TRANSFORMATION MICROYIELDING OF RETAINED AUSTENITE

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Abstract—The reversal in the temperature dependence of the elastic limit accurately determines the $M'_s$ temperature of retained austenite in 4340 steel. Two models, one based on an exponential distribution of pre-existing nucleation sites and another based on an autocatalytic-site potency distribution, were compared in predicting the constitutive behavior of the steel in the stress-assisted transformation regime ($T < M'_s$). The autocatalytic-site potency distribution is in better agreement with the experimental stress–strain behavior and predicts reasonable values of the carbon enrichment of the retained austenite due to tempering. The decrease in the chemical driving force for the transformation of retained austenite due to carbon stabilization determines the elastic limit of the steel in the stress-assisted transformation regime.

Résumé—Le renversement dans l’effet de la température sur la limite élastique détermine de façon précise la température $M'_s$ de l’austénite résiduelle dans l’acier 4340. Deux modèles, l’un basé sur une distribution exponentielle de sites de germination préexistants et l’autre sur une distribution de sites autocatalytiques en loi de puissance, ont été comparés vis-à-vis de leur capacité à prévoir le comportement de base de l’acier dans le régime de transformation assistée par la contrainte ($T < M'_s$). La distribution des sites autocatalytiques en loi de puissance est en meilleur accord avec le comportement expérimental contrainte-déformation, et elle préside des valeurs raisonnables de l’enrichissement en carbone de l’austénite résiduelle du au revenu. La diminution de la force motrice chimique de la transformation de l’austénite résiduelle due à la stabilisation du carbone détermine la limite élastique de l’acier dans le régime de transformation assistée par la contrainte.


1. INTRODUCTION

Deformation can stimulate the kinetics of solid state phase transformations through both the thermodynamic effect of the applied stress and the production of new catalyzing defects by plastic strain. For the case of martensitic transformations, these interactions are depicted in Fig. 1 [1]. Spontaneous transformation triggered by preexisting nucleation sites occurs on cooling to the $M_s$ temperature (Point A). Stress-assisted nucleation on the same sites will occur at the stress denoted by the solid line indicated. At a temperature designated $M'_s$, this stress reaches the yield stress $\sigma_y$ for slip in the parent phase (Point C). Above $M'_s$, new potent nucleation sites, introduced by plastic strain, trigger strain-induced nucleation (line CE). The temperature $M'_s$ thus defines an approximate boundary between the temperature regimes where the two modes of the transformation dominate: near $M'_s$ both modes will operate. Due to transformation plasticity, the observed yield stress follows the stress for stress-assisted transformation below $M'_s$ (line CA for athermal and line CA′ for isothermal martensitic transformation). A reversal in the temperature dependence of the flow stress thus provides a convenient determination of the $M'_s$ temperature. $M'_s$ is then a quantitative characterization of the stability against stress-assisted transformation. $M_s$ is the maximum temperature above which
martensitic transformation cannot be induced by deformation. Due to the interaction between stress triaxiality and transformation volume change, the $M_s^*$ and $M_d$ temperatures are stress-state dependent.

In metastable fully-austenitic steels $M_s^*$ can be conveniently determined from the reversal in the temperature dependence of the macroscopic (0.2%) flow stress [2]. However, when the austenite is in the form of a dispersed phase and in moderate amounts, such as retained austenite in 4340 steel, a complete reversal in the temperature dependence of the flow stress does not occur, thus making the determination of the $M_s^*$ temperature rather difficult. In this case, estimates of the $M_s^*$ temperature can be obtained from [3]:

1. transitions from smooth yielding to discontinuous yielding, and
2. local minima in the temperature dependence of the strength-differential effect.

On the other hand, the elastic limit is a more sensitive parameter that is expected to be controlled by the transformation in the stress-assisted region. Therefore, a reversal in the temperature dependence of the elastic limit should accurately determine the $M_s^*$ temperature for retained austenite. At the same time, the stress–strain behavior can be studied in the microyielding region and compared with models for stress-assisted transformation.

