Research Article

Nonequilibrium thermodynamic model of diffusion processes in the steel - carbon thin film tribological system

Abstract

A nonequilibrium thermodynamic model of dissipative processes in the tribological system steel – carbon thin film was developed. Cross coefficients and driving forces in the Onsager equation for the diffusion of carbon onto the friction surface of hypereutectoid steel are calculated. The thermodynamic conditions for the implementation of the selective transfer process in the tribological system under consideration are determined. Simple differential equations are obtained for the tribological system of carbon steel - graphite, which describe the effect of stresses on the diffusion of carbon, production based on nonequilibrium thermodynamics. It is shown, that the implementation of selective transfer requires the development of diffusion processes without the formation of excess phases. Therefore, carbon steel should be alloyed mainly with elements of the first group that increase the thermodynamic activity of carbon in steel - silicon, nickel, copper, cobalt and phosphorus. Recommendations are formulated on metallic materials choosing for minimal contact wear in contacted pairs of machines parts.

Keywords: nonequilibrium thermodynamics, hypereutectoid steel, diffusion, carbon, thin film, tribological system, minimal contact wear

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Introduction

The structure of the friction surfaces is dissipative, i.e. formed and maintained in a system with a large number of degrees of freedom using an external energy source.[1] An important feature characterizing the kinetics of structural changes in the metal surface during friction is the high heating and cooling rate of surfaces upon the transfer of mechanical energy to heat, significantly exceeding the heating and cooling rates under ordinary heat treatment conditions and the presence of significant diffusion fluxes of atoms in the surface layers.[2] The authors of[3] observed the diffusion of carbon atoms into the contact zone of steels and its precipitation in the form of graphite, which contributed to a decrease in the coefficient of friction and wear. A promising task is the theoretical analysis of carbon diffusion in a tribological system with graphite thin film and the implementation of the process of selective carbon transfer in this system.

The aim of this work is a nonequilibrium thermodynamic analysis of dissipative processes in the steel – carbon thin film (St – Ctf) tribological system with finding the values of thermodynamic forces, kinetic coefficients, and diffusion fluxes.

The basic equations of diffusion

To describe the kinetics of dissipative processes, one can use the equations of nonequilibrium thermodynamics.[4,5] Changes in a complex or composite system under constant external conditions can be described as a process of increasing entropy. The rate of increase of entropy σ can be represented by the sum of the products of flows and the corresponding forces for all transfer substrates in the amount of N:[4–6]

$$\sigma = \left(dS / dt \right) irrev = \sum_{k=1}^{N} J_k X_k \left(k = 1, .., N \right), \quad (1)$$

In the general case, the thermodynamic equations of motion have the form [4, 5]:

$$J_i = \sum_{k=1}^{N} L_{ik} X_k \left(i = 1, .., N \right), \quad (2)$$

where J_i – fluxes; X_k – thermodynamic forces; $L_{ik} = L_{ki}$ – kinetics coefficients of Onsager[6]; i, k – charge numbers (transfer substrates)

The main driving forces of phase transformations in nonequilibrium thermodynamics are the gradients of the chemical potentials of their components.[4-6] When considering a model nanoscale system, it is possible to use, as gradients, not gradients, but finite differences in chemical potentials ($-\Delta\mu_i$,) and other thermodynamic parameters[7,8] at known small distances.

If, for example, two charges are used as charges of the diffusion process in a carbon eutectoid steel - the concentration of carbon and iron, then, according to[2], the equations of motion take the form:

$$J_1 = L_{11} X_1 + L_{12} X_2 \quad (3.1)$$

$$J_2 = L_{21} X_1 + L_{22} X_2 \quad (3.2)$$

where J_1 – flux of carbon; J_2 – flux of iron; $X_1 = (-\Delta\mu_{Fe})$, $X_2 = (-\Delta\mu_C)$ – thermodynamic forces of iron and carbon. The potential drop has a "+" sign as it increases, and the flow is directed towards a decreasing potential, therefore the expressions for forces contain a "-" sign.

