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DETERMINATION OF THE PHASE COMPOSITION OF ALLOYS BY THE IMPROVED HILLERT METHOD

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ВСТАНОВЛЕННЯ ФАЗОВОГО СКЛАДУ СПЛАВІВ ЗА ВДОСКОНАЛЕНИМ МЕТОДОМ ХІЛЛЕРТА

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The Hillert method of computing activities of components along tie-lines in two-phase regions in ternary phase diagrams' isothermal sections has been enlarged to such regions, which do not contact the corresponding binary diagrams. This became possible by using the modified Hillert equation in which the change of the activity of a given element is a function of the slope of the corresponding tie-line only. As an example, it has been shown how such computations could be performed using an isothermal section of a Fe-C-X phase diagram where X is a carbideforming element and which contains several tie-line triangles.

Keywords: *phase diagram, diagram, isothermal sections, Hillert equation,* conodes, coordinate system of Skreinemakers.

Метод Хіллерта для розрахунку активності компонентів уздовж конод у двофазних областях та ізотермічних розрізів трифазних діаграм поширений на області, які не контактують із відповідними бінарними діаграмами. Це стало можливим завдяки використанню видозміненого рівняння Хіллерта, в якому зміна логарифму активності компонента є функцією лише нахилу конод для відповідних нод. Як приклад показано розрахунки фаз з використанням ізотермічних розрізів діаграми стану Fe-C-X, де X − карбідоутворюючий елемент, і в яких присутні кілька конодних трикутників.

Ключові слова: *фазова діаграма, діаграма, ізотермічні перерізи, рівняння Хіллерта, коноди, система координат Скрейнемакерса.*

Modern ideas in the field of graphitization of iron alloys are based on the phenomenological approach, which is not tied to specific physical models and, accordingly, is the most stable [1,2].

In ideal solutions, the chemical potential can be determined by the formula (when p=const):

$$\mu_i = \mu_i^0 + RT \ln N_i \quad (1)$$

where μ_i^0 is the chemical potential of component "i" in the standard state; R – universal gas table; T – temperature; N_i is the molar concentration of the component. For non-ideal systems, equation (1) turns into inequality (2):

$$\mu_i \neq \mu_i^0 + RT \ln N_i \quad (2)$$

N.Lewis proposed to replace the value of N_i with a fictitious value of a_i, i.e., thermodynamic activity (hereinafter referred to as activity), and convert inequality (2) into the equation [1]:

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (3)$$

This made it possible to create a method of activities. This method gained a new development after the appearance of the Hillert equation, which relates the thermodynamic activity of the component to the tangent of the angle of inclination of the cone. This conode connects the nodes, that is, the figurative points of the phases on the concentration simplex of the alloy. At the same time, the simplex is constructed in orthogonal coordinates, and the concentration axes are given in mole fractions of N_i.

General problems. In work [3] it is indicated that for isothermal sections in Skreinemakers coordinates, the Hillert equation takes the form:

$$\ln a_C - \ln a_C^0 = -n \quad (4)$$

where $n=tg\alpha$, α is the angle of inclination of the cone.

Skreinemaker's coordinates make it possible to significantly simplify the equation by using a smaller number of assumptions when replacing N_C with ν_C (respectively for *Fe-C-Si* or *Fe-C-Cr* – ν_{Fe}, ν_{Si} and ν_{Cr}) systems). With:

$$\gamma = \frac{N_C}{N_{Fe}};\ \gamma_{Si} = \frac{N_{Si}}{N_{Fe}};\ \gamma_{Cr} = \frac{N_{Cr}}{N_{Fe}}.$$

The analysis of conode triangles shows that with a known inclination of the conode triangle of ledeburite transformation, all three conodes meet at the vertices of the triangle, which unambiguously establishes the position of the points of thermodynamic activity of the alloys.

