

Estimation of Polyterms of a Density of Iron and Low-Alloyed Steels

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Abstract

In accordance with the approach most often implemented when creating applications, the density of steel is determined using the reduced diagram of Fe-C. Such an approach is not capable of providing high accuracy of polythermal density prediction. This is due to the fact that several empirical dependencies are used in calculating the density. As a result, according to the rules for determining the error for indirect measurements, the errors are summed up, and the polytherm of the steel density predicted will be made with an error significantly exceeding the errors of the empirical dependencies used. The problem of increasing the accuracy of forecasting polythermal density of low-alloy steels is solved. The solution of the problem is based on the development of the approach in the use of the size factor in the physics of solid and liquid pure metals for low-alloy steels. In this model, a transition is made from substitution and introduction solutions and chemical compounds that actually exist in steel to a conditional homogeneous medium from conditioned reduced atoms. Then, the volume of the conditioned reduced atom and the volume of the interatomic voids adjoining it are analyzed for heating from 298 K to the boiling point of low-alloy steel and pure iron, which is considered as the limiting case of low-alloy steel with zero impurity concentration. An equation is proposed for determining the critical point A_{c4} . On the basis of the model used in combination with empirical relationships for critical points in steel, a methodology has been developed for calculating the polytherm of iron density and low-alloy steels. A comparison of the results with known experimental data is presented. It is shown that the developed technique provides an average error in predicting the density of low-alloy steels in the range of $\pm 0.3\%$.

Keywords: density, estimated polyterm of density, iron, low-alloyed steel.

INTRODUCTION

In accordance with the approach, often implemented in the creation of applications, the density of steel is determined using the above diagram Fe-C. This diagram is considered similar to the real diagram of the state Fe-C, but depends on the content of alloying elements and the density is determined

additively depending on the content of phase components through empirical relationships for the densities of ferrite, austenite and cementite [1, 2]. This approach, with all its apparent rigor, is methodologically unable to provide high accuracy of density polytherms prediction. This is due to the fact that several empirical dependences are used in the calculation of density. For example, in the binary α - γ phase domain, four dependencies are used (for the density of ferrite, austenite, and two dependencies to account for the influence of alloying elements on the position of the state diagram lines). At the same time, according to the rules for determining the error in indirect measurements [3], errors are summed up, and the prediction of the steel density polytherm will be carried out with an error significantly exceeding the errors of the empirical dependences used.

In this paper we solve the problem of improving the accuracy of predicting the density of low-alloy steels polytherms. The solution of the problem is based on the use of the size factor in the physics of solid and liquid metals. This approach is developed by A. S. Basin [4] and E. S. Filippov [5] for pure metals and modified in this paper with respect to low-alloy steels.

DESIGN PROCEDURE (METHOD OF CALCULATION)

In the elementary crystal cell of iron the volume of the atom V_a and the volume of adjacent interatomic voids V_n , correlated with it make up the volume V . In relation to the standard state (298 K) the volume (standard) is determined by the equation:

$$V_{298} = V_a^{298} + V_n^{BBC} \quad (1)$$

where V_a^{298} and V_n^{BBC} are the respectively, the volume of the atom at a temperature of 298 K and atmospheric pressure and the volume of interatomic voids adjacent to the atom in a volume-centered cubic lattice (BCC).

By analogy with the dependence for pure metals [5], a General view of the dependence of the volume V on the temperature when heating low-alloy steel is shown in Fig. 1. Using V_{298} as a starting point has the advantage of having reliable experimental data for the standard state.

