diffusion-fundamentals.org

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Modeling of Diffusion Saturation of Titanium by Nitrogen Taking into Consideration Structural and Phase Transformations

Ya. Matychak, V. Fedirko, I. Pohrelyuk, O.Tkachuk

Physico-Mechanical Institute of National Academy of Sciences of Ukraine,
5, Naukova St., Lviv, 79601, Ukraine, E-Mail: matychak@ipm.lviv.ua

Diffusion in solids is often accompanied by structural and phase transformations. Nowadays it's very difficult to describe such processes analytically. It concerns either the nanosystems or the macroobjects. Titanium which is undergone polymorphic α⇔β transformation (change of crystalline lattice hcp→bcc) at $T_{\alpha\Leftrightarrow\beta}=882^0$C can be interesting for such investigations. Chemical-thermal treatment, particularly nitriding, is carried out, to improve the functional properties of the titanium alloys. But nitrogen is α–stabilizer and can stimulate structural transformations while nitriding. Earlier the kinetics of nitriding titanium and its alloys at the temperatures $T<T_{\alpha\Leftrightarrow\beta}$ has been investigated [1, 2]. Evolution of the microstructure during phase transformation because of the migration β–stabilizers has been investigated [3]. The aim of this work is to describe analytically the diffusive saturation of titanium by nitrogen at the temperature $T>T_{\alpha\Leftrightarrow\beta}$ taking into consideration phase and structural transformations.

Let us consider the isothermal saturation of titanium at $T>T_{\alpha\Leftrightarrow\beta}$. β⇔α phase structural transformation occurs on titanium surface because of its local oversaturation by nitrogen. In accordance with the phase diagram nitrogen solubility in α–phase is much more than in β-phase ($C_\alpha>C_\beta$), but contrary to the diffusion coefficients. Therefore the increase of volumetric quantity of α–phase ($f_\alpha^S(\tau)$) on the surface provides the increase of surface nitrogen concentration ($C^S(\tau)$). Following diffusion of nitrogen in the specimen bulk stimulates phase-structural changes also in the surface layer. Then $f_\alpha = f_\alpha(x,\tau)$ is the function of time and spatial coordinate x. Therefore it is possible to distinguish two zones in the diffusive zone: heterogeneous zone I ($0<x<Y(\tau)$), in which there is a microstructure change β⇔α except diffusive nitrogen dissolution and homogeneous zone II ($Y(\tau)\le x<\infty$), in which nitrogen diffusion is in β-phase (fig.1). On moving interface $Y(t)$ the nitrogen concentration is equal to maximum (C_β) its solubility in β-phase. Nitrogen diffusion in zone II is realized by the permanent diffusion coefficient $D_2=D_\beta$, and in zone I by the variable diffusion coefficient $D_1(x,\tau)$, depending on α–phase quantity. Taking into account equation, $f_\alpha(x,\tau)+f_\beta(x,\tau)=1$, it'll be presented $D_1(x,\tau)$ in such a kind:

$$D_1(x,\tau)=D_\alpha f_\alpha(x,\tau)+D_\beta f_\beta(x,\tau)=D_\beta-(D_\beta-D_\alpha)f_\alpha(x,\tau)\,. \qquad (1)$$

It is extremely difficult to describe the above-mentioned process analytically. It is a diffusive task of Stephen (with moved boundary) with the variable diffusion coefficient and non-stationary boundary conditions. Therefore let us offer its approximate solution. Take a linear law of nitrogen distribution in zone I, corresponding to the quasi-stationary state, and Gauss's law for zone II. Then

$$C_1(x,\tau) = C^S(\tau) - [C^S(\tau) - C_\beta] \cdot x / Y(\tau)\,, C_2(x,\tau) = C_\beta erfc\{[x - Y(\tau)]/[2\sqrt{D_\beta \tau}]\} \quad (2)$$

Phase-structural transformations on the surface are presented by the reaction of first order. Therefore for $C^S(\tau)$, $f_\alpha^S(\tau)$ at initial conditions $C^S(0) = C_\beta$, $f_\alpha^S(0) = 0$ we have:

$$C^S(\tau) = C_\beta + (C_\alpha - C_\beta) f_\alpha^S(\tau)\ ,\ f_\alpha^S(\tau) = 1 - \exp(-\lambda\tau) \quad (3)$$

Here λ is a parameter which characterizes rate of phase-boundary reaction.

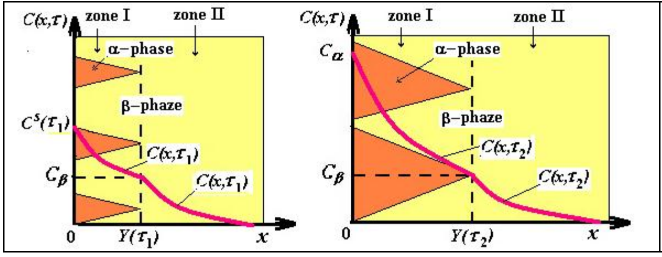

Fig.1. Evolution of nitrogen distribution in the diffusive zone ($\tau_2 > \tau_1$).

In accordance to nitrogen distribution in zone I (equation (1)) it'll be used a linear law of distribution volumetric quantity of α–phase: $f_\alpha(x,\tau) = f_\alpha^S[1 - x / Y(\tau)]$. Averaging volumetric quantity of α–phase on thickness of the zone I and taking into account equation (1), we'll have for the effective diffusion coefficient in zone I

$$\overline{D}_1(\tau) = D_\beta - (D_\beta - D_\alpha) f_\alpha^S(\tau)/2\,. \quad (4)$$

From equation of the mass balance ($J_1 = J_2$; J_1, J_2-diffusive flows) on the interface Y(t) and taking into account equation (2) we have:

$$\overline{D}_1(\tau) \cdot [C^S(\tau) - C_\beta] / Y(\tau) = D_\beta C_\beta / \sqrt{\pi D_\beta \tau}\ . \quad (5)$$

Consequently, evolution of zone of structural and phase transformations during the diffusive saturation of titanium by nitrogen is described by equation:

$$Y(\tau) = (C_\alpha - C_\beta) C_\beta^{-1} \sqrt{\pi D_\beta \tau} \cdot F(\tau)\,, F(\tau) = [1 - f_\alpha^S(\tau) \cdot (D_\beta - D_\alpha)/2D_\beta] \cdot f_\alpha^S(\tau)\,. \quad (6)$$

For continuous exposures

$$Y(\tau) = K\sqrt{\tau}\,, \quad \text{where} \quad K = [(C_\alpha - C_\beta) \cdot (D_\beta + D_\alpha) \cdot \sqrt{\pi}]/[2 D_\beta C_\beta]\ . \quad (7)$$

The experimental investigations have been proved correctness of the model conception. Analytical calculations describe satisfactorily the kinetics of transfer of the boundary which separates diffusive zone into two zones: zone with α-structure formed by nitrogen saturation and zone with α-structure formed by cooling to room temperature.

References

[1] Ya. Matychak, V. Fedirko, A. Prytula, I. Pohrelyuk, Defect and diffusion forum, 261-262 (2007) 47-54.

[2] Ya. Matychak, V. Fedirko, I. Pohrelyuk, O. Yaskiv, O. Tkachuk, Defect and diffusion forum, 277 (2008) 33-38.

[3] S. Malinov, I. Katzarov, W. Sha, Defect and diffusion forum, 237-240 (2005) 635-646.