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Diffusional Transformations: A Theory for the Formation of Superledges

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It is well known that the growth of proeutectoid ferrite in steels often occurs by the superledge mechanism, in which the piecewise displacement of the interface is accomplished by the motion of steps, whose heights can amount to several hundreds of lattice spacings. The present work is an attempt to understand the factors controlling the height (h) of experimentally observed superledges. A theory based on step nucleation is developed, which predicts a lower limit for h, for a specified set of transformation conditions and steel composition; published experimental data seems to be in good agreement with the theory, particularly with respect to the variation of h with transformation temperature. It is also shown that the critical height below which the nucleation of a ledge is not possible, is directly related to the free energy of the singular interface on which ledge motion is supposed to occur.

Es ist gut bekannt, daß das Wachstum von proeutektoidem Ferrit in Stahl oft durch den „Superklippen"-Mechanismus hervorgerufen wird, bei dem die stückweise Verschiebung der Grenzfläche von der Bewegung von Stufen begleitet ist, deren Höhe einige hundert Gitterabstände betragen kann. Es wird der Versuch unternommen, die Faktoren, die die Höhe (h) der experimentell beobachteten Klippen steuern, zu verstehen. Eine Theorie auf der Grundlage der Stufenkeimbildung wird entwickelt, die eine untere Grenze für h, für einen spezifischen Satz von Transformationsbedingungen und Zusammensetzung des Stahls vorhersagt; veröffentlichte experimentelle Werte scheinen in guter Übereinstimmung mit der Theorie zu sein, speziell bezüglich der Änderung von h mit der Transformationstemperatur. Es wird ebenfalls gezeigt, daß die kritische Höhe, unter der eine Keimbildung von Klippen nicht möglich ist, direkt mit der Freien Energie einer einzelnen Grenzfläche verknüpft ist, auf der die Klippenbewegung wahrscheinlich stattfindet.

1. Introduction

It has long been recognised that interfaces whose orientations correspond to sharp minima in interfacial free energy (i.e., *singular* interfaces) will tend to move by a step mechanism, rather than by the continuous displacement of every element of the structure of the interface [1, 2]. Cahn [2] has presented a general condition for predicting whether growth will be continuous or stepped; the occurrence of stepped growth depends on the existence of periodic equilibrium interface configurations [2] whose spacing would presumably correspond to that of the lattice planes parallel to the plane of the interface, so that the steps which accomplish growth would be expected to be of atomic height. However, it is now well established that the *diffusional* growth of proeutectoid ferrite in steels occurs by the movement of 'superledges' [3], whose heights can reach several hundreds of lattice spacings [4, 5]. There is no theory to explain either the absolute heights involved, or the experimentally observed (and well-behaved) variation in ledge height as a function of transformation temperature. Apart from their abnormal size, the superledges seem to behave in accordance with all the expected characteristics of stepped growth — in particular, their existence is

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usually associated with what are believed to be singular austenite/ferrite interfaces [3]. The present work is concerned with an effort to understand the superledge mechanism of growth; the proeutectoid ferrite transformation mentioned earlier is accompanied by a relatively low chemical free-energy change, and it was felt that the size of the superledges may be related to the difficulty of *nucleating* smaller ledges.

2. Model for Superledge Nucleation

Fig. 1 schematically illustrates a ferrite allotriomorph which has grown along the prior austenite grain boundary; for simplicity, the form of the illustrated section of the allotriomorph is considered to be maintained through at least a unit distance normal to the plane of the paper (this also applies to Fig. 2, which will be discussed later). One of the austenite/ferrite interfaces is assumed to be in a singular orientation, and ledge nucleation (ABCD) is proposed to occur at the corner 'A', since nucleation at a planar interface would be relatively difficult. If the chemical free-energy change (per unit volume) accompanying the nucleation of a ledge is given by $\Delta F_{\mathrm{v}}^{\mathrm{m}}$ and the energies (per unit length) of the positive and negative edges by S_+ and S_-, respectively, then nucleation of a ledge of unit depth becomes possible when condition (1) below for volume ABCD is satisfied,

$$|(\text{volume ABCD})|\,(\Delta F_{\mathrm{v}}^{\mathrm{m}})| > (S_+ + S_-)\ . \tag{1}$$

Since there are no restrictions on the ratio AB/BC, the ledge height is free to vary without affecting the above nucleation criterion, and the model is therefore not capable of predicting ledge heights, nor the variation of the latter with transformation temperature.

