Model for multiple stress-affected martensitic transformations, microstructural entropy and consequences on scatter in properties

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Abstract

Building on previous work on stress-affected martensitic transformations, a simple theory is presented to enable the calculation of the volume fractions of each martensite variant in an austenite grain, as a function of temperature. Polycrystalline austenite is dealt with by introducing specific textures, so that the orientation of the martensite in any region of the sample is defined. The calculations show that there is strong variant selection even with relatively small applied stresses, and the the evolution of overall volume fraction is dominated by the favoured variants. The notion of microstructural entropy, which indicates the level of heterogeneity in the microstructure is then used to indicate consequences on properties such as the scatter to be expected in toughness. These and further detailed consequences of stressaffected transformation are described.

1. Introduction

Displacive transformations such as bainite and martensite involve both a change in crystal structure and a physical deformation which is an invariantplane strain with a large shear component. They therefore react to stress much in the same way as slip or mechanical twinning. For example, the application of a stress favours certain slip systems over others, and the same applies to displacive transformations, since those plates which interact

Preprint submitted to Materials Science and Technology

June 3, 2013

favourably to relieve the applied stress grow in preference to others which oppose the external stress. An austenite grain in general can transform into 24 differently oriented martensite plates (variants), but *variant selection* is said to occur when some grow preferentially due to an external influence. The theory for variant selection is not well established for the following reasons.

The essential framework for dealing with the thermodynamics of stressaffected martensitic transformation was established by Patel and Cohen [1], by defining a mechanical free energy term ΔG_{MECH} which supplements the chemical free energy available for transformation, ΔG_{CHEM} so that the total driving force becomes

$$\Delta G = \Delta G_{CHEM} + \Delta G_{MECH} \tag{1}$$

where for an applied stress that is uniaxial [1],

$$\Delta G_{MECH} = s\tau + \delta\sigma_N \tag{2}$$

where s and δ represent the shear and dilatational strains due to transformation, the latter being normal to the martensite habit plane. The magnitudes of the shear stress τ on the habit plane, and σ_N normal to that plane, depend on the orientation of the plate relative to the applied stress. Therefore, the sign and magnitude of the mechanical driving force depends on the orientation of each of the 24 variants of martensite in any given grain of the parent phase with respect to the external stress. Strong variant selection has been shown to occur in the case of carbide precipitation [2] and bainitic transformations when the ratio $\Delta G_{MECH}/\Delta G$ is large [3].

Transformation under the influence of external stress leads to a differentiation of martensite variants during the evolution of transformation. In other words, it is as if there are many separate reactions starting at different temperatures. Classical Avrami theory [4–6] introduced the concept of extended volume when dealing with a single phase transformation, and the method has been adapted for multiple transformations [7–12]. The purpose of the present work was to develop to present a simple model capable of predicting the volume fractions of each kind of martensite as a function of the applied stress, and to assess the consequences of the results including the influence of the crystallographic texture in the parent phase.

2. Method

2.1. Multiple transformations

It is necessary to be able to estimate first, in each grain of austenite, the distribution of volume fractions of every one of the 24 individual variants of martensite, and to repeat this for every grain of austenite in a polycrystalline sample. Since every variant will be associated with a different ΔG_{MECH} , and hence a different martensite-start temperature (M_S) , it must be treated as a unique phase. Therefore, the number of different kinds of martensite (and M_S temperatures) will be $24 \times N_{\gamma}$ where N_{γ} is the number of austenite grains. These multiple transformations are not exclusive and can occur simultaneously.

The evolution of the martensite fraction f as a function of undercooling below M_S is described by the classical Koistinen and Marburger equation [13], the physical basis of which was revealed by Magee [14]:

$$1 - f = \exp\left[\underbrace{\overline{V}\phi \frac{d\{\Delta G\}}{dT}}_{\chi = -0.011} (M_S - T)\right].$$
(3)

where \overline{V} is the average volume per plate of martensite, and ϕ is the proportionality constant relating the change in the number of plates per unit volume of austenite to the corresponding change in driving force, $dN = -\phi d\{\Delta G\}$. The composite parameter χ was derived by Koistinen and Marburger fitting to experimental data [13].

