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Estimation of Temperature Dependences of Specific Heat Capacity of Low-Alloy Steels

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Abstract

The existing empirical polynomial temperature dependences of the specific heat of steels do not apply to the temperature range from 973 K to A_{C3}. The paper describes the solution of the problem of obtaining an equation that describes the temperature dependence of the specific heat of low-alloy steels in the temperature range from 973 K to A_{C3}. The equation obtained is a scaled equation for the specific heat in the vicinity of the Curie temperature. The solution of the equation is cross-linked with known empirical polynomial dependencies. A comparison of the results of calculations on the scaled equation for the specific heat in the vicinity of the Curie temperature with known experimental data is presented. It is shown that the average error in estimating the specific heat in the vicinity of the Curie temperature is about ± 1.5%. To evaluate the Curie temperature of low-alloy steels, an equation is proposed for the first time that allows this estimate to be performed depending on the chemical composition of the steel. The equation for estimating the Curie temperature of low-alloy steels is based on the Vonsovskii equation for calculating the Curie temperature of binary ferrimagnetic alloys. Approximation of the exchange integrals in the Vonsovskii equation was carried out approximately using the concentration dependences of the magnetic conversion temperature according to the diagrams of the state of the iron-doping element systems. Examples of a number steels show satisfactory agreement of the calculated and experimental values of the Curie temperature. Using a scaled equation for the specific heat in the vicinity of the Curie temperature, together with empirical polynomial temperature dependences for the specific heat of steels, it is possible to calculate the polytherms of the specific heat of low-alloy steels in the temperature range from 300 K to the solidus temperature.

Keywords: low-alloy steel, specific heat capacity, estimated polyterm of heat capacity, estimation of Curie temperature of low-alloy steel.

INTRODUCTION

Specific heat capacity in conjunction with other thermophysical properties of the material affects the accuracy of the results of computer simulations in calculations of temperature fields in products sold in packages of applied programs CAE (computer-aided engineering), providing automation of engineering calculations, implementation of imitating modeling of technological processes and physical phenomena, the optimization of products, etc.

The temperature dependence of the specific heat of low-alloy steel and technically pure iron has a pronounced maximum at the point of magnetic transformation. For carbon steels Curie point temperature is independent of the carbon content and is 770°C [1-4]. This allows to approximate experimentally obtained polytherms of heat capacity of carbon steels by polynomial dependences. This approach is used when carrying out the application of engineering calculations [5, 6]. For alloyed steels in CAE uses a table setting of known experimental data or methods for predicting thermal properties, including specific heat [7]. However, to date, the equation for calculating the Curie temperature of low-alloy steels has not been developed. Therefore, the use of polynomial models gives an error of up to 50 K in the position of the maximum specific heat of low-alloy steels [5].

The purpose of this work is to solve the problem of refining the existing method of calculating the temperature dependence of the specific heat capacity of steels using polynomial models by developing and taking into account when predicting the heat capacity of the equation that estimates the Curie temperature in low-alloy steels, and the scaled equation for the temperature dependence of the specific heat capacity of steel in the vicinity of the Curie temperature.

DESIGN PROCEDURE (METHOD OF CALCULATION)

Specific heat capacity of all low-alloy steels is determined by the empirical polynomial dependencies [8], in kJ/(kg K):

$$C_1(T) = 0{,}443 + 5{,}02 \cdot 10^{-4}(T-273) - \\ - 6{,}667 \cdot 10^{-7}(T-273)^2 + 1{,}202 \cdot (T-273)^3 \quad (1)$$

in the temperature range 293 – 973 K with an error of less than ±2.1% and

$$C_3(T) = 1{,}136 - 8{,}105 \cdot 10^{-4}(T-273) + \\ + 2{,}542 \cdot 10^{-7}(T-273)^2 + 7{,}127 \cdot 10^{-11}(T-273)^3 \quad (2)$$

with an accuracy of up to ±1.7% in the temperature interval T_{Ac3} ... T_S, where T, T_{Ac3}, T_S is temperature of, respectively, the current, point A_{C3} and solidus (K).

There are a number of equations for predicting A_{C3} and T_S in steels. Based on the comparative analysis given in [9], it can be assumed that for low-alloy steels the best prediction accuracy of A_{C3} is provided by the equation:

$$T_{Ac3} = 1198 - 219\sqrt{C} - 7Mn + 39Si - 31Ni - 55Mo - 41V \quad (3)$$

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

The solidus temperature of low alloy steel can be determined by the equation [10] (K):

$$T_S = \begin{cases} 1811-(478C+20{,}5Si+6{,}5Mn+500P+700S+5.5Al+2Cr+11{,}5Ni) \text{ if } C \le 0{,}09 \\ 1768-(20{,}5Si+6{,}5Mn+500P+700S+5.5Al+2Cr+11{,}5Ni) \text{ if } 0{,}09 < C \le 0{,}17 \\ 1800-(187{,}5C+20{,}5Si+6{,}5Mn+500P+700S+5.5Al+2Cr+11{,}5Ni) \text{ if } C > 0{,}17 \end{cases} \quad (4)$$

