Improved Thermodynamic Formula for Austenite/(Austenite+Cementite) Phase Boundary in Low Alloy Steels

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The phase boundary between two different phases is a criterion that defines the start and finish of phase transformation processes. Phase transformation kinetics is increased by adding alloying elements that increase the stability of the product phase. For example, Cr addition increases the stability of ferrite (α) transformed from austenite decomposition. The addition of an alloying element that increases the stability of the parent phase can suppress the formation of the product phase from the parent phase, e.g., Mn addition increases the austenite (γ) stability, resulting in a retarded ferrite transformation. This is due to the fact that the addition of an alloying element decreases or increases the driving force required for the phase transformation.1) The behavior of alloying elements during phase transformation can be classified into two types from a thermodynamic point of view: ortho-equilibrium (OE) and para-equilibrium (PE).2) OE is a full equilibrium situation, mainly observed at high temperature where the driving force for phase transformation is low and the diffusion of alloying elements is relatively fast. The alloying elements are fully partitioned between the parent phase and the product phase depending on the solubility in each phase. On the other hand, only the interstitial elements are partitioned, while no partitioning of an alloying element on substitutional sites occurs under PE conditions. The PE situation is generally observed in the low temperature region where the phase transformation kinetics is fast, and the diffusion of substitutional alloying elements is relatively slow.

Thermodynamic studies on the influence of alloying element partitioning on the phase boundaries of low alloy steels have been performed.3–11) The partitioning effects of alloying elements have been studied with respect to the phase boundary between γ and (γ+α) regions,8) known as the Aα3 temperature, curve, and the eutectoid transformation temperature (Aα2 temperature), which is determined by two phase boundaries, γ(γ+α) and γ(γ+cementite(θ)).9) Also, the influence of alloying element partitioning on the γ(γθ) phase boundary, i.e., the Acm temperature curve, has been studied and the following formula has been proposed.11)

\[ A_{cm}(^\circ C) = 224.4 + 992.4C - 465.1C^2 + 46.7C \]
\[ + 19.0CCr - 6.1Cl + 7.6Mn + 10.0Mo \]
\[ - 6.8CrMo - 6.9Ni + 3.7CNI - 2.7CrNi \]
\[ + 0.8Ni^2 + 16.7Si \]

However, this formula is limited to the hypo-eutectoid region with a carbon range from 0.2 to 0.7 mass%. Few or no formulae are available to predict the γ(γθ) phase boundary above the Aα1 temperature for the hyper-eutectoid region. Therefore, in this study, a thermodynamic based formula considering the effect of alloying element partitioning was proposed to predict the γ(γθ) phase boundary over a wide range of chemical compositions for low alloy steels.

The chemical composition range for the model proposed in this study is listed in Table 1. The maximum carbon content is 1.8 mass%, which can include both hypo- and hyper-eutectoid regions. Also, the effect of Cu addition was considered. Copper increases strengthening due to Cu precipitation and improves the hardenability and tempering resistance in HSLA steels.

First, the γ(γθ) phase boundary under OE conditions (hereafter called “AcmOE”) and the γ(γθ) phase boundary under PE conditions (hereafter called “AcmPE”) are calculated for alloy compositions in Table 1. Equations related to the chemical potentials for each element and all thermodynamic parameters such as free energy change between phases used to calculate AcmOE and AcmPE are adopted in the literature.3) Also detailed calculation procedures are described in the previous works.3–11) Thermodynamic calculation is carried out using a personal program code including the equations and the thermodynamic parameters. The actual γ(γθ) phase boundary (hereafter called “Acm^OPT”) is varied between two Acm temperatures calculated at OE and PE conditions depending on the effect of alloying element partitioning. Acm^OE−PE at the eutectoid temperature can be determined by comparison with the Acm^OE−PE temperature. The Acm^OE−PE temperature calculated by considering partitioned alloying elements9) indicates a tendency for alloy partitioning between PE and OE conditions, which directly relates to the alloy partitioning of Acm^PE−OE. The Acm^OE−PE temperature can be calculated by Eq. (8) in the reference.9)

Thus, the formalized Acm^OE−PE is given by:

\[ A_{cm}^{OE-PE} = A_{cm}^{OE} - \left( A_{cm}^{OE} - A_{cm}^{PE} \right) \left( \frac{A_{cm}^{OE} - A_{cm}^{PE}}{A_{cm}^{PE} - A_{cm}^{OE}} \right) \]

