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Martensite start temperature and the austenite grain-size

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Abstract The dependence of the martensite start temperature on the austenite grain-size is modeled based upon aspects of martensite nucleation and validated by data reported in the literature. The results obtained support the view that grain boundaries provide an environment for the formation of martensite embryos in annealed austenite. The model can account for a two-stage dependence of martensite start temperature on the austenite grain-size, considering that grain boundaries provide a suitable environment for martensite nucleation, and grain-size also has a stabilizing effect by limiting the volume of individual martensite units.

Introduction

The onset of martensite transformation occurs at a temperature, M_s, which is generally related to a steel's chemistry, either through empirical equations [1, 2] or phenomenological models that combine thermodynamic data and aspects of martensite nucleation [3–6]. This topic was comprehensively reviewed in the context of using neural network models to calculate M_s [7]. So, to pursue the analysis of the dependence of the martensite start temperature, M_s on the austenite grain-size is supported by both engineering and scientific interest, as modern structural steels generally depend on fine grained prior austenite.

The nucleation model [3] used in the previously cited works [4–6] is consistent with the notion that austenite grain boundaries provide a favorable environment for the formation of martensite embryos. Specifically, neural network analysis of the grain-size dependence of M_s in an HSLA steel [8] disclosed a positive dependence that, apparently, breaks down when the austenite grain-size is less than 5×10^{-3} mm [9]. A similar situation was observed with Fe–16 wt%Cr–10 wt%Ni steel that also transforms to lath martensite. Austenite grain refinement to 0.80×10^{-3} mm hinders multi-variant martensitic transformation into blocks and packets as observed in coarse-grained austenite (80×10^{-3} mm) [10]. This suggests that one might expect a change in the grain-size dependence of the martensite start temperature as the austenite grain-size approaches ultrafine values, 0.80×10^{-3} mm. On the other hand, grain boundaries provide a suitable environment for the initial nucleation of martensite [11–15]. In this context, Olson et al. [11] made the important observation that the experimental setup used to determine the martensite start temperature influences the M_s dependence on grain-size. M_s values determined by acoustic emission and electrical resistivity exhibit opposite trends, which were explained on the basis of martensite nucleation.

In recent papers by the present authors, new formal kinetics models have been successfully used to describe several aspects of the overall martensite transformation [16–20]. In this paper these ideas are extended to analyze the grain-size dependence of the martensite start temperature.

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Derivation of the main equations

Our model, to be derived below, is based on the fact that grain boundaries provide a suitable environment for martensite nucleation, but at the same time, a smaller grain-size has a stabilizing effect on the austenite by limiting the volume of individual martensite units.

In the following discussion, although not invoking any particular physical model, we depart from the classical embryo–nucleus concept by distinguishing embryos from nucleation sites. This distinction is based upon the following criterion: embryos are envisaged as structural configurations available in the austenite which might catalyze martensite nucleation. Nucleation sites, by contrast, are the specific structural configurations that are compatible with the nucleation barrier at a given temperature.

The classical experiment of Cech and Turnbull [21] on martensite transformation in small particles of FeNi alloy allowed Cohen and Olson [22] to express the probability that a particle of volume q contains a nucleation site at temperature T as

$$P_q(T) = 1 - \exp\left(-qn_V^T\right) \tag{1}$$

where n_V^T is the density of nucleation sites in the material at temperature T.

Subsequently, using data from [21], it was shown that [18]

$$n_V^T = n_V^0 \frac{\Delta G - \Delta G_0}{kT} \tag{2}$$

where n_V^0 is the density of embryos per unit volume of material, ΔG is the chemical driving force, $\Delta G_0 = \Delta G(T^*)$, and k is the Boltzmann constant. Hence, T^* is the highest temperature at which nucleation sites become viable.

In athermal martensite transformation, a nucleation site outright proceeds to a martensite unit [12]. Hence n_V^T can be equated to the number per unit volume of martensite units initially formed, N_V, so that T^* stands for the true athermal martensite start temperature. In bulk polycrystalline material, one expects grain boundaries to provide a suitable environment for the initial nucleation of martensite [11–15]. However, due to its displacive nature, martensite cannot cross or nucleate on a grain boundary.