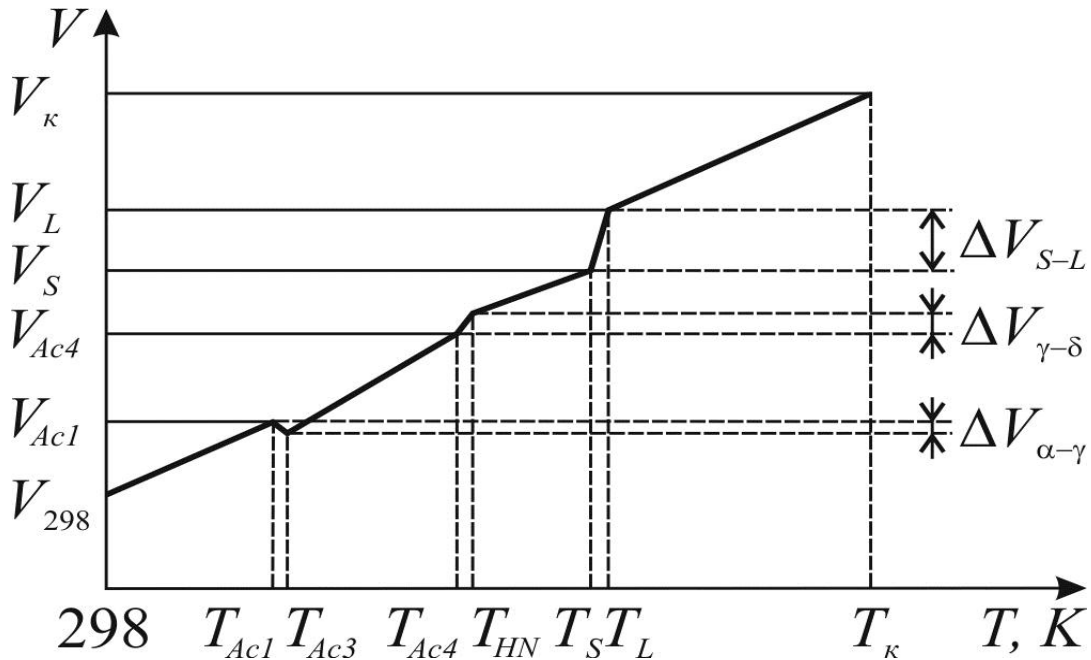


Figure 1. The general form of the dependence of the volume V on the temperature when the low-alloy steel is heated: T_{Ac1} , T_{Ac3} , T_{Ac4} , T_{HN} , T_S , T_L , T_c are the temperatures of the points: $Ac1$, $Ac3$, $Ac4$, HN lines in the $Fe-Fe_3C$, solidus, liquidus and boiling; V_{298} , V_{Ac1} , V_{Ac4} , V_S , V_L , V_K is the total volume of the atom and the adjacent interatomic voids, respectively, standard, at the points: $Ac1$, $Ac3$, $Ac4$, at solidus, liquidus and boiling temperatures

To use (1) in the general case (from pure iron to carbon and low-alloy steels), V_a^{298} , it's necessary to understand the volume of a conventional reduced atom, which is calculated for low-alloy steel taking into account the reduced volumes, both replacement atoms and introduction atoms. In this case, the reduced volume of substitution atoms is:

$$V_{a_{sub}} = \frac{4}{3} \pi \left(\frac{\sum_{j=1}^m r_{A_j^{sub}}^3 X A_j^{sub}}{\sum_{j=1}^m X A_j^{sub}} \right) \quad (2)$$

where $r_{A_j^{sub}}$ is the radius of the substitution atom for the coordination number CN (correlation number) 8 (for BCC lattice); $X A_j^{sub}$ is molar fraction of the substitution atom type A_j^{sub} ; m is the total number of substitution atoms of different types in steel.

Reduced volume of the embedding atom:

$$V_{a_{in}} = \frac{4}{3} \pi \left(\frac{\sum_{k=1}^q r_{A_k^{in}}^3 X A_k^{in}}{\sum_{k=1}^q X A_k^{in}} \right) \quad (3)$$

where $r_{A_k^{in}}$ is the radius of the atom of introduction of the form A_k^{in} for CN 6; $X A_k^{in}$ it's molar fraction of the atom of substitution of the form A_k^{in} ; k is the total number of atoms of introduction of different types in steel.

