TO THE MECHANISM OF DIFFUSION OF CHROMIUM AND MOLYBDENUM IN THE METAL OF WELDED JOINTS OF STEAM PIPELINES

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The concepts of the mechanism of diffusion of chromium and molybdenum in the metal of welded joints of steam pipelines from heat-resistant pearlite steels in long-term operation were widened. It is shown that diffusion movement of atoms of chromium and molybdenum occurs by vacancy and dumbbell mechanisms.

Keywords: *arc welding, heat-resistant pearlite steels, welded joints of steam pipelines, solid-phase reactions, activation energy, adhesion forces, diffusion movement*

During long service the physical-chemical processes occur in the metal of welded joints of elements of steam pipelines of heat-resistant pearlite steels (12Kh1MF, 15Kh1M1F) under the conditions of creep (T_{op} = 545–585 °C, P_{op} = 20–25 MPa), accompanying with development of structure, chemical and mechanical heterogeneities. The latter lead to degradation of metal and damage of welded joints. The similar processes occur as well in base metal of steam pipelines [1–5], however their intensity and, respectively, damage of steam pipelines is considerably lower than that of welded joints, the service life of which amounts 0.6–0.8 of life of the base metal.

In the process of long service the initial bainite-ferrite structure of welded joints, meeting the requirements of standard documents TU 14-3R-55–2001, is transformed to different-grain ferrite-carbide mixture without bainite component. The carbide reactions $M_3C \rightarrow M_7C_3 \rightarrow \rightarrow M_{23}C_6 \rightarrow M_6C$ and also coagulation of carbide phases occur which cause the formation of creep micropores at their interfaces with crystals of α-phase (Figure 1). The rate of presented solid-phase reactions is controlled by the level of segregation of atoms of chromium and molybdenum in the near-boundary zones of crystals of α-phase [6], which is limited by quantity of diffusion-moving atoms of chromium and molybdenum to the place of reactions running.

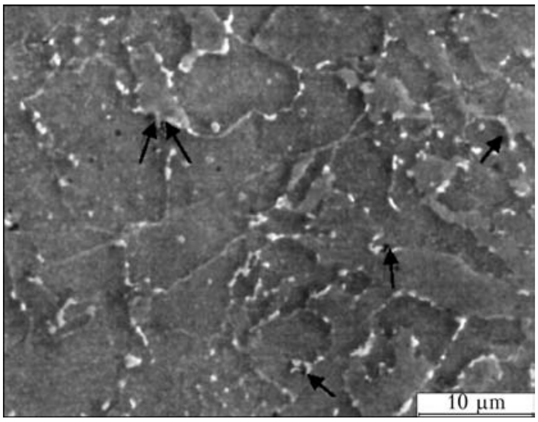

Figure 1. Microstructure of area of partial recrystallization of HAZ metal of welded joints of live steam (base metal — steel 12Kh1MF, service life — 170,000 h; pores are marked with arrows)

The purpose of this work is specification of mechanism of diffusion in metal of welded joints of steam pipelines, operated during long time under the creep conditions. The fundamentals of the theory of diffusion processes [7–12] as-applied to welded joints of heat-resistant steels with long-term operation (>250,000 h) under the creep conditions require further development.

The mechanism of diffusion movement of atoms of chromium and molybdenum at combined action of elastic and chemical forces in the crystals of α-phase under the creep conditions is connected with simultaneous formation and displacement of vacations and interstitial atoms. In the crystal of α-phase the exchange of place between atom and vacancy, located in the initial neighboring sites, occurs at transmitting the proper activation energy to the atom, required for loosening the crystal lattice for displacement of atom (ion) from nodal position to the site or occupation of the vacant place. The activation energy can be determined considering the potentials of interaction between the atoms.

