

SPECIFIC HEAT OF CEMENTITE IN THE TEMPERATURE RANGE 2—20°K

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By using the results of our earlier measurements of the specific heat of six carbon steels containing from 0.10 to 2.50 percent of carbon, the lattice and the electronic specific heats and the Debye temperature of these steels have been estimated as well as the respective values for cementite.

To about 15°K the specific heat of cementite may be represented by the formula: $C = \alpha T^3 + \gamma T$. The change in the lattice specific heat coefficient and Debye temperature has been estimated within the temperature range 15°—20°K.

The change in both the specific heat and thermodynamic functions of cementite has been calculated for the interval from 2°—20°K.

We have carried out a systematic study of specific heat of carbon steels with carbon contents from 0.10 to 2.50 percent [1]; the next step were the investigations on some Polish tool-steels [2].

The present study was taken, in order to get some information concerning the specific heat, Debye temperature and some thermodynamical properties of cementite on the basis of the results of our previous work.

TABLE I

No of the specimen	% of carbon contents weight	% of atomic carbon contents	% Fe ₃ C by weight	Mass [g]
I	0.10	0.46	1.49	133.257
II	0.25	1.15	3.75	121.257
III	0.45	2.06	6.74	142.176
IV	0.75	3.39	11.24	67.060
V	1.25	5.55	18.73	131.022
VI	2.50	10.65	37.47	86.300

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All the details concerning the preparation and the treatment of the specimens, the description of the calorimeter and measurement technique are fully given in the previous papers [1], [2].

Some physical data of the investigated specimens are given in Table I.

Discussion of the results

In the present work some additional measurements have been carried out and the temperature range has been extended in the direction of higher temperatures in order to get more experimental points as a supplement of the results, given in the paper [1].

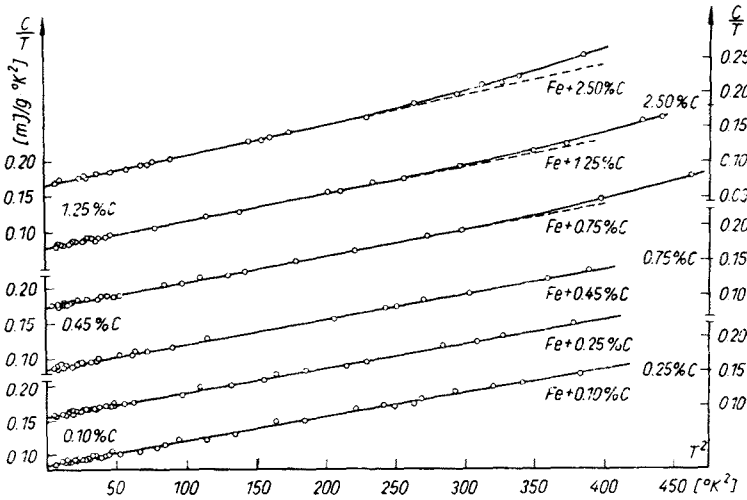


Fig. 1. Values of C/T versus T^2 for carbon steels

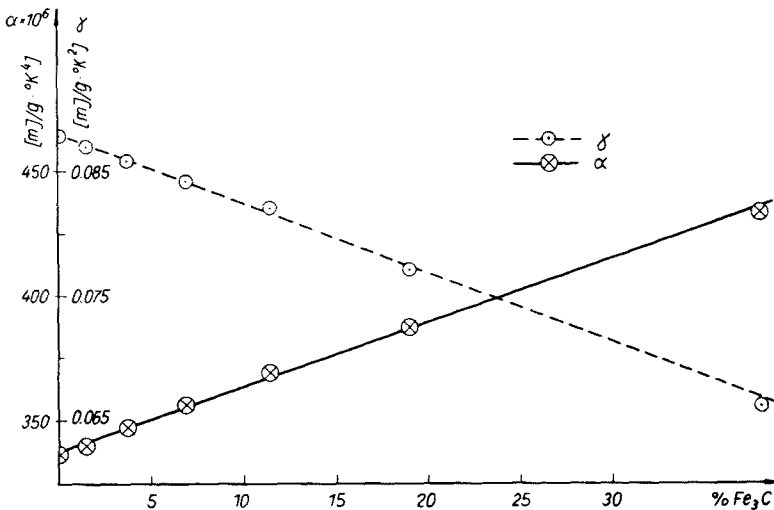


Fig. 2. Change in the specific heat coefficient with the cementite contents in the steels

The values of C/T versus T^2 for six previously investigated carbon steels with some additional measurement points are shown in Fig. 1.