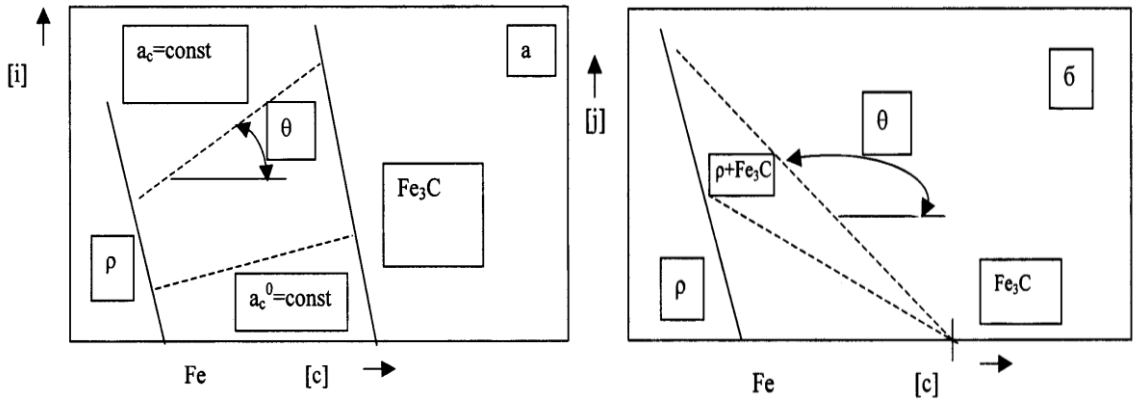
The aims of the work. Develop a method for calculating the phase state of systems for areas of triangular simplexes of three-component state diagrams M-C using the Hillert equation and Skreinemakkers coordinates.

Theoretical studies. Hillert's original Hillert's method turned out to be unsuitable for solving this problem, in contrast to the modified method, which uses the orthogonal

coordinate system of Skreinemakers. The reason for this is that the modified method does not require the definition and use of the coordinates of the corresponding nodes in the calculations. This opens up prospects for the application of this method in predicting the phase composition even when only individual data for the isothermal section of three-component systems are known. Work [4] proves that in three-component *Fe-C-Si* systems for the eutectic decay of austenite, similar expressions of the angle θ can be obtained for any alloys. The thermodynamic activity of a_c is related to a_c^o also equation of the Hillert formula type:

$$a_c = a_c^0 \exp(-tg\Theta), \quad (5)$$

and the value ($-tg\theta$) is negative for the variant shown in fig. 1 a, and positive for the option in fig. 1, b.



a **b**

Fig. 1. Conodes in Skreinemaker's coordinates [3]: a) for a solution ρ+cementite in the *Fe-C-i* system with a distribution coefficient of elements k_i>1,0 (ρ − iron phases α, γ and melt L); b) when k_j<<1.0

This behaviour of the as function a_c in the first version fully corresponds to the explanation that the carbide-forming element "*i*" by strengthening the metal-carbon chemical bond reduces the a_c. For the second option (when element j practically does not dissolve in cementite, it is necessary to take into account the variability of the composition of the cementite phase, where even minor changes in the carbon content significantly affect the activity of a_c. Consider two *Fe-C-Si* and *Fe-C-S* systems. Silicon lowers the ledeburite transformation temperature in the cementite system, but increases it in the *Fe–Si*–graphite system. The decrease in the value of $|a_c^0|$ does not exceed the growth of $|exp(-tg\theta)|$, and in general the value of a_c in formula (7) increases. This is

consistent with the well-known and practically proven statement that silicon is a graphitizer [2]. In the Fe-C-S system $a_c > a_c^0$, however, the decrease in value $\left|a_c^0\right|$ is greater by the modulus of growth $|exp(-tg\theta)|$, which leads to a general decrease in as when alloyed with sulphur, that is, sulphur in liquid cast iron is an anti-graphitizer. At high temperatures, cementite Fe_3C turns into bertolide Fe_3C_{1-x} (where x reaches tenths of a percent by mass [5]), which changes its characteristics under the influence of sulphur. Silicon increases the carbon concentration in cementite of variable composition. As the concentration of carbon increases, its thermodynamic activity increases sharply, which is due to the high density of isoactivity lines (Fig. 2). To the left of the point with a_c=0.825·1.134=0.935, the Fe-Si-graphite system is stable, and to the right Fe-Si-cementite, thus the bleaching effect of sulphur has both a kinetic and a thermodynamic nature.

When using the classical Hillert method [1,2] and its modifications [4,5], as already mentioned above, the most important initial value in the calculations of the activities a_i along the conode of the two-phase region of a given isothermal section of the three-component state diagram (angle h of the h-i-j system) is the activity a_i^o along the conode of the double *h-i* system of the same name. But this assumes that the considered two-phase region is located close to the diagram *h-i*. And if not, as shown in fig. 3? In this case, it is necessary to know the activity a_i^o along at least one conode of the three-component two-phase region α+β (see Fig. 3), and then this conode is taken as the basic one, although it is inclined to the h-i axis ($\upsilon_j=0$) and the latter is far from the region $\alpha+\beta$.