### 2. EXPERIMENTAL PROCEDURE

A tempered VAR 4340 steel (0.4 C, 0.46 Mn, 0.28 Si, 1.74 Ni, 0.89 Cr, 0.21 Mo, in wt%) was chosen to study the transformation effects of retained austenite by means of tensile testing. The essential heat treatment consisted of austenitizing at 1200°C for 1 h and oil quenching, followed by tempering at 200°C for 1 h. The resulting volume fraction of retained austenite was found to be 0.09 as measured by a vibrating-sample magnetometer [4]. The tensile specimens had a gage length of 16.25 mm and a diameter of 4 mm. Tensile testing was performed in an INSTRON 1125 machine.

The tensile elastic limit was determined as a function of temperature in order to measure the $M_s^*$ temperature of the retained austenite in the tempered 4340 steel. The technique, also described by Muir et al. [5], employed a load–unload procedure in order to monitor the load as a function of residual strain. This procedure was repeated with increasing load to determine the load that resulted in the first detectable positive residual strain. The strain was measured with an accuracy of $\pm 10^{-3}$ using sensitive strain gages mounted on the gage section of the tension specimens. Because the test was conducted as a function of temperature in a silicone–oil bath, a dummy strain gage mounted on an identical unloaded test specimen immersed in the bath as provided for temperature compensation.

### 3. RESULTS

#### 3.1. Temperature dependence of the elastic limit

The temperature dependence of the elastic limit is shown in Fig. 2. The 0.2% flow stress and smaller-strain offsets are also indicated in the same figure. A definite reversal of the temperature dependence occurs at or near 40°C designating the tensile $M_s^*$ temperature of the retained austenite. The 0.2% flow stress does not undergo a reversal, consistent with the behavior obtained from independent experiments with a single-specimen technique [3].

Figure 3 presents stress–strain curves obtained in the microyielding region at temperatures above and below $M_s^*$. Above $M_s^*$, the stress–strain curves have the normal downward-curving shape, while below $M_s^*$ the stress–strain curves have a sigmoidal shape characteristic of stress-assisted transformation.

![Fig. 2. Temperature dependence of the elastic limit (EL) and strain offsets between the elastic limit and the 0.2% flow stress in uniaxial tension for 4340 steel containing 9% retained austenite. The arrow indicates the $M_s^*$ temperature.](image-url)
3.2. Constitutive behavior in the microyielding regime

In the stress-assisted nucleation regime \((T < M_f^*)\) initial yielding is controlled by the transformation of the retained austenite. Therefore, the theory of martensitic nucleation can predict the constitutive behavior of the steel in the microyielding regime. The observed stress–strain behavior can be predicted by considering the effect of stress on the nucleation-site potency distribution. The stress-strain curve at \(T = 20{\degree}C\) is selected as representative of the stress-assisted transformation behavior. Two models for the nucleation-site potency distribution are compared. The first model assumes that the transformation is controlled by the pre-existing nucleation sites in the retained austenite. The second model assumes that the transformation is controlled by nucleation sites created due to autocatalysis during the quench from the solution temperature.

3.2.1. Exponential distribution of pre-existing nucleation-site potencies. According to this model the applied elastic stress assists the transformation kinetics by modifying the effective potency distribution of the pre-existing nucleation sites. Based on a dislocation–dissociation model of classical heterogeneous martensitic nucleation via elastic interactions with internal stress concentrations [6], the potency of a nucleation site can be expressed in terms of the thickness \(n\) (in numbers of crystal planes) of the nucleus that can be derived from the defect by barrierless dissociation. The critical \(n\) for nucleation at a given thermodynamic driving force per unit volume \(\Delta G^{\text{th}}\) is

\[
n = \frac{2\gamma_i/\rho}{\Delta G^{\text{th}} + E_{\text{str}} + W_i}
\]

where \(\gamma_i\) is the nucleus specific interfacial energy, \(\rho\) is the density of atoms in a closed-packed plane in moles per unit area, \(E_{\text{str}}\) is the elastic strain energy per unit volume associated with distortions in the nucleus interface plane, and \(W_i\) is the frictional work of interfacial motion. Based on this model, Cohen and Olson [7] derived the cumulative structural defect potency distribution \(N_i(n)\), from the Cech and Turnbull small particle experiments in Fe–30 Ni [8]

\[
N_i = V_i^n \exp(-2n) \quad (2)
\]

where \(N_i\) is the total number of nucleation sites of all potencies per unit volume and \(x\) is a constant.

