Communications

Metallurgical Thermodynamics and the Carbon Equivalent Expression

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The carbon equivalent expression is the most used expression in foundry ferrous metallurgy, but the relationship between carbon equivalent and metallurgical thermodynamics has not been recognized by most foundrymen. The carbon equivalent is used by foundrymen to predict various mechanical properties of cast iron, such as tensile strength[1] and hardness.[2] Some gray iron and ductile iron alloys have specifications on carbon equivalent as well as compositional restrictions.[3] A presentation by Franz Neuman[4] derived an expression for the carbon equivalent *via* metallurgical thermodynamics, but his derivation is quite different from the following derivation.

The carbon equivalent for a multicomponent iron-carbon base solution has the same activity as the equivalent amount of carbon in the binary iron-carbon solution. The carbon activity is related to the eutectic composition, and the austenite liquidus line and data regarding these values for Fe-C-Si melts are summarized by Heine.[5] The Henrian activity coefficient and interaction coefficients described in various metallurgical thermodynamics sources[6,7] will be used to derive the carbon equivalent expression. The Henrian activity approach, which is based upon infinitely dilute solutions, has been validated for iron-carbon saturated solutions, and interaction coefficients have been derived for such solutions.[4,6] The thermodynamics will be applied to a solution of iron-carbon-silicon-phosphorus, and the results will be compared to other carbon equivalent expressions presented in the literature.

In the quaternary (Fe-C-Si-P) solution, the Henrian activity of carbon is given by:

$$h_C = f_C \times \text{pct C} \qquad [1]$$

where:

h_C = Henrian activity of carbon

f_C = Henrian activity coefficient of carbon

pct C = weight percent carbon

The effects of carbon, silicon, and phosphorus upon the activity of carbon are included in the Henrian activity coefficient which can be expressed as:

$$f_C = f_C^C \times f_C^{Si} \times f_C^P \qquad [2]$$

where:

f_C^C = effect of carbon upon Henrian activity coefficient of carbon

f_C^{Si} = effect of silicon upon Henrian activity coefficient of carbon

f_C^P = effect of phosphorus upon Henrian activity coefficient of carbon

This is often represented in logarithmic form:

$$\log f_C = \log f_C^C + \log f_C^{Si} + \log f_C^P \qquad [3]$$

The effect of an element A upon the Henrian activity coefficient of another element B is represented by:

$$\log f_B^A = e_B^A \times \text{pct A} \qquad [4]$$

where:

e_B^A = interaction coefficient of element A upon element B

pct A = weight percent of element A

If the results of Eqs. [2], [3], and [4] are utilized in Eq. [1], it becomes, in logarithmic form:

$$\log h_C = \log \text{pct C} + \log f_C \qquad [5]$$

$$\log h_C = \log \text{pct C} + \log f_C^C + \log f_C^{Si} + \log f_C^P \qquad [6]$$

$$\log h_C = \log \text{pct C} + e_C^C \times \text{pct C} + e_C^{Si} \times \text{pct Si} + e_C^P \times \text{pct P} \qquad [7]$$

From the foundry viewpoint, the carbon equivalent results in the same Henrian activity in the multicomponent solution as carbon would have in the binary Fe-C solution; that is, Eq. [1] would be rewritten as:

$$h_C = f_C \times \text{CE} \qquad [8]$$

where:

h_C = Henrian activity of carbon

f_C = Henrian activity coefficient of carbon

CE = carbon equivalent weight percent

However, the logarithmic function of the activity coefficient will become:

$$\log f_C = e_C^C \times \text{CE} \qquad [9]$$

and then:

$$\log h_C = \log f_C + \log \text{CE} \qquad [10]$$

$$\log h_C = e_C^C \times \text{CE} + \log \text{CE} \qquad [11]$$

If the expressions for $\log h_C$ in Eqs. [7] and [11] are compared, one has:

$$\log \text{CE} + e_C^C \times \text{CE} = \log \text{pct C} + e_C^C \times \text{pct C} + e_C^{Si} \times \text{pct Si} + e_C^P \times \text{pct P} \qquad [12]$$

which can be converted to:

$$\log(\text{CE}/\text{pct C}) + e_C^C(\text{CE} - \text{pct C}) = e_C^{Si} \times \text{pct Si} + e_C^P \times \text{pct P} \qquad [13]$$