A very intensive transfer of a solid solution (mainly iron) should accompany the process of carbon diffusion in steel. This condition can be fulfilled because of an increase in the iron flux due to the cross coefficient L_{12}.

In the subsequent theory, the non-equilibrium theory of diffusion processes develops successfully, see e.g. works,[9–13] but diffusion processes in tribological systems are practically not considered.

Consequently, until now, questions remain open about the need to use the Onsager equations (1) for dissipative processes in tribological systems.

Description of contact diffusion process

We consider the dissipative processes that occur during friction in the system into carbon steel - carbon thin film. In our system, there are rubbing pairs — the doped α phase (F) and the carbon thin film (Ctf), in which flows of carbon, iron, an alloying element, and vacancies flow (Figure 1). We will use four quantities as charges — the concentrations of carbon, iron, an alloying element, and vacancies. The direction of the diffusion flux of atoms is determined by the distribution of pressure and temperature along the depth of the active surface layer.
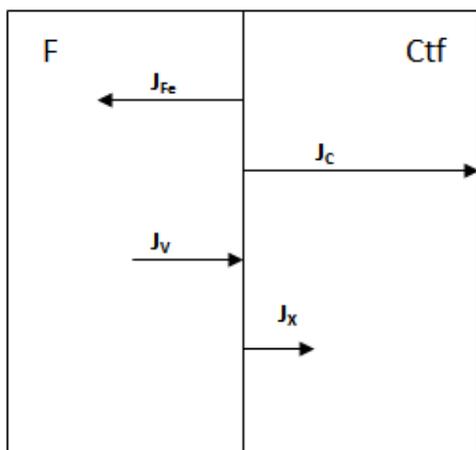

Figure 1 Scheme of the diffusion in the system Fe-C-X (alloying element) - Ctf.

Will consider that the volume of the system can change in general case, which is why condition of complete equality of streams 0 not executed:

$$J_{Fe} + J_X + J_C + J_V \neq 0. \tag{4}$$

According to (1), the thermodynamic equations for the fluxes take the form:

$$J_{Fe} = -L_{11}\Delta\mu_{Fe} - L_{12}\Delta\mu_c - L_{13}\Delta\mu_x - L_{14}\Delta\mu_v; \tag{5.1}$$

$$J_C = -L_{21}\Delta\mu_{Fe} - L_{22}\Delta\mu_C - L_{23}\Delta\mu_X - L_{24}\Delta\mu_V; \tag{5.2}$$

$$J_X = -L_{31}\Delta\mu_{Fe} - L_{32}\Delta\mu_C - L_{33}\Delta\mu_X - L_{34}\Delta\mu_V; \tag{5.3}$$

$$J_V = -L_{41}\Delta\mu_V - L_{42}\Delta\mu_C - L_{43}\Delta\mu_X - L_{44}\Delta\mu_V; \tag{5.4}$$

where J_{Fe}, J_C, J_X, J_V – fluxes of iron, carbon, alloying element and vacancies accordingly.

Being base on generals of nonequilibrium thermodynamics, it is possible to find the value of kinetic coefficients, so as it was executed in process.[15] In the conditions of complete equilibrium:

$$\Delta\mu_{Fe} = 0, \ \Delta\mu_C = 0, \ \Delta\mu_X = 0 \ \text{та} \ \Delta\mu_v = 0. \tag{6}$$

For the diagonal components of the system of equations (5.2) - (5.4) it is possible to write down:

$$L_{ik}L_{ki} = L_{ii}L_{kk}, \ i,k = 1\ldots4. \tag{7}$$

Taking into account Onsager's ratio, find connection between kinetic coefficients [14]:

$$L_{ik} = L_{ki} = \pm\sqrt{L_{ii} \times L_{kk}}, \qquad i,k = 1...4 \tag{8}$$

Next, we perform some specific calculations. First, let us consider the calculations of diffusion fluxes for the simplest case of a binary alloy of the Fe – C system.

