ANALYSIS OF THE EUTECTOID TRANSFORMATION INTO CARBON STEEL ON THE BASIS OF POSITIONS OF NON-EQUILIBRIUM THERMODYNAMICS

АНАЛИЗ ЭВТЕКТОИДНОГО ПРЕВРАЩЕНИЯ В УГЛЕРОДИСТОЙ СТАЛИ НА ОСНОВЕ ПОЛОЖЕНИЙ НЕРАВНОВЕСНОЙ ТЕРМОДИНАМИКИ

Dr. S. V. Bobyr [1], Prof. V. I. Bol'shakov [2], S.A. Sharfnadel[3],
Z. I. Nekrasov Institute of ferrous metallurgy[1], Prydniprovska state Academy of building and architecture [2], Department of science of investment trust[3] – Ukraine

Abstract: *The non-equilibrium thermodynamics analysis of the eutectoid transformation is executed into carbon steel. Onsager's equations of motion are built for the model thermodynamics system describing eutectoid transformation. Dependences of basic kinetic parameters of process are expected are speeds of height of pearlite and inter-plates distance from the size of subcooling became for the stationary process of eutectoid transformation.*

Keywords: *Non-Equilibrium Thermodynamics, Eutectoid Transformation, Diffusion, Equations Of Motion, Carbon Steel*

1. Introduction

In steel and cast iron, the kinetics of transformation of austenite largely determined by the diffusion of carbon, which allows them to refer to transformations controlled by diffusion [1-3]. Eutectoid transformation of austenite, as a kind of diffusion transformation, associated with a sharp change in the composition of the phases and the formation of colonies or aggregates of the two phases [3]. The value of S_0 perlite is the most important parameter for most of the steels does not depend on the grain size of austenite and varies from 1000 to 100 nm. (Fig. 1) [1, 8].

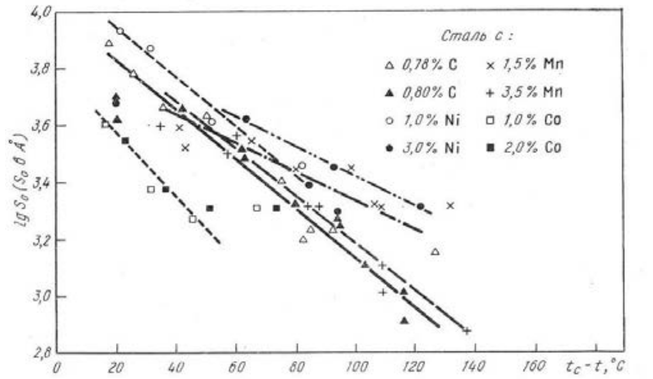

Fig.1. *The dependence of the average inter-plates distance of perlite from the size of subcooling to steels of different composition [1, 8].*

When the eutectoid decomposition of austenite the gain in free energy due to the conversion of austenite into perlite should be sufficient to cover the costs of education developed the interface between ferrite and cementite.

Accordingly, Zener derived the ratio:

$$S_0 = 2T\sigma/\rho Q\Delta T, \qquad (1)$$

An important kinetic characteristic of the eutectoid transformation of austenite is the growth rate of pearlite v. The value of growth rate was obtained by Mail [4] in the form: v = KS0-1. Zener received the expression for the growth rate of pearlite based mainly on considerations of dimensionality and some physico-chemical principles [5]. They were also justified the most general dependence of the rate of growth of pearlite from a temperature:

$$v \sim \Delta T^2 exp(-Q/RT)\,. \qquad (2)$$

Development of the model was performed by Zener Hillerton subject to the conditions of equilibrium defined by surface free energy [6].

Experimental results show, however, that the measured values inter-plates distance perlite is much greater than those values which give the model of Zener and Hillert [4, 7].

Onsager suggested [8] that the determinant of the growth rate of pearlite is diffusion in the ferritic phase, and Turnbull considered the diffusion along the boundaries of the colonies [9]. Kahn found that it is impossible to reach an equilibrium redistribution of the components in the perlite, however it is possible to calculate the growth rate and the degree of redistribution components, if known, the distance between the plates [10]. You still want a physical principle to fix this distance.