The effect of the applied stress on the potency distribution can be found by adding a mechanical driving force term \(\Delta G^m\) to the chemical driving force term \(\Delta G^{\text{th}}\) of equation (1), to obtain the total driving force

\[
\Delta G = \Delta G^{\text{th}} + \Delta G^m.
\]

The mechanical driving force \(\Delta G^m\) is related to the applied stress by

\[
\Delta G^m = \sigma \left( \frac{\Delta G}{\delta\Delta G} \right). \quad (4)
\]

At a given stress level, the value of \(\Delta G^m\) changes with the orientation of the nucleus relative to the stress axis. The mechanical driving force due to a uniaxial elastic stress \(\sigma\) is then expressed as

\[
\Delta G^m = \frac{1}{2} \left( \gamma_t \sin(2\theta) \cos x + \epsilon_t [1 + \cos(2\theta)] \right) \quad (5)
\]

where \(\gamma_t\) and \(\epsilon_t\) are the transformation shear and normal strains, \(\theta\) is the angle between the applied stress axis and the normal to the habit plane, and \(x\) is the angle between the shear direction of the transformation and the maximum shear direction of the applied stress resolved on the habit plane.

In considering stress effects on the potency distribution, two limiting cases should be considered. A fully-biased distribution which is based on the assumption by Patel and Cohen [9] that nucleation sites are of the optimum orientation for maximum interaction with the applied stress such that \(\Delta G^m = \Delta G_{\text{max}}^m\) for all sites. An opposite limit is to consider a fully-random distribution, based on the assumption made by Olson et al. [10] that the nucleation sites are randomly oriented. The actual behavior should be bounded by these two limits. Olson et al. found that in the stress-assisted regime the effect of the applied stress is approximately one third (1/3) of that predicted by the fully-biased distribution model. Therefore, the potency distribution of nucleation sites \(N_i(\sigma)\), under an applied elastic stress \(\sigma\), is given by the following expression

\[
N_i(\sigma) = N_i \exp \left( \frac{2\gamma_i/\rho}{\Delta G^{\text{th}} + \Delta G_{\text{max}}^m + W_i + E_{\text{str}}} \right) \quad (6)
\]

where \(\Delta G^m\) is \(\Delta G_{\text{max}}^m\) for the fully-biased case and \(\Delta G_{\text{max}}^m/3\) for the fully-random distribution.

The probability that a particle of volume \(V_p\) will contain at least one nucleation site is

\[
f = 1 - \exp(-N_i V_p) \quad (7)
\]

For a large number of particles with average volume \(V_p\), the fraction of particles containing martensite due to single-nucleation events is given by the probability defined above. For stress-assisted transformation, yielding is controlled entirely by the transformation, and then \(f\) and \(\epsilon\) are linearly related

\[
f = \frac{\epsilon}{\epsilon_1} \quad (8)
\]

Fig. 3. Stress–strain curves in the microyielding region for temperatures above and below the tensile M_f temperature. 4340 steel containing 9% retained austenite.
where $\epsilon_i$ is the plastic strain at the completion of the stress-assisted transformation ($f = 1$).

Combining equations (4), (6), (7), and (8) we obtain the stress–strain relation in the stress-assisted region

$$\sigma = \frac{2\pi\gamma_i}{\rho} \ln \left[ \frac{1}{N_0 V_p} \ln (1 - \epsilon_i) \right] - \Delta G^{th} - W_i - E^m$$

(9)

where $(\partial \Delta G/\partial \sigma)$ has the values of $(\partial \Delta G/\partial \sigma)_{max}$ and $1/3(\partial \Delta G/\partial \sigma)_{max}$ for the fully-biased and fully-random distributions of nucleation sites, respectively.

