Calculation of liquidus temperature for steel by Le Châtelier-Shreder and van Laar-Bowen equations

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Abstract

This paper deals with the calculation of temperature of liquid phase in the Fe-admixture binary systems. Two cases are considered in the calculations:

1. equilibrium of pure δ-iron with ideal melt of alloying element containing iron according to the Le Châtelier-Shreder equation,
2. ideal solid solution of δ-ferrite with ideal melt of alloying element containing iron according to modified van Laar-Bowen equation by distribution coefficients.

Decrease of melting point of δ-iron in the binary systems is calculated as the difference between melting point of pure δ-iron and melting point of δ-iron containing 1 wt.% of alloying element. The melting point decrease for the polycomponent system (steel) is calculated as a sum of individual (binary) melting point decreases, which, consequently, gives the melting temperature of low-alloyed steels.

Key words: decrease of melting point, binary system Fe-X, liquidus temperature, steel, distribution coefficients, ideal systems

1. Introduction

Melting point is an important parameter in steel casting because from it the optimal casting temperatures are derived and the course of solidification process can be predicted.

Heterogeneous processes such as melting or solidification are described by the melting point of δ-iron, temperature of melt and the decrease of melting point of δ-iron due to the presence of impurities and alloying elements [1–4]. The melting point of δ-iron $T^{\mathrm{TAV}}_{\delta-\mathrm{Fe}}$ is 1811 K, the molar heat of melting at melting point $\Delta H^{\mathrm{TAV}}_{1811,\delta-\mathrm{Fe}}$ is 13 806 J·mol^{-1}, molar entropy at melting point $\Delta S^{\mathrm{TAV}}_{1811,\delta-\mathrm{Fe}}$ is 7.62 J·mol^{-1}·K^{-1} [5].

2. Calculation of melting point decrease of iron in binary systems

The fundamental principle of melting point calculation takes stand on equality of chemical potentials of iron and alloying elements at phase equilibrium δ-iron↔melt:

$$\mu^{\delta}_{\mathrm{Fe}} = \mu^{\mathrm{l}}_{\mathrm{Fe}}, \tag{1}$$

$$\mu^{0\delta}_{\mathrm{Fe}} + RT\ln x^{\delta}_{\mathrm{Fe}} = \mu^{0\mathrm{l}}_{\mathrm{Fe}} + RT\ln x^{\mathrm{l}}_{\mathrm{Fe}} \tag{2}$$

$$\text{if} \quad \Delta\mu^{0}_{\mathrm{Fe}} = \mu^{0\mathrm{l}}_{\mathrm{Fe}} - \mu^{0\delta}_{\mathrm{Fe}} = \Delta G^{\mathrm{TAV}}_{\mathrm{Fe}} \tag{3}$$

$$\text{if} \quad \Delta G^{\mathrm{TAV}}_{\mathrm{Fe}} = \Delta H^{\mathrm{TAV}}_{\mathrm{Fe}} - T\Delta S^{\mathrm{TAV}}_{\mathrm{Fe}}, \tag{4}$$

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$$\ln \frac{x^{\delta}_{\mathrm{Fe}}}{x^{\mathrm{l}}_{\mathrm{Fe}}} = \frac{\Delta H^{\mathrm{TAV}}_{\mathrm{Fe}}}{R} \left(\frac{1}{T^{\mathrm{l}}} - \frac{1}{T^{\mathrm{TAV}}_{\delta-\mathrm{Fe}}} \right), \tag{5}$$

$$T^{\mathrm{l}} = \frac{\Delta H^{\mathrm{TAV}}_{\mathrm{Fe}}}{\Delta S^{\mathrm{TAV}}_{\mathrm{Fe}} + R \ln \frac{x^{\delta}_{\mathrm{Fe}}}{x^{\mathrm{l}}_{\mathrm{Fe}}}}. \tag{6}$$

1) If iron and alloying element behave in melt ideally and the solidified phase is pure δ-iron, i.e. $x^{\delta}_{\mathrm{Fe}} = 1$, then the melting point can be calculated using Le Châtelier-Shreder equation derived below in Eq. (7):

$$T^{\mathrm{l}} = \frac{\Delta H^{\mathrm{TAV}}_{\delta-\mathrm{Fe}}}{\Delta S^{\mathrm{TAV}}_{\delta-\mathrm{Fe}} - R \ln \left(1 - x^{\mathrm{l}}_{i}\right)}. \tag{7}$$

It is common practice to express the change in melting point for 1 wt.% of alloying element as follows:

$$x^{\mathrm{l}}_{i,w_i=1\%} = \frac{\frac{1}{M_i}}{\frac{1}{M_i} + \frac{100-1}{M_{\mathrm{Fe}}}}, \tag{8}$$

where $M_{\mathrm{Fe}} = 55.847\ \mathrm{g \cdot mol^{-1}}$ [5].

