Note

Thermodynamic Formula for the A_{cm} Temperature of Low Alloy Steels

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The decomposition of austenite to ferrite or cementite begins at the equilibrium phase boundary of austenite/(ferrite+austenite) or austenite/(cementite+austenite) in binary Fe–C phase diagram. The temperature values on the phase boundaries of austenite/(ferrite+austenite) and austenite/(cementite+austenite) at a certain carbon content are called A_{e3} and A_{cm} temperatures of the steel, respectively. The A_{e1} temperature is defined as the eutectoid temperature corresponding to the intersection point of two phase boundaries: austenite/(ferrite+austenite) and austenite/(cementite+austenite). Many thermodynamic studies have been performed to calculate the phase diagrams, which provide us with various basic information for predicting the quantitative kinetics of phase transformations in low alloy steels.^{1–7)} The partitioning effects of alloying elements such as Ni, Cr, and Mo occurring during the austenite decomposition on the phase diagrams of the steels have been investigated with ortho-equilibrium (OE) and para-equilibrium (PE) models in low alloy steels. The schematic drawing of the Fe–Fe₃C phase diagram calculated by using the OE and PE models is illustrated in Fig. 1. The phase boundaries calculated with OE model are generally shown at the higher temperatures than those by PE model.

Recently, Lee and Lusk⁷⁾ have analyzed the experimental A_{e1} temperatures of 85 low alloy steels, obtained from the US Steels Atlas of I–T diagrams,⁸⁾ using thermodynamic

Fig. 1. Schematic drawing of the Fe–Fe₃C phase diagram calculated by ortho-(OE) and para-(PE) equilibrium models.

models. They have realized that the measured A_{e1} temperatures are located between two theoretical A_{e1} temperatures predicted using OE and PE models and suggested a new thermodynamic model for better prediction of the measured A_{e1} temperatures. This fact means that two phase boundaries of austenite/(ferrite+austenite) and austenite/(cementite+austenite) are also located between the calculated phase boundaries by OE and PE models. However, the austenite/(ferrite+austenite) boundary calculated by OE model shows a good match as compared with the experimental A_{e3} data.²⁾ This seems reasonable since the ferrite transformation usually occurs at relatively high temperatures at which substitutional and interstitial atoms can quickly diffuse and thus become partitioned.⁶⁾ Therefore, the actual phase boundary of austenite/(cementite+austenite) should be located between the theoretical phase boundaries around the A_{e1} temperature, leading to the actual A_{e1} temperatures between two equilibrium phase boundaries. Nevertheless, up to now, the thermodynamic formula for predicting the actual A_{cm} boundaries in low alloy steels has not been proposed yet.

We have, therefore, derived a new formula to predict the accurate A_{cm} temperature of the low alloy steels, assuming that the partitioning effect of substitutional elements linearly reduces below A_{e1} temperature, resulting in no partitioning of alloy elements at room temperature (T_0).⁹⁾ The thermodynamic formula for predicting the accurate A_{cm} temperatures of low alloy steels has been newly suggested as follows:

$$A_{cm} = A_{cm}^{PE} + (A_{cm}^{OE} - A_{cm}^{PE}) \left(\frac{A_{e1} - A_{e1}^{PE}}{A_{e1}^{OE} - A_{e1}^{PE}} \right) \left(\frac{A_{cm}^{PE} - T_0}{A_{e1} - T_0} \right) \dots\dots(1)$$

where A_{cm}^{OE} , A_{cm}^{PE} , A_{e1}^{OE} , and A_{e1}^{PE} mean the A_{cm} and A_{e1} temperatures predicted by OE and PE models, respectively. A_{e1} is the calculated temperature by the A_{e1} formula.⁷⁾

In order to calculate the A_{cm} temperature using a complicated Eq. (1), however, the OE and PE thermodynamic models are still necessary. For the sake of simplicity and short calculation time, a simple A_{cm} formula (Eq. (2)), which is applicable to the chemical range of Table 1, was generated by regressing about 50 000 A_{cm} temperatures obtained by Eq. (1) with respect to the steel chemistry in mass percent.

$$A_{cm} (^{\circ}\text{C}) = 224.4 + 992.4C - 465.1C^2 + 46.7Cr + 19.0CCr - 6.1Cr^2 + 7.6Mn + 10.0Mo - 6.8CrMo - 6.9Ni + 3.7CNi - 2.7CrNi + 0.8Ni^2 + 16.7Si \dots\dots\dots(2)$$

The square value of the multiple correlation coefficient, R^2 was 0.998837. The A_{cm} temperatures of all 50 000 steels were calculated using Eq. (2) and were compared with the A_{cm} values calculated by Eq. (1). The regression was successfully made within $\pm 3^{\circ}\text{C}$.