There is a quite distinct linear change of C/T with T^2 for all the specimens up to about $15^\circ\text{--}16^\circ\text{K}$, thus in this temperature range the specific heat may be represented by the formula

$$C = \alpha T^3 + \gamma T$$

The α — lattice and γ — electron coefficients are given in Table II. The change of specific heat coefficients with the cementite contents in the steel is shown in Fig. 2.

The linearity of the changes of both specific heat coefficients may be explained by the fact that the contribution of cementite in the steel structure is also linear function of the carbon contents.

The increase in carbon contents results in an increasing role played by cementite in the steel structure and simultaneously causes an increase in the lattice and decrease in the electronic heat coefficients. Table II contains the values of α -lattice coefficient, measured in $\text{mJ/g } ^\circ\text{K}^4$, and γ -electron coefficient, measured in $\text{mJ/g } ^\circ\text{K}^2$.

The change in the molar heat of cementite with temperature within the range $2^\circ\text{K--}15^\circ\text{K}$ may be represented by the formula $C = 6.25 T + 0.111 T^3$ $\text{mJ/mole } ^\circ\text{K}$.

Above 15°K the lattice component of the cementite specific heat raises more strongly, than below 15°K . The value of Debye temperature θ_D up to 15°K is nearly constant and within the temperature range $15^\circ\text{--}50^\circ\text{K}$ there is a decrease in θ_D amounting to about 7%.

TABLE II

No of specimen	% of carbon by weight	$\alpha \times 10^6 \text{ mJ/g}^\circ\text{K}^4$	$\gamma \text{ mJ/g}^\circ\text{K}^2$
I	0.10	34 ₀	0.086 ₉
II	0.25	34 ₇	0.085 ₈
III	0.45	35 ₆	0.084 ₂
IV	0.75	36 ₉	0.082 ₀
V	1.25	38 ₇	0.077 ₁
VI	2.50	43 ₄	0.066 ₂

From the iron-carbon equilibrium diagram it is obvious that the solubility of carbon in iron at room temperature is rather small; according to Vensen [3] and Piling [4] this solubility does not exceed 0.006%. Wert [5] gives in his paper the solubility $10^{-4}\%$. Of course many admixtures and impurities in iron may result in the increase in solubility of carbon. On the basis of the linear course of the functions C/T versus T^2 shown in Fig. 1, one may assume that within the temperature range up to about 15°K the specific heat of cementite may be also represented as

$$C_1 = \alpha_1 T^3 + \gamma_1 T$$

where C_1 is the specific heat of cementite in $\text{mJ/g}^\circ\text{K}$, α_1 — the lattice and γ_1 — the electronic specific heat coefficients, respectively.

The total specific heat of steel, containing y % of carbon by weight C_2 may be represented as $C_2 = wC_1 + zC$ where C is the specific heat of pure iron, w — the amount of Fe_3C in one gram of steel (g), z — the amount of iron in one gram of steel (g). Consequently the specific heat of steel equals

$$C_2 = (w\alpha_1 + z\alpha)T^3 + (w\gamma_1 + z\gamma)T = \alpha_2 T^3 + \gamma_2 T$$

where: γ — is the electronic heat coefficient of iron,

α — is the lattice heat coefficient of iron

$\gamma_2 = (w\gamma_1 + z\gamma)$ the electronic specific heat coefficient of steel, $\alpha_2 = (w\alpha_1 + z\alpha)$ the lattice specific heat coefficient of steel. One gram of carbon binds 13.99 g of iron giving 14.99 g of cementite, therefore the amounts of cementite and iron in the steel are accordingly equal: $w = 0.1499 y$, $z = (1 - 0.1499 y)$, hence

$$\gamma_1 = \frac{\gamma_2 - (1 - 0.1499 y)\gamma}{0.1499 y} \quad (I)$$

$$\alpha_1 = \frac{\alpha_2 - (1 - 0.1499 y)\alpha}{0.1499 y} \quad (II)$$

By using the formulas I and II one can estimate both the electronic and lattice specific heat coefficients of cementite using the measurement results of specific heat of steels and pure iron.