During determination of minimum activation energy of displacement of vacancies the characteristics of field of alternated elastic stresses and relaxation of structure, adjacent directly to the vacancy, were taken into consideration. It was established that activation energy is close to 0.4–0.5 of the energy of crystal lattice of α-phase related to one atom. The least is the activation energy for the area of incomplete recrystallization of HAZ of welded joints characterized by the presence of significant structural and chemical heterogeneity, the level of which is higher than that of analogue levels of activation energy of other regions of HAZ metal and also the weld metal and base metal. The most intensive energy is required for base metal not subjected to welding heating.

Let us represent the frequency of displacement of vacancies using migration as-applied to the crystal of α-phase in the form of known expression

$$v_V = C\nu \exp(-E_A/RT), \quad (1)$$

where E_A is the activation energy of migration, J/(g·atom); ν is the pre-exponential multiplier, close to 10^{13} s^{-1}; C is the eight-coordination number; $R = 8.3$ J/(g·atom) is the gas constant; T is the temperature, °C.

The directed displacement of vacancies to the place of atoms of the first coordination sphere was taken as the effect of stressed state of the system.

The coefficient of self-diffusion of vacancies under the creep conditions can be determined by separation in crystal of two parallel planes of 1 mm^2 area, located at the distance close to the parameter of crystal lattice of α-phase ($a =$ $= 0.25$ nm). It was assumed that concentration of vacancies at one plate K_1 is larger than K_2 concentration of vacancies in another one. Then, the directed flow of vacancies from their higher concentration to lower one can be represented in the form of specified expression [7]

$$J = -\frac{1}{6} v' b^2 \frac{dK_V}{dx}, \quad (2)$$

where v' is the frequency of migration of vacancies; b is the parameter of crystal lattice; K_V is the surface concentration of vacancies; symbol «–» is the direction of displacement of vacancies to the side of their lower concentration.

Considering the coefficients, close by their values, of diffusion movement (migration) of vacancies and atoms [11], and also their similar activation mechanism in the crystals of α-phase, depending on the temperature, the activation energy of displacement of vacancies for the given creep conditions can correspond to activation energy of movement of atoms of chromium, i.e. 2.5–2.9 eV, which is close to the data of work [12].

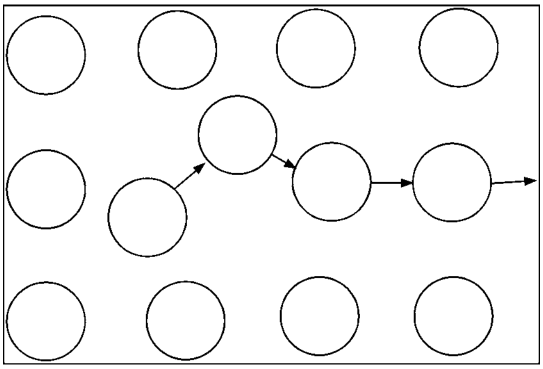

Figure 2. Scheme of dumbbell mechanism of movement of atoms in the crystal of α-phase

During testing period of welded joints under the creep conditions above 250,000 h and the presence of partial degradation of their metal the intensity of movement of atoms of chromium and molybdenum will be provided due to a larger extent to the dumbbell mechanism, and to a lower extent — to vacancy mechanism. This movement is promoted by the slipping of dislocations under the conditions of gradient of chemical potential [13]. The movement occurs by the formation of configurations of the type of moving dumbbells by interstitial atoms with each of neighboring atoms (Figure 2). The dumbbell mechanism of movement is realized in the presence in α-phase crystals of creep pores of 0.5–1.7 μm size (Figure 3), and also polygonal structure of crystals (Figure 4).

