previous models [1-3] of nitrogen diffusion in titanium allowed obtaining the concentration profile only for the diffusion zone, without accounting the formation of compound layer. In this approach one can determine the approximate thickness of the nitrided layer, but it cannot be said nothing about the distribution of nitrogen concentration in the compound layer.

In this paper we took into consideration not only the processes in the diffusion zone, but also the growth and evolution of new phases. In order to account the phase structure of the compound layer, the diffusion problem with two moving boundaries has been solved both numerically and analytically.

1. NITRIDING KINETICS

We have used a simplified physical model of the formation and growth of the nitrided layers in the titanium [4]. The model is constructed taking into account the reaction-diffusion processes at nitriding temperatures below β -transformation, i.e below 882 °C (Fig. 1). After absorption by the sample surface, the nitrogen diffuses into the bulk and forms the concentration gradient. Thus, the nitrogen is introduced into α -phase in the surface layer which is called a diffusion zone $\alpha(N)$. After reaching the solubility limit 7.6% for zone $\alpha(N)$, see Fig. 1, the new Ti_2N -phase starts to form. When the concentration of nitrogen reaches 12.8%, that is the solubility limit for Ti_2N -phase, the Ti_2N -phase transforms to TiN . As a result the surface layer consists of phases TiN , Ti_2N , $\alpha(N)$ and α -titanium as it is schematically shown in Fig. 2. Therefore, in proposed model we take into consideration that besides the diffusion zone $\alpha(N)$ there is a compound layer, which consists from TiN and Ti_2N . In addition, we should take into account that the boundaries between the above mentioned phases are movable.

The presented model allows for above-mentioned requirements and gives a possibility to simulate quantitatively the kinetics of the formation of nitrided layers under different experimental conditions.

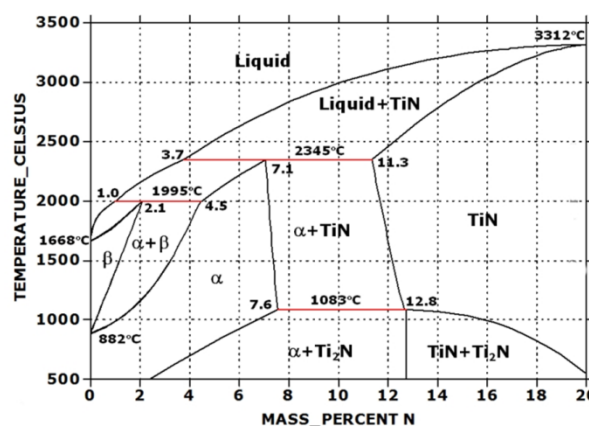


Fig. 1. Binary Ti-N phase diagram

2. ANALYTICAL MODEL

Let us consider one dimensional case, wherein the concentration varies only along axis x [5-7]. The processes in each phase are described by equations:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2}, \quad i = \alpha, \gamma, \varepsilon, \quad (2.1)$$

where D_i – diffusion coefficients.

Separate our problem into two stages. The first stage is a formation of α -phase and processes on the surface of the metal. For this stage we write the initial and boundary conditions:

$$C(x, 0) = C_0, \quad 0 < x < \infty, \quad (2.2)$$

$$D \frac{\partial C(0, t)}{\partial x} = \alpha (C(0, t) - C_{eq}), \quad t > 0, \quad (2.3)$$

$$C(x \rightarrow \infty, t) = 0, \quad t > 0, \quad (2.4)$$

where α – kinetic constant of reaction.

The solution of the diffusion equation for α -phase with conditions (2.2)-(2.4) is:

$$\frac{C - C_{eq}}{C_0 - C_{eq}} = \text{Erfc} \left(\frac{x}{2\sqrt{D_\alpha t}} \right) + \exp \left(\frac{\alpha x}{D_\alpha} + \frac{\alpha^2 t}{D_\alpha} \right) \times \text{Erfc} \left(\frac{x}{2\sqrt{D_\alpha t}} + \alpha \sqrt{\frac{t}{D_\alpha}} \right). \quad (2.5)$$

It will take some time t^* until concentration on the surface reaches C_s . This value is maintained during the process. Such behavior of the concentration on the surface is caused by the absorption effects. Schematically, it is shown on Fig. 3.

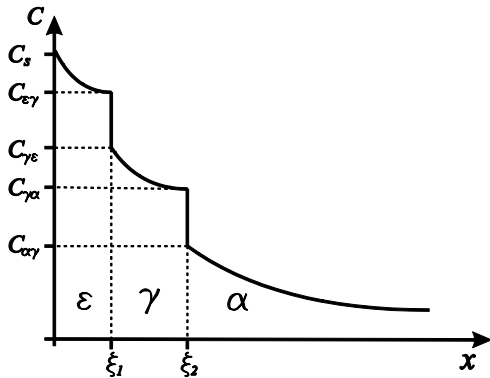


Fig. 2. Scheme of the phase growth during nitriding of the titanium

Time t^* can be obtained from the transcendental equation:

$$\frac{C_s - C_{eq}}{C_0 - C_{eq}} = \exp\left(\frac{\alpha^2 t^*}{D_\alpha}\right) \cdot \operatorname{Erfc}\left(\alpha \sqrt{\frac{t^*}{D_\alpha}}\right). \quad (2.6)$$

Derive the concentration distribution at the beginning of the second stage by substituting this value of time into the solution (2.5).

