Determination of Parameters for Fitting the Dilatation Curve of Austenite-Martensite Transformation in Cr-Ni Steels

Hai QIU, Jingga QI, Fuxin YIN and Kazuo HIRAOKA

Fundamental Studies on Technologies for Steel Materials with Enhanced Strength and Functions, Consortium of JRCM (The Japan Research and Development Center for Metals), National Institute for Materials Science, Tsukuba, Ibaraki 305-0047 Japan.

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1. Yamamoto’s Model Based on Dilatation Curve

In the austenite–martensite transformation, martensite begins to form at a certain temperature denoted as $M_s$ temperature, and this transformation proceeds upon continuous cooling. Magee1) discussed the driving force for martensite nucleation from the viewpoint of thermodynamics, and gave an expression for the volume fraction of martensite, $f_m$, as a function of temperature, $T$, as the following.

$$f_m = 1 - \exp(-\frac{\bar{V} \phi (\partial \Delta G_v^{\delta - \alpha} / \partial T)(M_s - T)}{b})$$............................(1)

where $\bar{V}$ is the average volume of the newly formed martensite plates due to temperature variation $dT$, $\phi$ a proportionality constant, $\Delta G_v^{\delta - \alpha}$ the driving force (free energy) for the formation of martensite.

Koistinen and Marburger2) measured the contents of martensite and retained austenite in carbon steels by X-ray technique, and proposed empirically an equation for $f_m$ (actually identical to Eq. (1)).

$$f_m = 1 - \exp(-b(M_s - T))$$............................(2)

where $b=0.011$, and temperature is in °C. Following work by other researchers3,4) shows that $b$ is a material constant varying with chemical compositions. These results convincingly support Eq. (1), and demonstrate that Eq. (1) describes adequately the kinetic process of austenite–martensite transformation in steels.

$f_m$ in the cooling process can be measured by in situ equipment, such as in situ X-ray equipment. However, in addition to high cost, sometimes measurement is unavailable since such in situ equipment is not conventional. It is desired to apply Eq. (2) to directly determine $f_m$ at any temperature, if $b$ and $M_s$ are known.

As temperature decreases in the austenite region, sample will shrink proportionally. The proportional coefficient is generally denoted as expansion coefficient. We refer to this reduction in volume as the shrinkage caused by the expansion coefficient. When temperature falls down below $M_s$, austenite transforms into martensite, making the sample expand because of the difference in volume between austenite and martensite. The newly formed martensite also shrinks as temperature decreasing like austenite. Therefore, the total volume variation in the austenite–martensite transformation region, is dependent on the sum of the three variations (shrinkage of the retained austenite and the newly formed martensite, and the expansion of austenite–martensite transformation). Apparently, the total volume change is directly correlated to the $f_m$. If their relations can be expressed in equations, $f_m$ can be deduced from the experimental data of dilatation. Based on this idea, Yamamoto et al.5) proposed a simple model to determine $b$ and $M_s$ from the dilation curve schematically represented in a solid line in Fig. 1. Their model is briefly summarized as the following equations.

$$d_{i+1} = d_i - (f_m \alpha_m + f_s \alpha_s) \Delta T$$...............(3)

$$E_{i+1} = d_{i+1} + e_{\gamma-m} f_m$$...........................(4)

where $i$ represents $i$-th experimental point, $d$ the shrinkage caused by the expansion coefficient, $E$ the total dilatation at a temperature, $\alpha_m$ the expansion coefficient of martensite, $\alpha_s$ the expansion coefficient of austenite, $f_m$ the volume fraction of martensite expressed with Eq. (2), $f_s$ the volume fraction of austenite, $\Delta T$ the temperature variation between any two temperatures, $e_{\gamma-m}$ the strain due to the lattice volume difference between austenite and martensite. Note that $f_m + f_s = 1$. This implies that this model is only applicable to the austenite–martensite dual phase steels.

There are five unknown variables, $b, M_s, \alpha_m, \alpha_s, e_{\gamma-m}$ in Eqs. (2)–(4). We only have experimental data of $E$ vs. $T$. Yamamoto et al.5) assumed that line AB as shown in Fig. 1 is single austenite region, and $\alpha_s$ is the gradient of line AB. Similarly, $\alpha_m$ is given by the gradient of line GH, $b, M_s$ and $e_{\gamma-m}$ cannot be determined directly from the experimental data. We set an initial value to them, and then substitute them and the experimental $\alpha_m, \alpha_s$ into Eqs. (2)–(4) to give a calculated value of $E$. Adjust $b, M_s, e_{\gamma-m}$ until best fitting the experimental dilatation vs. temperature curve.

In the utilization of Yamamoto’s model, sometimes unusual $f_m$ was found, and in some cases $f_m$ was not unique for a given material. This is induced by the unreasonable points listed below.