We find the coefficient of diffusion D depending on the temperature from Arhenius equation

$$D = D_0 \exp(E_D/RT), \quad (3)$$

where D_0 is the pre-exponential multiplier characterized according to Frenkel by the distance between atoms in the lattice of α-phase and also by period of oscillation or frequency of atom oscillations; E_D is the dependence of coefficient of diffusion on temperature determined as a sum of

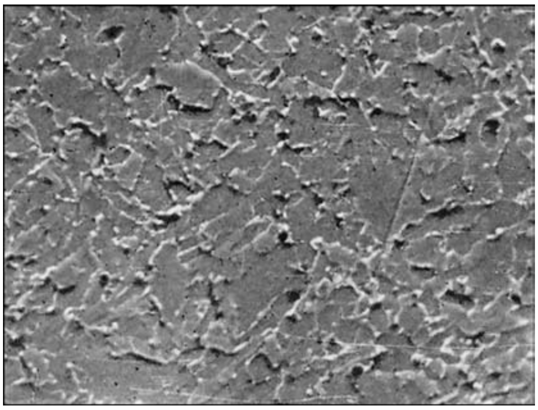

Figure 3. Microstructure (×2500) of weld metal with creep pores (alloy 08KhMF, service life — 190,000 h)

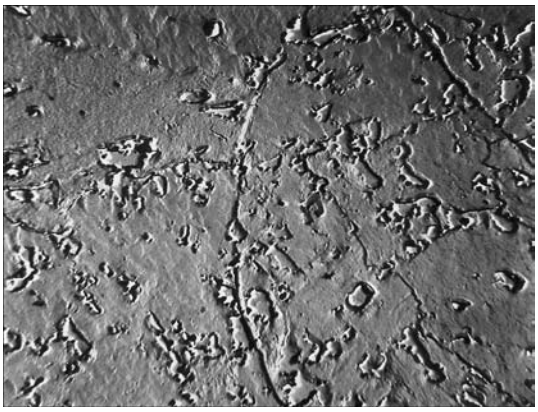

Figure 4. Polygonal structure (×6000) of crystal of α-phase of the area of partial recrystallization of HAZ metal of welded joint of steel 15Kh1M1F (service life — 186,000 h)

enthalpies of formation of vacancies E_{f1} and activation energy of jump of atom E_{v1}, i.e. $E_{f1} + E_{v1}$ (vacation mechanism) and as a sum of enthalpies of formation of vacancies and movement of atom (dumbbell mechanism) $E_{f2} + E_{v2}$. The values D_0 for chromium in the structure of welded joints of steel 15Kh1M1F amount to $(14.2–17.1)\cdot10^{-3}$ cm²/s, which corresponds to the length of ordinate, cut off by Arrhenius straight line at $1/T = 0$ (or $\ln D_0$).

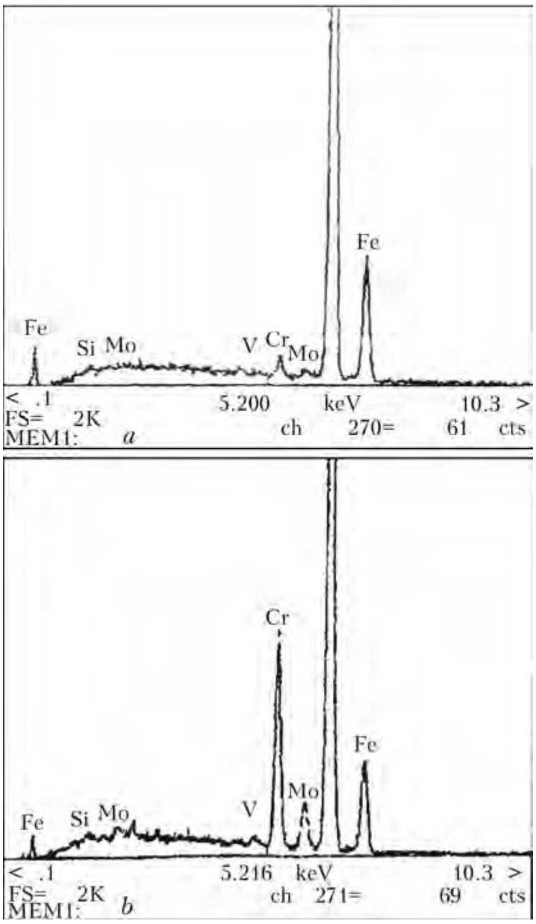

Figure 5. Spectrum of α-phase crystal of 08KhMF alloy weld metal: *a* — initial; *b* — after 276,000 h service (welded joint of steel 15Kh1M1F)

Let us suppose that $E_D = (E_{f1} + E_{v1}) + (E_{f2} + E_{v2})$. For the metal of welded joints of steels 15Kh1M1F and 12Kh1MF in long-term operation under the creep conditions, E_D = 220–270 kJ/mol, that greatly depends on their structural and chemical heterogeneity.