The second stage includes the formation and growth of new phases. It is needed to redefine the solution for α -phase, to find solutions for γ -, and ε -phase and also to find interphase boundary motion equations. Usually the solutions can be found in such form:

$$C_i(x, t) = A_i + B_i \cdot \operatorname{Erf}\left(\frac{x}{2\sqrt{D_i t}}\right), \quad (2.7)$$

where A_i and B_i – constants, which are determined from boundary conditions. Write these boundary conditions:

$$\begin{cases} C_\alpha(\xi_2, t) = C_{\alpha\gamma}; \\ C_\alpha(\infty, t) = 0; \end{cases} \quad (2.8)$$

$$\begin{cases} C_\gamma(\xi_1, t) = C_{\gamma\varepsilon}; \\ C_\gamma(\xi_2, t) = C_{\gamma\alpha}; \end{cases} \quad (2.9)$$

$$\begin{cases} C_\varepsilon(0, t) = C_s; \\ C_\varepsilon(\xi_1, t) = C_{\varepsilon\gamma}. \end{cases} \quad (2.10)$$

Then:

$$C_\alpha(x, t) = \frac{C_{\alpha\gamma}}{\operatorname{Erfc}\left(\frac{\xi_2}{2\sqrt{D_\alpha t}}\right)} \operatorname{Erfc}\left(\frac{x}{2\sqrt{D_\alpha t}}\right), \quad (2.11)$$

$\xi_2 < x < \infty$

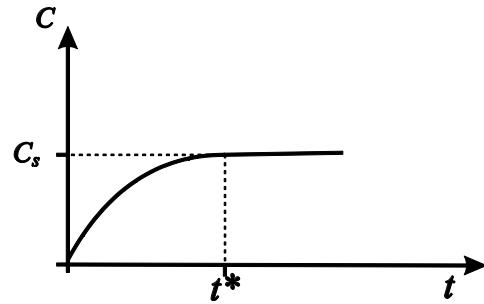


Fig. 3. Scheme of the concentration growth on the surface during the first stage

$$C_\gamma(x, t) = C_{\gamma\varepsilon} - \frac{C_{\gamma\varepsilon} - C_{\gamma\alpha}}{\operatorname{Erf}\left(\frac{\xi_1}{2\sqrt{D_\gamma t}}\right) - \operatorname{Erf}\left(\frac{\xi_2}{2\sqrt{D_\gamma t}}\right)} \times \left(\operatorname{Erf}\left(\frac{\xi_1}{2\sqrt{D_\gamma t}}\right) - \operatorname{Erf}\left(\frac{x}{2\sqrt{D_\gamma t}}\right) \right), \quad \xi_1 < x < \xi_2, \quad (2.12)$$

$$C_\varepsilon(x, t) = C_s + \frac{C_{\varepsilon\gamma} - C_s}{\operatorname{Erf}\left(\frac{\xi_1}{2\sqrt{D_\varepsilon t}}\right)} \cdot \operatorname{Erf}\left(\frac{x}{2\sqrt{D_\varepsilon t}}\right), \quad (2.13)$$

$$0 < x < \xi_1.$$

The phase boundary, as it is known, is shifted proportionally to the square root of time:

$$\xi_{1,2} = 2b_{1,2}\sqrt{D_{\varepsilon,\gamma}t}. \quad (2.14)$$

We have two pairs of equations for determining the unknown coefficients of $b_{1,2}$. The first pair of equations (2.13) and (2.12) describes the concentration distribution in the ε - and γ -phase.

The second pair of equations is a balance equation on the boundaries of phases:

$$\begin{cases} (C_{\varepsilon\gamma} - C_{\gamma\varepsilon}) \frac{d\xi_1}{dt} = -D_\varepsilon \left(\frac{\partial C_\varepsilon}{\partial x}\right)_{C_{\varepsilon\gamma}} + D_\gamma \left(\frac{\partial C_\gamma}{\partial x}\right)_{C_{\gamma\varepsilon}}; \\ (C_{\gamma\alpha} - C_{\alpha\gamma}) \frac{d\xi_2}{dt} = -D_\gamma \left(\frac{\partial C_\gamma}{\partial x}\right)_{C_{\gamma\alpha}} + D_\alpha \left(\frac{\partial C_\alpha}{\partial x}\right)_{C_{\alpha\gamma}}. \end{cases} \quad (2.15)$$