Equation (9) can be fitted to the experimental stress–strain curve for $T = 20^\circ C$, with $N_0 V_p$ and $\Delta G^{th}$ the parameters to be determined from the best fit. The strain $\epsilon_i$ can be determined from a linear extrapolation of the high-temperature elastic limit ($T > M_f^*$) to lower temperatures. For $T = 20^\circ C$ this extrapolation gives $\epsilon_i = 0.17%$. At this strain the stress would reach the elastic limit of the steel in the absence of transformation (the slip-controlled elastic limit). For $\epsilon > \epsilon_i$, plastic yielding by slip introduces new nucleation sites in the retained austenite and the transformation becomes strain-induced. Thus, pure stress-assisted transformation operates up to $\epsilon = \epsilon_i$.

The frictional work of interfacial motion in equation (9) was estimated using the expression given by Kuroda [11]: $W_i = 1.310 \times 10^4 X_e^{3.1}$. For 0.40 wt%C in 4340 steel, this gives $W_i = 1000$ J/mol. The remaining parameters in equation (9) are taken as $E_m = 500$ J/mol, $\rho = 3 \times 10^{-5}$ mol/m$^2$, $\gamma_i = 0.15$ J/m$^2$, and $\lambda = 0.866$ [6, 7].

Figure 4 compares the experimental stress–strain curve at $T = 20^\circ C$ with the curve calculated using equation (9). Although the calculated $\sigma$–$\epsilon$ curve possesses the sigmoidal shape of the experimental $\sigma$–$\epsilon$ curve, it does not fit the data well at low and high strains. In particular, the assumption of the exponential nucleation-site potency distribution fails to account for a non-zero value of the elastic limit as well as to predict the onset of rapid work hardening as $\epsilon_i$ approaches unity. The parameters determined from the best fit are: $N_0 V_p = 1.48 \times 10^4$ and $\Delta G^{th} = -1687$ J/mol for the fully-biased distribution and $N_0 V_p = 5.44 \times 10^4$ and $\Delta G^{th} = -1811$ J/mol for the fully-random orientation distribution. The chemical driving forces calculated above can be compared with the value $\Delta G^{th} = -3028$ J/mol, estimated using the THERMOCALC system [12] for the composition of 4340 steel at room temperature. The values of $\Delta G^{th}$ determined from the best fit imply a very large reduction in $\Delta G^{th}$ which cannot be accounted for by carbon stabilization of the retained austenite. In view of these considerations, we conclude that the exponential distribution of the pre-existing nucleation sites does not satisfactorily describe the constitutive behavior of the steel in the microyielding region. The next section presents an alternative model, based on the distribution of nucleation sites created by autocatalysis, during the initial quench hardening of the steel.

3.2.2. Nucleation-site potency distribution of autocatalytic sites. In this model the applied plastic assists the transformation kinetics by modifying the effective potency distribution of autocatalytic sites. The following assumptions are employed:

1. The nucleation sites created by autocatalysis are much more plentiful than the pre-existing sites, i.e. $f_{CA} \gg N_i$, where $p$ is the autocatalytic factor [13], $f_{CA}$ is the fraction transformed during quenching, and $N_i$ is the density of the pre-existing sites. Then, since $f_{CA} \simeq 1$, the number of available nucleation sites $N_i$ is

$$N_i = p.$$  

2. The potency of the autocatalytic sites has been described by a Gaussian distribution [14], as shown in Fig. 5(a). For the behavior at $f_{CA} \simeq 1$, a linear approximation is adopted for the cumulative distribution of nucleation sites [Fig. 5(b)]

$$p = C_1 + C_2 n$$

where $C_1$ and $C_2$ are constants.

3. Furthermore, the distribution is truncated at $n = n_{Q}$ due to the consumption of sites during quenching and $n = \Delta p$ [Fig. 5(c)]. The potency of the nucleation sites at room temperature $n_{Q}$, as calculated from equation (1) is 6.5.