Consistent with the foregoing arguments, we envisage martensite nucleation to occur within the volume of influence of a grain boundary. The concept of "volume of influence" was introduced by Khachaturyan et al. [12]. They have shown by computer simulations using Phase Field Microelasticity (PFM) that the martensitic transformation may initiate not from a defect, e.g., a dislocation, itself but within the neighborhood of this defect. This neighborhood, associated with the elastic field of the defect, would correspond to the so called "volume of influence" of the defect. Since grain boundaries are themselves "defects" it is to be expected that they have their own volume of influence. Therefore, one may write

$$P_a(T) = 1 - \exp(-an_s) \tag{3}$$

where P_a is the probability of finding a nucleation site associated with the grain boundary of a grain with grain boundary area a, and n_s is the number of embryos per unit of grain boundary area. As $S_V = a/q$, where q is the grain volume, this probability can be expressed as

$$P_a(T) = 1 - \exp(-qn_sS_V) \tag{4}$$

S_V is a standard stereological parameter, usually determined by lineal analysis on a metallographic section. S_V depends inversely on the mean grain intercept distance, and decreases with increasing grain-size. As the nucleation site density is low, one may approximate Eq. 4 as

$$P_a(T) \cong qn_sS_V \tag{5}$$

Admitting that the volume of influence of the grain boundaries where an initial nucleation event occurs has a thickness λ, then, for present purposes, it is reasonable to take the probability of a nucleation event to be proportional to λS_V. We choose this proportionality factor arbitrarily to be equal to one. In any case, this proportionality factor will be lumped with other unknown parameters. The net probability, P, of a nucleation event taking place in a specific grain results from multiplying the probability, P_a, of finding a nucleation site on the grain boundary, with the probability of a nucleation event taking place within the volume of influence. This yields

$$P(T) = \lambda S_V P_a(T) \cong q\lambda n_s S_V^2 \tag{6}$$

and n_V^T may be identified from Eq. 6 as

$$n_V^T = n_s\lambda S_V^2 \tag{7}$$

The number of nucleation sites per unit volume initially available at the martensite start temperature is

$$n_V^0 = n_s^0\lambda S_V^2 \tag{8}$$

where n_s^0 is the initial number per unit area of embryos at the grain boundaries.

Combining the above equations, and using the approximation that at temperatures close to M_s, the chemical driving force, varies linearly with the temperature, one obtains the probability that n_V nucleation sites are available at temperature T,

$$P_{n_V}^T = n_s^0 \cdot \lambda \cdot S_V^2 \cdot q \cdot \frac{\Delta S}{k}\frac{T^* - T}{T} \tag{9}$$

Here, ΔS is the change in entropy for the transformation. Recalling that in an athermal reaction a nucleation site spontaneously propagates as martensite, one can relate the probability, Eq. 9, to the initial number of martensite plates per grain, $q \cdot N_V$, where N_V is the number of martensite plates per unit of volume. Henceforth, the austenite grain-size relates to the experimental M_s temperature as

$$S_V^{-2} = \Gamma_1 \cdot \frac{T^* - M_s}{M_s} \tag{10}$$

Here Γ_1 is defined by

$$\Gamma_1 = \frac{n_s^0 \cdot \lambda \cdot \varphi}{N_V^{M_s}} \cdot \frac{\Delta S}{k} \tag{11}$$

where φ is a factor introduced for completeness, taking into consideration the well known autocatalytic aspect of martensite kinetics, and $N_V^{M_s}$ is the total number of martensite units per unit volume initially formed at M_s. Γ_1 lumps together all unknown parameters in Eq. 10.

Equation 10 provides a basic relationship that relates a fundamental aspect of the reaction (nucleation event) to measurable parameters of practical interest (M_s and S_V) and allows direct determination of T^* if the experiment allows detection of nucleation events. More frequently, however, M_s temperatures are determined by monitoring volumetric changes in a dilatometer or resistometer. Let m be the fraction of grain volume transformed by the initially formed martensite units. Assuming austenitic grains with tetrakaihedron shape, the average volume is given by $q = (8/(3S_V))^3$, which is an expression obtained in [23]. Using these approximations in Eq. 11, one finds the following relationship between the austenite grain-size, expressed as S_V, and the experimental M_s, determined by monitoring volumetric changes, becomes

$$S_V = \Gamma_2 \frac{T^* - M_s}{M_s} \tag{12}$$

where

$$\Gamma_2 = \left(\frac{8}{3}\right)^3 \cdot \frac{m \cdot n_s^0 \cdot \lambda \cdot \varphi}{V_V^{\text{offset}}} \cdot \frac{\Delta S}{k} \tag{13}$$

Here V_V^{offset} is an offset volume fraction related to the sensitivity of the experiment, or pre-defined to ensure the comparability of results obtained on independent runs [24], and the other parameters were defined before. Γ_2 lumps together all unknown parameters in Eq. 10.

Results and discussion

Comparison of Eqs. 10 and 12 shows opposing trends caused by different aspects of the reaction involved. Equation 10 relates M_s to the catalyzing effect of grain boundaries, because more grain boundary area provides more chances for nucleation to occur. On the other hand, Eqs. 12–13 reflect limitations imposed by the grain-size on the allowable volume of a martensite unit. If martensite size is limited, a larger number of martensite units would be needed to comprise a detectable fraction transformed in fine-grained rather than in coarse-grained austenite. Further cooling below T^* would be required to reach the experimental M_s in the case of fine-grained austenite. This apparent dichotomy is well documented by the experimental results in [11].

