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Research of the thermal-tension condition and the elemental composition gradient changes of binary systems produced by combined ion-plasma method

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Abstract. To increase the life cycle of the constructional steel products working at high temperatures in air environment the combined ion-plasma method of surface modification was elaborated. Using the method described in the paper, constructional steel J24056 samples with different refractory metal coatings such as molybdenum and tantalum and film-thickness up to 10 microns were prepared. The calculations of the temperature distribution and the tension on the depth of the specified sample brand coated steel were performed. The research of oxygen distribution in the surface layer after high temperature annealing in an air atmosphere has been conducted. An estimation model of the oxygen distribution within the grains in a binary steel-coating system is proposed in the paper.

1. Introduction

To increase the life cycle of constructional steel products [1], working in the conditions of the high temperatures in an oxygen atmosphere, a combined ion-plasma method of surface modification that includes ion implantation and ion-plasma magnetron sputtering was developed. Ion implantation is performed before magnetron sputtering to improve an adhesion of the constructional steel surface [2-4]. It should be noted that the ion implantation of modifier material before its sputtering improves an adhesion from 5 to 10 times, which has a significant influence on the physical, mechanical and performance properties of the products [5]. The main problems discussed in the paper are the temperature and tension distribution in a binary «steel-coating» system calculation, mass transfer of small impurities inside the grain model creation, the combined ion-plasma method elaboration, explanation of modifier material selection, as well as study of the structure and composition of the binary «steel-coating» system after annealing in air atmosphere.

2. The temperature distribution

For the research of the thermal-tension condition of constructional steel J24056 with the coating, as modifier materials were selected the following elements: titanium, nickel, chromium, vanadium, molybdenum, tantalum, tungsten and niobium [6, 7]. The selection of these elements as modifier materials was determined by their protective properties [8-11]. For the development of the constructional steel products modification method and determination the conditions of their subsequent operation, the information about the dynamic field of temperature distribution is required. Application of both the energy conservation laws and Fourier's law to analysis for heat conductivity in the motionless isotropic environment led to the differential equation of heat conductivity, which connects the temporal and spatial changes of temperature [12]. During the incidence of heat flow onto a flat plate, the problem of the temperature distribution can be considered as one-dimensional because of the uniform distribution of heat flow on the surface area of the plate and the plate area being much greater than the thickness of the layer under study (surface area is much greater than the thickness of the modifier layer).

3. Distribution of internal tensions caused by the temperature gradient

Consider the tensions occurring in the material during thermal heating. Initially, consider the two-layer plate which is heated by gas flow unevenly on one side. The wave of dynamic tension along the OX axis quickly fades; however, there is tension in the cross direction of the OX axis. This tension is caused by the temperature gradient along the OX axis and the heterogeneity of the properties in multi-layered samples. The corresponding components can be determined from the following expression (1) [13]:

$$\sigma_z = \sigma_y = \frac{\alpha(T)E(T)}{1-\mu} T(x) + C_1 + C_2 x \tag{1}$$

Here $\alpha(T)$ is the coefficient of thermal expansion, E is the elastic modulus, μ is the Poisson's coefficient, C_1 and C_2 is the constants that are defined from a condition that the resultant force and the resultant moment are equal to zero [13]. It is necessary to take into account the boundary conditions, similarly, σ_z [13]:

$$\sigma_z = \sigma_y = -K(x)T(x) + \frac{K(x)}{h}\int_0^h T dx + \frac{3K(x)(x-\frac{h}{2})}{\frac{h^3}{4}}\int_0^h T(x-\frac{h}{2})dx \tag{2}$$

Here $K = \frac{\alpha(x)E}{1-\mu}$. This type of tension is responsible for a small grid of cracks formation on a sample surface. Moreover, the change of linear expansion coefficient renders a significant influence on the cracks formation. It takes place due to the process of heating and temperature variation that is also considered in the calculation scheme. Thus, σ_y and σ_z tensions are the most destroying. As the calculations of tensions in the cross direction versus the sample depth indicated, the lowest tensions occur in the following materials: tungsten, molybdenum, chromium and tantalum. Additional tests in terms of chemical hardness narrowed the choice of materials to molybdenum and tantalum.