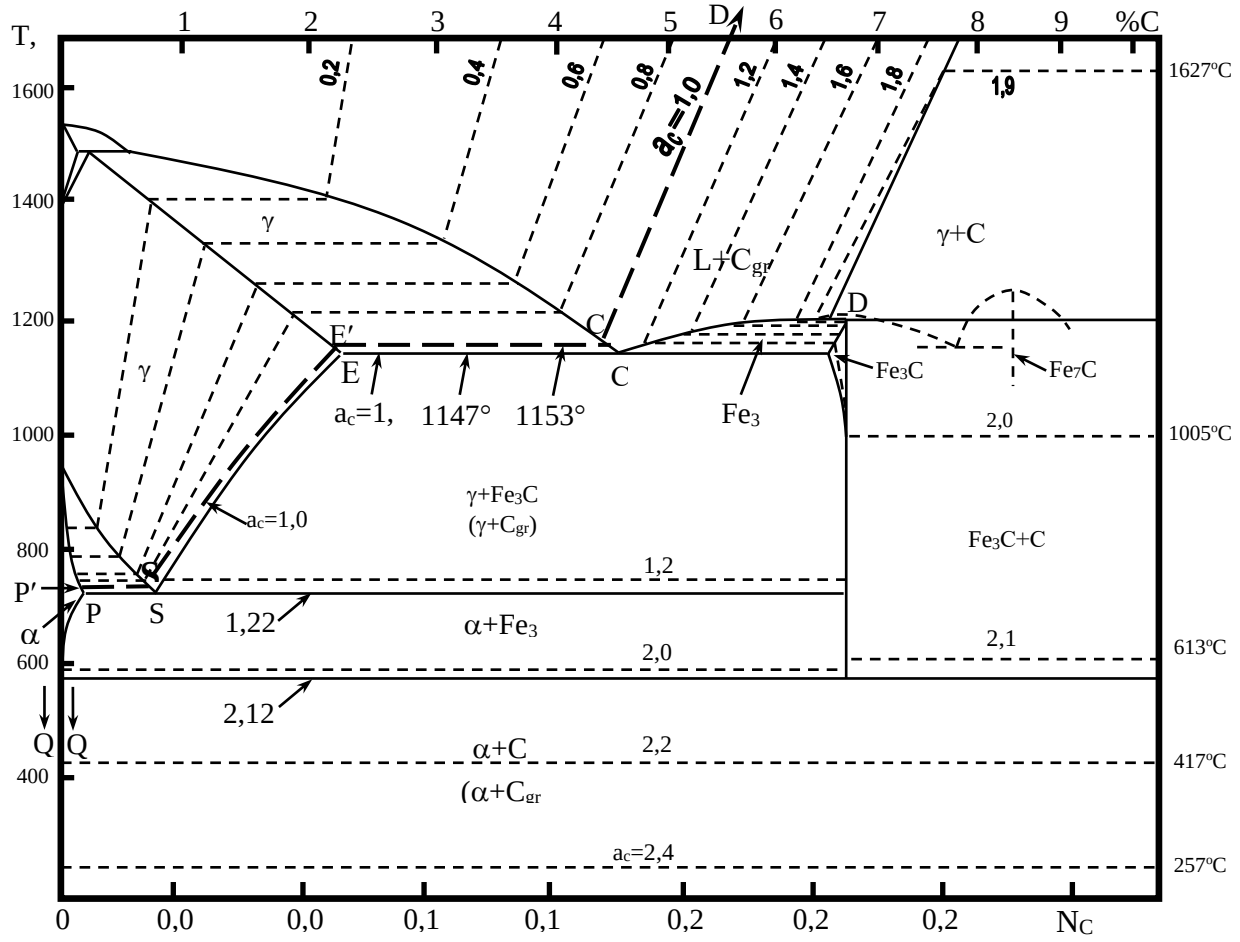


Fig. 2. Diagram of the state of melt+cementite with the applied scale a_c^0 at the selected standard state of carbon – graphite (a_c^{zp}≡*1,0*)