Further validation of Eq. 12 was accomplished using the experimental results reported in [24] concerning the application of a high-resolution dilatometer to determine the onset of martensite transformation in Fe–5 wt% Ni–2.3 wt% Mn–0.13 wt% C, which proceeds without bursts. An offset method [25] was used to determine the temperatures T_{off} to reach a designated offset volume fraction transformed $V_{V_{\text{off}}} = 0.01$. The plot in Fig. 1 shows data from [24] plotted in accordance with Eq. 12. Fitting $T^* \approx 609$ K, a correlation coefficient of 0.98 was obtained. M_s^0 in [24] and T^* are equivalent. Hence, we ascribe the difference (~26 K) between the values M_s^0 and T^* to the different methods used in the calculation. Yang and Bhadeshia [24] applied Fisher's partitioning model [26] combined with an empirical equation to determine M_s^0. More important, however, remains the fact that the values of either T^* or M_s^0 are nearly 100 K less than the value of 723 K calculated using a thermodynamic frame work based upon the stored free energy of martensite [24].

The model can account for a two-stage dependence of martensite start temperature on the austenite grain-size. Stages in a plot of property versus some experimental variable, such as M_s vs. S_V, must result from some intrinsic change, or transition, in the nucleation of martensite. For instance, one such change related to microstructure, is the

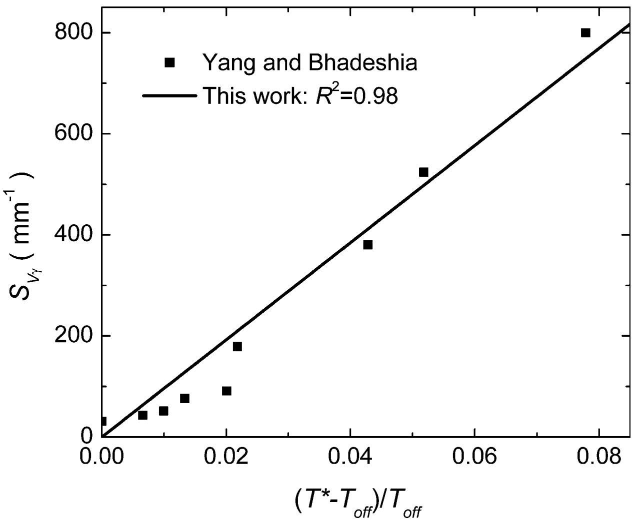

Fig. 1 Experimental data from Yang and Bhadeshia [24] plotted after present model, Eq. 12, with T_{off} substituted for M_s, and $V_{V_{\text{off}}} = 0.01$

suppression of multi-variant transformation in Fe–16 wt% Cr–10 wt% Ni as described by Takaki et al. [10]. The formalism described above supports such a transition if the condition $\lambda \cdot S_V = 1$ was satisfied by grain refinement. For comparison, the observed transition reported in [8] develops at about $S_V = 400$ mm^{-1} giving $\lambda \approx 2.5 \times 10^{-3}$ mm. This result is compatible with 0.8×10^{-3} mm reported by Takaki et al. [10]. Nonetheless, at present, one cannot be more conclusive about this issue.

Summary and conclusions

In summary, a formal kinetic approach is used to derive a relationship between the austenite grain-size and the onset of athermal martensite. The approach is tantamount to acknowledging that a grain boundary provides a source of martensite embryos in annealed austenite [11–15]. However, three parameters, n_s, λ, and φ could not be individually analyzed at this time, so, in its present form, the present model contains two fitting parameters, Γ and T^*. In spite of this limitation, the model allows determination of T^* directly from measurable quantities.

It is also well established [27, 28] that the austenite grain-size limits the size of martensite units and contributes to austenite stabilization. This effect is expected to be more pronounced in the case of lenticular martensite that partitions the austenite grains. Nevertheless, it is appropriate to recall that Eq. 2 and, related forms, are given in terms of a difference in driving force, $\Delta G - \Delta G_0$, so that a containment effect on driving force would not influence the value of T^*, which depends solely on the propagation of available nucleation sites. Therefore, the model can account for a two-stage dependence of martensite start temperature on the austenite grain-size, considering that grain boundaries provide a suitable environment for martensite nucleation, and that the austenite grain-size limits the size of the martensite units and contributes to austenite stabilization.

In conclusion, we reiterate the importance of considering martensite kinetics as well as the effect of the martensite characteristics used in the experiment to ascertain M_s. Our model accounts for:

- The influence of austenite grain-size on the initial rate of martensite transformation;
- The influence of the experiment used to determine the start of the reaction;
- Possible changes in the variation of M_s caused by grain refinement.

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