4. The mass transfer of small impurities inside the grain

As a result of the binary «steel-coating» system heating in an air atmosphere the oxygen diffuses from the gas phase into the surface layers of the product. In contrast with the iron atoms and the other metals the oxygen atoms are small-sized and their diffusion is carried out mainly by interstitial mechanism.

To explain and quantify the elemental composition is used the kinetic equation (3) which determines the concentration of atoms of type B in the binary system of the atoms of type A and B under the influence of the temperature gradient and internal tensions.

$$\frac{\partial c_B^i}{\partial x} = -\frac{\partial}{\partial x} D_B^i \frac{\partial c_B^i}{\partial x} \; [1 + (\frac{P}{E})^2] + \frac{\partial c_B^i}{\partial x} (D_A^i \frac{\partial c_A^i}{\partial x} - D_B^i \frac{\partial c_B^i}{\partial x}) \; [1 + (\frac{P}{E})^2] + 2 \frac{\partial}{\partial x} \frac{c_B^i c_A^i}{kT^2} (\frac{D_B^i E_B^i}{c_A^i} - \frac{c_B^i D_B^i E_B^i}{c_A^i} - D_A^i E_A^i)[1 + (\frac{P}{E})^2] \frac{\partial T}{\partial x} \quad (3)$$

Here c_A^i and c_B^i is the concentration of atoms of type A and B respectively, $D_B^i = D_{0B}^i \; exp(-E_B^i / kT)$ and $D_A^i = D_{0A}^i \; exp(-E_A^i / kT)$ is diffusion coefficients of atoms of type B and A (see table 1). P is the internal tensions in the material, E is the Young's modulus, T is the temperature, k is the Boltzmann constant, E_B^i and E_A^i is the activation energy of interstitial diffusion mechanism. The first term in equation (3) describes the concentration mechanism of interstitial diffusion mechanism, the second – counter flows of components A and B, the third term describes the thermal diffusion on the interstitial mechanism. The diffusion coefficients of nitrogen and oxygen atoms ($D_0 \; exp(-E_A / kT)$) borrowed from [14].

To determine the distribution of elements concentrations, equation (3) must be supplemented by the influence of the mutual recombination mechanisms, when vacancy and interstitial atom disappear, as well as sinks of point defects on dislocations and grain boundaries. Basic mechanisms of elements redistribution in the surface layers associated with the point defects flows: vacancies and interstitials atoms. To calculate the concentration of vacancies and interstitial atoms consider the grain disposed on the surface as the model. Let the section of grain be rectangular. To calculate the concentration of point defects in this case, we use the following system of equations (4-5):

$$\frac{\partial C_{iB}}{\partial t} = exp(-E_i / kT) - ZC_V C_{iB} + \frac{\partial}{\partial x}(-D_i \frac{\partial C_{iB}}{\partial x}) + \frac{\partial}{\partial y}(-D_i \frac{\partial C_{iB}}{\partial y}) - K_i C_{iB} \quad (4)$$

$$\frac{\partial C_V}{\partial t} = exp(-E_V / kT) - ZC_V C_V + \frac{\partial}{\partial x}(-D_V \frac{\partial C_V}{\partial x}) + \frac{\partial}{\partial y}(-D_V \frac{\partial C_V}{\partial y}) - K_V C_V \quad (5)$$

Here $C_{iB} = exp(-E_i / kT)$ and $C_V = exp(-E_V / kT)$ is respectively the concentration of thermodynamic equilibrium vacancies and interstitial atoms at high temperature [15], $Z = 4\pi r_V v_i Z$ is the proportionality coefficient in the recombination; D_i and D_V is respectively the diffusion coefficients of interstitials and vacancies, $r_i = (\rho D_{0i} \; exp(-E_i / kT)) / 2$ and $r_V = (\rho D_{0V} \; exp(-E_V / kT)) / 2$ is the he rate of interstitials and vacancies annihilation on dislocation sinks [16], v_i is the hopping frequency.

The most intense annihilation mechanisms are the mutual recombination and annihilation of the dislocation at sinks. The next type of sinks is the grain boundary, which is limited. Vacancy concentration inside the grain will be higher than at the sinks. Therefore, point defects will move to the sinks, i.e. to the surface and grain boundaries. Schematically, the vacancies flows are represented in figure 1. Since the surface and grain boundaries are effective sinks of vacancies, the concentration of equilibrium vacancies decreases at the sinks. As a result of this process there are significant gradients vacancies, that stimulates the atoms diffusion. If the alloy contains several types of atoms, the equilibrium vacancy gradient leads to a flow of atoms, which in turn brings to a redistribution of the elements in the alloy.