The least error in determining the liquidus temperature T_L low alloy steel gives the equation [11] (K):

$$\begin{aligned} T_L = {} & 1812-78C-12Si-5Mn-1{,}5Cr-4Ni-5Cu- \\ & -2Mo-2V-1{,}5W-2Al-2Co-10Ti-150B-6Zr- \\ & -30P-25S-80O_2-90N_2-1300H_2. \end{aligned} \quad (5)$$

For binary ferromagnetic alloys, the Curie temperature can be determined by the equation Vonsovskogo [12]:

$$T_c = \frac{Z}{2k}\left[A_1 + 2n_2(A_1 - A_{12}) + n_2^2(A_1 + A_2 - 2A_{12})\right] \quad (6)$$

where Z is the coordination number, k is the Boltzmann constant; A_1, A_2 and A_{12} are the exchange integrals, respectively, for the neighborhoods of type A – A, B – B, A – B (A and B - are atoms of different components of the alloy); n_2 is the concentration of atoms of grade B.

Equation (6) can be written in the form:

$$T_c = \frac{Z}{2k}A_1 + F \quad (7)$$

where $F = \frac{Z}{2k}\left[2n_2(A_1 - A_{12}) + n_2^2(A_1 + A_2 - 2A_{12})\right]$ is the functionality.

For iron-based alloys of (7), if $n_2 = 0$ it is follows that the Curie temperature of the iron $T_c = \frac{Z}{2k}A_1$. Given that for iron $T_c = 1043$ K, for binary iron alloys equation (7) takes the form:

$$T_c = 1043 + F. \quad (8)$$

The numerical values of the functional F at different concentrations of alloying elements in the iron – based binary alloy matrix can be estimated approximately from the concentration dependences of the magnetic transformation temperature according to the diagrams of the state of the iron-alloying element systems.

When using the expression (8) for a multicomponent system, i.e. for low-alloy steel, it is necessary to take into account the contributions to the formation of T_c of various functional F of alloying elements and impurities. In the first approximation, molar fractions of these chemical elements can be used for this purpose. Taking into account the above, the data given in [1-4, 13], based on the expression (8) the equation for predicting the Curie temperature of low-alloy steel, depending on the content of the chemical elements determining this temperature, (K):

$$T_c = \frac{1}{\sum\limits_i XB_i}\begin{bmatrix} \left(-7{,}5Mn - Mn^2\right)\cdot XMn - \left(-0{,}1Si + 1{,}5Si^2\right)\cdot XSi - 36Ti\cdot XTi - 4Al\cdot XAl - \\ -\left(5Mo + 0{,}2Mo^2\right)\cdot XMo + 0{,}5Zr\cdot XZr + \left(10{,}5V - 0{,}4V^2\right)\cdot XV + \\ +\left(14Co - 0{,}17Co^2\right)\cdot XCo - \left(0{,}82Cr + 0{,}4Cr^2\right)\cdot XCr - \left(4{,}8Ni - 0{,}6Ni^2\right)\cdot XNi - \\ -11Cu\cdot XCu - 100N\cdot XN - 22P\cdot XP - 4As\cdot XAs \end{bmatrix} + 1043 \quad (9)$$

where $\sum\limits_i XB_i$ is the sum of the molar fractions of the chemical elements present in the steel, which are considered in equation (9); B_i is the symbol of the i–th chemical element in (9).

Equation (9) reflects the different concentration dependence of the temperature of the magnetic transformation on the respective diagrams of binary systems of iron-alloying element with correlation coefficients $R > 0.95$ and the case when $Mn \le 2{,}5$ %; $Si \le 3$ %; $Ti \le 2{,}5$ %; $Al \le 5$ %; $Mo \le 5$ %; $Zr \le 5$ %; $V \le 2{,}5$ %; $Co \le 5$ %; $Cr \le 9$ %; $Ni \le 4$ %; $Cu \le 1$ %; $N \le 0{,}05$ %; $P \le 0{,}5$ % and $As \le 0{,}5$ %.

Experimental values of Curie temperature for a number of steels (chemical composition of steels is given in table. 1) and the results of calculations on the equation (9) are presented in table. 2.