However, this equation applies to the case where there is a unique M_s . To deal with multiple transformations occurring in the same austenite grain, the simultaneous transformations adaptation [7–11] of the extended volume concept of Avrami theory [4–6] applies. The method has been widely applied, including to martensitic transformation by [12]; we therefore follow [12] but avoid complexity by dealing directly with the Koistinen and Marburger equation. So for 24 different martensitic reactions happening at the same time in a given austenite grain, and in a temperature interval dT [15]:

$$df_{1} = \chi \left(1 - \sum_{i=0}^{24} f_{i} \right) dT, \quad \text{with} \quad df_{1} = 0 \quad \text{if} \quad M_{S_{1}} < T$$

$$\vdots$$

$$df_{24} = \chi \left(1 - \sum_{i=0}^{24} f_{i} \right) dT, \quad \text{with} \quad df_{24} = 0 \quad \text{if} \quad M_{S_{24}} < T \quad (4)$$
(5)

with each equation obtained by differentiating equation 3. The fraction from individual austenite grains are then summed over all the N_{γ} austenite grains, assuming that there is no interaction between the grains. Equations like these are perfect for numerical interpretation by reducing the temperature in small intervals and updating the terms at each step.

2.2. Calculation of stress-affected M_S temperatures

In the discussion that follows, the stress-free start temperature is defined as M_S° , and that influenced by stress as M_S^{σ} . To a good approximation, the chemical driving force varies linearly with temperature and may be written as:

$$\Delta G_{CHEM} = a_1 T + a_2 \tag{6}$$

where a_1 and a_2 are constants. At the martensite-start temperature, it has a critical value ΔG_{M_S} required to trigger transformation, then in the absence of stress,

$$\Delta G_{M_S} = a_1 M_S^\circ + a_2. \tag{7}$$

Recalling that $\Delta G = \Delta G_{CHEM} + \Delta G_{MECH}$, it follows that under the influence of stress, the case for stress-affected transformation becomes:

$$\Delta G_{M_S} = a_1 M_S^{\sigma} + a_2 + \Delta G_{MECH}.$$
(8)

On combining equations 7 and 8 we see that

$$\Delta G_{MECH} = a_1 (M_S^{\sigma} - M_S^{\circ}) = a_1 \Delta M_S \tag{9}$$

so that a knowledge of the mechanical free energy enables the change in the martensite-start temperature to be estimated. The coefficient a_1 was estimated to be $0.174 \,\mathrm{J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$ for a typical low-alloy steel of composition Fe-1Mn-0.2C wt% using thermodynamic calculations [16] and is not expected to be sensitive to alloy composition in the class of low-alloy steels, so is assumed constant in the present analysis; if the need arises, it is easy to calculate using our standard and freely available software for specific steels [16].

There are examples in the literature, originating from the pioneering work by Patel and Cohen [1], where the mechanical driving force is expressed in a simple manner as a function of stress, for example that it equals $-0.86\sigma \text{ J} \text{ mol}^{-1} \text{ MPa}$ for martensite induced in uniaxial tension with a stress σ [17–19]. However, these assume that the martensite that forms will be at an optimum orientation consistent with the maximum interaction with the applied stress. On the other hand, what is required here is to calculate the mechanical free energy term for each of the 24 variants of martensite per grain of austenite.

The applied system of stresses can be described by a 3×3 stress tensor σ_{lm} which when multiplied by the unit normal to the martensite habit plane gives the traction **t** describing the state of stress on that plane. The traction can then be resolved into σ_N and τ in the normal manner [20]:

$$\sigma_N = |\mathbf{t}| \cos\{\theta\}$$

$$\tau = |\mathbf{t}| \cos\{\beta\} \cos\{\phi\}$$
(10)

where $|\mathbf{t}|$ is the magnitude of \mathbf{t} , θ is the angle between the habit plane normal and \mathbf{t} , β the angle between \mathbf{t} and the direction of the maximum resolved shear stress, and ϕ the angle between the latter and the direction of shear for the martensite plate concerned. Substituting these terms into equation 2 gives the mechanical free energy. Throughout this work, the set of parameters which represent the crystallography of an individual plate of martensite, i.e., the shape deformation, the habit plane indices, the orientation relationship with the austenite, are identical to those used in previous studies [3].