Although there are some thermodynamic calculations of

Table 1. Chemical composition range used for generating A_{cm} temperatures.

Chemistry	C	Mn	Si	Ni	Cr	Mo
Range (wt.%)	0.2–0.7	0.0–1.5	0.0–0.3	0.0–2.8	0.0–1.5	0.0–0.6

A_{cm} temperatures, there seems to be no confirmation with the experimental A_{cm} temperatures probably because of the difficulty in measuring A_{cm} temperature below A_{c1} temperature. Thus, we have measured the equilibrium volume fractions of pro-eutectoid ferrite formed at the several different isothermal temperatures below A_{c1} temperature by image analysis and then compared them with the calculated ones using the proposed A_{cm} equation (Eq. (2)).

The dilatometric tests of AISI 5140 steel were performed using tiny plates of $10 \times 3 \times 1 \text{ mm}^3$. The specimens were austenitized at 900°C for 10 min and quenched to the isothermal holding temperature of 610, 640, 670, and 700°C between A_{c1} (736°C) and B_s (593°C) temperatures. They were held for enough long time to finish the pearlitic transformation at each temperature based on the Atlas I-T diagram, and then quenched to room temperature by blowing a nitrogen gas.

The quenched samples were mechanically polished and etched with a 2% Nital solution, and the ferrite-pearlite microstructure was observed using an optical microscope. The equilibrium volume fraction of the pro-eutectoid ferrite was measured from the microstructures by an image analyzer because it gives a point of austenite/(cementite + austenite) boundary, that is, the carbon concentration at which the cementite starts to precipitate at the isothermal holding temperature based on a simple lever rule. The relation between the A_{cm} temperature and the equilibrium volume fraction of the pro-eutectoid ferrite (V_f^{eq}) is illustrated in Fig. 2. The carbon concentration of the austenite increases with the precipitation of the pro-eutectoid ferrite, but it can not exceed the austenite/(cementite + austenite) boundary, where the cementite starts to form.

As shown in Fig. 3, the higher the isothermal holding temperature the more volume fraction of pro-eutectoid ferrite (white parts). The equilibrium volume fractions of the pro-eutectoid ferrite calculated by OE and PE models are

compared with the measured ones in Table 2. The measured ferrite volume fractions are located between the calculated ones by OE and PE models at any temperature and are closer to the ferrite fractions calculated by the OE model with increasing the isothermal holding temperature, because of more active partitioning of alloying elements. This result shows the evidence that the actual austenite/(cementite + austenite) phase boundary below A_{c1} temperature is located between the austenite/(cementite + austenite) phase boundaries calculated by OE and PE models, respectively.

The equilibrium volume fractions of the ferrite calculated by the formulae of A_{cm} temperature are compared with the measured ones in Fig. 4. The ferrite volume fractions calculated by Eq. (2) shows a good agreement with experimental ones, though the measured ferrite volume fraction shows a little deviation from the calculated one by Eq. (2). This deviation is probably due to the regressed equation based on about 50 000 different chemistry of the low alloy steel. Therefore, Eq. (2) can be used to determine the equilibrium volume fraction of ferrite as a function of temperature using a lever rule. This new A_{cm} equation would be contributed to the precise and fast calculation of the A_{cm} temperature in low alloy steels.

Table 2. Equilibrium volume fractions of pro-eutectoid ferrite obtained by thermodynamic models and experimental measurement with an isothermal holding temperature in AISI 5140 steel.

Temp. ($^\circ\text{C}$)	610	640	670	700
V_f^{eq} (OE)	0.000	0.000	0.040	0.206
V_f^{eq} (PE)	0.357	0.419	0.471	0.515
V_f^{eq} (exp)	0.125	0.204	0.252	0.302

Fig. 2. Relation between the A_{cm} temperature and the equilibrium volume fraction of pro-eutectoid ferrite (V_f^{eq}) by using a lever rule. V_f^{eq} is $b/(a+b)$ above A_{c1} and $d/(c+d)$ below A_{c1} temperature, respectively.

Fig. 4. Variation in equilibrium volume fraction of ferrite with an isothermal holding temperature in AISI 5140 steel. Four big markers are the measured fractions.

Fig. 3. Optical microstructures of the specimens isothermally transformed at different temperatures in AISI 5140 steel. (a) 610°C , (b) 640°C , (c) 670°C , and (d) 700°C . White parts are pro-eutectoid ferrite and dark parts are pearlite.

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