Under the above set of assumptions, the cumulative distribution of nucleation sites is given by the linear approximation as

$$N_i(\sigma) = C_1[\eta(\sigma) - n_{Q}],$$

(10)

The potency under an applied stress $\sigma$ in the present tensile testing is given by

$$\eta(\sigma) = -\frac{2\pi\gamma_i}{\rho} \frac{\Delta G^{th} + W_i + E^m + \Delta G^c}{\Delta G^{th}}.$$  

(11)

where the chemical driving force $\Delta G^{th}$ and the frictional work of interfacial motion $W_i$ are now evaluated for the tempered condition and are different from the corresponding $\Delta G^{th}$ and $W_i$ of equation (1) due to carbon enrichment of the retained austenite.
Fig. 5. Potency distribution of autocatalytic sites. \( p \) is the autocatalytic factor, \( n \) is the structural potency of nucleation sites, and \( n_{\text{RT}} \) is the potency of nucleation sites at room temperature, immediately after the steel is quenched from the solution temperature to room temperature. The Gaussian distribution of autocatalytic sites is shown in Fig. 3(a), the linearization in Fig. 3(b) and the truncation of the distribution at \( n_{\text{RT}} \) due to the consumption of sites during quenching in Fig. 3(c).

During heat treatment, since \( \Delta G^{\text{act}} \) and \( W_f \) are functions of carbon content, we can write

\[
\Delta G^{\text{act}} + W_f = F(X_c)
\]

where \( F(X_c) \) is a function of the mole fraction carbon \( X_c \).

Combining equations (7) and (10) the fraction of particles to transform is given by

\[
f = 1 - \exp\left\{-C_2V_p[n(\sigma) - n_{\text{RT}}]\right\}.
\]

Finally, the stress–strain relation in the microyielding region can be found by combining equations (4), (8), (11), (13), and (14) to obtain

\[
\sigma = \frac{1}{(\partial \Delta G/\partial \sigma)} \left[ \frac{(-2\lambda/p)(C_2V_p)}{n_{\text{RT}}(C_2V_p) - \ln(1 - \epsilon/\epsilon_0) - F(X_c) - E^{\text{RT}}} \right]
\]

where \( (\partial \Delta G/\partial \sigma) \) takes the values of \( (\partial \Delta G/\partial \sigma)_{\text{max}} \) and \( 1/3 (\partial \Delta G/\partial \sigma)_{\text{max}} \) for the fully-biased and fully-random distributions of nucleation sites respectively. Equation (14) will be fitted to the experimental stress–strain curve for \( T = 20^\circ C \), with \( F(X_c) \) and \( C_2V_p \) the parameters to be determined from the best fit.

Figure 6 compares the experimental stress–strain curve at \( T = 20^\circ C \) with the curve calculated using equation (14). Although the model predicts a higher elastic limit, it agrees very well at higher plastic strains, especially in the rapid work hardening region. The rapid increase in the rate of work hardening is suggestive of the exhaustion of available nucleation sites at strains close to \( \epsilon_0 \). This, however, does not necessarily imply complete transformation of the retained austenite, since a single nucleation event is generally not expected to give rise to complete transformation of film-like austenite particles. Complete transformation would require more than one nucleation event per particle, the probability of which is negligible. It is estimated that at \( T = 20^\circ C \) only approximately 30% of retained austenite transforms up to \( \epsilon = \epsilon_0 \), while the fraction of austenite particles containing martensite is approaching unity.

Using non-linear curve-fitting, the values of the parameters for the best fit are: \( C_2V_p = -2.614 \), and \( F(X_c) = \Delta G^{\text{act}} + W_f = -1455 \text{ J/mol} \) for the fully-biased distribution model and \( C_2V_p = -6.871 \), and \( F(X_c) = -1845 \text{ J/mol} \) for the fully-random distribution model.