Calculation of diffusion fluxes for the case of a binary alloy of the Fe – C system

Let us find the values of diffusion fluxes for the case of a binary alloy of the Fe – C system with 1.5% C at 950 ° C.

Taking into account relations (3), we obtain the following equations of motion with three independent coefficients L_{11}, L_{12}, and L_{22}[8]:

$$J_{Fe} = -L_{11}\Delta\mu^*_{Fe} - L_{12}\Delta\mu_c \tag{9.1}$$

$$J_{\tilde{N}} = -L_{21}\Delta\mu^*_{Fe} - L_{22}\Delta\mu_c \tag{9.2}$$

where $\Delta\mu^*_{Fe} = \Delta\mu_{Fe} - \Delta\mu_v$ – redused thermodinamic force.

$$\Delta\mu_{Fe} = -RT \ln \frac{C'_{Fe}}{C_{Fe}} = -10168 \ln \frac{0,939}{0,937}$$
$$= -21,8 \, J, \tag{10}$$

where C_{Fe} – iron concentration in metastable equilibrium (Figure 2); C'_{Fe} – iron concentration at stable equilibrium; R – universal gas constant;

$$\Delta\mu_C = -RT \ln \frac{a^G_C}{a^C_C} = -10168 \ln \frac{1,00}{1,06} = 592,4 \, Äæ, \tag{11}$$
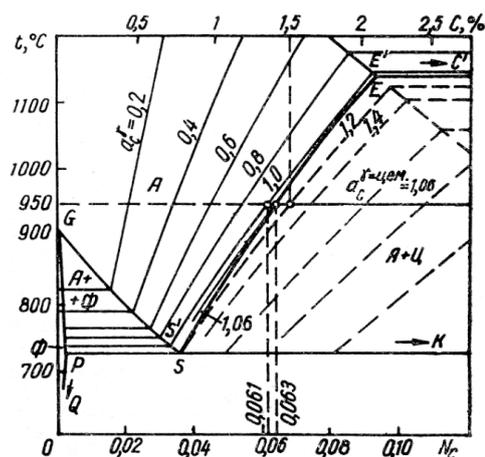

Figure 2 Part of the Fe-C state diagram with plotted carbon isoactivity lines in a metastable system.[8]

where a^C_C – the value of the thermodynamic activity of carbon in cementite when choosing graphite as the standard state of carbon, a^G_C =1,00 (Figure 2).

As is known from,[15] the kinetic coefficients L_{ii} are related to the diffusion coefficients D_i by the relation:

$$L_{ii} = C_i D_i \ / \ RT, \qquad (12)$$

where C_1 – iron concentration in alloy (0,934); C_2 – carbon concentration in alloy (0,066).

The temperature dependences of the self-diffusion coefficients of iron and carbon diffusion in austenite are:[16]

$$D_{Fe}^{\gamma} = 5,8 \exp\left[\frac{-309500}{RT}\right] cm^2 \ / \ s \qquad (13.1)$$

$$D_{C}^{\gamma} = (0,07 + 0,06\%C) \exp\left[\frac{-134000}{RT}\right] cm^2 \ / \ s \qquad (13.2)$$

At a temperature

$950°C: D_1 = D^{\gamma}_{Fe} \approx 3,84 \cdot 10^{-13} cm^2 \ / \ s; D_2 = D^{\gamma}_{C} \approx 3,15 \cdot 10^{-7} cm^2 \ / \ s.$

Using relations (9) and (7), we find the values of the kinetic coefficients for our system:

$$L_{11} = 3,53 \times 10^{-17}; L_{22} = 2,04 \times 10^{-12}; L_{12} = -0,85 \times 10^{-14}.$$

Therefore, the system of equations (5) takes the form:

$$J_C = -0,85 \times 10^{-14} (\Delta \mu_{Fe} - \Delta \mu_v) + 2,04 \times 10^{-12} \Delta \mu_C, \qquad (14)$$

It follows from equations (11) that the iron flux having the opposite sign significantly increases due to the cross coefficient L_{12} and the significant value of the thermodynamic force $\Delta \mu_C$. A positive carbon flux is slightly reduced due to the cross coefficient L_{12}.