To deal with polycrystalline austenite, samples of 500 grains were arranged with respect to a reference set of coordinates in order to generate a variety of crystallographic textures, including random, Goss, Cube and Copper, using a method described elsewhere [21]. As a consequence, 24×500 values of the mechanical free energy were calculated for the exact orientation of each martensite plate in the polycrystalline sample. Fig. 1 illustrates

the distribution of ΔG_{MECH} for the most favoured variant in each austenite grain, as a function of the texture and of the direction of the applied stress (20 MPa). Clearly, the nature of the interaction of the overall interaction of martensite with stress will be different as a function of the austenite texture, but in some cases (Goss and Copper), the orientation of the stress axis is important to specify.

3. Results and Discussion

Given the calculated mechanical free energy terms and the theory for calculating the fraction of transformation contributed by each variant to individual austenite grains, and summing over all the 24×500 austenite grains, it becomes possible to predict many features of the evolution of martensite as a function of stress. Fig. 2a shows the distribution within the polycrystalline sample, of the volume fractions of martensite variants. In the absence of stress, each plate within an austenite grain could contribute equally, resulting in a fraction $\frac{1}{24} \equiv 0.042$ so any deviation from this is a consequence of variant selection, i.e., the favouring of particular orientations of martensite which better comply with the applied stress. The distribution broadens as the stress is increased, because particular variants then are strongly biased, resulting in large volume fractions. But surprisingly, the frequency of variants that contribute little to the volume fraction of transformation also increases. As will be seen later, this is because the dominant variants consume most of the austenite in the early stages of transformation, resulting in little austenite left for unfavourable variants to grow.

These results have consequences on mechanical properties. If large parts of austenite transform into few variants, then blocks of identically oriented plates would form. These large, crystallographically homogeneous regions, are known to be detrimental to toughness because they permit the undeviated propagation of cleavage cracks [22–26], and a coarse block size also results in a reduction of strength [27].

The dispersion of volume fractions represents a microstructural heterogeneity, the extent of which can be defined in terms of a parameter known as *microstructural entropy* [28] which has its origins in statistical theory [29, 30]. Thus, for a random variable X assuming the value *i* with probability $p_i = 1, \ldots, n$, the entropy of X, as a logarithmic measure of the mean



Figure 1: $\langle 100 \rangle_{\gamma}$ pole figures showing austenite grain orientations relative to the sample (s) axes, together with the distribution of mechanical free energy terms ($\sigma = 20 \text{ MPa}$) for the most favoured variant in each of the 500 austenite grains. The axes $x \parallel [100]_{\text{s}}$, $y \parallel [010]_{\text{s}}$ and $z \parallel [001]_{\text{s}}$ refer to the direction along which the tensile stress is applied. (a,b) Radom γ texture. (c,d) Cube texture. (e,f) Goss texture. (g,h) Copper texture.

probability, is given by:

$$H\{X\} = -\sum_{i=1}^{n} p_i \ln\{p_i\}$$
(11)

which has a maximum when all the probabilities are identical. If volume fractions (V_i) are substituted for probabilities, the n the resulting microstructural entropy is known to correlate strongly with scatter in toughness values [28]. Thus, the microstructural entropy within each austenite grain is defined on the basis of equation 11 as:

$$H = \left[-\sum_{i=1}^{24} V_i \ln\{V_i\} \right] / \ln\{24\}$$
(12)

where the $\ln\{24\}$ term normalises H to vary between 0 and 1, with 0 representing the case where the whole of the austenite grain transforms into a single variant of martensite, and 1 for the case where all variants are equally represented (i.e., a uniform microstructure).

Fig. 2b shows the distribution of 500 values of microstructural entropy as a function of the applied stress; the microstructure becomes ever more non-uniform as the stress is increased, indicating a detrimental effect of stress-affected transformation on the scatter to be expected in mechanical properties.

