The influence of the high temperature annealing on the small impurities segregation in J24056 grain steel

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Abstract

In the process of constructional steel products operation in conditions of high temperatures, chemical elements segregation occurs, which leads to the surface characteristics changing and influences their operation period. This paper is aimed in developing the model of mass transfer and redistribution of small-sized atoms (carbon, oxygen) in the binary system “steel-coating” after high temperature annealing in air atmosphere. It is estimated, that carbon concentration inside the grain increases up to 2.81%, at the grain boundaries it reaches 0.44%, while oxygen concentration increases in average up to 16%. The main mechanisms, leading to the redistribution of small-sized impurities, are non-equilibrium flows of point defects to the surface and grains boundaries.

Keywords: mass transfer model; segregation; small-sized impurities; carbon; oxygen; high temperature annealing

1. Introduction

Theoretical and experimental investigation of chemical elements segregation in constructional steel products working in the conditions of the high temperatures is an important issue of modern materials science thanks to the influence of diffusion processes on the physical, chemical and operational material characteristics [1]. Of great scientific interest are the mechanisms of chemical elements redistribution, including small-sized impurities [2, 3], occurring on the boundaries and inside the grain and having much influence on the metal products [4], alloys [5], low-alloyed [6] and austenitic steels [7] operational characteristics. The frontmost investigation directions of chemical elements segregation, caused by high temperature influence, include the forecasting of materials strength

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characteristics [8], caused by the character and the depth of elements redistribution at the boundaries and inside the grain [9]. To calculate the elements redistribution at the grain boundary, physics-and-mathematical models of this mechanism are developed, various mathematical methods, such as Monte Carlo simulation [10], are implemented.

Theoretical importance of the research of elements thermo diffusion at the boundaries and inside the grain, caused by high temperature influence, is that the authors developed and verified the mass transfer model for small-sized carbon and oxygen impurities in constructional steel J24056 (the analogue of Russian steel 38X2MYuA), as well as in the binary system “steel-coating”. To describe the processes of mass transfer in the systems with small-sized impurities on the base of statistical physics approaches, we obtained kinetic equation of point defects diffusion – vacancies and interstitial atoms in the area of temperature gradient taking into account the velocity of their annihilation at dislocation areas. It was found out, that mass transfer of small-size carbon and oxygen impurities is performed mainly by the interstitial mechanism. High degree of the computational results convergence with the experimental data proves practical importance of the research thanks to the possibility of using its results for the investigation of high temperature influence on the operational characteristics of constructional steel J24056 products.

2. Model of small-sized impurities mass transfer in binary system

The result of heating in air atmosphere is the diffusion of carbon and oxygen in surface layers of steel J24056. Carbon and oxygen atoms, comparing with atoms of iron and other metals, are small-sized, and their diffusion, is carried out mainly by the interstitial mechanism. To explain and numerically describe the elemental composition we use kinetic equation (1), which describes the concentration of atoms type B in binary system from type A and B atoms under the influence of temperature gradient and internal stresses. The first addend in equation (1) describes the diffusion concentration mechanism by the interstitial mechanism; the second addend describes counterflows of A and B components; the third addend describes thermo diffusion by the interstitial mechanism. Diffusion coefficients are taken from [11].

\[ \frac{\partial c_B^i}{\partial x} = - \frac{\partial}{\partial x} D_B^i \frac{\partial c_B^i}{\partial x} [1 + \left( \frac{P}{E} \right)^2] + \frac{\partial c_B^i}{\partial x} \left( D_A^i \frac{\partial c_A^i}{\partial x} - D_B^i \frac{\partial c_B^i}{\partial x} \right) [1 + \left( \frac{P}{E} \right)^2] + 
\]

\[ + 2 \frac{\partial}{\partial x} \left( \frac{c_B^i}{c_A^i} \right) \left( \frac{D_B^i E_B^i}{c_A^i} - \frac{c_B^i D_A^i E_A^i}{c_A^i} - D_A^i E_A^i \right) [1 + \left( \frac{P}{E} \right)^2] \frac{\partial T}{\partial x} \]

(1)

where \( c_A^i \) and \( c_B^i \) is concentrations of atoms types A and B, \( D_B^i = D_{0B} \exp(- E_B^i / kT) \) and \( D_A^i = D_{0A} \exp(- E_A^i / kT) \) are diffusion coefficients, \( k \) is Boltzmann constant, \( E_B^i \) and \( E_A^i \) is diffusion activation energy by the interstitial mechanism. To calculate the distribution of elements concentration, equation (1) should be added by the influence of inter-recombination mechanisms, when vacancy and interstitial atom disappear, and also by the annihilation areas of point defects at dislocations and grain boundaries. The main mechanisms of elements redistribution in the surface layers are connected with point defects flows: vacancies \( V \) and interstitial atoms. To calculate the concentration of vacancies and interstitial atoms let us take the grain, located at the surface, as a model. Let grain section be rectangular. For calculating point defects concentration, in this case take the following equation system:

\[ \frac{\partial C_{ib}}{\partial t} = \exp(- E_i / kT) - ZC_Y C_{ib} + \frac{\partial}{\partial x} \left( - D_i \frac{\partial C_{ib}}{\partial x} \right) + \frac{\partial}{\partial y} \left( - D_i \frac{\partial C_{ib}}{\partial y} \right) - r_i C_{ib} \]  