The diffusion movement of atoms is mostly provided by elastic forces and chemical potential $\mu = \mu_0 + kT \ln C_m$, where C_m is the concentration of diffusive atoms of chromium and molybdenum. Let us write the chemical force as a change of chemical potential and concentration (symbol «–» shows that force is directed to the equalizing of chemical potential and concentration):

$$f_{\rm ch} = \left(\frac{\partial\mu}{\partial x}\right)T = -\frac{kT}{C_m}\left(\frac{\partial C_m}{\partial x}\right)T. \qquad (4)$$

Under the influence of chemical force $f_{\rm ch}$ the diffusive movement of flows of atoms of chromium and molybdenum occurs. Let us write $f_{\rm ch} = f_{\rm ch.\,Cr} + f_{\rm ch.\,Mo}$ for the crystal of α-phase. In the metal of welded joints as a non-stationary system the processes of diffusion are expressed by the Fick second law:

$$\begin{cases} \dfrac{\partial \mathrm{Cr}}{\partial t} = \dfrac{\partial}{\partial x} D \dfrac{\partial \mathrm{Cr}}{\partial x}, \\[2ex] \dfrac{\partial \mathrm{Mo}}{\partial T} = \dfrac{\partial}{\partial x} D \dfrac{\partial \mathrm{Mo}}{\partial x}, \end{cases} \qquad (5)$$

where x is the average displacement of diffusive atoms of chromium and molybdenum, determined experimentally.

We will find, respectively, the approximate value of coefficient of diffusion D for chromium and molybdenum through the square of average displacement:

$$D = x^2/2t. \qquad (6)$$

The values of average drift velocities and also coefficients of diffusion of chromium and molybdenum in the metal of welded joints, long time operated under creep conditions, are significantly different. This is proved by the presence of segregations along the boundaries of grains of α-phase (Figures 5 and 6) which promotes the transition of chromium and molybdenum into carbides and formation of new carbides [6]. The average value of segregation of chromium is considerably higher than similar segregation of molybdenum (Figure 7). It is known that diffusion mobility of atoms of molybdenum is higher than diffusion mobility of atoms of chromium [14]. However, in the presence of atoms of chromium, vanadium, silicon and manganese and also possibility of molybdenum to form new carbides

(Mo_2C) the intensity of formation of its segregation along the boundaries of grains of α-phase is significantly decreased.

In α-phase crystals of area of incomplete recrystallization of HAZ metal of welded joints of steel 15Kh1M1F after their testing under the creep conditions during 270,000 h, the carbide phases contained about 64 % V, 82 % Mo, 49 % Cr. The amount of VC carbides increased approximately by 10–15 % as compared to initial ones. In the coagulating carbides (mainly) $M_{23}C_6$ (a = = 1.05722 nm) the slow substitution of atoms of chromium by atoms of molybdenum occurs [1, 8].

Diffusion movement of atoms of molybdenum, chromium and iron with atomic radii 0.139, 0.127 and 0.126 nm, respectively [15] is different. This difference is provided by different level of activation energy, that is due to the force of bond between atoms in the lattice (lattice energy). In the presence of significant structural and chemical heterogeneity, there is a sense to determine separately the diffusion movement of atoms for each area of HAZ metal and also separately for weld and base metal.