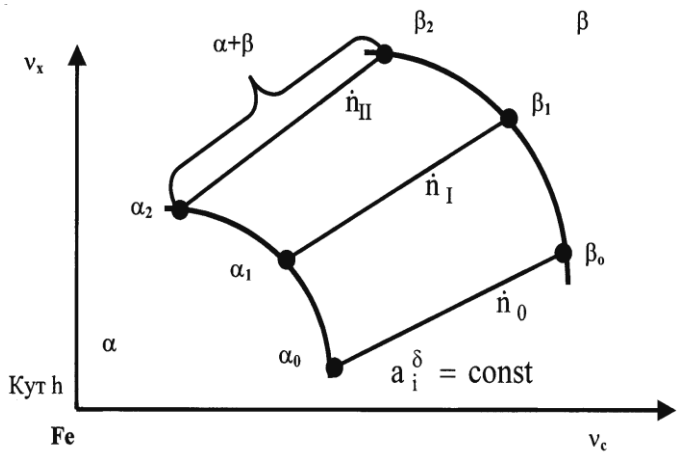


Fig. 3. Scheme for calculating the activity ai along the anodes α+β in the two-phase region of the isothermal section of the state diagram of the ternary system *h-i-*j (angle *h*), where *j* is an additional alloying element affecting the activity of component *i*. The case when the area α+β is not adjacent to the dual system *h*-i (orthogonal Skreinemakers coordinates $v_i=X_i/X_h$ and $v_j=X_j/X_h$ - with the same scale division price; here X is the content of the component in mole fractions)

Isothermal section in fig. 3 is made in Skreinemaker's coordinates because it allows the very simple and accurate Hillert-Zhiguts equation to be used in calculations, which

does not contain the coordinates of nodes or figurative points of alloys:

$$a_i = a_i^0 \cdot \exp(-\dot{n}) \quad (6)$$

where a_i^o is the activity of the component along the base ("zero") conode at $X_j=0$ (binary system *h-i*, when the area $\alpha+\beta$ is adjacent to the binary diagram *h-i* along this conode); ń is the tangent of the angle of inclination of the conode of the two-phase equilibrium in the studied system *h-i-j*.

This allows, in turn, for the case shown in Fig. 3 to calculate a_i along the node $\alpha_I\beta_I$ according to the equation:

$$\ln a_i^I = \ln a_i^\delta - \dot{n}_I + \dot{n}_0 \quad (7)$$

where $\dot{n}_I$ and $\dot{n}_O$ are the tangents of the angles of inclination of the cones $\alpha_I\beta_I$ and $\alpha_0\beta_0$, respectively; a_i^δ is the known value a_i along the base node $\alpha_0\beta_0$.

Similarly, for the $\alpha_{II}\beta_{II}$ node, the calculation is carried out according to the equation:

$$\ln a_i^{II} = \ln a_i^\delta - \dot{n}_{II} + \dot{n}_O \quad (8)$$

where $\dot{n}_i$ is the slope of the conode $\alpha_{II}\beta_{II}$.

It is easy to make sure that the original Hillert equation [6,7], which includes the coordinates of the nodes (not to mention the significant approximations that were required in its derivation), is not suitable for such calculations, because when moving from the node $\alpha_0\beta_0$ to conode $\alpha_I\beta_I$, and after to conode $\alpha_{II}\beta_{II}$ these coordinates change significantly.

The proposed methodological approach is also suitable for calculation in the field of *Fe-C-X* systems, where *X* is a strong carbide-forming element, such as *W*, *Mo*, *V*, and *Ti*, which synthesize salt-like carbides of the *MC* and M_2C types. In this case, calculations show that the activity of carbon in them is a very small fraction of unity, which indicates a very high strength of metal–carbon bonds. The value of a_c in this case can serve as a measure of the exothermicity of the SHS process, synthesizing hard alloys and carbide steels that contain the indicated carbides (the lower a_c, the higher the heat of reaction). The topic of this work did not include establishing the corresponding quantitative dependencies because modern science does not yet have an appropriate set of initial

calculation data for the chain activity of “components their chemical potentials partial free energies of components free energy of the system”.

Conclusions. Hillert's method is also extended to the nodes of two-phase regions of triangular simplexes of three-component *M-C* state diagrams, when these regions are distant from those sides of the specified triangles, which in the two-component simplex describe the growth of the content of the component we are studying when calculating its activity. Hillert's original method turned out to be unsuitable for solving this problem, unlike a modified method that uses the orthogonal Skreinemakers coordinate system. The reason for this is that the modified method does not require the definition and use of the coordinates of the corresponding nodes in the calculations.

This opens up prospects for the application of this method in predicting the phase composition even when only individual data for the isothermal section of three-component systems are known.

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