From the calculated value of \( F(X_c) \) the extent of carbon enrichment of the retained austenite due to tempering can now be estimated. From equation (12) and using THERMOCALC to express the chemical driving force as a function of carbon \( \Delta G^{\text{act}} = \Delta G^{\text{act}}(X_c) \), we find that \( X_c = 0.026 \) or 0.57 wt% C for the fully-biased distribution model and \( X_c = 0.022 \) or 0.46 wt% for the fully-random distribution model. This corresponds to the carbon content of the retained austenite after tempering. Similar levels of carbon enrichment of the retained austenite have been observed by Barnard et al. [15] in a 0.26 C, 2 Cr, 1.98 Mn, 0.5 Mo, 0.01 Ni steel by means of atom probe/field-ion microscopy.

The slope \( \partial \sigma/\partial T \) in the stress-assisted transformation regime can now be calculated and compared with the experimental slope of 15.2 MPa/K for the temperature dependence of the elastic limit from Fig. 2. The slope \( \partial \sigma/\partial T \) is related to the entropy change \( \Delta S^{\text{act}} \) for the martensitic transformation through the relation

\[
\frac{\partial \sigma}{\partial T} = \frac{\Delta S^{\text{act}}}{(\partial \Delta G/\partial \sigma)}
\]

![Fig. 6. Comparison of experimental stress-strain curve at \( T = 20^\circ C \) with the model based on the distribution of autocatalytic sites [equation (14)].](image-url)
\( \Delta S^* \) was evaluated at room temperature for the carbon content estimated above. For the two limits we have \( \Delta S(0.57 \text{ wt}\% \text{C}) = 4.609 \text{ J/mol} \cdot \text{K} \) and \( \Delta S(0.46 \text{ wt}\% \text{C}) = 4.755 \text{ J/mol} \cdot \text{K} \) which gives \( \Delta \sigma/\Delta T = 5.3 \text{ MPa/K} \) for the fully-biased distribution and \( \Delta \sigma/\Delta T = 16.5 \text{ MPa/K} \) for the fully-random distribution. The actual behavior is therefore bracketed by these two limits but is closer to the fully-random distribution of nucleation sites.

The parameter \( C_3 \) in the model corresponds to the slope \( dp/dn \) of the autocatalytic-site potency distribution. Using \( V_p = 3 \times 10^{-45} \text{ m}^3 \) from TEM observations of retained austenite by Rao and Thomas [16] and the result \( C_2 = -6.871 \) from above, we get \( C_2 = 2.3 \times 10^{14} \text{ m}^3 \) which is in very good agreement with the value \( dp/dn = 8 \times 10^{13} \text{ m}^3 \) obtained by Lin [14] for a Fe-29.5 Ni alloy.

The reduction of the driving force due to the carbon enrichment is

\[
d(\Delta G) = (\Delta G^m + W_f) - F(X_f) = 183 \text{ J/mol}.\]

The stress required to compensate for the decrease in the chemical driving force can be calculated from the condition

\[
\sigma \left( \frac{\partial \Delta G}{\partial \sigma} \right) = d(\Delta G)
\]

and is \( \sigma = 641 \text{ MPa} \). This transformation stress is then the elastic limit of the tempered steel in the stress-assisted transformation regime.

**4. CONCLUSIONS**

1. The reversal in the temperature dependence of the elastic limit provides an accurate determination of the \( M_s^* \) temperature for retained austenite. It was found that for 4340 steel austenitized at 1200°C and temperature at 200°C, the \( M_s^* \) temperature in uniaxial tension is 40°C.

2. Two models, one based on an exponential distribution of pre-existing nucleation sites and another based on an autocatalytic-site potency distribution, were compared in predicting the constitutive behavior of the steel in the stress-assisted transformation regime (\( T < M_s^* \)). The autocatalytic-site potency distribution is in better agreement with the experimental stress-strain behavior and predicts reasonable values of the carbon enrichment of the retained austenite due to tempering. The retained austenite would be enriched from 0.40 to 0.46 wt\% C.

3. The decrease in the driving force due to carbon stabilization must be compensated by a mechanical driving force contribution, which then determines the elastic limit of the steel in the stress-assisted transformation regime.

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