(2)

In the previous model,11) the partitioning effect of alloying elements linearly decreases below the Aα1 temperature, and no partitioning occurs at low temperature. Similarly, it is known that the alloying elements can be fully partitioned at high temperature. The partitioning of the alloying elements is strongly dependent on temperature, so the actual Acm temperature with the temperature-dependent partitioning effect of alloying elements (Acm^OPT) is obtained as follows:
where $T_0^{\text{low}}$ is the low standard temperature for full PE conditions (=25°C), $T_0^{\text{high}}$ is the high standard temperature for full OE conditions, and $Ae_1$ is the temperature for the maximum equilibrium carbon solubility on the γ(γθ) phase boundary in a binary Fe–Fe₃C system (=1147°C). $T_0^{\text{low}}$ and $T_0^{\text{high}}$ are determined in order to separate the partitioning behavior with temperature.

A large number of combinations of alloying elements in Table 1 were used to calculate the $A^{\text{OPT}}_e$ temperature according to Eq. (3). A simple formula for $A^{\text{OPT}}_e$ temperature prediction has been generated by regression analysis as

$$A^{\text{OPT}}_e = \begin{cases} A^{\text{OE}}_e & \text{for } A^{\text{OE-PE}}_e \geq T_0^{\text{high}} \\ A^{\text{OE}}_e - (A^{\text{OE}}_e - A^{\text{OE-PE}}_e) \left( \frac{T_0^{\text{high}} - A^{\text{OE-PE}}_e}{T_0^{\text{high}} - A^{\text{OE}}_e} \right) & \text{for } A^{\text{OE-PE}}_e < A^{\text{OE}}_e < T_0^{\text{high}} \\ 0 & \text{for } A^{\text{OE-PE}}_e < A^{\text{OE}}_e \end{cases}$$

(3)

where $A^{\text{OPT}}_e$ is the calculated $A_e$ temperature. “Ac_e” is the $A_e$ temperature experimentally measured. The compositions of the alloys used for comparison are within the composition range in Table 1 except for one alloy (0.81C-3.69Ni-0.78Cr). The $A^{\text{OPT}}_e$ temperatures calculated using the previous formula are too low for the same reason illustrated in Fig. 1. There is no doubt that the prediction accuracy could be lowered when exceeding the composition range of data used to derive the equations.

The equilibrium volume of proeutectoid cementite can be obtained from the γ(γθ) phase boundary. The measured equilibrium $Acm$ temperature obtained using the newly proposed formula are in an acceptable range relative to the experimental data considering the non-equilibrium nature of the experiment. The compositions of the alloys used for comparison are within the composition range in Table 1 except for one alloy (0.81C-3.69Ni-0.78Cr). The $Acm$ temperatures calculated using the previous formula are too low for the same reason illustrated in Fig. 1. There is no doubt that the prediction accuracy could be lowered when exceeding the composition range of data used to derive the equations.

**Figure 1** compares the $\gamma(\gamma\theta)$ phase boundaries calculated by the previous formula (Eq. (1)) and the proposed formula (Eq. (4)) for the binary Fe–Fe₃C alloy system. The experimental data points of the $\gamma(\gamma\theta)$ phase boundary were measured from Fe–Fe₃C alloys with different carbon contents higher than 0.8 mass%. The $\gamma(\gamma\theta)$ boundary curve calculated by Eq. (1) is underestimated compared with the experimental data because the thermodynamic data used to derive Eq. (1) were limited to the hypo-eutectoid composition range of the low alloy steels. The results calculated using Eq. (4) are in good agreement with experimental data, which indicates that Eq. (4) can overcome the inaccuracies of the previous formula for hyper-eutectoid region.

Twelve $Acm$ temperatures of various Fe–C–X alloys measured experimentally were collected from the literature. Those $Acm$ temperatures are higher than the equilibrium $Acm$ temperatures since the $Acm$ temperature is measured during continuous heating. Overheating beyond the equilibrium temperature is required to complete the dissolution of all cementite particles. The calculated equilibrium $Acm$ temperatures are compared with the measured $Acm$ temperatures for various Fe–C–X alloys as shown in **Fig. 2**. The equilibrium $Acm$ temperatures obtained using the newly proposed formula are in an acceptable range relative to the experimental data considering the non-equilibrium nature of the experiment. The compositions of the alloys used for comparison are within the composition range in Table 1 except for one alloy (0.81C-3.69Ni-0.78Cr). The $Acm$ temperatures calculated using the previous formula are too low for the same reason illustrated in Fig. 1. There is no doubt that the prediction accuracy could be lowered when exceeding the composition range of data used to derive the equations.