2. Preconditions and means for resolving the problem

In [11, 12] as such a principle was used the law of conservation of energy during transformation of austenite and the diffusion of carbon balance. The result is a characteristic equation of the second degree relative to the thickness of the perlite $\Delta=S_0/2$:

$$(\alpha_1 + \alpha_2)q\gamma D_x/\Delta^2 = \alpha\,(T - T_c) - C\gamma dT/dt\,. \qquad (3)$$

From equation (4) imply an expression characterizing inter-plates distance of pearlite in non-equilibrium $\gamma\rightarrow\alpha$+c – transformation:

$$S_0 = 2\sqrt{[(\alpha_1+\alpha_2)q\gamma D_x]/(\alpha(T-T_c) - C\gamma dT/dt)}\,, \qquad (4)$$

where $\Delta T = T - T_c$ - is temperature difference between sample and environment;

dT/dt is the cooling rate of the sample;

α – heat transfer coefficient;

q – the specific amount of heat released during the formation of perlite;

γ – the density of iron-carbon steel;

α_1 and α_2 – concentration coefficients.

If the transformation of austenite takes place in isothermal conditions, it can be assumed that dT/dt = 0. In this case, equation (3) takes the following simple form:

$$S_0 = 2\sqrt{[(\alpha_1+\alpha_2)q\gamma D_x]/(\alpha\Delta T)}. \qquad (5)$$

From equation (5) it follows that inter-plates distance depends on the diffusion coefficient of carbon along the X-axis, hypothermia alloy ΔT and the concentration coefficients α_1 and α_2.

Themselves concentration coefficients are also dependent on the subcooling ΔT. When ΔT = 0, $\alpha_1 + \alpha_2 = 0$. If you increase the subcooling of the concentration ratios increase. The maximum value of the coefficients $\alpha_1 = 1$ and $\alpha_2 = 1$.

At small ΔT one can write approximately:

$$\alpha_1 + \alpha_2 = \alpha'\Delta T, \qquad (6)$$

where α' is some constant value.

Then at low subcooling of the alloy ΔT:

$$S_0 = \sqrt{\alpha' q\gamma D_x/\alpha}. \qquad (7)$$

At deep subcooling $\alpha_1 + \alpha_2 \sim 2$ и $S_0 \sim \sqrt{D_x/\Delta T}$.

The final calculated expression for inter-plates distances has the form: when $\Delta T > \Delta T_0$,

$$\lg S_0 = K_1 - 0{,}5\lg\Delta T - 0{,}4343Q/2RT;$$

if $\Delta T \le \Delta T_0$,

$$\lg S_0 = K_2 - 0{,}4343Q/2RT, \qquad (8)$$

where K_1 and K_2 – are some constants ($K_2 = K_1 - 0{,}5 \lg \Delta T_0$);

ΔT_0 – the point “sewing” of equations.

In this paper, we obtain the following expression for the growth rate of pearlite:

$$v = \sqrt{\alpha(\alpha_1 + \alpha_2)\Delta T D_z / q\gamma}\ . \qquad (9)$$

After substitution of the expressions for the diffusion coefficient as a function of temperature, the temperature dependence for the rate of growth of pearlite was found in the form:

$$v = \Delta T \sqrt{\alpha\alpha' A \exp(-Q/R(T_e - \Delta T))/q\gamma}, \qquad (10)$$

where it is considered that the diffusion of carbon occurs in isothermal conditions at a temperature $T_e - \Delta T$ [here T_e = 996 K – the equilibrium temperature of the eutectoid transformation, R = 8,314 J/(mol·K)].

According to the authors built the model, the growth rate of pearlite in the direction of the axis X has a maximum value when the subcooling ΔT = 149,3 ° C, if we assume that the diffusion of carbon occurs in the ferrite. In the Z axis direction, the growth rate of pearlite is theoretically maximum value when the subcooling ΔT = 99,6 ° C, if we consider the diffusion in austenite. Note that the maximum on the experimental dependence of the growth rate of pearlite with a greater degree of accuracy is described by the diffusion of carbon in ferrite than in austenite, which corresponds to the Onsager's conjecture [19]. The calculated dependence of $S_0 \sim \sqrt{D_x/\Delta T}$ coincides with sufficient accuracy with the experimental values of inter-plates distance of pearlite.