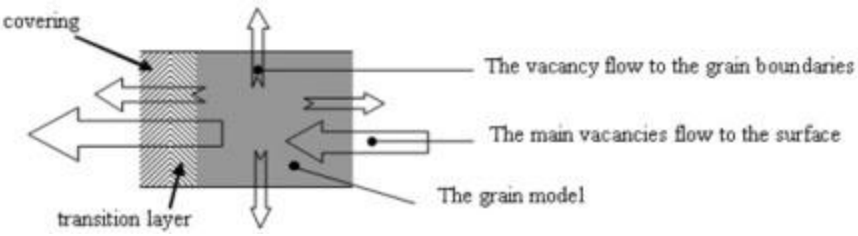

Figure 1. The scheme of the vacancies flows distribution.

Redistribution of impurities can be explained by the presence of point defects gradients at the grain boundary. Grain boundary is an intense vacancies sink, so the average profile of the vacancies distribution in the grain boundary changes its shape. As a result, two streams of impurities occur: one is directed transversely to the surface, and the second parallel to it, i.e. is directed to a grain boundary (see figure 1). The oxygen concentration in the grain area (see figure 2) was calculated according to the basis of equations (4) and (5). The theoretical studies indicate that the oxygen concentration leads to increasing in the interior area of the grain. The calculation on grain rectangular shape shows an increase in oxygen concentration of 35%.

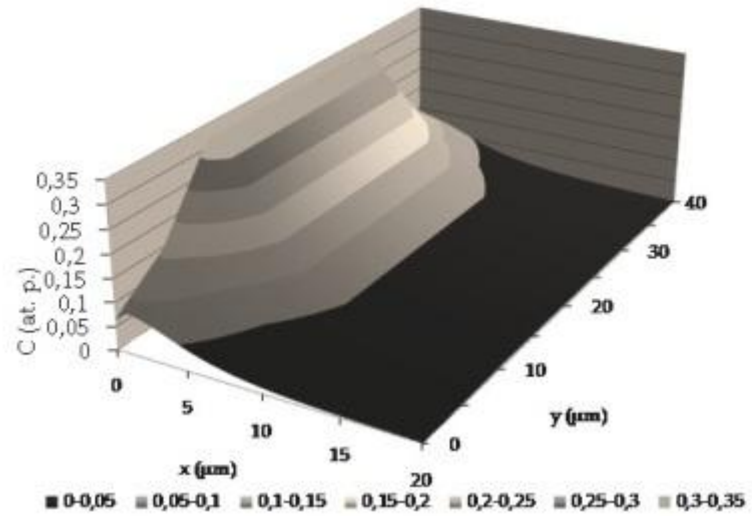

Figure 2. The oxygen distribution in steel J24056 after 60 minutes annealing, the calculation data of rectangular shape grains.

5. The oxygen influence on the structure and composition of the binary «steel-coating» system surface after heating in air atmosphere

To study the oxygen influence on the life cycle of the coating, the samples were annealed for 30-70 minutes at a temperature of 900°C in air atmosphere. As an annealing result, the oxygen diffusion in the surface layers and its redistribution within microcrystal grains [17], which is known in the literature as the segregation elements term, takes place. At high temperatures occurs the segregation of small impurities inside the grain. The calculations have shown that the oxygen concentration in the interior area of the grain is increased by reducing the concentration at the boundary. In addition, the concentration of oxygen can be increased to 40%. As it is shown by experimental SEM studies, the oxygen concentration increases within the grains and reduces to the boundaries (see figure 3). To compare the results of a numerical calculation with the experimental results, the analysis of the surface layer composition with the aid of the SEM microprobe in a straight line was carried out. The results of calculation correlate well with the experimental results.