(1) For some cases, retained austenite is present within the line GH, and thus the gradient of line GH is not equal to $\alpha_m$. For the steels with lower $M_s$, we only obtain dilatation

![Fig. 1. Schematic dilatation curve.](image-url)
curves ranging from A to F, sometimes from A to a certain point between C and F. For this case, reference datum has to be cited for $\alpha_{\text{eq}}$ instead of experimentally determination.

(2) To uniquely determine $b$, $M_s$, and $e_{\gamma-m}$, at least three equations are required. However, Yamamoto et al.\(^\dagger\) gave only two equations (Eq. (3) and Eq. (4)). This means that $b$, $M_s$, $e_{\gamma-m}$, are not uniquely determined even if the calculated dilatation curve well fit the experimental dilatation curve. This is the main reason for making large error.

(3) Error analysis was not performed for the calculated and the experimental dilatation, and so the minimum error cannot be ensured.

2. Proposed Method for the Determination of Variables

Equations (3) and (4) are discrete formulae, and hard for mathematically deduction. Assume that an infinitesimal temperature variation $dT$ induces dilatation variation $dE$ as illustrated in Fig. 1. We can rewrite Eqs. (3) and (4) as

$$dE = [\alpha_{\text{m/f}} + \alpha_{\gamma}(1-f_{\text{m}})]dT + e_{\gamma-m}d_{\text{m}}$$ ...........................................(5)

The first term in the right side of Eq. (5) is the shrinkage caused by the expansion coefficient, and the second term is due to the austenite–martensite transformation. Integrate Eq. (5) from $M_s$ to any temperature $T$ as

$$\int_{E_{\text{eq}}}^{E} dE = \int_{M_s}^{T} [\alpha_{\text{m/f}} + \alpha_{\gamma}(1-f_{\text{m}})]dT + \int_{0}^{f_{\text{m}}} e_{\gamma-m}d_{\text{m}}$$ ...........................................(6)

where the integration limits of $E$ and $f_{\text{m}}$ correspond to the temperature $T$, and $E=E_0$ and $f_{\text{m}}=0$ for the $M_s$ point. Substitute Eq. (2) into Eq. (6), leading to

$$E = E_0 + (e_{\gamma-m} - \alpha_{\text{m}}M_s - (\alpha_{\gamma} - \alpha_{\text{m}})b)$$

$$+ \alpha_{\text{m}}T + \frac{b - e_{\gamma-m}}{1 - (\alpha_{\gamma} - \alpha_{\text{m}})} e^{-K_{\text{m}}(T-Ms)}$$ ...........................................(7)

The determination for each variable in Eq. (7) is as follows.

(1) $\alpha_{\gamma}$: $\alpha_{\text{eq}}$ is equal to the gradient of line AB.

(2) $\alpha_{\text{m}}$: Perform dilatation test to cool a sample down to room temperature, and then dropping the sample into the liquid nitrogen to reduce the content of retained austenite. Reheat the quenched sample up to a certain temperature lower than the phase transformation temperature, and record the dilatation against temperature. The gradient of this dilatation curve is taken as an approximation of $\alpha_{\text{m}}$.

(3) $M_s$: Eq. (7) shows that dilatation $E$ exponentially increases rapidly around $M_s$. In practical experiments, however, expansion around $M_s$ is slow (see curve $M_s$ CD in Fig. 1), and there is no such $M_s$ point as demonstrated in Eq. (7). For calculation, we should idealize the experimental data.

The data idealization briefly includes: ① fit curve DF with Boltzmann function $y=(A_2 + (A_1 - A_2)(1+\exp(-x-x_0)/dx))$, where $A_1$, $A_2$, $x_0$ and $dx$ are variables; ② extrapolate the fitting curve (dotted line $DM_{\text{cal}}$); ③ fit line AB, and determine the cross-point with the extrapolated curve in ②, which is the $M_s$ point for calculation, denoted as $M_{\text{cal}}$, $(M_{\text{cal}}, E_0)$; ④ add the fitted data (line $DM_{\text{cal}}$) to the experimental data (curve DFGH) to create idealized data (curve $M_{\text{cal}}$ DFGH). The procedures of ①–④ are easily performed with the commercial software Origin.

(4) $b$, $e_{\gamma-m}$. The method of least squares is used to determine $b$ and $e_{\gamma-m}$. Assume $J$ as error between the calculated ($E_i$) and experimental ($e_i$) dilatation for $n$ experimental points, given by

$$J = \sum_{i=1}^{n} (E_i - e_i)^2$$ ...........................................(8)

Take $\partial J/\partial e_{\gamma-m}=0$, giving

$$e_{\gamma-m} = -\sum_{i=1}^{n} C_i D_i / \sum_{i=1}^{n} C_i^2$$ ...........................................(9)

where $C_i = 1 - \exp[-b(M_s - T_i)]$, $D_i = E_{i0} - \alpha_{\text{m}}(M_s - T_i)$ - $C_i(\alpha_{\gamma} - \alpha_{\text{m}})b - e_{\gamma-m}$.