The comparison of experimental data with results of calculations, however, demonstrates that different authors proposed methods of calculating the growth rate of pearlite colonies require consideration of additional factors [2, 4, 13, 14]. B. Lyubov as such an additional factor used, concentration of stresses occurring in front of the pearlitic transformation [2]. Taking into account the influence of the concentration of stresses significantly increases the calculated value of the speed of lateral growth of pearlite colonies and brings it closer to the experimental value for highly pure of eutectoid steel [2] (Fig.2).

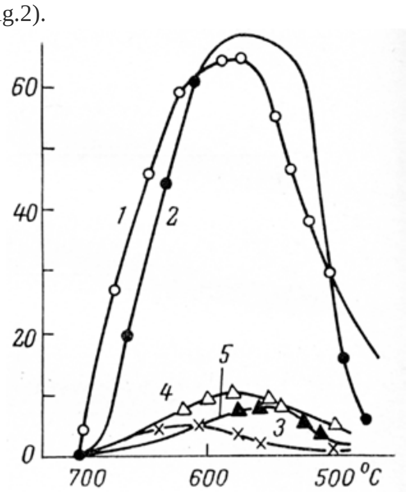

Fig. 2. The speed of lateral growth of pearlite:
1 - the estimated data B. Lyubov [2];
2 - experimental data for high purity eutectoid steel;
3 - data calculated by the formula Zener (2);
4 - data calculated by formula (10);
5 - experimental data for industrial steel.

Theory eutectoid transformation continues to evolve recently, see eg. [13-16], however, the pearlite transformation from the basis of nonequilibrium thermodynamics is still not addressed. Consequently, matters of non-equilibrium thermodynamic descriptions of the eutectoid transformation of austenite. The aim of this work is the development of diffusional model eutectoid transformation of austenite on the basis of the positions of nonequilibrium thermodynamics with the finding of the dependence of main kinetic parameters of the process – the rate of growth of pearlite and inter-plates distance – on the magnitude of supercooling of steel for the stationary process.

3. The equations of motion and basic ratios

Nonequilibrium thermodynamics provides the necessary apparatus for the analysis of diffusion processes in iron-carbon alloys [17-19]. In the general case, the thermodynamic equations of motion have the form [18]:

$$J_i = \sum_{\kappa=1}^{N} L_{ik} X_k \ \text{(i=1,..,N)}, \qquad (11)$$

where Ji – streams, Xk is the thermodynamic force; Lik = Lki – Onsager's kinetic coefficients [19]; i,k – the numbers of charges (substrate transfer).

The main driving forces of phase transitions in nonequilibrium thermodynamics are the gradients of the chemical potentials of the components [17-19]. When considering discontinuous systems as thermodynamic forces are being utilized finite differences of the chemical potentials ($-\Delta\mu_i$,), during the transition from metastable state to stable [20-23]. If, for example, as charges process carbids education to use two quantities, the concentration of carbon and iron, according to (11), the equations of motion take the form:

$$J_1 = L_{11}X_1 + L_{12}X_2 \qquad (12.1)$$

$$J_2 = L_{21}X_1 + L_{22}X_2, \qquad (12.2)$$

where J_1 is the carbon flux characterizing the rate of formation of carbides; J_2 – flow iron;

$X_1 = (-\Delta\mu_{Fe})$, $X_2 = (-\Delta\mu_C)$ – – thermodynamic forces of the iron and carbon. The difference of potential has the sign "+" in its increase, and the flow is directed in the direction of decreasing potential, so the expression for the forces contain a " – " character.

In the present work the generalization of the equations characterizing the growth of pearlite colonies based on the application of methods of non-equilibrium thermodynamics.

To do this, equation (12) from the work of the authors [12], characterizing the growth rate of pearlite colonies present in the form of:

$$dX/dt = D_x[(C'_{\text{ф}} - C'_{\text{ц}})/(C'_{\text{ф}} - C_{\text{ф}}) + (C'_{\text{ф}} - C'_{\text{ц}})/(C_{\text{ц}} - C'_{\text{ц}})]/\Delta$$

$$= (D_x/\Delta)(-\Delta\varphi), \qquad (13)$$

where D_x is the diffusion coefficient of carbon in austenite along the x axis at a predetermined temperature T;

Δ - the thickness of a layer of austenite have different carbon concentration;