It was established that activation energy of chromium, diffusion mobility of which is the most significant in the crystals of α-phase, is differed from the activation energy of other elements. The chemical coefficients of diffusion D_{Cr} and D_{Mo} considering the data of work [10] were determined through the coefficients of self-diffusion D^*_{Cr} and D^*_{Mo} which were found experimentally (Figure 6):

$$\begin{cases} D_{\mathrm{Cr}} = D^*_{\mathrm{Cr}}\left(1 + \dfrac{d\ln f_{\mathrm{Cr}}}{d\ln \gamma_{\mathrm{Cr}}}\right) = D^*_{\mathrm{Cr}}\,\dfrac{d\ln a_{\mathrm{Cr}}}{d\ln \gamma_{\mathrm{Cr}}}, \\ D_{\mathrm{Mo}} = D^*_{\mathrm{Mo}}\left(1 + \dfrac{d\ln f_{\mathrm{Mo}}}{d\ln \gamma_{\mathrm{Mo}}}\right) = D^*_{\mathrm{Mo}}\,\dfrac{d\ln a_{\mathrm{Mo}}}{d\ln \gamma_{\mathrm{Mo}}}, \end{cases} \tag{7}$$

where a_{Cr}, a_{Mo} is the activity of components of chromium and molybdenum; $f = a/\gamma$ is the coefficient of activity; γ is the molar concentration of chromium and molybdenum; $1 + \dfrac{d\ln f}{d\ln \gamma}$ is the thermodynamic factor.

The parameters a and f were found basing on the data of segregation of chromium and molybdenum (see Figures 5 and 6) the level of which considerably changed with time.

It was assumed that temperature dependence of coefficients of self-diffusion of chromium and molybdenum can be described for given steels using the following equation [14]:

$$D = 0.2\exp\left(-\frac{33T_{\mathrm{melt}}}{RT}\right)\ [\mathrm{cm^2/s}].$$

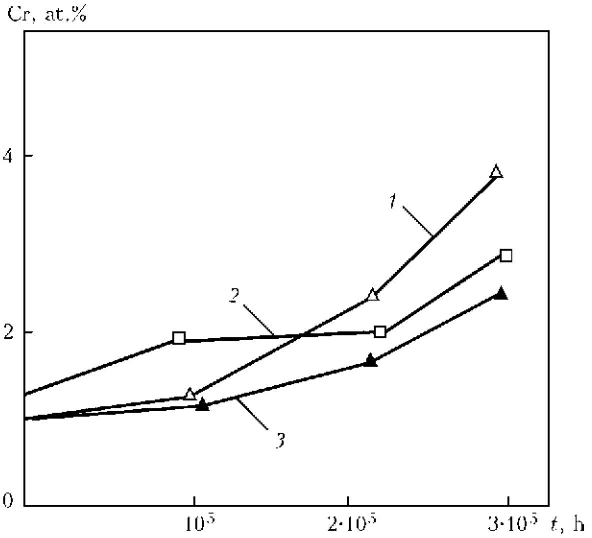

Figure 6. Dependence of local segregation of chromium in near-boundary zone of α-phase crystal on time t at the area of partial recrystallization (*1*), overheat of HAZ metal (*2*) of steel 15Kh1M1F welded joint of live steam pipeline, and in the area of weld metal (*3*)

Under the conditions of long operation the values of activation energy will differ, as well as values of pre-exponential multiplier, which can vary within the limits of 0.01–4 $\mathrm{cm^2/s}$, the coefficient in numerator will also change, respectively.

It was established that value of averaged coefficient of diffusion D_{Cr} in the metal of welded joints of steel 15Kh1M1F (testing period of 276,000 h) amounts approximately from $(2.3–2.7)^{-12}$ to $(3.1–3.3)^{-14}$ $\mathrm{cm^2/s}$. The value of this coefficient depends greatly on conditions of operation of welded joints (starts/stops of energy units, overheats) and also their structure, chemi-