(2)

\[ \frac{\partial C_Y}{\partial t} = \exp(- E_Y / kT) - ZC_Y C_{ib} + \frac{\partial}{\partial x} \left( - D_Y \frac{\partial C_Y}{\partial x} \right) + \frac{\partial}{\partial y} \left( - D_Y \frac{\partial C_Y}{\partial y} \right) - r_Y C_Y \]  

(3)
where \( C_{ii} = \exp(-E_i / kT) \), \( C_V = \exp(-E_V / kT) \) is the concentration of vacancies and interstitial atoms thermodynamically equilibrium at high temperature [12]; \( Z = 4\pi r_i \nu_i \) is coefficient of proportionality during the recombination; \( D_j \), \( D_V \) is diffusion coefficient of vacancies and interstitial atoms; \( r_i = (\rho D_{ij} \exp(-E_i / kT)) / 2 \), \( r_V = (\rho D_{0V} \exp(-E_V / kT)) / 2 \) is annihilation velocity of vacancies and interstitial atoms at dislocation areas [13], \( \nu \) is jump frequency. The most intensive annihilation mechanisms are inter-recombination and annihilation at dislocation areas. Another type of annihilation areas is the grain boundary. This type of стоков is limited. Vacancies concentration inside the grain is higher than at the annihilation areas. As a result, point defects will move towards the annihilation areas, to the surface and the grain boundaries. Schematically, vacancies flows are presented in Fig. 1.

![Fig. 1. The scheme of the vacancies flows distribution.](image)

The surface and the grain boundaries are efficient vacancies annihilation areas, so the concentration of equilibrium vacancies decreases at the annihilation areas. As a result, significant vacancy gradients appear. Этот процесс стимулирует atoms diffusion. Если в сплаве имеются несколько сортов атомов, то градиент неравновесных vacancies leads to the atom flow occurrence, with results in elements redistribution in the alloy.

Redistribution of the impurity can be explained by the presence of point defects gradients at the grain boundary. The grain boundary is an intensive vacancies annihilation area, so average profile of vacancies distribution at grain boundary changes its form. As a result, two impurity flows appear: one is directed perpendicular to the surface, another is parallel to it, and that is, it is directed to the grain boundary (Fig. 1).

3. Results and discussion

On the base of equation system (1, 2 and 3) were carried out calculations of carbon and oxygen concentration at the grain center and boundary in steel 124056, modified with molybdenum according to the combined ion-plasma method [14], during 60 minutes after annealing at temperature 900º C (Fig. 2). The calculation results for the rectangular grain are given in Fig. 2 (a, b). For comparing the calculation results with the experimental data, the analysis of composition in the surface layer by scanning electron microscope with X-ray energy-dispersive spectrometer Jeol JCM-5700 at the grain center and boundary was carried out (Fig. 3). The calculation results correlate well with the experimental data (table 1). As it can seen from the experimental data, there is significant carbon redistribution inside the grains. Its initial concentration in steel 124056 is from 0.3% to 0.42%, after molybdenum covering and high temperature annealing, carbon and oxygen redistribution occur. In steel without coating carbon concentration after annealing inside the grain increases to 8.48%, at the grain boundary it averages 0.19%, in systems with the coating inside the grain it is 2.81% and 0.44% correspondently. After annealing, oxygen concentration in steel without coating in the grain center averages 35.24%, at the grain boundary it is 4.32%, in molybdenum-modified steel it is 16.08 % and 4.26% correspondently.
Fig. 2. Carbon distribution in steel J 2405 6 after the annealing, calculation data for the rectangular grain, (a) along axis OX, (b) along axis OY.

Fig. 3. Microimage of steel J24056 grain (a) and its element analysis in the grain center in point 7 (b).

Table 1. Chemical elements concentration at the boundary and inside the grain

| Chemical element | C (wt., %) | O (wt., %) | Fe (wt., %) |
|------------------|-----------|-----------|------------|
| Grain boundary   |           |           |            |
| Point 1          | 0.68      | 4.63      | 94.69      |
| Point 2          | 0.14      | 2.71      | 97.14      |
| Point 3          | 0.73      | 6.50      | 92.77      |
| Point 4          | 0.50      | 4.67      | 94.83      |
| Point 5          | 0.17      | 2.79      | 97.04      |
| Average value    | 0.44      | 4.26      | 95.29      |
| Internal grain area |       |          |           |
| Point 6          | 3.73      | 17.21     | 79.06      |
| Point 7          | 3.63      | 19.98     | 76.39      |
| Point 8          | 2.67      | 12.75     | 84.57      |
| Point 9          | 1.93      | 15.99     | 82.08      |
| Point 10         | 2.08      | 18.09     | 79.83      |
4. Conclusion

As a result of high temperature annealing, in steel J24056 grain with pre-formed molybdenum coating grain area redistribution of small-sized impurities occurs, in such a case, annealing at temperature 900°C during 60 minutes leads to the carbon concentration increasing to 8.5% for steel without coating and to 2.8% for steel with molybdenum coating. Increasing of oxygen concentration in steel without coating in the grain center averaging 35% is caused by oxygen adsorption during high temperature annealing. Molybdenum covering decreases the intensity of oxygen adsorption; however, its concentration in the grain center reaches in average 16%. The developed model of small-sized impurities mass transfer with close agreement with experimental data explains the carbon and oxygen redistribution in the grain area. The main transfer mechanism is point defects gradients, occurring at the grain boundaries, while coating elements, as a result of high temperature annealing diffuse into the steel internal areas.

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