$C'_{\text{ф}}$ и $C'_{\text{ц}}$ – and the concentration of carbon in ferrite and austenite near cementite plates, respectively, at temperature T (Fig.3);

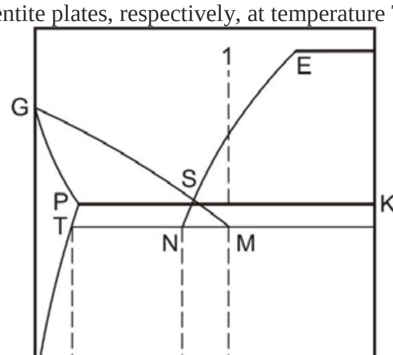

Fig. 3. Diagram of the eutectoid transformation of steel composition 1.

$C_{\text{ц}}$ – content of carbon in cementite (~6,67 %);

$C_{\text{ф}}$ - the amount of carbon in the ferrite at a given temperature T;

$-\Delta\varphi$ is the thermodynamic force of the lateral growth of pearlite. It is determined by the concentrations of carbon in ferrite and cementite and has a dimensionless size.

The second equation, characterized our system, the balance equation of heat (16) from [12] we written in the form:

$$C\gamma dT/dt = \alpha \Delta T - (q\gamma/\Delta)\, dX/dt, \quad (14)$$

where α is the transfer coefficient;

ΔT – temperature difference of the sample (T) and the cooling medium;

q – the specific amount of heat released during the formation of perlite; γ – the density of steel.

If the charge process eutectoid pre-rotation of the austenite to use two variables – the temperature of the sample T and the thickness of the plates of perlite X, then, according to (3), Onsager's equations of motion should have the symmetric form (3), where

$J_1 = -dX/dt$ is the flow value of the perlite layer (increasing the absolute values of the thermodynamic forces of growth of pearlite stream increases in absolute value);

$J_2 = -C\gamma dT/dt$ is the heat flow in the sample (by reducing the temperature of the sample flow positive);

$X_1 = (-\Delta\varphi)$, $X_2 = (-\Delta T/T)$ – thermodynamic forces of growth of pearlite and temperature [24].

In order for equation (13) correspond to equations (12.1), it must contain the additional term $L_{12}(-\Delta T/T)$; the value of the coefficient $L_{11} = (D_x/\Delta)$:

$$J_1 = (D_x/\Delta)(-\Delta\varphi) + L_{12}(-\Delta T/T), \quad (15.1)$$

where L_{12} is the cross - ratio, whose value is still unknown.

Thus we introduce the (perceived) service dependence of growth rate the pearlite layer not only on the concentrations of carbon in phases, and temperature.

By substituting the expression (51) in energy equation (5), find an expression for the flow of heat J_2:

$$J_2 = (q\gamma/\Delta)((D_x/\Delta)(-\Delta\varphi) + L_{12}(-\Delta T/T)) - \alpha T(-\Delta T/T) = (q\gamma D_x/\Delta^2)(-\Delta\varphi) + (q\gamma L_{12}/\Delta - \alpha T)(-\Delta T/T). \quad (15.2)$$

Comparing between equations (12.2) and (15.2), we get:

$$L_{21} = q\gamma D_x/\Delta^2. \quad (16)$$

Using the kinetic coefficients of the relations, the Onsager's cross-links Lik = Lki [19], we find, that

$$L_{12} = L_{21} = q\gamma D_x/\Delta^2; \quad (17)$$

whereas $L_{22} = q^2\gamma^2 D_x/\Delta^3 - \alpha T$. (18)

The system of equations (6) takes the form:

$$J_1 = (D_x/\Delta)(-\Delta\varphi) + q\gamma D_x/\Delta^2(-\Delta T/T) \quad (19.1)$$

$$J_2 = (q\gamma D_x/\Delta^2)(-\Delta\varphi) + (q^2\gamma^2 D_x/\Delta^3 - \alpha T)(-\Delta T/T). \quad (19.2)$$

In accordance with (19.1) on the growth rate of pearlite affects not only the thermodynamic power concentration, but the temperature gradient of the sample and the environment.