The problem seems to arise because of the failure to recognise that the negative edge at A should act as a *pivot* during nucleation, when the interface at AB attempts forward motion. The dissipation of solute away from the austenite/ferrite interface should become increasingly difficult as the interface shape changes from that of a positive edge, to a planar interface or a negative edge. This is because the volume of austenite available in the immediate vicinity of the ferrite, for the absorption of solute, decreases in the order of interface shape listed above. Hence, the rise in solute concentration in the austenite at the interface, due to the initial establishment of the allotriomorph, can be expected to be relatively high at the corner A. The subsequent nucleation of a ledge can therefore be better represented as in Fig. 2a, where the edge A restricts interface motion during nucleation. Fig. 2b, which is a transmission electron micrograph illustrating the growth of a proeutectoid ferrite allotriomorph in an Fe–0.39 C–4.08 Ni–2.05 Si (wt%) steel (isothermally transformed at 514 °C for 120 s),

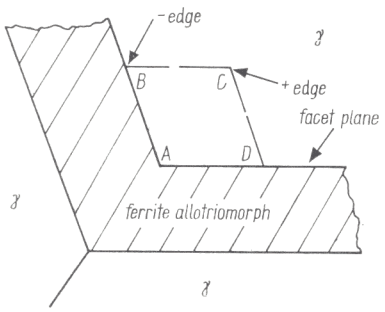


Fig. 1. Schematic diagram illustrating the nucleation of a ledge

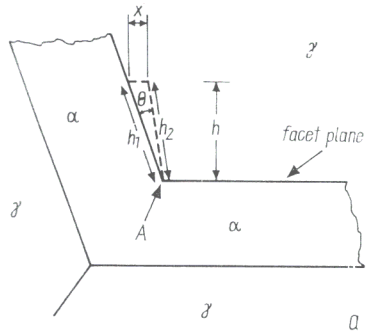
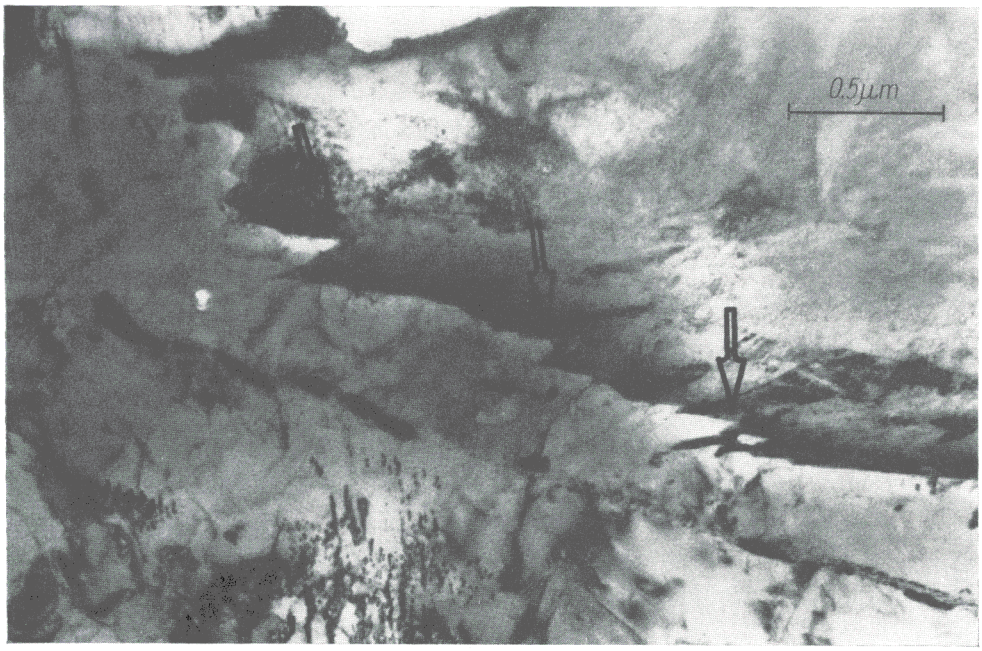


Fig. 2. a) Schematic diagram illustrating the nucleation of an inclined ledge on a proeutectoid ferrite allotriomorph. b) Transmission electron micrograph illustrating inclined growth ledges on a proeutectoid ferrite allotriomorph in an Fe–Ni–Si–C steel



b

shows that the situation envisaged in Fig. 2a is realistic. The growth ledges (arrowed) are seen to be inclined, with the negative edges lagging behind the corresponding positive edges. Further evidence on the shape of superledges involved in the growth of proeutectoid ferrite can be obtained from the in-situ photoemission electron microscopy observations of Edmonds and Honeycombe [6], which clearly demonstrate the existence of inclined superledges.

