Simulation of oxide phases formation under pulsed electron beam

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Abstract. This paper presents the mathematical model of evolution phase composition in the TiNi+Si system under impulsive electron beam. It was assumed that the initial coating contains small concentration of molecular oxygen. This model is one-demensional, and takes into account the phenomena of diffusion, chemical reactions, and thermal effects of chemical reactions. Results of the numerical modeling had show that the oxide of titanium and triple solution TiNiSi formed in significant amounts, and triple solution preferentially forms in the substrate. Other oxides must be formed in trace amounts.

1. Introduction

Nitinol is well studied and frequently used in practice medicine for a long time. However, its nitinol employment is restricted by use in medicine neat complicated rather the high toxicity of nickel. To avoid the toxic effect of nickel the various protective coatings are used. Special attention has been paid to the adhesive strength of coatings and methods of its increase [1, 2]. The coatings can be formed in by different ways: by chemical, electroplating, electron beam exposure reaction, and etc. One of methods consists in the coating deposition using the ion plasma technique [3] with the subsequent treatment it with the a low-energy high-current electron beam [4-6]. The formation of the protective coating is difficult to observe directly, so hence the important question of the development of a mathematical model of the this process is very important. In this paper introduces a the one-dimensional mathematical model of the dynamics evolution of phase composition in the system under impulse action of a low-energy electron flow. The model takes into account the phenomena of diffusion, chemical reactions, and thermal effects of chemical reactions and allows to study the element's redistribution.

2. Mathematical formulation of the problem

We suppose a that NiTi-sample with the thick silicon coating of thickness h undergoes the pulsed electron beam processing. A small amount of molecular oxygen presents in the surface layer of the coating. Provided that the parameters of the electron beam are identical across the surface of the same sample the problem can be considered a as one-dimensional problem (Figure 1).
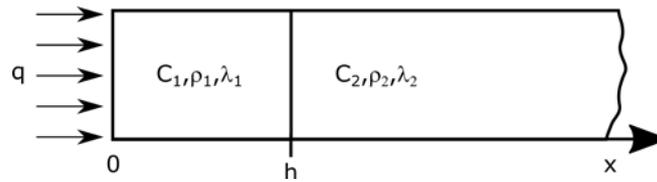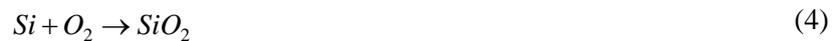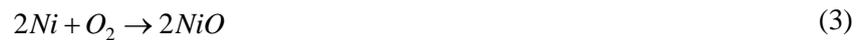
Figure 1. Illustration to the problem formulation.

Chemical reactions during the processing are described to this system of equations:

$$Ti + O_2 \rightarrow TiO_2 \tag{1}$$

$$Ti + Ni + Si \rightarrow TiNiSi \tag{2}$$

$$2Ni + O_2 \rightarrow 2NiO \tag{3}$$

$$Si + O_2 \rightarrow SiO_2 \tag{4}$$

The rates of these reactions are denoted as φ_i where $i = 1\ldots4$.

In such formulation, the dynamics of the specimen temperature in the sample in such a formulation is described by one-dimensional heat thermal conductivity equation:

$$c_k \rho_k \frac{\partial T_k}{\partial t} = \frac{\partial}{\partial x}\left(\lambda_k \frac{\partial T_k}{\partial x}\right) + W_{ch}, \tag{5}$$

where k is the index, $k = 1, 2$, c_1, ρ_1 are the density and heat capacity of the coating, c_2, ρ_2 are the density and heat capacity of the substrate, T_1, T_2 are the temperature of the coating and the substrate, respectively, t is the time, x is the spatial coordinate, λ_1, λ_2 are thermal conductivities of the coatings and substrate, W_{ch} is the total heat source associated with the thermal effect of chemical reactions in the specimen, $W_{ch} = \sum\limits_{i=1}^{4} Q_{ch,i}\varphi_i$, $Q_{ch,i}$ is the thermal effect of the i-th reaction.

Concentrations of free compounds elements of (Si, Ti, Ni and O_2) follow from determined by the diffusion equations:

$$\frac{\partial C_j}{\partial t} = \frac{\partial}{\partial x}\left(D_j \frac{\partial C_j}{\partial x}\right) + \sigma_j, \tag{6}$$

where, C_j are the molar concentrations of elements Si, Ti, Ni and O_2, $j = 1,2,3,4$; D_j are their diffusion coefficients, which depend on the temperature corresponding to the Arrhenius law: $D_j = D_{0j}\exp(-E_{dj}/RT)$, D_{0j} are frequency factors, E_{dj} are the activation energies, R is the gas constant, σ_j are the sources or sinks related to chemical reactions.