For the present calculation the following results of the measurements of "armco" iron [1] have been accepted:

$$\alpha = 0.0188 \text{ mJ/mole } ^\circ K^4 = 0.000336 \text{ mJ/g } ^\circ K^4$$

$$\gamma = 4.90 \text{ mJ/mole } ^\circ K^2 = 0.0877 \text{ mJ/g } ^\circ K^2.$$

The measurement results of the heat coefficients of carbon steels are listed in Table II, and the calculation results of the specific heat of cementite are given in Table III.

TABLE III

No of the specimen	% of carbon	γ Fe_3C mJ/g $^\circ K^2$	$\alpha \times 10^6$ Fe_3C mJ/g $^\circ K^4$
I	0.10	0.037 ₃	60 ₀
II	0.25	0.036 ₈	64 ₀
III	0.45	0.036 ₃	63 ₇
IV	0.75	0.037 ₁	63 ₁
V	1.25	0.031 ₂	60 ₈
VI	2.50	0.030 ₄	59 ₇

By using the data from Table III the mean values of the specific coefficients of cementite have been calculated; the results are as follows:

$$\gamma = 0.0384 \text{ mJ/g } ^\circ K^2 \text{ and } \alpha = 0.000612 \text{ mJ/g } ^\circ K^4$$

The mole heat coefficients are:

$$\gamma = 6.25 \text{ mJ/mole } ^\circ K^2 \text{ and } \alpha = 0.111 \text{ mJ/mole } ^\circ K^4$$

Debye temperature $\theta_D = 259.5$ $^\circ K$.

It is quite clear from Fig. 1 the specific heat of steels containing 0.75%, 1.25% and

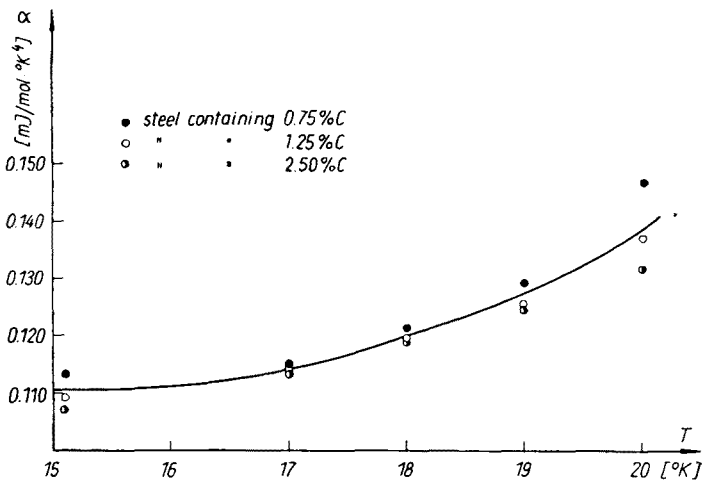
2.50% of carbon, above 15°K significantly deviates from the formula $C = \alpha T^3 + \gamma T$. Since the values of the specific heat of iron fulfil the Debye law up to 20°K, the deviation between 15° and 20°K is due to the specific heat of cementite.

The specimens with lower carbon contents do not show this deviation, because the change in the specific heat of small amounts of cementite present in the specimens gives rise to the change in the specific heat of steel smaller than the measurement error.

Using the values of the specific heat from the smoothed C/T versus T^2 curves, the lattice and electronic specific heat coefficients of cementite and the Debye temperature θ_D have been estimated. The results of the calculations have been listed in Table IV. The graph α versus T for the cementite is given in Fig. 3.

TABLE IV

T °K	% C	α mJ/mole °K ⁴	θ_D [°K]
17	0.75	0.115	256.7
	1.25	0.114	257.3
	2.50	0.113	257.3
18	0.75	0.121	252.0
	1.25	0.119	253.9
	2.50	0.119	253.9
19	0.75	0.129	246.8
	1.25	0.125	249.3
	2.50	0.124	249.8
20	0.75	0.147	236.5
	1.25	0.137	242.0
	2.50	0.132	245.4

Fig. 3. α versus T graph for the cementite

The graph in Fig. 4 represents the change of Debye temperature of cementite with temperature within the temperature range 15° to 20°K.

By using the calculated values of α and γ for cementite one can draw the curve specific heat as a function of the temperature. The results of the calculation of the specific heat of cementite are summarized in Table V.