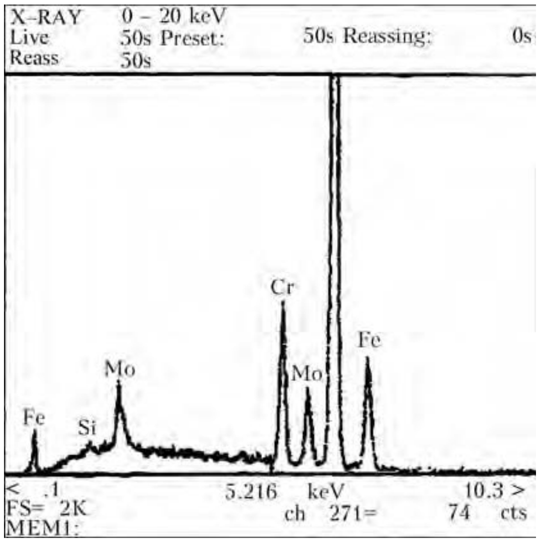

Figure 7. Spectrum of near-boundary zone of α-phase grain for area of partial recrystallization of steel 12Kh1M1F welded joint of steam pipeline (service life — 275 637 h)

cal composition and other factors. The intensity of formation of segregations of molybdenum amounts about 0.3–0.4 of intensity of segregation of chromium (Figure 7). In the metal of welded joints after their test time of about 270,000 h the tendency towards decrease of diffusion mobility of atoms of chromium and increase of diffusion mobility of atoms of molybdenum was observed, that requires additional study. The decrease in mobility of chromium and increase in molybdenum mobility is connected with appropriate changes of gradients of chemical potentials.

During determination of coefficients of diffusion the error was considered predetermined by difference in chemical composition of specimens of diffusion pair, gradient of concentration in the crystal of α-phase where coefficient of diffusion is determined; peculiarities of interface phases; heterogeneity of chemical composition of steel; structural heterogeneity and sizes of grains.

The values of chemical coefficients of diffusion for different structural areas of welded joints are considerably differed. Taking into account the coefficients it was found that the diffusion processes under the creep conditions are most intensive at the area of partial recrystallization of HAZ metal (see Figure 6), which is proved by the data of surface microprobe analysis (see Figure 7).

It should be noted that it is the diffusion movement of atoms of chromium and, at the least extent, of atoms of molybdenum that leads to the formation of near-boundary zones of segregation in the grains of α-phase (see Figures 5 and 6). The increase of concentration of mentioned elements was predetermined by the energy of bonding, average heat energy *kT*, frequencies of jumps of atoms of chromium and molybdenum, displacement of vacancies, which is, in its turn, determined by the difference of chemical potentials and caused by the presence of significant chemical and structural heterogeneity in the metal of welded joints.

The chemical heterogeneity as segregation, predetermined by diffusion of atoms of chromium and molybdenum, was revealed by electron-probe microanalysis of working surface of sections with application of scanning electron microscope JSM-820 with the Link AN 10185S system of X-ray microanalyzer.

The presence of local zones of segregation, occupying from several atomic layers to approximately 0.1 μm (at shifting of its coherency) along the boundaries of crystals of α-phase does not cause the noticeable changes of properties. The basic effect of segregation zones is the increase in rate of carbide reactions $M_3C \rightarrow M_7C_3 \rightarrow M_{23}C_6$ and also coagulation of $M_{23}C_6$, which is determined by concentration in the zones of chromium and molybdenum, which leads to degradation and damage of metal of long-time operated elements of steam pipeline systems and mostly their welded joints [2–6, 13, 14, 16]. It is possible to decrease the intensity of considered diffusion processes by producing of welded joints with decreased initial structural and chemical heterogeneity, which will allow increasing the stability of structure of welded joints, decreasing their damageability and increasing the service life by approximately 15–20 % [2, 3].

CONCLUSIONS

1. During determination of parameters of diffusion processes the mechanism of diffusion of chromium and molybdenum in the metal of long-operated welded joints of steam pipelines of heat-resistant pearlite steels was specified.

2. It was established that diffusion movement of atoms of chromium and molybdenum in the metal of welded joints occurs by two integrated mechanisms: vacancy and dumbbell.

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