The concentrations of the reaction products are determined by the kinetic equations:

$$\frac{dC_m}{dt} = \sigma_m, \tag{7}$$

where C_m are the molar concentration of the compounds TiNiSi, TiO_2, NiO, SiO_2; $m = 5,6,7,8$

The system is completed by with boundary and initial conditions:

$$x = 0: \quad -\lambda_1 \frac{\partial T_1}{\partial x} = q(t), \quad \frac{\partial C_j}{\partial x} = 0, \ j = 1\ldots4$$

$$x = h: \lambda_1 \frac{\partial T_1}{\partial x} = \lambda_2 \frac{\partial T_2}{\partial x}, \ T_1 = T_2,$$

$$D_j \left. \frac{\partial C_j}{\partial x} \right|_{x=h-0} = D_j \left. \frac{\partial C_j}{\partial x} \right|_{x=h+0}, \ j = 1 \ldots 4$$

$$x \to \infty: \ \frac{\partial T_2}{\partial x} = 0, \frac{\partial C_j}{\partial x} = 0, \ j = 1 \ldots 4$$

$$t = 0: \ T_1 = T_2 = T_0, \ C_j = C_{j0}, \ j = 1 \ldots 8$$

where $q = E / t_{imp}$ is the external heat flux, t_{imp} – impulse duration.

The reaction rates:

$$\varphi_1 = k_{01} \exp(-E_{a1} / RT) C_2 C_4,$$

$$\varphi_2 = k_{02} \exp(-E_{a2} / RT) C_1 C_2 C_3,$$

$$\varphi_3 = k_{03} \exp(-E_{a3} / RT) C_3^2 C_4,$$

$$\varphi_4 = k_{04} \exp(-E_{a4} / RT) C_1 C_4.$$

follow from the equations (1)-(4), the Arrhenius law and the law of mass action. The reaction rate constants, activation energies of chemical reactions () and heats of the reactions was were determined by means of known thermodynamical formulae [10].

According to above we shall obtain:

$$\sigma_1 = -\varphi_2 - \varphi_4, \ \sigma_2 = -\varphi_1 - \varphi_2, \ \sigma_3 = -\varphi_2 - 2\varphi_3,$$

$$\sigma_4 = -\varphi_1 - \varphi_3 - \varphi_4, \ \sigma_5 = \varphi_2,$$

$$\sigma_6 = \varphi_1, \sigma_7 = 2\varphi_3, \sigma_8 = \varphi_4.$$

In accordance with experiments [2, 5] it was assumed for in the calculations made: the thickness of the substrate is 1 cm, the coating thickness is of 200 nm, the sample is subjected to 5 times the pulse exposure, the pulse duration – is 150 ms, pause time is 0.02, the energy density in the beam was varied, and was about 20 J/cm^2.

Initial concentrations of the reagents are $C_{01} = 0.08296$ mol/cm^3, $C_{02} = 0.0535$ mol/cm^3, $C_{03} = 0.06548$ mol/cm^3, $C_{04} = 0.015$ mol/cm^3 (Figure 2).
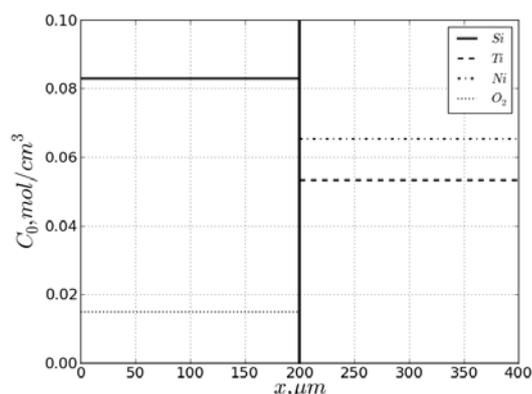

Figure 2. The initial concentrations. The vertical line shows the interface between the coating and substrate.