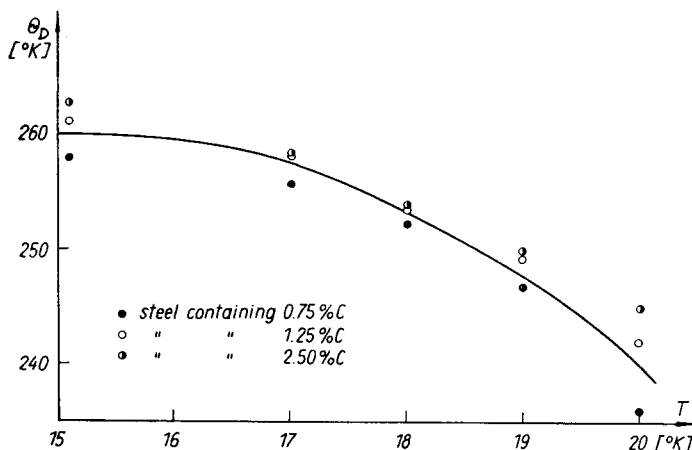


Fig. 4. Change in Debye temperature of cementite with temperature within the temperature range 15° to 20°K

TABLE V

The change of the molar heat of the cementite with temperature

T °K	$C_e = \gamma T$ mJ/mole °K	$C_s = \alpha T^3$ mJ/mole °K	$C = C_e + C_s$ mJ/mole °K
2	12.50	0.89	13.39
3	18.75	2.99	21.74
4	24.99	7.10	32.09
5	31.24	13.88	45.12
6	37.49	23.98	61.47
7	43.73	38.07	81.81
8	49.99	56.83	106.8
9	56.24	80.91	137.2
10	62.49	111.0	173.5
11	68.74	147.7	216.5
12	74.99	191.8	266.8
13	81.24	243.9	325.1
14	87.48	304.6	392.1
15	93.73	374.6	468.4
16	99.98	454.6	554.6
17	106.2	560.1	666.3
18	112.5	669.8	812.3
19	118.7	871.1	989.8
20	125.0	1112	1237

Fig. 5 shows the molecular heat of cementite *versus* temperature, electronic and lattice specific heats being separated.

The growth of the lattice molar heat of cementite in comparison with molar heat of pure iron is a result of quite different crystallographic structure of the cementite. At higher

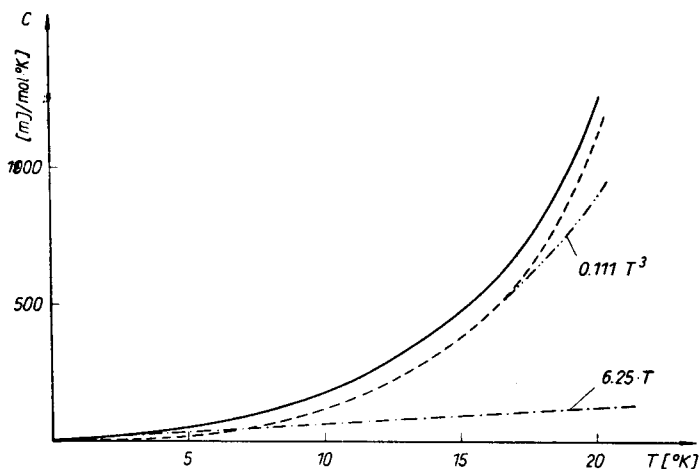


Fig. 5. Molar heat of cementite *versus* temperature

temperatures above the range of the present investigation one may expect a further growth of the lattice specific heat as a result of the vibration contribution by light carbon atoms in the cementite lattice. One can not exclude the additional growth of the heat capacity as a result of jumps of carbon atoms between the adjacent vacancies of the lattice or the cooperation with the lattice defects.

It is quite clear that the extension of the specific heat measurements to higher temperatures beyond 20°K may throw some light on the problem of the stability of carbon atoms in cementite.

The study of the electronic coefficient of the specific heat may supply us with valuable information concerning the structure of the energy bands. The knowledge of the electronic specific heat coefficients enables us to estimate the density of states near the Fermi surface. The type of the function of the density of states $N(E)$ being different, the density of states near the Fermi surface may be represented by the formula

$$N(E) \approx \frac{3\gamma}{\pi^2 kR}$$

In the ferromagnetic metals the band $3d$ is composed of two energy subbands, one totally filled is occupied by five electrons with no contribution to the specific heat, and second, occupied by the remaining electrons, belongs to the band $3d$ and with quite opposite spin orientation.