The values used in (3) $r_{A_k^{in}}$ for the coordination number 6 are characteristic of the embedding atoms in BCC and FCC lattices. The atoms of the implementation of the change of position of centers of atoms substitution in the crystal lattice, such as is known for carbon [6], which modifies the atomic radius defined as half of the interatomic distance between the centers of the closest atoms. The atomic volume changes accordingly. In this model the formation of density (1) subject to the foregoing and the requirement of preservation of the molar volume upon dissolution of the impurities, the amount of the contingent given atom V_a^{298} is determined by the equation

$$V_a^{298} = V_{a_{sub}} - V_{a_{in}} \left(\frac{\sum_{k=1}^q X A_k^{in}}{\sum_{j=1}^m X A_j^{sub}} \right) \quad (4)$$

where the last term of the equation (4) determines the fraction of the volume of atoms of introduction correlated with one atom of substitution.

In accordance with (4), the transition from the actual steel solutions of substitution and introduction to a conditionally homogeneous medium described (1) and consisting of a conditionally reduced atom in a crystal lattice with a volume determined by (4) and adjacent to the atom of interatomic voids is carried out.

On the basis of the law of conservation of mass, the mass of the conditional reduced atom under consideration is formed additively taking into account the molar fractions of the

masses of all chemical elements of steel, i.e. both replacement atoms and introduction atoms:

$$\mu_a = \sum_{i=1}^n \mu_i X_i \quad (5)$$

where μ_i is the mass of the atom i -th species (amu); X_i is the mole fraction of the i -th atom; n is the total number of varieties of chemical elements in steel, $n = m + q$.

Through the packing density of the BCC lattice $k^{BCC} = 0,125\pi\sqrt{3}$ [7], the volume of interatomic voids adjacent to the reduced atom is determined at a temperature of 298 K [5]:

$$V_n^{BCC} = \left(\frac{1 - k^{BCC}}{k^{BCC}} \right) V_{a_{sub}}^{298} \approx 0,47022V_{a_{sub}}^{298}. \quad (6)$$

According to Fig. 1 the change of metal volume in the considered model is determined by the system of equations:

$$V(T) = \begin{cases} \frac{T - 298}{T_L - 298} \Delta V_{solid}^\alpha + V_{298} & \text{at } T \leq T_{Ac1}; \\ V_{Ac1} - \frac{T_{Ac1} - T}{T_{Ac3} - T_{Ac1}} \Delta V_{\alpha-\gamma} & \text{at } T_{Ac1} < T \leq T_{Ac3}; \\ V_{Ac1} - \Delta V_{\alpha-\gamma} + \frac{T - 298}{T_L - 298} \Delta V_{solid}^\gamma & \text{at } T_{Ac3} < T \leq T_{Ac4}; \\ V_{Ac4} + \frac{T - T_{HN}}{T_{HN} - T_{Ac4}} \Delta V_{\gamma-\delta} & \text{at } T_{Ac4} < T \leq T_{HN}; \\ V_{Ac4} + \Delta V_{\gamma-\delta} + \frac{T - 298}{T_L - 298} \Delta V_{solid}^\delta & \text{at } T_{HN} < T \leq T_S; \\ V_S + \frac{T - T_S}{T_L - T_S} \Delta V_{S-L} & \text{at } T_S < T \leq T_L; \\ V_L + \frac{T - T_L}{T_k - T_L} \Delta V_{liq} & \text{at } T_L < T \leq T_k. \end{cases} \quad (7)$$

where $V_{Ac1} = \frac{T_{Ac1} - 298}{T_L - 298} \Delta V_{solid}^\alpha + V_{298}$;

$$V_{Ac4} = V_{Ac1} - \Delta V_{\alpha-\gamma} + \frac{T_{Ac4} - 298}{T_L - 298} \Delta V_{solid}^\gamma;$$

$$V_S = V_{Ac4} + \Delta V_{\gamma-\delta} + \frac{T_S - 298}{T_L - 298} \Delta V_{solid}^\delta \text{ and}$$

$$\Delta V_{S-L} = V_L - V_S.$$

T_k is the boiling point of steel, which in the model can be estimated by the empirical formula for a homogeneous substance [8] by the equation:

$$T_k = 56,321\mu_a \text{ (K)}. \quad (8)$$

On the basis of statistical processing of experimental data [9-13] and analysis of volume ratios [5], $\Delta V_{solid}^\alpha, \Delta V_{\alpha-\gamma}$,

