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Model of the Hardness Prediction for the Diffusion Nitriding

Vladimír Horák¹, Vladimir V. Kulish², Vojtěch Hrubý¹, and Tereza Mrázková¹

¹*Department of Mechanical Engineering, University of Defence,
Kounicova 65, 662 10 Brno, Czech Republic*

²*School of Mechanical and Aerospace Engineering, Nanyang Technological University,
50 Nanyang Avenue, Singapore 639798*

Abstract. The plasma nitriding process produces a hard near-surface thin layer of the nitrided material. The thickness of the diffused layer, produced in the course of this process, is between 0.001 and 0.6 mm. The paper presents a diffusion model of plasma nitriding that allows one to predict the material hardness distribution within the near-surface layer as a function of time for a modified nitrogen diffusion coefficient. The temperature dependence of the diffusion coefficient are considered in the paper. Hence, the model involves the reaction rates of nitrides formation. The one-dimensional transient diffusion model is then applied to a thin nitride layer. The solution thus obtained is compared with experimental data for a decrease of hardness as a function of depth and time, until the core hardness is reached.

Keywords: Diffusion, Nitriding, Hardness, Logistic Function.

PACS: 81.65.Lp

INTRODUCTION

The plasma nitriding of steel, as the process of chemical action of gaseous nitrogen, causes a creation of nitrides in the surface layer of material. Nitriding technology is widely used to increase the surface hardness, the fatigue resistance, as well as the surface treatment and corrosion protection. The thickness and composition of a surface layer are given by the course of nitrogen diffusion into a microstructure of a nitrided material and by the system of proceeding chemical reactions during the nitriding process.

The nitriding process is strongly affected by the furnace atmosphere temperature and vacuum pressure. The thickness of the nitrided layer is determined by the holding time of nitriding. All these parameters need to be included in a mathematical model of the nitriding process.

THEORETICAL BACKGROUND OF THE PROBLEM

Molecular diffusion is referred to as the penetration of molecules or atoms in a material due to a molar concentration gradient c .

The rate of diffusion $dn/d\tau$ of a substance is proportional to the isoconcentration surface area A and is expressed by Fick's first law of diffusion as the molar diffusion flux in the direction x normal to the isoconcentration surface

$$\frac{dn}{d\tau} = -D A \frac{dc}{dx}, \quad (1)$$

where D is the diffusion coefficient expressing the ability of particles to diffuse into the material. This coefficient is a function of pressure and temperature.

The unsteady-state diffusion describes Fick's second law of diffusion determining the concentration distribution during the transient diffusion in the form

$$\frac{\partial c}{\partial \tau} = D \frac{\partial^2 c}{\partial x^2}. \quad (2)$$

The partial differential equation (2) is of the parabolic type. The integration of this equation with respect to the initial and boundary conditions is used to determine the concentration distribution within a material. There are a number of analytic solutions of equation (2) for the time-dependent, one-dimensional diffusion. Such solutions are given in books by Crank [1] and Carslaw and Jaeger [2].

The practically important solution is for the diffusion through a semi infinite solid with constant surface concentration. Boundary conditions: for $\tau = 0$, $c = c_0$ and for $\tau > 0$, $c = c_s$ at $x = 0$ and $c = c_0$ at $x = \infty$ (see Figure 1). Application of these boundary conditions to equation (2) yields the solution

$$\frac{c - c_0}{c_s - c_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{D\tau}}\right) \quad (3)$$

where c is the concentration at distance x after time τ . The expression erf is the Gaussian error function [3].

The resulting concentration profiles at three different time moments are shown in Figure 1.

FIGURE 1. Concentration Profiles for Unsteady-state Diffusion at Three Different Times

The nitrided material hardness distribution should be corresponding to the concentration profile of the diffusing nitrogen.

Because the nitriding process proceeds in a thin layer for a relatively long exposure time and for the above mentioned invariable boundary conditions, the problem can be simplified as the one-dimensional quasi-stationary solution that can be easily applied for bodies of simple shapes: plane, cylindrical, and spherical.

In the case of the steady state diffusion through a plane wall (see Figure 2), the isoconcentration surfaces are planes parallel to the wall surface and perpendicular to the x axis.

FIGURE 2. Schematic of Diffusion through the Plane Wall

The differential equation of Fick's law of diffusion (1) can be easily solved by the separation of variables. By integrating we obtain

$$\frac{dn}{d\tau} = -D A \frac{c - c_s}{x} \quad (4)$$

This molar diffusion flux causes the change in the molar concentration within the volume of layer of thickness x due to diffusion. Thus is

$$\frac{dn}{d\tau} = x A \frac{dc}{d\tau} \quad (5)$$

By comparing the right sides of equations (4) and (5) and separating the variables we can integrate

$$\int \frac{1}{c - c_s} dc = -\frac{D}{x^2} \int d\tau \quad (6)$$

By integrating equation (6) for the initial conditions, as shown in Figure 2, we obtain

$$\ln(c - c_s) - \ln \Delta c_0 = -\frac{D}{x^2} \tau \quad (7)$$

and by rearranging the equation for the concentration distribution within the plane wall in the final form

$$\frac{c - c_s}{c_0 - c_s} = \exp\left(-\frac{D \tau}{x^2}\right) \quad (8)$$

Concentration profiles obtained from solving equation (8) for three different time moments are shown in Figure 3.