Table 1. The chemical composition of the steels, mass %

Element	Steel grade			
	Low-alloy steel [14]	Modified 9Cr-1Mo steel [15]	9Cr-1Mo [16]	100Cr6 [17]
Cr	1,50	8,55	8,44	1,40
Mo	0,50	0,88	0,94	–
V	0,10	0,21	0,001	–
Nb	0,10	0,08	–	–
C	0,25	0,10	0,10	1,02
Mn	0,20	0,51	0,46	0,31
Cu	–	0,18	0,11	0,10
Si	0,20	0,32	0,49	0,22
N	–	0,035	–	–
Ni	–	0,15	0,17	0,086
P	–	0,012	0,008	0,019
S	–	0,005	0,049	0,002
Ti	–	0,002	–	–
Al	–	0,007	0,011	–
Zr	–	0,001	–	–
Co	3,00	–	–	–
B	0,03	–	–	–

Table 2. Experimental and calculated values of the Curie temperature, °C

Curie temperature	Steel grade			
	Low-alloy steel	Modified 9Cr-1Mo steel	9Cr-1Mo	100Cr6
Experimental data	790,2 [1] [14]	741 [15]	740±5 [16]	769[2] [17]
Calculation data (8)	790,0	741,2	741,5	768,4

Notes: [1] – maximum temperature on the differential thermal analysis curve; [2] – the value is determined by the schedule given in [17].

As can be seen from on the table 2, the calculated Curie temperature values are close enough to the experimental data, which indicates the possibility of using the equation (9) in determining the Curie temperature of low-alloy steels.

The heat capacity at Curie temperature has a jump [18]:

$$\Delta C = -\frac{a^2 T_c}{2b} \tag{10}$$

where a, b are the coefficients of the decomposition of the thermodynamic potential in Landau's theory by degrees of the order parameter.

Taking into account that in the considered method of calculation of specific heat capacity ΔC at heating of various low-alloyed steels is counted from one level defined by the equation (1), and the contribution ΔC to the total heat capacity at Tc is predominant, then, on the basis of (10) it can be considered that the specific heat capacity of low-alloy steel at T_c is approximately proportional to T_c, i.e. is given by the expression:

$$C_c = k_c T_c \tag{11}$$

where k_c is the coefficient.

From (11) it follows that for iron at $T_c = 1043$ K and $C_c = 1{,}5$ kJ/(kg·K) [19] $k_c = 1{,}483 \cdot 10^{-3}$ kJ/(kg·K^2). This k_c value is assumed, in the first approximation, for low-alloy steels.

Scaling of the heat capacity in the vicinity of the Curie temperature can be carried out by the equations:

$$C_2(T) = \begin{cases} C_c\left[1-\left(\frac{T_c - T}{T_c}\right)^{\alpha 1}\right] \text{ at } T \le T_c \\ C_c\left[1-\left(\frac{T - T_c}{T_c}\right)^{\alpha 2}\right] \text{ at } T > T_c \end{cases} \tag{12}$$

where α_1 and α_2 are coefficients. Using the least squares method, it is obtained $\alpha_1 = 0{,}36$ and $\alpha_1 = 0{,}36$ that the best agreement of equation (12) with the experimental data is provided.

The crosslinking of the solution of equation (12) and dependencies (1) and (2) is carried out by equating (1) and (12), and (2) and (12) to find the temperatures at which these equations are performed.

The heat capacity of various liquid steels is practically independent of the temperature and is in a narrow range: from 0.75 to 0.85 kJ/(kg K), and the spread of values does not go beyond the experimental errors, and the average value coincides with the heat capacity of pure iron, i.e. 0.825 kJ/(kg K) [20]. Therefore, in the developed technique, the heat capacity of the liquid low-alloy steel is assumed to be equal to, kJ/(kg K):

$$C_L = 0{,}825 \cdot \tag{13}$$

Assuming a linear change in the specific heat of steel in the interval (T_S ... T_L) you can write the equation

$$C_4(T) = C_3(T_S) + \frac{C_L - C_3(T_S)}{T_L - T_S}. \tag{14}$$

Solutions of equations (1) - (14) determine the temperature dependence of the specific heat of low-alloy steels.

RESULTS AND DISCUSSION

Solutions of the system of equations (1) - (14) are shown in Fig. 1 - 4. Since low-alloy steel can be considered a dilute solution based on iron, the solution of equations (1) - (14) should be valid for pure iron. For Fig. 1 experimental data [19] and the calculated polytherm of specific heat of iron are presented.