We assume the following values for thermal parameters: $c_1 = 0.7136 \frac{J}{mol \cdot K}$, $\rho_1 = 2.33$ g/cm^3,

$c_2 = 0.227 \frac{J}{mol \cdot K}$, $\rho_2 = 6.45$ g/cm^3, $\lambda_1 = 1.49 \frac{W}{cm \cdot K}$, $\lambda_1 = 0.18 \frac{W}{cm \cdot K}$.

The results of the formal evaluation of the formal kinetic parameters of for the reactions are presented in the Table. 1, the values of diffusion parameters values are shown in the Table 2.

Table 1. Formal-kinetic parameters for reaction

Reaction	ΔH, J/mol	E_d, J/mol	$k_0, \frac{1}{s}$
$Ti + O_2 \rightarrow TiO_2$	-50049	322707	$2.133 \cdot 10^{16}$
$Ti + Ni + Si \rightarrow TiNiSi$	-1430	27650	$0.8 \cdot 10^5$
$2Ni + O_2 \rightarrow 2NiO$	-47818	351900	$1.5 \cdot 10^9$
$Si + O_2 \rightarrow SiO_2$	-40179	316680	$3.188 \cdot 10^9$

Table 2. Diffusion parameters

Substance	$D_{0i}, \frac{cm}{s^2}$, $x \le h$	E_a, J/mol, $x \le h$	$D_{0i}, \frac{cm}{s^2}$, $x > h$	E_a, J/mol, $x > h$
Si	1800	$11 \cdot 10^4$	$3 \cdot 10^4$	$1 \cdot 10^5$
Ti	6.4	$123 \cdot 10^3$	2	$15 \cdot 10^4$
Ni	190	$185 \cdot 10^3$	$6 \cdot 10^{-4}$	$9 \cdot 10^4$
O_2	0.21	$292 \cdot 10^3$	0.049	$84 \cdot 10^3$

The resulting system of equations was solved numerically. Thermal conductivity heat equations (5) and diffusion equations (6) are solved using an the implicit finite difference schemes and double sweep method, the kinetic equations (7) – was solved by Euler method.

3. Examples
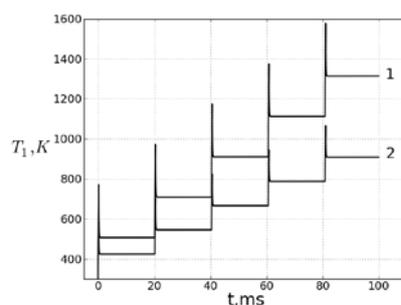Changing the temperature in the point $x = 0$ is illustrated in Figure 3.

Figure 3. The temperatures at the point $x = 0$.
$1 - E = 25$ J/cm^2, $2 - E = 15$ J/cm^2.

Quite naturally, the temperature rises sharply in times during of exposures, and rapidly decreases in the pauses between them that is quite naturally. In the during early stages of exposure, diffusion of free elements is insignificant due to the low average temperature of the sample medium of free diffusion of elements is insignificant. Further, the redistribution element concentration near the boundary interface

between the coating and the substrate becomes conspicuous, and with further increase in of the temperature accelerates the process accelerates (Figure 4).
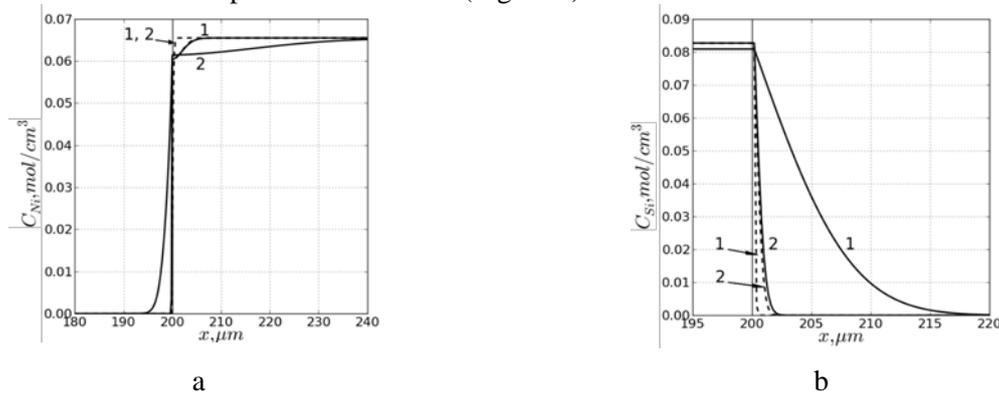

| a | b |

Figure 4. The concentration profiles, a – Ni, b – Si. $1 - t = 2 \cdot 10^{-2}$ s., $2 - t = 3 \cdot 10^{-2}$ s The solid line corresponds to the $E = 25$ J/cm^2, dashed – $E = 15$ J/cm^2. The vertical line shows the interface between the coating and substrate.