FIGURE 3. Concentration Profiles for Quasi-stationary Solution of Diffusion at Three Different Times

Applying of the same procedure to the cylindrical wall of surface radius r_s , we obtain the equation for the concentration distribution at distance x from the surface after time τ in the form valid for the concave side of the surface

$$\frac{c - c_s}{c_0 - c_s} = \exp \left(- \frac{D \tau}{\left(\ln \frac{r_s + x}{r_s} \right) \left(r_s + \frac{x}{2} \right) x} \right) \quad (9)$$

and for the convex surface of the cylinder

$$\frac{c - c_s}{c_0 - c_s} = \exp \left(- \frac{D \tau}{\left(\ln \frac{r_s}{r_s - x} \right) \left(r_s - \frac{x}{2} \right) x} \right) \quad (10)$$

The one-dimensional quasi-stationary solution of the concentration distribution for the spherical wall of surface radius r_s at distance x from the surface after time τ for the concave surface of the sphere is given by

$$\frac{c - c_s}{c_0 - c_s} = \exp \left(- \frac{D \tau}{\left(\frac{1}{r_s} - \frac{1}{r_s + x} \right) \left(r_s^2 + r_s x + \frac{x^2}{2} \right) x} \right) \quad (11)$$

and for the convex spherical surface

$$\frac{c - c_s}{c_0 - c_s} = \exp \left(- \frac{D \tau}{\left(\frac{1}{r_s} - \frac{1}{r_s - x} \right) \left(r_s^2 - r_s x + \frac{x^2}{2} \right) x} \right) \quad (12)$$

The comparison of concentration profiles obtained from solving equations (8), (9), (10), (11), and (12), i.e. for flat, cylindrical (concave and convex), and spherical (concave and convex) surfaces, is shown in Figure 4a.

FIGURE 4a. Concentration Profiles for Flat, Cylindrical, and Spherical Surfaces, $r_s = 7$ mm

In general, concentration profiles for the above cases are almost identical as seen from Figure 4a for the surface radius $r_s = 7$ mm. If we want to have some partial differences, it is necessary to apply these equations for a smaller surface radius, e.g. $r_s = 3.5$ mm as shown in Figure 4b.

FIGURE 4b. Concentration Profiles for Flat, Cylindrical, and Spherical Surfaces, $r_s = 3.5$ mm

Anyway, if we want to apply the principle of one-dimensional quasi-stationary diffusion for describing the nitriding process, where the diffused layer produced in the course of this process is between 0.001 and 0.6 mm, it is evident that we can apply the flat surface solution for any nitriding shape.

This conclusion agrees well with the one drawn in [4], where the generalized equation of energy transport has been analyzed. In that work the Laplace operator was written in its most general form, to account for the geometry effect.

Now we are looking for a universal representation (approximation) of solution (3) in terms of elementary functions. It is evident that the logistic function in the form

$$\frac{c - c_0}{c_s - c_0} = \frac{1}{1 + a \exp[b(x - k \tau)]} \quad (13)$$

is the best candidate for such an approximation.

We are now looking for the parameters a , b , and k , to provide the best fit.

Firstly, because for $x = 0$ and $\tau = 0$ $c = c_s$, it immediately follows that $a = 1$.

Then, $b = 4/\sqrt{\pi}$ provides the best fit, to account for the coefficient $2/\sqrt{\pi}$ in the definition of the error function.

Yet, to account for the physical properties of the material the diffusion coefficient must be included (it dictates the slope of the solution). In view of this, the

final expression for the parameter b becomes $b = 4/\sqrt{\pi D}$.

Finally, the parameter k describes the propagation of the diffusion front inside the material. In other words, it determines how fast the position of isoconcentration surfaces changes. Obviously, k depends not only on the physical state of the material in question but also on temperature.

MODEL OF THE HARDNESS FOR DIFFUSION NITRIDING

It is possible to assume, that the material hardness distribution within the near-surface layer corresponds to the concentration profiles by diffusion.

Effect of Holding Time of Nitriding

The nitrided steel hardness HV distribution for four different holding times of nitriding is shown in Figures 5. The hardness achieved on the surface HV_s decreases with the depth x until core hardness HV_0 is reached. The nitriding creates a high surface hardness and a sharp transition zone between nitrided surface and the core material.

Results of the hardness distribution testing for 4, 9, 15, and 40 hours of nitriding processed at the temperature 500 °C are given for the steel of the material number 32CrMoV12-10. The surface hardness $HV_s = 1140$ and the core hardness $HV_0 = 520$.