Take $\partial J/\partial b=0$, resulting in

$$e_{\gamma-m} = \left\{ \sum_{i=1}^{n} (C_i E_i + D_i F_i) + \left( \sum_{i=1}^{n} C_i E_i + D_i F_i \right)^2 \right\}^{-1} \left\{ \sum_{i=1}^{n} C_i E_i \right\}$$ ...........................................(10)

where $E_i=(\alpha_{\gamma} - \alpha_{\text{m}})C_i - bM_s(\alpha_{\gamma} - \alpha_{\text{m}})(1-C_i)$, $F_i=bM_s(1-C_i)$.

$e_{\gamma-m}$ is plotted against $b$ with Eqs. (9) and (10), respectively, the cross-point of the two curves corresponds to the optimum $b$ and $e_{\gamma-m}$.

3. Verification of the Modified Model

The longitudinal dilatation ($\Delta l/l$) of samples with 3 mm in diameter and 10 mm in length prepared from 12 alloys listed in Table 1 was measured with Formastor-F dilatometer. The samples were experienced with two identical thermal cycles (heating up to 1 300°C from room temperature, heating rate 20°C/s, cooling down to 20°C, cooling rate 12°C/s). The sampling time for recording data is 0.5 s. The samples after thermal experiences merely consist of martensite and retained austenite.

The five variables, $b$, $M_s$, $\alpha_{\text{eq}}$, $\alpha_{\gamma}$, $e_{\gamma-m}$, were determined directly from the experimental dilatation vs. temperature curves, and the corresponding values are summarized in Table 1. Figure 2 gives two instances of the calculated and the experimental dilatation curves for N1 and N5. The range of martensitic transformation from $M_s$ to 20°C varies with the chemical compositions for the steels used. Apparently, N5 has a longer curve than N1 for the temperature range of $M_s$ to 20°C. Although the lengths of dilatation curves are different, the calculated $E$ with Eq. (8) perfectly agrees with the experimental dilatation curves for all the alloys used. The values of $f_{\text{m}}$ at 20°C determined with Eq. (2) using the variables in Table 1 are compared with the experimental $f_{\text{m}}$ values measured with magnetization method in Fig. 3. The consistency of the calculated values with the experimental values in Figs. 2 and 3 demonstrates that the proposed method for determining the variables is rational.
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Table 1. The samples used.

| sample No. | chemical composition | b   | ε_{P,M} | α_{MN} | α_{M} | M_{col} (°C) |
|------------|----------------------|-----|---------|--------|-------|--------------|
| N1         | 0.01C-14Cr-9Ni       | 0.02710 | 0.00915 | 1.439E-05 | 2.234E-05 | 56.2         |
| N2         | 0.01C-14Cr-8Ni       | 0.02878 | 0.00780 | 1.244E-05 | 1.690E-05 | 121.0        |
| N3         | 0.01C-14Cr-7Ni       | 0.02672 | 0.00821 | 1.324E-05 | 2.164E-05 | 179.7        |
| N4         | 0.01C-14Cr-6Ni       | 0.02777 | 0.00771 | 1.287E-05 | 2.182E-05 | 219.6        |
| N5         | 0.01C-14Cr-5Ni       | 0.02845 | 0.00758 | 1.275E-05 | 2.196E-05 | 236.2        |
| N6         | 0.01C-14Cr-4Ni       | 0.02605 | 0.00793 | 1.390E-05 | 2.333E-05 | 277.5        |
| N7         | 0.05C-14Cr-9Ni       | --     | --      | 2.264E-05 | --     | --           |
| N8         | 0.05C-14Cr-8Ni       | 0.01410 | 0.00953 | 1.559E-05 | 2.170E-05 | 75.8         |
| N9         | 0.05C-14Cr-7Ni       | 0.01598 | 0.01005 | 1.491E-05 | 2.401E-05 | 109.9        |
| N10        | 0.05C-14Cr-6Ni       | 0.02009 | 0.00824 | 1.491E-05 | 2.208E-05 | 150.5        |
| N11        | 0.05C-14Cr-5Ni       | 0.02035 | 0.00786 | 1.335E-05 | 1.927E-05 | 187.2        |
| N12        | 0.05C-14Cr-4Ni       | 0.01777 | 0.00774 | 1.338E-05 | 1.994E-05 | 222.3        |

Note: No dilatation due to phase transformation in the heating and cooling process of N7

Fig. 2. Experimental and calculated dilatation curves of N1 and N5.

Fig. 3. Comparison of the calculated f_{m} with the experimental f_{m} measured with the magnetism method at 20°C.

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