$$\Delta V_{solid}^\gamma, \Delta V_{\gamma-\delta}, \Delta V_{solid}^\delta, \Delta V_{S-L} \text{ and } \Delta V_{liq} \text{ in (7) obtained the}$$

following dependence: $\Delta V_{solid}^\alpha = 0,104V_{a_{sub}}^{298}$,

$$\Delta V_{solid}^\gamma = 0,19V_{a_{sub}}^{298}, \Delta V_{solid}^\delta = 0,2V_{a_{sub}}^{298},$$

$$\Delta V_{liq} = 0,246V_{a_{sub}}^{298}, \Delta V_{\alpha-\gamma} = 3,5 \cdot 10^{-3}V_{298} \text{ and}$$

$$\Delta V_{\gamma-\delta} = 4,5 \cdot 10^{-3}V_{298}.$$

For pure iron and low alloy steel at the liquidus temperature can be written expression for the average density of atoms that form in the solid phase of the substitution solution:

$$\rho_L^{at} = \sum_{j=1}^m \left[\left(\mu_{A_j^{sub}} X A_j^{sub} \right) / \left(\frac{4}{3} \pi r_{A_j^{sub}}^3 N_A \right) \right] \quad (9)$$

where $\mu_{A_j^{sub}}$ is the atomic mass of the chemical element of

the form A_j^{sub} ; N_A is the number of Avogadro; $r_{A_j^{sub}}$ is the

radius of the atom of substitution of the form at CN 8 for the melt of pure iron or CN 12 for the melt of steel, as in the melt of pure iron placement of atoms corresponds to BCC-like (CN close to 8), but in the presence of carbon in the matrix of liquid iron formed areas with a dense packing of atoms, similar to HCC-like [14] (CN close to 12).

As is known, the molar volume of steel at T_L can be determined in the approximation of the additive effect of alloying elements and impurities on the molar volume of pure iron [13]. Deviation from this rule is observed only at high concentrations of dissolved elements [5]. In accordance with the above, normalizing (9) with respect to the density of liquid iron, we obtain an approximate expression for the density of low-alloy steel at the liquidus temperature in g / cm^3 :

$$\rho_L^{st} = \frac{7,04\mu_{Fe}}{\frac{4}{3}\pi r_{Fe}^3 N_A} \rho_L^{at} \quad (10)$$

where 7,04 is the density of liquid iron, g / cm^3 [4, 9, 11]; μ_{Fe} is the atomic mass of iron (amu); r_{Fe} is metal radius of iron for CN 8 (pure iron) or CN 12 (low-alloy steel).

If we write (10) only for Fe, Cr, Ni, Mn, Mo and Si (at mass concentrations not exceeding 5% for each element) and make the transition from molar fractions in (10) to mass concentrations, as well as to the dimension of the density of steel in kg/m^3 , we have the equation:

$$\rho_L = 69Fe + 66,5Cr + 71,3Ni + 58,6Mn + 51,6Mo + 57,3Si \quad (11)$$

where the chemical elements represent the mass concentration in the steel.

The coefficients for variables in (11) are close to the corresponding coefficients in the empirical equation for the density of liquid steel [15]:

$$\rho = \left(\begin{matrix} 69,4Fe + 66,3Cr + 71,4Ni + \\ + 57,2Mn + 51,5Mo + 49,3Si \end{matrix} \right) - 0,86(T - 1550). \quad (12)$$

Given that the equations of type (12) are usually obtained by statistical processing of the results of industrial melting, the compliance of the considered coefficients can be considered satisfactory, which confirms the applicability of (10) to estimate the density of low-alloy steel at T_L .