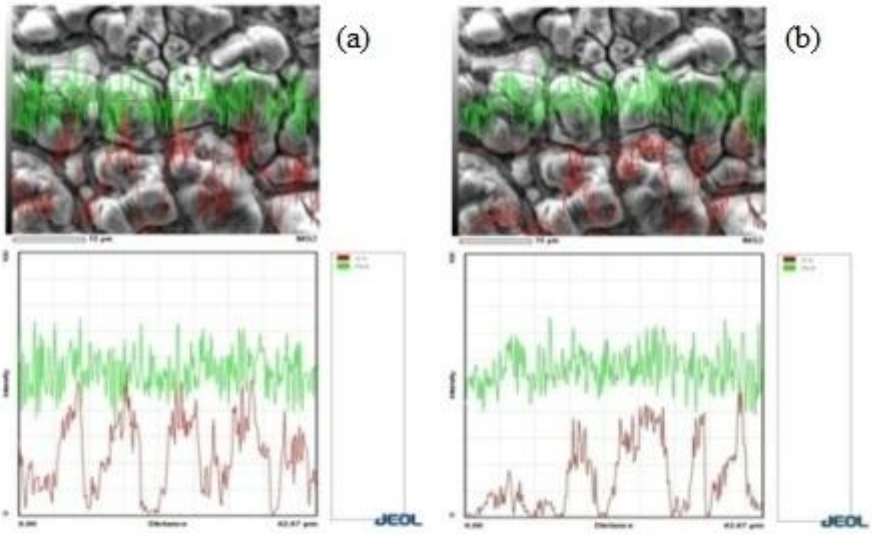

Figure 3. The elements distribution in the molybdenum-steel system after annealing at 900°C (a) within the grains (b) along the grains boundary

6. The combined ion-plasma method of surface modification

The combined ion-plasma method was realized on the NNV-6 installations together with the ADVAVAC VSM-200 installation. Technological process of ion implantation with the subsequent magnetron sputtering is performed step-by-step and includes the samples preparation, ionic cleaning, ion implantation, ion-plasma sputtering, cooling. The modes of combined ion-plasma method were defined experimentally for each type of coating material [18]. Superficial structural modification was performed according to the described method. Transition layers between the coatings and the matrix were analyzed with the scanning electron microscope JEOL JCM-5700 (see figure 4).

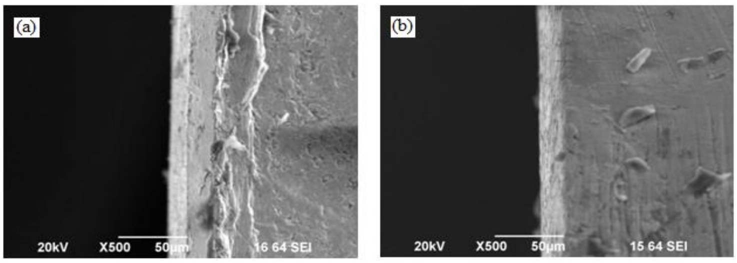

Figure 4. SEM micrograph of a cross-section of the binary «steel-coating» system with molybdenum (a) and tantalum (b) as a modifier material

During the analysis of different areas between the coatings and the matrix on the occurrence of micro-cracks, inclusions and heterogeneity regions, the best quality of the molybdenum adhesion was revealed. In accordance with the combined ion-plasma method of surface modification were obtained calibration plates for laser cutting «LaserMat-4200» installation. The plates modified by combined ion-plasma method were subjected to the field tests which have been carried out at plant of a bridge metalwork of NPO Mostovik LLC in the Omsk city. The estimated tests demonstrated at least the twofold increase in the term of plates operation, and in some cases it increased from 2 to 4 times, the enhance of periods of between-repairs interval.

7. Conclusion

To reduce the tensions caused by rapid heating and cooling, molybdenum and tantalum are the most appropriate coatings from the point view of its thermal characteristics.

The experimental and theoretical studies indicate that the segregation of small impurities (oxygen) leads to increasing in its concentration in the interior area of the grain. The experimental data of oxygen concentration in the grains increased to 40%, calculated on grain rectangular shape shows an increase in oxygen concentration of 35%, which indicates good correlation developed model. The combined ion-plasma method of surface modification including ion implantation with the subsequent magnetron sputtering was elaborated. The empirically optimized coating mode provides the improving of constructional steel products efficiency in a high-temperature exposure, thus increasing the life cycle of the calibration plates for the laser cutting «LaserMat-4200» installation twice.

Acknowledgments

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