The total density of states is equal to the sum of the densities of states of the not totally filled subbands $3d$ and the band $4s$. Owing to the small density of states in the band $4s$ the

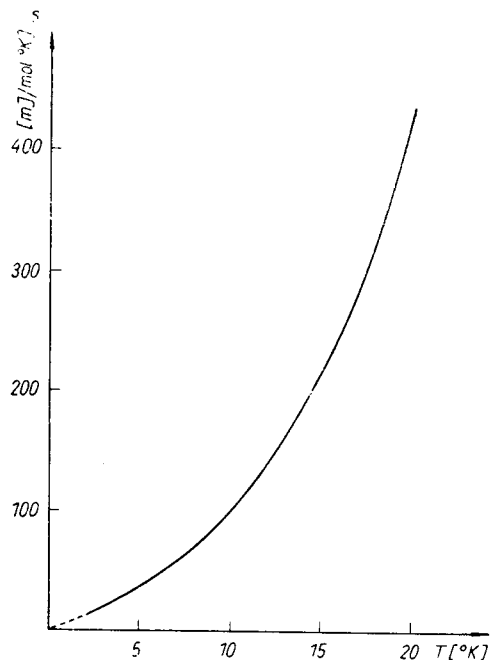


Fig. 6. Entropy vs. temperature diagram of cementite

TABLE VI

The thermodynamical functions of cementite

T °K	S mJ/mole °K	$(H-H_0)$ mJ/mole	$\left(\frac{F-H_0}{T}\right)$ mJ/mole °K
2	12.61	12.5	6.36
3	19.65	29.2	9.92
4	27.28	55.0	13.53
5	36.23	97.0	16.83
6	45.77	148.7	21.07
7	56.68	220.0	25.28
8	69.22	312.0	30.22
9	83.51	434.2	35.27
10	99.77	588.0	40.97
11	118.32	781.7	47.26
12	139.32	1021	54.24
13	162.94	1316	61.71
14	189.36	1673	69.86
15	218.85	2105	78.52
16	251.67	2616	88.17
17	286.42	3225	96.72
18	328.31	3963	108.15
19	376.82	4864	120.82
20	433.68	5976	134.88

contribution of the electrons belonging to this band may be neglected in the first approximation, thus the density of states in the band $3d$ may be represented by the formula $N(E)_{3d} \cong 2N(E)$.

The density of states near the Fermi surface of iron estimated on the study of γ coefficient obtained from the specific heat measurements on "armco" iron is equal to $4.15 \text{ at}^{-1}\text{eV}^{-1}$. The electronic specific heat coefficient of one mole iron contained in cementite equals $2.80 \text{ mJ/mole } ^\circ\text{K}^2$ and the corresponding density of states equals $1.76 \text{ at}^{-1}\text{eV}^{-1}$. From the results of the specific heat measurements one can obtain the thermodynamic functions of the substance. Thus the thermodynamic functions of cementite have been calculated up to 20°K .

The entropy $\int_0^T C \frac{dT}{T}$ has been obtained by applying the graphical method of integrating the function $C/T = f(T)$. The entropy — temperature diagram of cementite is shown in Fig. 6.

The enthalpy difference has been obtained by integrating the graph molar heat of cementite *versus* temperature (see Fig. 5). The estimated values of entropy S , enthalpy $(H-H_0)$ and the free energy function F are listed in Table VI.

The values of the thermodynamical functions within the temperature range $0^\circ\text{--}2^\circ\text{K}$ have been obtained by extrapolation of the specific heat of cementite up to 0°K by using the formula $C = 6.25T + 0.1111T^3 \text{ mJ/mole } ^\circ\text{K}$.

REFERENCES

- [1] J. Mazur, W. Zacharko, *Acta Phys. Polon.*, **32**, 501 (1967).
- [2] J. Mazur, W. Zacharko, *Acta Phys. Polon.*, **33**, 657 (1968).
- [3] J. Yensen, *Amer. Inst. Electr. Eng.*, **43**, 145 (1924).
- [4] W. P. Piling, *Trans. Amer. Inst. Min. Met. Eng.*, **70**, 254 (1924).
- [5] C. A. Wert, *J. Metallurgic.*, **2**, 1242 (1950).