The structure of liquid metal is formed in accordance with the principle of the best use of space by two opposite fluctuations in atomic density: clusters with dense packing and absolutely chaotic packing [16]. In this case, the volume of the atom and adjacent interatomic voids at T_L is:

$$V_L = \frac{\mu_a}{\rho_L^{st} N_A}. \quad (13)$$

Polytherm density of metal (pure iron or low alloy steel) is determined by the equation:

$$\rho(T) = \frac{\mu_a}{V(T) N_A}. \quad (14)$$

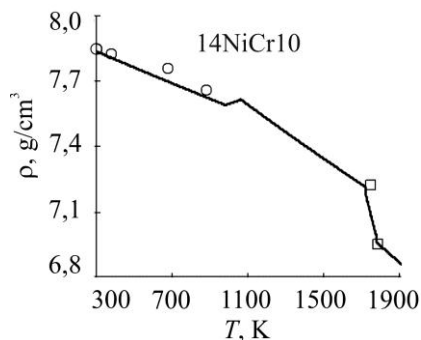
To calculate the metal radii of the elements at different coordination numbers required for calculations by equations (1) – (14), we used the Pauling equation given in [17].

To predict the temperatures T_{Ac1} , T_{Ac3} , T_S , T_L used empirical equations according to [18, 19].

Based on the analysis of double diagrams of the iron – alloying element with a correlation coefficient of 0.95, the equations for calculating the temperatures of the points Ac_4 and the HN line of the iron – cementite diagram taking into account the influence of alloying elements are obtained:

$$T_{Ac4} = 1665 + 670C + 7,9Mn + 25Ni + 5,55Co + 12,9Cu; \quad (15)$$

$$T_{HN} = 1665 + 1065C + 8,9Mn + 28,6Ni + 6,2Co + 11,9Cu. \quad (16)$$



Equations (15), (16) are applicable in the case: $Mn \leq 4\%$; $Ni \leq 4\%$; $Co \leq 5\%$; $Cu \leq 2\%$; $C \leq 0,16\%$ for (15) and $C \leq 0,1\%$ for (16). When, $C > 0,16\%$ i.e. for steels that do not have $\delta + \gamma$ an area, when performing calculations in accordance with (1) – (16), it is necessary to use an additional to (1) – (16) conditional mathematical constraint $T_{Ac4} = T_{HN} = T_S$.

RESULTS AND DISCUSSION

Solutions of the system of equations (1) - (16) are shown in Fig. 2 - 4. For fig. 2 experimental data and calculated polytherm of pure iron density are presented in Fig. 3, 4 calculated density polytherms for a number of steels are presented.

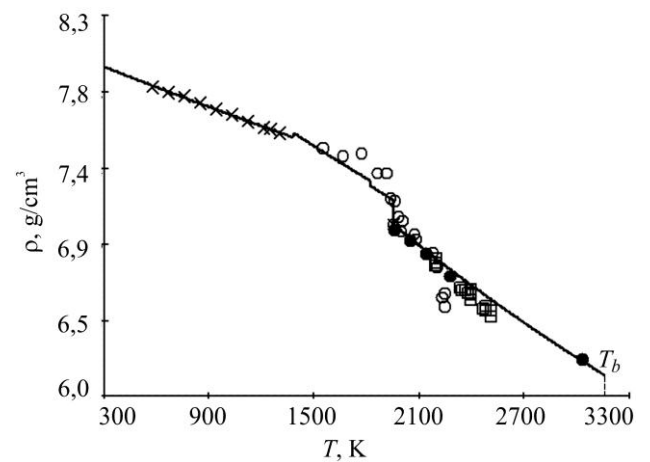


Figure 2. Calculated polytherm of pure iron density from equations (1) – (16) and experimental data: \times – [11]; o – [9]; \square – [10]; \bullet – [12]

As can be seen from Fig. 2, the calculated polytherm density of pure iron is in satisfactory agreement with the experimental data.

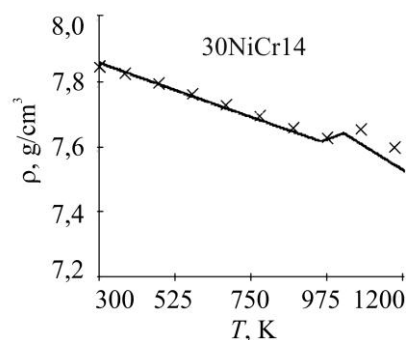


Figure 3. Calculated polytherms of the density of steels 14NiCr10 and 30NiCr14 according to equations (1) – (16) and experimental data: o – [20]; \square – [13]; x – [21]