Derive two transcendental equations for determining $b_{1,2}$ by substituting (2.12) and (2.13) into (2.15):

$$C_{\varepsilon\gamma} - C_{\gamma\varepsilon} = \frac{C_s - C_{\varepsilon\gamma}}{\sqrt{\pi} b_1 \exp(b_1^2) \operatorname{Erf}(b_1)} - \frac{C_{\gamma\varepsilon} - C_{\gamma\alpha}}{\sqrt{\pi} b_1 \sqrt{\varphi_1} \exp(b_1^2 \varphi_1) \operatorname{Erf}(b_1 \sqrt{\varphi_1})}, \quad (2.16)$$

$$C_{\gamma\alpha} - C_{\alpha\gamma} = \frac{C_{\gamma\varepsilon} - C_{\gamma\alpha}}{\sqrt{\pi} b_2 \exp(b_2^2) \operatorname{Erf}(b_2)} - \frac{C_{\alpha\gamma} - C_0}{\sqrt{\pi} b_2 \sqrt{\varphi_2} \exp(b_2^2 \varphi_2) \operatorname{Erf}(b_2 \sqrt{\varphi_2})}, \quad (2.17)$$

where $\varphi_1 = D_\varepsilon / D_\gamma$, $\varphi_2 = D_\gamma / D_\alpha$.

Thus, the positions of interphase boundaries $\xi_{1,2}$ can be obtained from (2.14) if we determine the values of $b_{1,2}$ from (2.16) and (2.17) at a given time. And if we know the positions of interphase boundaries the concentration profiles can be calculated in each phase from, (2.11)-(2.13).

3. RESULTS

For comparing the calculated results with experimental ones we have used the data about microhardness distribution along a depth of Ti plate after nitriding in

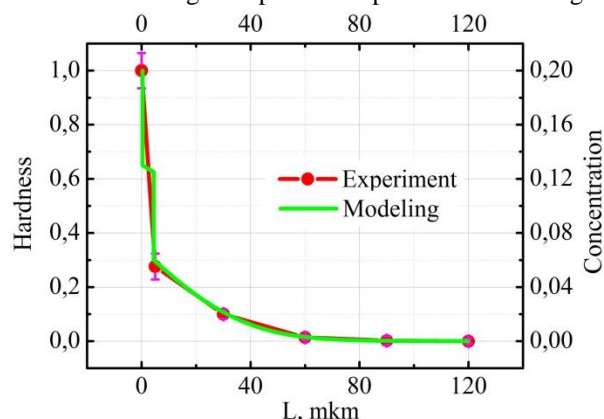


Fig. 4. Comparison of simulated and experimental results

non-self-maintained gaseous discharge [8]. The correlation between concentration and microhardness is given by expression [9]:

$$\frac{H - H_0}{H_s - H_0} \propto \frac{C - C_0}{C_s - C_0}, \quad (3.1)$$

where H – a microhardness value at a given point, H_0 – a microhardness value at infinity (microhardness of pure material), H_s – a surface microhardness, C – a concentration value at a given point, C_0 – a microhardness value at infinity (initial concentration of working gas in the sample), C_s – a concentration at the surface. We have suggested for calculating that $C_0 = 0$ and $C_s = 0.2$. The duration t of the nitriding process was set equal to 20 minutes as it was in experiment carried out in [8].

As it can be seen in Fig. 4 the simulation is in good agreement with experimental results.

CONCLUSIONS

The diffusion problem with two moving boundaries has been solved both numerically and analytically. A good agreement between the numerical modeling, analytical modeling and experimental results have been obtained.

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МОДЕЛИРОВАНИЕ ДИФФУЗИИ ГАЗОВ В МЕТАЛЛЫ НА ПРИМЕРЕ АЗОТИРОВАНИЯ ТИТАНА В НЕСАМОСТОЯТЕЛЬНОМ ГАЗОВОМ РАЗРЯДЕ

И.А. Мисирук, А.И. Тимошенко, В.С. Таран

Исследована кинетика азотирования как с использованием компьютерного моделирования, так и аналитически, путем решения диффузионного уравнения. Моделирование процессов диффузии реализовано с учетом формирования новых фаз и существования подвижных границ между ними. Получено хорошее соответствие между численным моделированием, аналитическим моделированием и экспериментальными результатами.

МОДЕЛЮВАННЯ ДИФУЗІЇ ГАЗІВ У МЕТАЛИ НА ПРИКЛАДІ АЗОТУВАННЯ ТИТАНУ В НЕСАМОСТІЙНОМУ ГАЗОВОМУ РОЗРЯДІ

І.О. Місірук, О.І. Тимошенко, В.С. Таран

Досліджено кінетику азотування як з використанням комп'ютерного моделювання, так і аналітично, шляхом розв'язання дифузійного рівняння. Моделювання процесів дифузії реалізовано з урахуванням формування нових фаз та існування рухливих границь між ними. Отримано хорошу відповідність між чисельним моделюванням, аналітичним моделюванням та експериментальними результатами.