$$T^{\mathrm{l}(9)}_{w_i=1\%} = \frac{\Delta H^{\mathrm{TAV}}_{\delta-\mathrm{Fe}}}{\Delta S^{\mathrm{TAV}}_{\delta-\mathrm{Fe}} - R \ln (1 - x^{\mathrm{l}}_{i,w_i=1\%})}. \tag{9}$$

2) If iron and alloying element behave ideally in both melt and solid phases the basis of melting point calculation is given by van Laar-Bowen equation in its general form:

$$T^{\mathrm{l}} = \frac{\Delta H^{\mathrm{TAV}}_{\delta-\mathrm{Fe}}}{\Delta S^{\mathrm{TAV}}_{\delta-\mathrm{Fe}} + R \ln \frac{1 - x^{\delta}_{i}}{1 - x^{\mathrm{l}}_{i}}}. \tag{10}$$

a) If the equilibrium distribution coefficient of i-th alloying element in iron is taken as isothermal ratio of molar fractions of i-th alloying element in solid x^{δ}_{i} and liquid phase x^{l}_{i} [4, 6] then the calculation of melting temperature for 1 wt.% of admixture can be carried out as follows:

$$k_i = \frac{x^{\delta}_{i}}{x^{\mathrm{l}}_{i}}, \tag{11}$$

$$T^{\mathrm{l}(12)}_{w_i=1\%} = \frac{\Delta H^{\mathrm{TAV}}_{\delta-\mathrm{Fe}}}{\Delta S^{\mathrm{TAV}}_{\delta-\mathrm{Fe}} + R \ln \frac{1 - k_i x^{\mathrm{l}}_{i,w_i=1\%}}{1 - x^{\mathrm{l}}_{i,w_i=1\%}}}. \tag{12}$$

b) If the limiting equilibrium distribution coefficient of i-th admixture in iron is inserted into Eq. (10), the following formula for melting temperature can be derived:

$$k^{\mathrm{lim}}_{i} = \lim_{x_i \to 0} \frac{x^{\delta}_{i}}{x^{\mathrm{l}}_{i}}, \tag{13}$$

$$T^{\mathrm{l}(14)}_{w_i=1\%} = \frac{\Delta H^{\mathrm{TAV}}_{\delta-\mathrm{Fe}}}{\Delta S^{\mathrm{TAV}}_{\delta-\mathrm{Fe}} + R \ln \frac{1 - k^{\mathrm{lim}}_{i} x^{\mathrm{l}}_{i,w_i=1\%}}{1 - x^{\mathrm{l}}_{i,w_i=1\%}}}. \tag{14}$$

The melting temperature decrease of δ-iron caused by the addition of 1 wt.% of alloying element can be calculated as the difference between melting point of pure iron and the temperature of melt containing 1 wt.% of admixture:

$$\Delta T_{w_i=1\%} = T^{\mathrm{TAV}}_{\delta-\mathrm{Fe}} - T^{\mathrm{l}}_{w_i=1\%} = 1811 - T^{\mathrm{l}}_{w_i=1\%}. \tag{15}$$

The values of melting temperature decrease for 1 wt.% of the individual alloying elements for

1) $k_i = 0$, Eq. (9),

2a) $k_i = k^{\mathrm{P(E)}}_{i}$, Eq. (12),

where $k^{\mathrm{P(E)}}_{i}$ is the distribution coefficient of admixing element in iron at the peritectic or eutectic temperature. Alternatively, temperature of minimum on the solid and liquid curves can be used (Fe-V, Fe-Cr, Fe--W);

2b) $k_i = k^{\mathrm{lim}}_{i}$, Eq. (14)

are summarized in Table 1 in columns 6–8. To compare the calculated values with experimental ones, the data from different authors are given in columns 9–11.

3. Calculation of melting temperature decrease of iron in polycomponent (steel) systems

If no interaction between alloying elements is presumed the rule of additivity can be applied, i.e. the total temperature decrease is the sum of individual temperature decreases for each alloying element:

$$\Delta T_{\mathrm{total}} = \sum \Delta T_{w_i=1\%} \times \%i, \tag{16}$$

$$T^{\mathrm{l}} = T^{\mathrm{TAV}}_{\delta-\mathrm{Fe}} - \Delta T_{\mathrm{total}} = 1811 - \Delta T_{\mathrm{total}}. \tag{17}$$

4. Discussion

The melting point decreases of iron calculated using Le Châtelier-Shreder equation are too high due to

Table 1. Melting point decrease of binary systems (iron-admixture) for 1 wt.% of admixing element $\Delta T^{\mathrm{l}}_{w_i=1\%}$ taken from literature and calculated for 1) $k_i = 0$, 2a) $k_i = k_i^{\mathrm{P(E)}}$, 2b) $k_i = k_i^{\mathrm{lim}}$