We next consider the phase transformation of austenite in the special conditions of stationary growth of pearlite colonies when you can accept that $\Delta T \approx$ const, $dT/dt \approx 0$. In this case, equation (19.2) becomes:

$$J_2 = (q\gamma D_x/\Delta^2)(-\Delta\varphi) + (q^2\gamma^2 D_x/\Delta^3 - \alpha T)(-\Delta T/T) = 0. \quad (20)$$

At small ΔT one can write approximately, as it was done in [12]: $\Delta\varphi = \kappa\Delta T/T$, (21)

where K – coefficient of proportionality.

By analogy with the previously obtained solutions [25], we introduce the following notation:

$$\Delta_0 = \sqrt{\kappa q\gamma D_x/\alpha T}; \quad (22)$$

$$\Delta_l = q\gamma/k, \quad (23)$$

is a characteristic parameter of the system.

Equation (20) can now be represented as:

$$\Delta^3 - \Delta_0^2\Delta - \Delta_0^2\Delta_l = 0. \quad (24)$$

When Δl=0, as might be expected, the solution of equation (24) $\Delta = \Delta_0$.

We receive known solution for pearlitic transformation of austenite [12].

If $\Delta l \neq 0$, we must find the roots of equations of 3rd degree.

For solutions of equation (15) we introduce the normalization $\Delta_0 = 1$.

Equation (24) then takes the form:

$$\Delta^3 - \Delta - \Delta_l = 0. \quad (25)$$

The roots of the equation (16) is equal to [25]:

$X_0 = A+B$, $X1,2 = -(A+B)/2 \pm i\sqrt{3}(A-B)/2$

$$A = \sqrt[3]{\Delta_l/2 + \sqrt{Q}}, \quad B = \sqrt[3]{\Delta_l/2 - \sqrt{Q}},$$

where A and B are any values of the cube roots of complex numbers, satisfying the equality $AB = -P/3$; $Q = \Delta_l^2/4 - 1/27$.

If Q>0, then the solution of equation (25) are valid and two complex roots. In our case, in the valid region, there is one root of the equation (25).

To a solution of the equation of state (16) was negled, it can be represented graphically. We introduce two auxiliary functions $У_1$ и $У_2$, where: $У_1 = X^2$, $У_2 = 1 + \Delta l/X$.

The solution of equation (25) can be found graphically in the form of: $У_1 = У_2$. (26)

Plot the graphs of functions $У_1$ and $У_2$ on the coordinate axis with different values of Δl (in units of Δ_0) (Fig.4).

Thus, in accordance with expressions (22) and (23), we take into account that Δ_l = const and Δ_0 is changed depending on the temperature of the transformations of austenite.

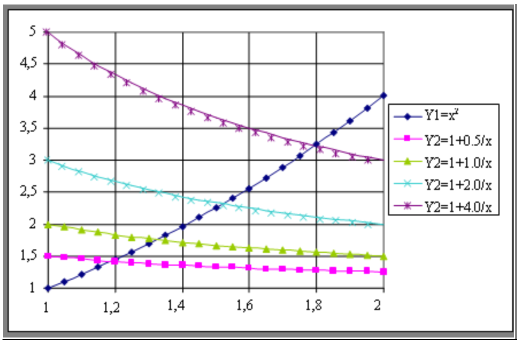

Fig. 4. *Graphical solution of the equation of state (26).*

As can be seen from figure 2, in the valid region sous-exists one solution of equation (3.39). For small Δ_l (<0,5) root Xk is in a region close to 1 ($Xk \to \Delta_0$), at the increase Δ_l (in units of Δ_0) the value of the root increases. . For large values Δ_l is the root *Xk* is approximately equal to

$$Xk \approx \sqrt[3]{\Delta l/\Delta_0}. \quad (27)$$

Inter-plates distance of perlite at stationary growth process, we find by the formula:

$$S_0 = 2X\kappa \times \Delta_0 = 2\kappa Xk\sqrt{\Delta l D_x/\alpha T}. \quad (28)$$

Using equations (19.1) and (27) – (28), we find also a refined expression for the rate of growth of pearlite in an isothermal transformation:

$$dX/dt = \frac{kDx}{S_0}\frac{\Delta T}{T}\left(1 + \frac{2\Delta l}{S_0}\right) \quad (29)$$

Formula (29) is a more accurate expression for determining the rate of growth of pearlite in eutectoid transformation than previously obtained by the authors, the expression (12) in the article [12].