The free-energy change resulting from the formation of the nucleus illustrated in Fig. 2a is given (for a unit depth normal to the plane of the diagram) by

$$\Delta F = \sigma x + S_+ + \Delta F_{\mathrm{v}}^{\mathrm{m}}(xh/2) \,, \tag{2}$$

where σ is the interfacial energy per unit area of *facet plane* (i.e., the interface in singular orientation). In (2), the difference in orientation between h_1 and h_2 has been ignored, since the angle θ must be small at the nucleation stage. If $A = xh/2$, then on differen-

tiating (2) with respect to the volume of the nucleus we get

$$\frac{\mathrm{d}(\Delta F)}{\mathrm{d}A} = \frac{\mathrm{d}h}{\mathrm{d}A}\frac{\partial(\Delta F)}{\partial h} + \frac{\mathrm{d}x}{\mathrm{d}A}\frac{\partial(\Delta F)}{\partial x} = \frac{2\sigma}{h} - 2\Delta F_{\mathrm{v}}^{\mathrm{m}} . \tag{3}$$

Following classical nucleation theory, the growth of an embryo into a successful nucleus becomes feasible beyond the critical point given by

$$\frac{\mathrm{d}(\Delta F)}{\mathrm{d}A} = 0 \quad \text{so that} \quad h^* = \frac{\sigma}{\Delta F_{\mathrm{v}}^{\mathrm{m}}}, \tag{4}$$

where h^* is the critical nucleus height which has to be exceeded for the successful nucleation of a viable ledge. h^* therefore provides a lower limit for the size of superledges in any steel, the composition of which determines the magnitude of $\Delta F_{\mathrm{v}}^{\mathrm{m}}$ for a specified transformation temperature. All experimental measurements should therefore exceed the calculated value of h^*. An upper limit can also be postulated, since ledges larger than a few times h^* would themselves be sites for further step nucleation, and would therefore tend to degenerate into a number of smaller ledges (whose heights would, of course, exceed h^*).

3. Analysis of Published Experimental Data

The analysis was based on published experimental data (taken from [4, 5]) on the variation of superledge height as a function of transformation temperature in a variety of low-alloy steels, all of which exhibit the classical 'interphase precipitation' reaction (3). The primary advantage of such data is that $\Delta F_{\mathrm{v}}^{\mathrm{m}}$ does not alter with the progress of transformation, since both ferrite and carbides form nearly simultaneously, so that the average composition of the austenite remains constant. That there is no gross enrichment of the residual austenite at any stage of the reaction is also reflected in the fact that the transformation to proeutectoid ferrite and carbides is known to reach completion in the particular steels chosen for analysis.

The most prominent facet plane associated with the diffusional growth of ferrite in austenite is known to be $(111)\gamma \,||\, (011)\alpha$ [7], and there is evidence to suggest that the superledges involved in proeutectoid ferrite growth operate on this plane [3]. The energy attributed to an interphase interface in the $(111)\gamma \,||\, (011)\alpha$ orientation is about 0.2 J/m² [8], and this is taken to be equal to σ in the present calculations. Indeed, it was found that on plotting the experimentally observed ledge heights versus $\sigma/\Delta F_{\mathrm{v}}^{\mathrm{m}}$, and systematically varying σ, the slope of the straight line through the origin became the theoretically expected value of unity only when $\sigma = 0.195$ J/m², in good agreement with the value of 0.2 J/m² normally associated with the $(111)\gamma \,||\, (011)\alpha$ interface.