**Figure 2** compares the volume of proeutectoid cementite calculated using Eqs. (1) and (4) with the measured results. The lever rule was used to calculate the volume of proeutectoid cementite from the $\gamma(\gamma\theta)$ phase boundary, as was used for the proeutectoid ferrite calculation. First, the mass fractions for proeutectoid cementite and austenite ($W_\theta$ and $W_\gamma$) were calculated.

$$W_\theta = \frac{C_{\gamma\theta} - C_0}{(6.69 - C_0)}$$

$$W_\gamma = 1 - W_\theta$$

(5)

where $C_0$ is the mass percent carbon in the AISI 52100 (≈0.92) and $C_{\gamma\theta}$ is the mass percent carbon on the $\gamma(\gamma\theta)$ phase boundary at a given temperature. Therefore, $C_{\gamma\theta}$ is influenced by the partitioning of alloying elements since the
alloy partitioning influences the $\gamma(\gamma+\theta)$ phase boundary. $C_{\gamma\theta}$ can be obtained by solving Eq. (4) for $C$ as the temperature and amounts of alloying elements except for C are given. The exact volume fraction of proeutectoid cementite ($V_\theta$) is expressed as follows:

$$V_\theta = \frac{W_\theta}{\rho_\theta} = \frac{W_\gamma}{\rho_\gamma + W_\theta/\rho_\gamma}$$

where $\rho_\theta$ and $\rho_\gamma$ are the densities of cementite and austenite. The alloy partitioning varied from PE to mixed (PE+OE), and finally reached to OE conditions as raising temperature influences the $\gamma(\gamma+\theta)$ phase boundary (Ae1 temperature) as seen in Eq. (3) and brings about the change of the cementite volume fraction. The calculated volume curve, obtained using Eq. (4), matches well with the measured data points. Figure 3(b) shows the microstructure of the quenched sample after holding at 800°C, where the small spherical white particles are the proeutectoid cementite.

As found in Figs. 1 to 3, the formula proposed in this study accurately predicts the $\gamma(\gamma+\theta)$ phase boundary in the high temperature hyper-eutectoid region. Thus, the use of Eq. (4) in the low temperature hypo-eutectoid austenite region was also verified. Figure 4 shows the calculated volumes of proeutectoid ferrite below the Ae1 temperature compared with the experimental results. The calculated volume curve using Eq. (4) is similar to that using Eq. (1), showing good accuracy. Similar to the calculation in Fig. 3, the mass fractions for proeutectoid ferrite and austenite ($W_\alpha$ and $W_\gamma$) were calculated from the Fe–C phase diagram of the alloy as

$$W_\alpha = \frac{C_{\gamma\theta} \cdot C_\alpha}{C_{\gamma\theta}}$$
$$W_\gamma = 1 - W_\alpha$$

The carbon solubility in ferrite was ignored. The exact volume fraction of proeutectoid ferrite ($V_\alpha$) is given by

$$V_\alpha = \frac{W_\alpha}{\rho_\alpha} = \frac{W_\alpha}{\rho_\alpha + W_\gamma/\rho_\gamma}$$

where $\rho_\alpha$ is the density of ferrite. In this case, the alloy partitioning also influences $C_{\gamma\theta}$ and finally $V_\alpha$.

In conclusion, OE and PE thermodynamic calculations were carried out to predict the $\gamma(\gamma+\theta)$ phase boundary for hypo- and hyper-eutectoid low alloy steels. The temperature variation of the partitioning effect of substitutional alloying elements on the actual $\gamma(\gamma+\theta)$ phase boundary was considered. A new Ae1 temperature formula was proposed as a function of chemical composition based on the thermodynamic calculations, which could predict the accurate $\gamma(\gamma+\theta)$ phase boundary of various low alloy steels not only in the high temperature hyper-eutectoid region, but also in the low temperature hypo-eutectoid region. It is anticipated that the proposed formula can be useful for the calculation of various phase transformations of multi-component austenite with wide ranges of temperature and composition.

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