To simplify the relation to the desired form the log (CE/pct C) term must be reduced by using the logarithmic series. The first step is to convert CE/pct C to:

$$\text{CE}/\text{pct C} = (\text{CE} - \text{pct C})/\text{pct C} + 1 \qquad [14]$$

Now if one sets:

$$(\text{CE} - \text{pct C})/\text{pct C} = x \qquad [15]$$

where x is a number less than 1, the logarithmic series expression

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$$\log(x+1) = (x - \tfrac{1}{2}x^2 + \cdots)/2.302 \quad [16]$$

can be reduced, when the higher order terms are neglected, to:

$$\log(x+1) \cong 0.434x \quad [17]$$

and thus a simplified expression for log (CE/pct C) obtained from Eqs. [14] through [17] is:

$$\log(\text{CE}/\text{pct C}) = 0.434(\text{CE} - \text{pct C})/\text{pct C} \quad [18]$$

A proper assumption needs to be made about the carbon level to obtain an expression similar to the standard carbon equivalent expression. The carbon level selected was 3.5 pct because

(a) The carbon level of most cast irons ranges from 3.0 to 4.0 pct.

(b) Cast iron is an Fe-C-Si alloy, and the effect of Si upon the eutectic carbon level (4.26 pct) reduces the eutectic carbon by about 0.32 per percent silicon.[7] A cast iron nominally contains 2 pct Si and is usually slightly hypoeutectic.

Equation [18], with the application of 3.5 pct for the carbon level in the denominator of the right-hand side expression, becomes:

$$\log(\text{CE}/\text{pct C}) = 0.124(\text{CE} - \text{pct C}) \quad [19]$$

The interaction coefficients for carbon, silicon, and phosphorus selected were 0.159, 0.085, and 0.088. The carbon value was from an expression derived by Healy[8] which is:

$$e_C^C = 0.092 + 118/T \quad [20]$$

where:

$$T = \text{temperature (K)}$$

The silicon and phosphorus values are derived from those reported by Elliott, Gleiser, and Ramakrishna (Reference 6, page 487) for graphite saturated iron solution and adjusted for a Fe-C-Si solution with a molecular weight of 49. The use of Eq. [19] and the selected interaction coefficients in Eq. [13] result in:

$$0.283\,(\text{CE} - \text{pct C}) = 0.085 \text{ pct Si} + 0.088 \text{ pct P} \quad [21]$$

and:

$$\text{CE} - \text{pct C} = 0.30 \text{ pct Si} + 0.31 \text{ pct P} \quad [22]$$

or:

$$\text{CE} = \text{pct C} + 0.30 \text{ pct Si} + 0.31 \text{ pct P} \quad [23]$$

This expression of carbon equivalent is nearly equal to those commonly used,[9] such as:

$$\text{CE} = \text{pct C} + \tfrac{1}{3}(\text{pct Si} + \text{pct P}) \quad [24]$$

The difference between Eqs. [23] and [24], the theoretical and empirical equations for carbon equivalent, can be further reduced. The interaction coefficients were developed at 1600 °C and most foundry metals are cast at lower temperatures, such as 1500 °C (2732 °F). According to Pehlke[10] the interaction parameter will vary linearly with the reciprocal of absolute temperature, and after this adjustment is made, Eq. [23] at 1500 °C becomes:

$$\text{CE} = \text{pct C} + 0.32 \text{ pct Si} + 0.33 \text{ pct P} \quad [25]$$

The expression derived by Neumann[4] is:

$$\text{CE} = \text{pct C} + 0.31 \text{ pct Si} + 0.33 \text{ pct P} + 0.4 \text{ pct S} - 0.027 \text{ pct Mn} \quad [26]$$

S. L. Karsay[11] strongly recommends the value of 0.31 for the silicon coefficient, and Heine[5] uses the value of 0.317 for the effect of silicon on the eutectic carbon equivalent.

The agreement between the coefficients of silicon and phosphorus in Eqs. [24], [25], and [26] as well as the other recommended values for the silicon coefficient is remarkable. The recommended range of compositions for the carbon equivalent expression would be the same as those for most gray, ductile, and compacted graphite irons. Adjustments for other elements can be made in a similar manner if the interaction coefficient in an iron-carbon saturated melt is known.

It is satisfying to know that the carbon equivalent expression, validated by experience through the years, can also be derived from basic metallurgical thermodynamics. This procedure used will permit the derivation of coefficients for other elements upon the carbon equivalent expression from the interaction coefficients.

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