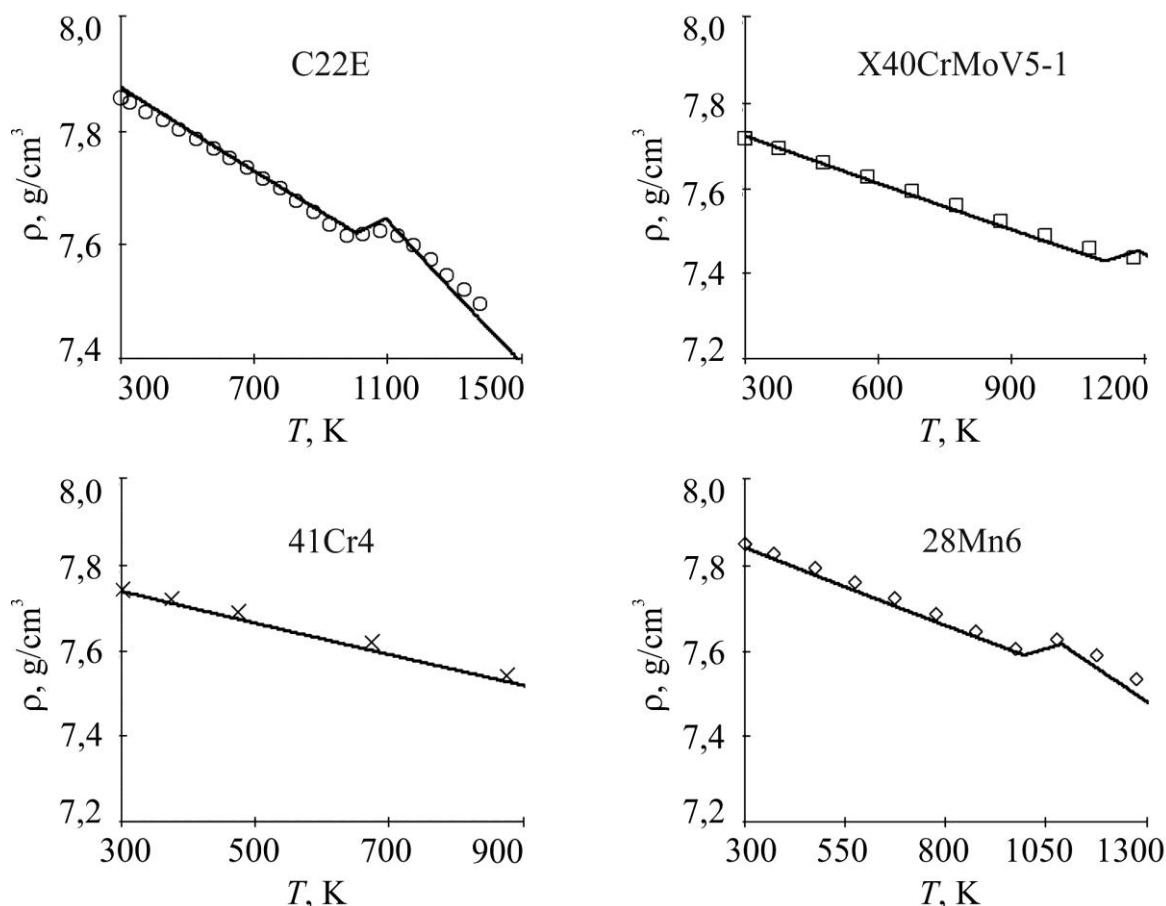


Figure 4. Calculated polytherms of the density of steels C22E, X40CrMoV5-1, 41Cr4 and 28Mn6 according to equations (1) - (16) and experimental data: o –[21]; □ –[20]; x –[20]; ◇ –[21]

Comparison of experimental and calculated data shown in Fig. 3, 4, shows that the average error in predicting the density of steels according to the equations (1) – (16) is about $\pm 0.3\%$.

CONCLUSION

Based on the use of the size factor in the physics of solid and liquid metals and alloys in combination with empirical dependences for critical points in steel, a method for calculating the density of iron and low-alloy steels polytherms is developed, which provides an average error in predicting the density of steels within $\pm 0.3\%$.

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