Prediction of Martensite Volume Fraction in Fe–Cr–Ni Alloys

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Martensitic stainless steels, such as those in the AISI type 4xx series, have good corrosion resistance, good edge retention, high strength, high hardness, and good wear resistance.1) Maintaining control over the amount of martensite is important when designing alloy compositions and determining heat treatment conditions, because of the contribution of martensite to the mechanical and electrochemical properties in these stainless steels. Dilatometric analysis has been widely used for determining quantitative volume properties in these stainless steels. Dilatometric analysis is to demonstrate an analytical model for predicting the volume change for a single iron (or substitutional) atom. Physically a\textsubscript{AFe} and a\textsubscript{AM} indicate the absolute volume of the unit cell of martensite and austenite, which consist of two iron atoms and four iron atoms respectively. Dividing the absolute volume of the unit cell by the number of iron atoms in the unit cell gives the volume per one iron atom.

The equations for the lattice parameters of austenite and martensite with the effect of the alloying elements are as follows:

\[ a_A = \left( a_{A,Fe} + \sum_i k_i^a X_i \right) \left[ 1 + \alpha_a (T - 298) \right] \]  \hspace{1cm} (mm) \hspace{1cm} \text{(3)}
\[ a_M = \left( a_{M,Fe} + k_M^{MC} X_C + \sum_i k_i^m X_i \right) \left[ 1 + \alpha_m (T - 298) \right] \] \hspace{1cm} \text{(4)}
\[ c_M = \left( a_{M,Fe} + k_M^{MC} X_C + \sum_i k_i^m X_i \right) \left[ 1 + \alpha_m (T - 298) \right] \] \hspace{1cm} \text{(5)}

where a\textsubscript{A,Fe} is the lattice parameter of austenite, a\textsubscript{A} is the lattice parameter of martensite in the a-axis, k\textsubscript{i} are the lattice parameters of martensite in the c-axis, \(V'\) is the initial volume fraction of austenite (=1.0), and \(V_M\) is the volume fraction of martensite. The volumetric change in Eq. (2) is based on the relative volume change for a single iron atom. The unit cell volume of martensite characterized by \(a_M\) and \(c_M\) is the unit cell volume at the standard temperature, and delta (\(\Delta\)) means the change of sample length or the change in volume from the standard temperature condition.

The volumetric transformation strain equation for martensite formation from austenite can be derived by considering the crystal structures of austenite and martensite, i.e. face-centered cubic for austenite transforming to body-centered tetragonal for martensite.

\[ \left( \frac{\Delta l}{l_0} \right)_{A \to M} = \frac{1}{3} \left( \frac{1}{3} V' - 1 \right) \] \hspace{1cm} \text{(1)}

\[ = \frac{1}{3} \left( (1/2)a^2_M c_M V' + (1/4)a^3_M (V' - V_M) - 1 \right) \] \hspace{1cm} \text{(2)}

Table 1 summarizes the coefficients for the alloying element effects for the austenite lattice parameter. Table 2 gives the coefficients for the martensite lattice parameter. These coefficients were obtained from the literature data of Fe–Mn,\textsuperscript{9) Fe–C,\textsuperscript{13) Fe–Cr,\textsuperscript{14) Fe–Ni,\textsuperscript{15) Fe–C–Cr.\textsuperscript{10)}}}
Fe–Ni–C\(^{11}\)) and Fe–Mn–Cr–C\(^{12}\)) alloys. The amount of Si, P, N, and other element could affect the lattice parameter in alloy steels, but only the major elements listed in Tables 1 and 2 were considered since the focus of the present study is on Fe–Ni–Cr alloys.

Figure 1 shows the calculation method used to convert the strain change to an increment of martensite volume between two data points on the dilation curve. The theoretical transformation strain could be derived as a function of temperature and volume fraction by combining Eqs. (2) to (5). The strain change due to only the incremental increase of the martensite volume fraction (\(\Delta e^M\)) is calculated by removing the theoretical thermal strain change (\(\Delta e^T\)) from the measured strain change (\(\Delta e^{\text{measured}}\)). The thermal strain change during cooling is negative since it reduces the distance between neighboring atoms and vice versa for heating process. The incremental increase of the martensite volume fraction is calculated by comparing the measured strain change with the theoretical strain change related to martensite formation.

Four dilation curves of Fe–Cr–Ni stainless steel alloys\(^{16–18}\)) (labeled S1 to S4) that have different chemical compositions (as shown in Table 3) were selected to verify the analytical model proposed in the present study. Figure 2 shows the four dilation curve changes due to the martensite transformation below each martensite start (\(M_s\)) temperature. In each case the cooling rates were high enough to obtain full martensite without other diffusion-controlled transformational products above the \(M_s\) temperature. The martensite transformations of the S3 and S4 curves were completed above room temperature, while the martensite transformation was not completed at room temperature for the S1 and S2 curves. The comparison between the dilation curve and the thermal expansion coefficient of martensite was used to determine the completion of the martensite transformation. Table 4 gives the thermal expansion coefficients of austenite and martensite of Fe–Cr–Ni alloys\(^{16–18}\)).
The carbon atoms located in the interstitial sites have a greater effect on the volume change as compared to the alloying elements, which occupy substitutional sites. This larger effect of carbon on the martensite transformation strain can be explained, since carbon atoms occupy interstitial sites in the body-centered tetragonal martensite to form.

By comparing with the calculation of pure iron, the addition of Ni produces expansion and the additions of Mn and Cr produce contraction. The effect of each alloying element on the lattice parameters of both austenite and martensite causes the total transformation strain change. The effect of Ni on the expansion of the martensite lattice parameter is larger than that of the austenite lattice parameter; thus, the transformation strain of martensite formation from austenite is slightly larger due to the addition of Ni. In contrast, Mn and Cr additions slightly reduce the transformation strain of martensite, because the addition of Mn or Cr is relatively more effective in expanding the austenite lattice parameter.

In summary, an analytical model to predict martensite volume fraction from dilatometric data for Fe–Cr–Ni stainless steel alloys has been proposed by considering the effect of alloying elements on the lattice parameters of austenite and martensite. The appropriate coefficients of alloying elements and thermal expansion coefficients were selected from the experimental data of Fe–Cr–Ni-based alloys in literature. The importance of alloying element for dilatometric analysis was confirmed by comparing the predicted results of the calculations considering all alloy elements and just carbon effects with measured martensite volume fraction at room temperature. Each effect of an alloying element on the transformation strain of martensite formation from austenite was also considered. It is anticipated that the present analytical approach would be useful to investigate the transformation kinetics of Fe-based alloys containing high-alloying elements.

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