As direct calculations show, for

$$\Delta \mu_v = 0 : J_{Fe} = -5,03 \times 10^{-12}, J_C = 1,21 \times 10^{-9} cm^2 \ / \ s.$$ In the absence of cross-links, the flux of iron has a much smaller value: $J_{Fe} = -0,76 \times 10^{-15} cm^2 \ / \ s.$

The influence of alloying elements on the carbon diffusion in the tribological system

The change in the thermodynamic activity of carbon in steel upon alloying with component i can be found by the procedure[20,21] from the equation:

$$\Delta \mu_C^i = \ln\left(\frac{a_C}{a_{C_0}}\right) = \beta i N_i \qquad (15)$$

where β_i – the coefficient of influence of the element on the thermodynamic activity of carbon in steel; Ni – element content in steel in atomic fractions.

The β_i value is calculated through the interfacial distribution coefficient of the alloying element $Ki = Ni (K) / Ni (\alpha)$ and the atomic fraction of carbon in steel Nc[17]:

$$\beta i = -\frac{(Ki - 1) + (Nc(K) - KiNc(\alpha))}{(Ki - 1)Nc + (Nc(K) - KiNc(\alpha))} \qquad (15)$$

With a small error for low alloy steels, one can take $Nc\ (K) = 0.25$, $Nc\ (\alpha) = 0.001$, the carbon content in undoped steel phases, taken from the Fe – C state diagram.

Alloying hypereutectoid steel with elements of the first group, which are slightly soluble in cementite ($K<1$), such as silicon, nickel, copper, and aluminum, increases the thermodynamic activity of carbon in steel. This helps to increase the diffusion flux of carbon from the metal to the graphite thin film and prevents its dissolution. The carbide-forming elements of the second group — chromium, manganese, molybdenum, vanadium, are concentrated in cementite ($K>1$) and reduce the thermodynamic activity of carbon in steel.[17–20] This will reduce thermodynamic forces for carbon diffusion.

Consider, for example, the effect of 1% silicon on the thermodynamic strength of carbon in steel with 1.5% C ($N_C = 0.066$, $N_{Si} = 0.018$, $N_{Fe} = 0.916$) taking into account the results of.[18,19]

Using the distribution coefficient of silicon between the α-phase and cementite (0.25), we find equations for calculating the influence coefficients β_{Si}:

$$\beta_{Si} \approx -1 / \left(-0,75 Nc + 0,25\right) \qquad (16)$$

where from $\beta^{\alpha}_{Si} \approx 5; \beta^{\alpha}_{Si} N_{Si} = 0,09,$

$$\Delta \mu_C = -10168 \times 0,09 = 875 J.$$

If 1.0% Cr is present in the steel, as an ordinary addition, then its effect on the thermodynamic activity of carbon will be negative. Using the distribution coefficient of chromium between the α phase and K_{Cr} carbide equal to 4, we find the equations for calculating the influence coefficients β_{Cr}

$$\beta_{Cr} = -3,246 / \left(3,0 Nc + 0,246\right) \qquad (17)$$

where from $\beta^{\alpha}_{Cr} = -7,3; \beta^{\alpha}_{Cr} N_{Cr} = -0,088$

In order for our carbon tribological system to selectively transfer carbon from metal to graphite thin film, and not *vice versa*, it is necessary that the thermodynamic activity of carbon in steel exceed 1.0 when graphite is chosen as the standard state. For this, steel should be alloyed with elements of the first group. In a first approximation, the following thermodynamic condition must be satisfied for alloying elements in steel:

$$\sum_i \Delta \mu_C^i = \sum_i \beta i N_i \geq 0 \qquad (18)$$

If condition (18) is not satisfied, then in the process of friction a decrease in the thickness of the graphite thin film occurs and the selective transfer process is violated.