By applying the quasi-stationary solution given by equation (8), we obtain the hardness approximation in the form

$$\frac{HV - HV_s}{HV_0 - HV_s} = \exp\left(-\frac{D^* \tau}{x^2}\right) \quad (14)$$

where D^* is the modified coefficient of diffusion as the coefficient of nitriding.

Results of the quasi-stationary approximation (14) for $D^* = 0.0004$ (mm²/h) in comparison with experiment are shown in Figure 5a. It is seen that results of approximation do not correspond to the experiment very well.

If we want to improve the quasi-stationary approximation, it is necessary to apply the empirical member k into equation (14) as

$$\frac{HV - HV_s}{HV_0 - HV_s} = \exp\left(-\frac{D^* \tau}{x^{2+k\tau}}\right) \quad (15)$$

Results of the given approximation (15) for $D^* = 0.00009$ (mm²/h) and $k = 0.05$ (1/h) in comparison with the experiment are shown in Figure 5b.

FIGURE 5a. Hardness Profiles Approximation by Equation (14) for Various Time of Nitriding, Steel 32CrMoV12-10

FIGURE 5b. Hardness Profiles Approximation by Equation (15) for Various Time of Nitriding, Steel 32CrMoV12-10

FIGURE 5c. Hardness Profiles Approximation by Equation (16) for Various Time of Nitriding, Steel 32CrMoV12-10

The best results give the approximation by the logistic function (13) applied for the hardness profile approximation in the form

$$\frac{HV - HV_0}{HV_s - HV_0} = \frac{1}{1 + \exp\left[\frac{4}{\sqrt{\pi D^*}}(x - k\tau)\right]} \quad (16)$$

Results of this approximation are given in Figure 5c for $D^* = 1.0 \text{ (mm}^2\text{)}$ and $k = 0.072 \text{ (mm/h)}$ in comparison with the experimental data.

Combined Effect of Nitriding Temperature and Holding Time

Results of the hardness distribution testing for various nitriding temperatures and nitriding holding time are shown in Figures 6 for the steel of the material number X2CrNiMo17-12-2. The surface hardness $HV_s = 1400$ and the core hardness $HV_0 = 220$.

Results of the improved quasi-stationary approximation (15) are given in Figure 6a for $k = 0.05 \text{ (1/h)}$ and for the nitriding coefficients, which are depending on temperature as:

$$D^* (450^\circ\text{C}) = 0.0000008 \text{ (mm}^2\text{/h)}$$

$$D^* (460^\circ\text{C}) = 0.000008 \text{ (mm}^2\text{/h)}$$

$$D^* (490^\circ\text{C}) = 0.00001 \text{ (mm}^2\text{/h)}$$

$$D^* (510^\circ\text{C}) = 0.0001 \text{ (mm}^2\text{/h)}$$

Even this improved quasi-stationary approximation (15) does not correspond very well with the experimental data, namely for longer times of nitriding as seen in Figure 6a.

FIGURE 6a. Hardness Profiles Approximation by Equation (15) for Varied Nitriding Temperatures and Different Time of Nitriding, Steel X2CrNiMo17-12-2

The logistic function (13) provides a very good approximation for various nitriding temperatures and nitriding holding time as shown in Figure 6a. This approximation is given for the nitrided material constant $D^* = 2.7 \text{ (mm}^2\text{)}$ and for the propagation velocities of nitriding front inside the material, which depend on temperature as:

$$k (450^\circ\text{C}) = 0.0009 \text{ (mm/h)}$$

$$k (460^\circ\text{C}) = 0.0026 \text{ (mm/h)}$$

$$k (490^\circ\text{C}) = 0.0033 \text{ (mm/h)}$$

$$k (510^\circ\text{C}) = 0.0085 \text{ (mm/h)}$$

FIGURE 6b. Hardness Profiles Approximation by Equation (16) for Varied Nitriding Temperatures and Different Time of Nitriding, Steel X2CrNiMo17-12-2

CONCLUSIONS

In this work, a universal representation for an exact solution has been found in terms of elementary functions. It has been demonstrated that the logistic function describes the process with accuracy less than two per cent. Moreover, only one parameter is sufficient to provide the best fitting of experimental data.

The simple model developed in this study can, therefore, become a powerful tool for analyzing the process of nitriding in a wide range of applications.

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REFERENCES

1. J. Crank, *The Mathematics of Diffusion*, Oxford: Clarendon Press, 1975, pp. 11-103.

2. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford: Clarendon Press, 1959, pp. 50-230.
3. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, Washington, D.C.: National Bureau of Standards, Applied Mathematics Series – 55, 1972, pp. 295-300.
4. Kulish, V. V., An Analytical Solution of the Generalized Equation of Energy Transport in One-Dimensional Semi-Infinite Domains, *Journal of Mathematical Problems in Engineering*, Volume 2004, Issue 3, pp. 185-195.