Because the $\Delta F_{\mathrm{v}}^{\mathrm{m}}$ term refers to nucleation (i.e., the formation of a very small amount of ferrite, which hardly leads to any significant change in the composition of the remaining austenite), it has to be calculated as in [9, 10] (its significance is illustrated in Fig. 1 of [9], and Fig. 1 of [10]). The details of the calculations for $\Delta F_{\mathrm{v}}^{\mathrm{m}}$ have already been stated in [10] (additional data in [11 to 13]), but the following approximations should be noted:

(i) To simplify the calculations, substitutional alloying elements are assumed not to partition between the ferrite and the austenite. Any errors due to this should be most significant at the highest of temperatures (i.e., at low supersaturations), but should in any case be small, since the analysis is confined to low-alloy steels (i.e., less than 1 wt% of alloying element content).

(ii) The presence of very small additions of Niobium has been ignored, due to the lack of pertinent thermodynamic data. This should not cause any significant errors in $\Delta F_{\mathrm{v}}^{\mathrm{m}}$.

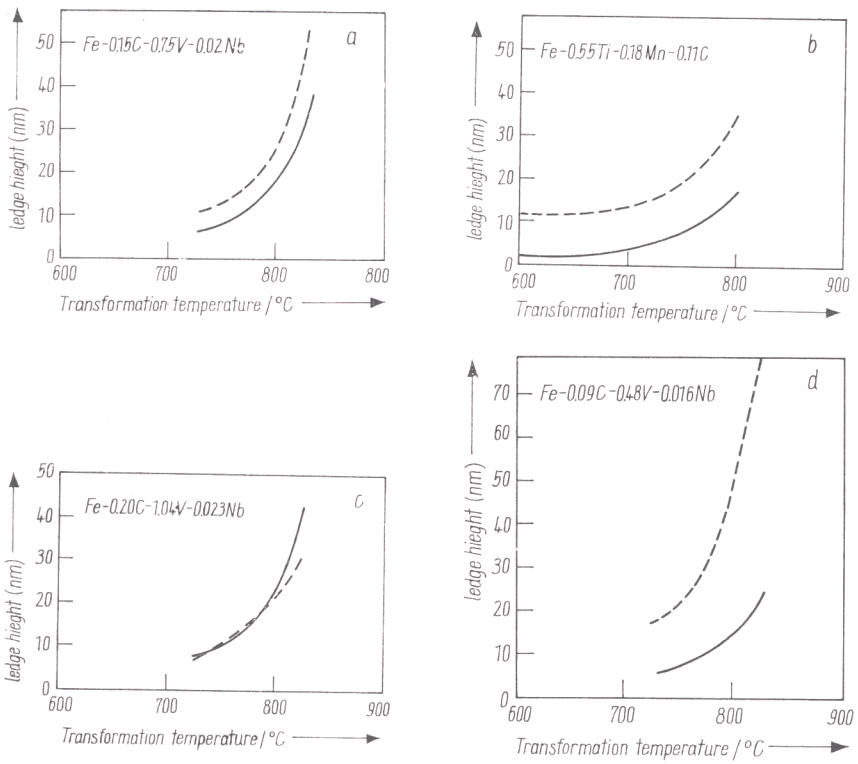


Fig. 3. Diagrams comparing the calculated minimum possible ledge height (continuous curves) with the experimental results of [4, 5] (dashed lines)

The results are presented in Fig. 3, where the dashed lines represent the published experimental information taken from [4, 5]. It is evident that in most cases, the measured ledge heights exceed the predicted minimum values of h^*; more significantly, the calculated and experimental curves both show strikingly similar trends, as a function of transformation temperature. One feature which is not fully understood is the variation in the separation between the experimental and theoretical curves, when comparing different steels. In fact, the way in which experimental data have been compared with the theory is approximate, since there is no reason why stepped growth should be confined to just one kind of a singular interface — low-energy interfaces other than the $(111)_\gamma \parallel (011)_\alpha$ have been theoretically predicted [7]. Furthermore, the precise geometry of ledge nucleation may also vary from the situation envisaged in Fig. 2, although this would not be expected to alter the form of (4) (there would presumably be a premultiplying 'shape factor'). Finally, a proper test of the theory requires a knowledge of the local crystallography in addition to the related ledge height data.

4. Conclusions

A nucleation based theory has been developed to explain the height of steps involved in the diffusional growth of ferrite, and to predict the variation of the expected ledge height with transformation temperature. The theory is in good agreement with ex-

perimental data in the sense that the observed step heights exceed the calculated minimum values (the theory also explains the temperature dependence of h), but it has not been possible to fix a well defined upper limit to h.

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