Assessment of the effect of stresses on carbon diffusion in a tribological system

If, as the charges of the dissipation process in a tribological system, two values are used - the concentration of carbon particles and the micro deformation of steel ε, then, according to (2), the equations of motion take the form:

$$J_1 = L_{11} X_1 + L_{12} X_2 \qquad (19.1)$$

$$J_2 = L_{21} X_1 + L_{22} X_2 \qquad (19.2)$$

where $X_1 = \Delta \varphi_C$ – the thermodynamic force for carbon is a change in the chemical potential in the friction section, $X_2 = \sigma$ is the local stress (pressure) in the friction section.

The system of equations (19) describes the contribution of tensions and strains to carbon diffusion. However, in it we still do not know the coefficients of the equations associated with tensions. We find their values in the uniaxial tension approximation.

Then the coefficient L_{22} characterizes the direct relationship:

$$J_2 = d\varepsilon / dt = L_{22}\sigma. \qquad (20)$$

where ε – steel deformation in the axis direction X.

Consider that with uniaxial compression[20]

$$\sigma_\alpha = E\varepsilon, \qquad (21)$$

where E – modulus of steel resiliency ($\sim 2{,}17 \cdot 10^5$ Мпа),

Then expression (20) can be transformed as follows:

$$d\varepsilon/dt = L_{22}\sigma = L_{22}E\varepsilon = \frac{V}{L}\varepsilon, \qquad (22)$$

where the following values are entered: v – is the strain propagation velocity in steel (~ 1000 m/s)[20]; L – is the characteristic distance over which micro deformation extends (the size of the protrusions deformed during friction). We assume that the size of the protrusions is of the order of the thickness of the graphite thin film (~ 100 nm).

From equation (22) we find that the coefficient L_{22} is equal to:

$$L_{22} = \frac{V}{LE}. \qquad (23)$$

The cross coefficients $L_{12} = L_{21}$ for a nonequilibrium thermodynamic system are found with sufficient accuracy by the formulas proposed in[21]:

$$L_{12} = \sqrt{L_{11}L_{22}} = \sqrt{\frac{D_C C_C}{RT} \frac{v}{LE}} \qquad (24)$$

Thus, we have obtained simple differential equations for a tribological system that describe the effect of tension on carbon diffusion, derived from nonequilibrium thermodynamics. From the system of equations (19) it follows that the significant temperature and stress gradients arising during friction increase the diffusion rate of alloying elements and carbon. Moreover, as can be seen from Figure 1 and the system of equations (5), the diffusion fluxes of the alloying element can be directed towards the contact of the conjugated pair of carbon steel - carbon thin film.

In,[2] it was shown that for the implementation of selective transfer, the development of diffusion processes of alloying elements without the formation of excess phases is necessary. In our case, such alloying elements are elements of the first group that do not form compounds with carbon. Therefore, carbon steel should be alloyed mainly with elements of the first group, which increase the thermodynamic activity of carbon in steel and do not form other excess phases - silicon, nickel, copper, cobalt and phosphorus. Although aluminum increases the thermodynamic activity of carbon in steel, it can form solid oxide inclusions that contribute to abrasive wear of steel at the contact point. Therefore, the aluminum content in the steel should be limited.

Conclusion

1. The expediency of applying the equations of nonequilibrium thermodynamics to the analysis of dissipative processes in the composite tribological system of steel - graphite thin film is shown.

2. An example is given of calculating the values of thermodynamic forces and kinetic coefficients for diffusion fluxes in a simple tribological system carbon steel (1.5% C) - graphite at 950 ° C.