It was detected that triple solution preferentially forms in the substrate due to the greater mobility of silicon than nickel (Figure 5).
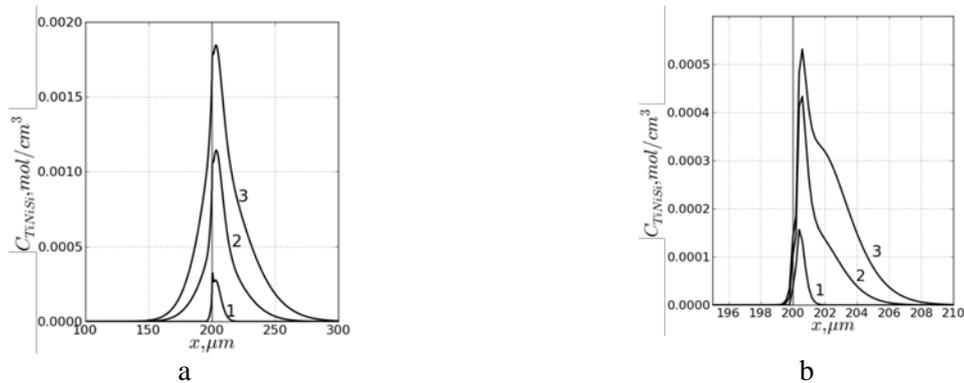

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Figure 5. The concentration profiles $TiNiSi$ a – $E = 25$ J/cm^2, b – $E = 15$ J/cm^2. $1 - t = 3 \cdot 10^{-2}$ s., $2 - t = 4.5 \cdot 10^{-2}$ s, $3 - t = 5 \cdot 10^{-2}$ s. The vertical line shows the boundary between the coating and the substrate.

Contained in the coating oxygen reacts with titanium to form titanium oxide (Figure 6). This reaction has the following character: up to a certain point of time titanium oxide practically does not form, then its concentration increases markedly during some microseconds (Figure 6b).
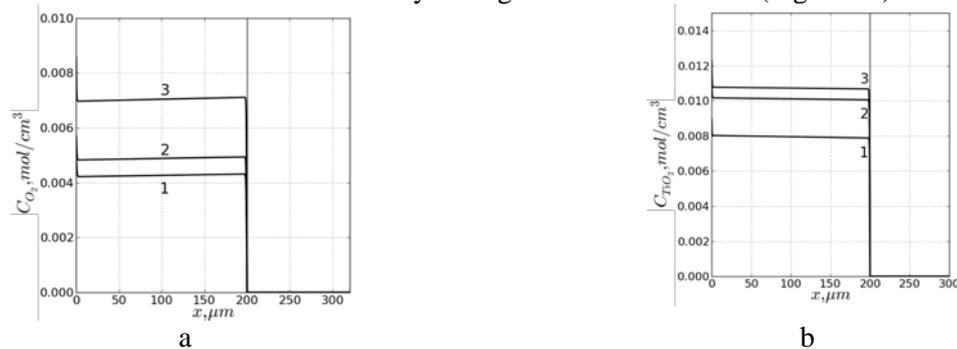

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Figure 6. The concentration profiles, a – O_2, b – TiO_2. $1 - t = 8.1 \cdot 10^{-2}$ s., $2 - t = 8.2 \cdot 10^{-2}$ s, $3 - t = 8.3 \cdot 10^{-2}$ s. The vertical line shows the interface between the coating and the substrate.

The oxides of nickel and silicon do not form (in the numerical experiment, their concentrations do not exceed 10^{-9} mol/cm^3).

4. Conclusion

In response a pulsed electron beam on the sample of Nitinol with silicon doped and oxygen near the surface layer of a solid solution and oxide.

Thus, numerical experiments had show that during impulse electron beam action on the sample of Nitinol with silicon coating containing initial Oxygen, solid solution and oxide are generated in the surface layer. Small concentrations of the oxides of nickel and silicon appearing in the heated zone should not affect the properties of the sample.

Modeling suggests that the oxides of nickel and silicon should not affect the properties of the sample, since the assumed values of processing parameters must be formed in trace amounts.

References
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