Alloying element	M_i (g·mol^{-1})	$x^{\mathrm{l}}_{i,w_i=1\%}$	$k_i^{\mathrm{P(E)}}$ [6]	k_i^{lim} [6]	$\Delta T^{\mathrm{l}}_{w_i=1\%}$					
					1)	2a)	2b)	[6]	[7]	[8]
1	2	3	4	5	6	7	8	9	10	11
B	10.811	0.0496	0.07	0.045	95.2	89.0	91.2	98	–	90
C	12.0107	0.0449	0.17	0.19	86.4	72.6	70.9	86.6	65	73
N	14.007	0.0387	0.28**	–	74.7	54.7	–	–	–	–
O	15.9994	0.0341	0.17	0.15	66.0	55.3	56.6	–	–	11 for 0.16 %
Al	26.9815	0.0205	0.85	0.88	40.0	6.2	4.9	11.8	–	3
Si	28.0855	0.0197	0.82	0.66	38.5	7.1	13.4	13.9	8	12
P	30.9738	0.0179	0.31	0.14	35.0	24.4	30.2	32.3	30	28
S	32.065	0.0173	0.013	0.062	33.8	33.4	31.8	30.5	25	30
Ti	47.867	0.0116	0.62	0.35	22.8	8.7	14.9	14.9	–	18
V	50.9415	0.011	1*	0.87	21.6	0.0	2.8	2.9	2	2
Cr	51.9961	0.0107	1*	0.9	21.0	0.0	2.1	2.1	1.5	1
Mn	54.9380	0.0102	0.72	0.69	20.0	5.7	6.3	6.2	5	3
Ni	58.6934	0.0095	0.77	0.69	18.7	4.3	5.8	5.6	4	3.5
Co	58.9332	0.0095	0.85	0.84	18.7	2.8	3.0	3	–	1.8
Cu	63.546	0.0088	0.52	0.78	17.3	8.4	3.8	3.8	5	7
As	74.9216	0.0075	0.39	0.21	14.7	9.0	11.7	11.8	–	14 for 0.5 %
Nb	92.9064	0.006	0.27	0.37	11.8	8.6	7.5	7.5	–	–
Mo	95.94	0.0058	0.99	0.73	11.4	0.1	3.1	3.1	–	2
Sn	118.71	0.0047	0.26	0.28	9.3	6.9	6.7	6.7	–	10 for 0.03 %
Ta	180.948	0.0031	0.32	0.44	6.1	4.2	3.4	3.5	–	–
W	183.84	0.0031	1*	0.83	6.1	0.0	1.0	0.9	–	< 1

Remarks: * value of distribution coefficient at minimum on the curves of solidus and liquidus; ** value of $k_{\mathrm{N}}^{\mathrm{P(E)}}$ taken from [8]

the fact that the solid phase obtained during solidification is not, typically, pure δ-iron.

The binary systems of chromium-iron, vanadium-iron and tungsten-iron show minimum on the solid and liquid curves at which the temperature distribution coefficients are equal one. Consequently, values of melting point decrease calculated according to Eq. (15) are zero. In this case, therefore, it is recommended to read the melting point decrease directly from the phase diagrams. They are 1.26 ℃ per 1 wt.% of chromium, 2.4 ℃ per 1 wt.% of vanadium and 0.68 ℃ per 1 wt.% of tungsten. Another possibility is to calculate the melting point decrease using limiting distribution coefficients as it is done in Table 1, column 8. The calculated melting point decreases (Table 1, columns 7 and 8) agree reasonably with the literature values in Table 1, columns 9–11.

5. Conclusion

The van Laar-Bowen equation (12), modified by (16), (17), (values from Table 1, column 7), is recommended for the calculation of the melting point decrease of δ-iron (1 wt.% of admixture) – Eq. (18).

It is recommended to calculate melting point decrease of low-alloyed steels, such as deep-drawing, transformer, micro-alloyed or structural steels, according to the following formula:

$$\begin{aligned} T^{\mathrm{l}}_{\mathrm{steel}} &= 1811 - 72.6 \times \%\mathrm{C} - 7.1 \times \%\mathrm{Si} - 5.7 \times \%\mathrm{Mn} \\ &- 24.4 \times \%\mathrm{P} - 33.4 \times \%\mathrm{S} - 2.1 \times \%\mathrm{Cr} \\ &- 2.8 \times \%\mathrm{V} - 6.2 \times \%\mathrm{Al} - 8.4 \times \%\mathrm{Cu} \\ &- 4.3 \times \%\mathrm{Ni} - 2.8 \times \%\mathrm{Co} - 8.6 \times \%\mathrm{Nb} \\ &- 4.2 \times \%\mathrm{Ta} - 8.7 \times \%\mathrm{Ti} - 9 \times \%\mathrm{As} \\ &- 1 \times \%\mathrm{W} - 6.9 \times \%\mathrm{Sn} - 54.7 \times \%\mathrm{N} \\ &- 0.1 \times \%\mathrm{Mo} - 55.3 \times \%\mathrm{O} - 89 \times \%\mathrm{B}. \end{aligned} \tag{18}$$

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