3. It is shown how alloying elements affect the magnitude of diffusion fluxes in the tribological system of alloyed carbon steel - graphite. The necessary thermodynamic condition for the existence of selective transfer in this system is found.

4. Simple differential equations are obtained for the tribological system of carbon steel - graphite, which describe the effect of stresses on the diffusion of carbon, production based on nonequilibrium thermodynamics.

5. It is shown that the implementation of selective transfer requires the development of diffusion processes without the formation of excess phases; therefore, carbon steel should be alloyed mainly with elements of the first group that increase the thermodynamic activity of carbon in steel - silicon, nickel, copper, cobalt and phosphorus.

Conflicts of interest

The author state that there is no conflict of interest.

References

1. L S Czesnek. Mechanics and microphysics of abrasion of surfaces. *Moscow Mashinostroenie*.1979;263.

2. LM Ry`bakova, LI Kuksenova. Structure and wear resistance of metal. Moscow *Mashinostroenie*. 1982;212.

3. Nakajima K, Isogai A. Structure change of a metal surface during the break-in period. *Wear*. 1968;11(3):223.

4. I Prigozhin, Vvedenie v termodinamiku neobratimy`kh proczessov, *Moskva IL*. 1960.

5. S de Groot, P Mazur. Neravnovesnaya termodinamika. *Moskva Mir*. 1964.

6. L Onsager. Reciprocal Relations in Irreversible Processes. *I Phys Rev*. 1931;37(4):405.

7. AI Veynik. Termodinamika Minsk. *Vyisheyshaya shkola*. 1968.

8. AA Zhukov, RL Snezhnoj, Diffuzionny`e proczessy` v metallakh. *Kiev Naukova dumka*. 1966.

9. V Vovk, G Schmitz, R Kirchheim. Nucleation of product phase in reactive diffusion of Al/Co. *Phys Rev*. 2004;l69(10):104102.

10. AM Gusak, TV Zaporozhets, Yu O Lyashennko, et al. Diffusion Controlled Solid State Reactions: in Alloys. *Thin Films And Nanosys-tems Berlin Willey VC*. 2010.

11. D Bombac, I H. Katzarov, D L Pashov, et al. Theoretical evaluation of the role of crystal defects on local equilibrium and effective diffusivity of hydrogen in iron. *Journal Materials Science and Technology*. 2017;33(13)1505–1514.

12. A Van der Ven, JC Thomas, B Puchala, et al. First-Principles Statistical Mechanics of Multicomponent Crystals. *Annual Review of Materials Research*. 2018;48:27–55.

13. D D Vvedensky. Transformations of Materials. 2019.

14. SV Bobyr. Calculation of Diffusion Flows for the Formation of Phases in Alloys Iron-Carbon-Alloying Element. *Physics and Chemistry of Solid State*. 2019;20(2);196–201.

15. BS Bokshtejn, Diffuziya v metallakh. *Moskva Metallurgiya*. 1978.

16. LN Larikov, VI Isajchev, Diffusion in metals and alloys. Directory. *Kiev Naukova dumka*. 1987.

17. GI Sil`man. Method for calculating state diagrams of ternary systems using coefficients of interfacial distribution of elements. Part 1. Two-Phase Equilibrium. *Zhurnal fizicheskoj khimii*. 1985;57(2):307–313.

18. MA Krishtal, AA Zhukov, RL Snezhnoj, et al. Thermodynamics, physical kinetics of structure formation and properties of iron and steel. *Moskva Metallurgiya*. 1971.

19. G I Sil`man. Uglerodny`e e`kvivalenty` e`lementov v chugunakh. *MiTOM*. 2002;44(1–2).

20. MV Belous, MP Braun. Fizika metallov. *Kiev Vishha shkola*. 1986.

21. SV Bobyr. Using the Principles of Nonequilibrium Thermodynamics for the Analysis of Phase Transformations in Iron-Carbon Alloys. Chapter in book Nonequilibrium Particle Dynamics. *London Intechopen*. 2019.