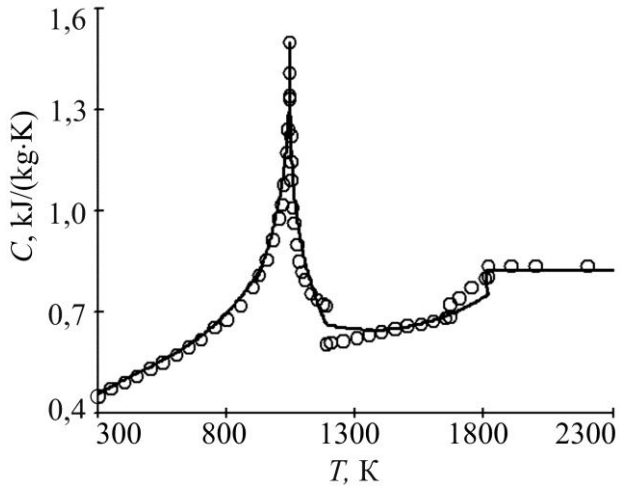

Figure 1. Experimental data (o – [19]) and the results of calculating the polytherm of the specific heat of pure iron according to equations (1) – (14)

Presented in Fig. 1 experimental data are recommended and obtained in [19] by statistical processing of 41 iron specific heat polytherms experimentally obtained by different researchers.

As seen in Fig. 1 compliance of experimental and calculated results can be considered satisfactory. For fig. 2-4 results of

calculations on equations (1) – (14) and experimental data for a number of steels are given.

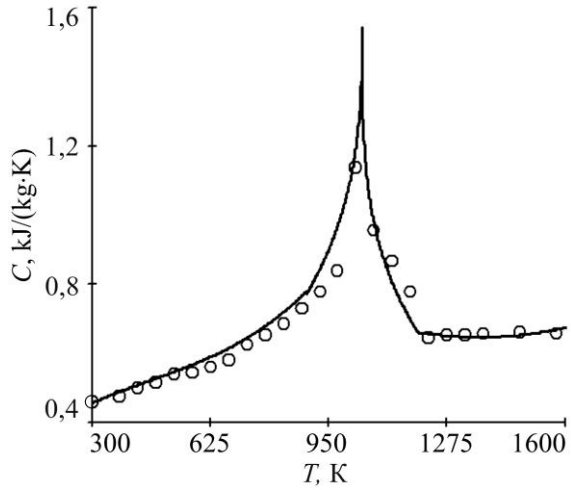

Figure 2. Calculated polytherm of specific heat of steel C15 and experimental data: o – [20]

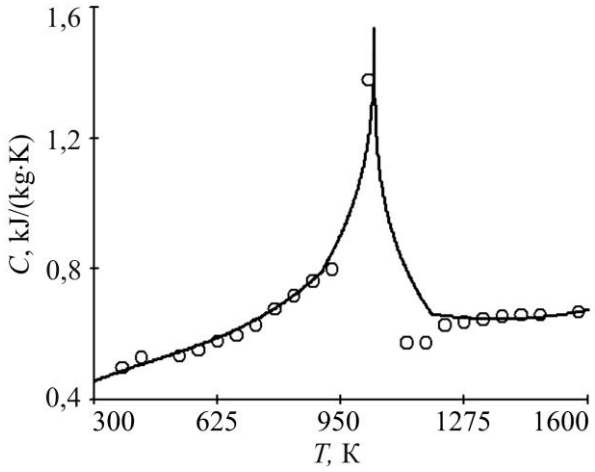

Figure 3. Calculated polytherm of the specific heat of steel 30NiCr14 and experimental data: o – [20]

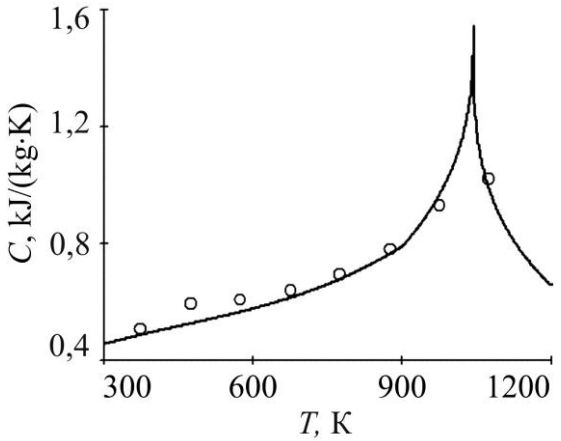

Figure 4. Calculated polytherm of specific heat of 14MoV6-3 and experimental data: o – [21]

The average relative standard deviation of the calculated specific heat polytherms from the experimental values for all steels and iron considered in the vicinity of the Curie temperature (Fig. 1 - 4) is about of ± 1.5%.

CONCLUSION

In addition to the known empirical polynomial equation of temperature dependence of specific heat capacity of low-alloy steels (1), (2), valid in temperature ranges, respectively, 293 ... 973 K and A_{c3} ... T_S, for the temperature range from 973 K to A_{c3}, a scaled equation of temperature dependence of the specific heat of steel in the vicinity of the Curie temperature (12) is proposed.

Using the obtained equation for calculating the Curie temperature depending on the chemical composition of steel (9), a refined method for calculating the specific heat polytherms of low – alloy steels according to the equations (1) - (14) is developed, which provides an overall average error in predicting the specific heat capacity not exceeding the error of the empirical equations (1) and (2).

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