The evolution of total volume fraction is illustrated in Fig. 2c where $M_S^\circ = 140^\circ$ C. The effect of stress is spread the temperature range over which transformation occurs, a phenomenon which also occurs when the steel is chemically heterogeneous or where transformation occurs in a temperature gradient [31]. Recalling that in the absence of stress, the 24 variants in an individual austenite grain would each have a fraction ≈ 0.04 , Fig. 3 shows that most of the austenite in the polycrystalline sample transforms into those variants which are favoured by the applied stress. There is, therefore, strong variant selection. Furthermore, the approximate linear and empirical relationship reported in previous work, between the number of active variants and the ratio $\Delta G_{MECH}/\Delta G$ [3], is consistent with the trend in Fig. 3, although in the case of martensite, the ratio of the mechanical to total driving force is not relevant because the chemical driving force at the onset of transformation is essentially fixed to the value ΔG_{MS} . It is the absolute value ΔG_{MECH} which determines variant selection.



Figure 2: Stress-affected martensitic transformation from a random distribution of five hundred grains of austenite. (a) Distribution of martensite fractions. (b) Microstructural entropy as a function of the applied tensile stress. (c) Volume fraction of martensite as a function of temperature and applied stress.



Figure 3: Total volume fraction of martensite "favoured" variants in all austenite grain, i.e., those whose individual volume fractions exceed 0.04, as a function of tensile stress.

Calculations were conducted to investigate further the influence of austenite texture on subsequent martensitic transformation. It turns out that the volume fraction obtained as a function of transformation temperature is very insensitive to the austenite texture (Fig. 4a), presumably because much of the reaction is dominated by the most favoured variants. There are, nevertheless, significant difference expected in the microstructure as shown in the distribution of volume fractions, Fig. 4b.



Figure 4: Data for all textures for a stress of 200 MPa applied along the z-axis. (a) Volume fractions; there is no significant different between the four textures. (b) Frequency distributions.

4. Possible Experiments

The calculations presented here can in practice be subjected to experimental probes. Modern electron back-scatter diffraction (EBSD) on a scanning electron microscope can, in combination with orientation imaging, produce quantitative characterisations of the data presented in Fig. 2a. The data presented in Fig. 2c can readily be measured using dilatometry in the case of the sample which undergoes martensitic transformation in the absence of external stress. When transformation occurs under the influence of stress, variant selection means that the strains measured during dilatometry are no longer isotropic [32]. It would be necessary in those circumstances to characterise strains along the three of the principal axes of the sample in order to deduce the true volume fraction of martensite. The relationship between the scatter in mechanical properties and the measured microstructural entropy is likely to be most significant the the steel is in the ductile-to-brittle transition temperature range.

5. Conclusions

It now becomes possible to calculate with a simple algorithm, not only the crystallographic orientations of martensite plates but also the overall volume fraction of each variant of martensite in each grain of austenite, given the orientations of the austenite grains relative to the sample reference frame. The advent of electron back scattered diffraction makes it possible to quantitatively determine the volume fractions calculated in the present work. The computer program used in the calculations is freely available on [33] and may be used to better assess diffraction data.

The work presented in this paper focuses on stress-affected transformation leading to a different martensite-start temperature depending on the orientation of the plate relative to the system of stresses. However, it is of generic value and applies to any scenario in which the steel is heterogeneous in the following contexts:

- differences in M_S temperatures caused by the fact that chemical composition may vary with position.
- When macroscopic measurements are made, the temperature may not be homogeneous, in which case the transformation temperature in different regions of the sample will not be identical. This can be treated in using the simultaneous transformation equations 5 expressed as a function of time instead of temperature.
- When transformation occurs under the influence of magnetic fields which are not homogeneously applied.
- There are alloys in which both α' and ε martensite form when the samples are deformed [34]. The method can in principle be applied to such scenarios to estimate the relative volume fractions of the two phases.

A further conclusion is that variant selection can be expressed quantitatively by stating both the crystal orientation of the variant and how dominant it becomes by quoting its volume fraction. The microstructural entropy term then in principle helps relate, for example, the scatter in toughness to the development of microstructure. Acknowledgments: The authors are grateful to Professor Dong Woo Suh of GIFT, POSTECH, for helpful discussions and comments. Drs Kundu and Chintha acknowledge support from Tata Steel Ltd. HKDHB is grateful to the World Class University Programme of the National Research Foundation of Korea, Ministry of Education, Science and Technology, project number R32–2008–000–10147–0.

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