4. DISCUSSION OF RESULTS

Use the known dependence of the diffusion coefficient on temperature [27]:

$$D = A\exp(-Q/RT), \quad (30)$$

where Q is the activation energy ($Q \approx 134$ kJ/mol);

R is constant (R = 8,314 J/(mol·K)).

After substituting known values for the parameters of steel and given that $k \approx 2{,}0$, we find the calculated dependence of the growth rate of pearlite on the magnitude of subcooling of the alloy (Fig. 5). This figure shows for comparison the dependence of the growth rate of pearlite from the size of subcooling, calculated by the formula Zener (1) [4, 5].

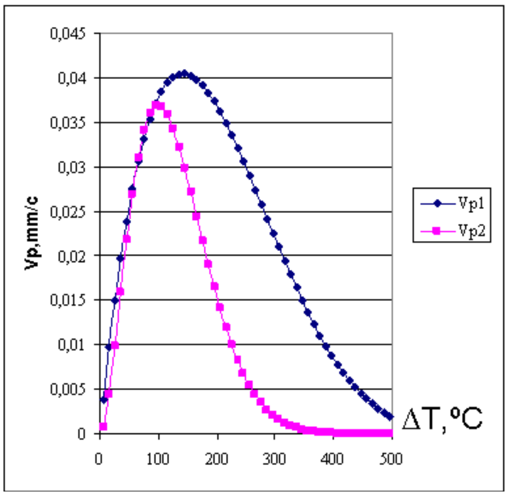

Fig. 5. *The dependence of the growth rate of pearlite from the size of subcooling, calculated by the formula (29) present work (Vp1) and Zener formula (2) [4, 5] (Vp2).*

Consider the change in the growth rate of pearlite (20) if we change the value of the overcooling of the alloy. When ΔT = 0, as it should be, dX/dt = 0. If you increase the subcooling, the rate of formation of pearlite increases, passing through a maximum at a certain value of ΔT.

According to the constructed model, the growth rate of pearlite in the direction of the axis X has a maximum value when the supercooling ΔT = 140,0 ºC. Calculated according to the formula breakdown, the growth rate of pearlite is theoretically maximum value when the subcooling ΔT = 96 ° C. Therefore, the theoretical expression (29) allows a more accurate way to describe max and the course of the experimental curve for the rate of formation of pearlite, presented in the works [2, 15] for high purity eutectoid steel.

Obtained in this section an expression for the growth rate of the perlite has considerable value when supercooling 300...400 °C, thereby determining the possibility of formation of pearlite in the temperature range. Indeed, in [15] revealed the formation of pearlite in carbon steels in the temperature range 375...325 °C. The calculated dependence inter-plates distance of perlite according to the formula (28) from the size of subcooling of steel is shown in Fig. 6. The same figure shows the experimental points from [15].

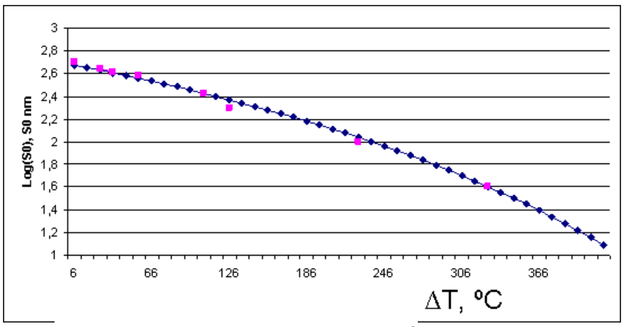

Fig. 6. *The calculated dependence of inter-plates distance of perlite from the size of subcooling of steel (■ – experimental points from [15], p. 122).*

There is quite good agreement of the calculated dependence with the results of recent experiments, indicating the adequacy of the proposed model.

INSIGHTS

1. Application of methods of nonequilibrium thermodynamics to the analysis of the eutectoid transformation of austenite have helped to clarify previously obtained by the authors of the equation of motion of the system and find new, more accurate theoretical expression for the rate of growth of pearlite and inter-plates distance.

2. The theoretical expression for the rate of growth of pearlite, obtained in the present work, allows to more accurately describe the high and the pilot of the curve for the rate of growth of pearlite, presented in the works [2, 15] for high purity eutectoid steel.

3. The obtained dependence for inter-plates distance distances of perlite on the magnitude of subcooling become sufficiently relevant experimental results of work [15] for carbon steel.

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