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Nucleation theory for high-carbon bainite

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Abstract

There is a great deal of interest in high-carbon (≥0.8 wt.%) bainite, both in the context of cast irons and in the development of novel very strong and tough steels. In this paper we investigate whether the theory describing the nucleation of bainite is appropriate for this new class of materials.

Keywords: Bainite; Nucleation; Steel; Kinetics

1. Introduction

There is considerable technological interest in high-carbon bainite in steels containing sufficient silicon to suppress the precipitation of cementite. In austempered ductile cast irons the carbon concentration in the austenite prior to the formation of bainite can be in excess of 1 wt.% [1–7]. It has also been discovered recently that bainite with a strength in excess of 2.3 GPa and a toughness of some 30 MPa $m^{1/2}$ can be obtained in high-carbon steels by transformation at very low temperatures [8,9].

It would be useful to design these kinds of materials using phase transformation theory, as has been done in the past for lower carbon steels [10–13]. To make comprehensive calculations requires a reliable nucleation model for bainite. The first such model was developed in 1981 [14,15] based on a dislocation mechanism and was validated on a large amount of published data on low-carbon steels.

The purpose of the work presented here was to see if the same nucleation model [15] can be used without modification for much higher carbon steels. We shall begin with martensitic nucleation in order to set the scene for bainitic nucleation, to be followed by new experimental data for very high carbon steels, and finally with an analysis of the data in terms of nucleation theory.

2. Martensitic nucleation

It is highly likely that martensite nucleates by a mechanism involving the dissociation of dislocations. This is straightforward to understand in the context of the transformation of a face-centred cubic crystal structure (e.g. austenite) into a hexagonal close-packed (h.c.p.) martensite. The essential difference between these two lattices is that the {1 1 1} planes of the f.c.c. structure are stacked in the sequence ...*ABCABC*... whereas the corresponding {0 0 0 1} planes of the h.c.p. ε-martensite structure follow the sequence ...*ABABAB*.... At constant density, all that is required to achieve the transformation is the change in stacking sequence, which can be achieved by the passage of a Shockley partial dislocation on successive close-packed planes. It is for this reason that a single f.c.c. stacking-fault has frequently been considered to be a nucleus for ε-martensite. The fault may then thicken into a plate via a pole mechanism [16]. Confidence in the mechanism was enhanced when Brooks et al. [17,18] were able to demonstrate that there is in fact a dilatation normal to the fault plane, corresponding to the expected change in density during transformation.

The corresponding faulting mechanism of nucleation for body-centred cubic (b.c.c.) α' martensite is more complex since the transformation strain is not an invariant-plane strain [19]. But the essential features of the mechanism remain unchanged, i.e. the nucleus relies on the development of faults by the propagation of partial dislocations.

The free energy of a unit area of fault is [19]:

$$G_F = n\rho(\Delta G_{CHEM} + G_{STRAIN}) + 2\sigma \quad (1)$$

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where n is the number of close-packed planes participating in the faulting process and ρ the spacing of the close-packed planes on which the faulting is assumed to occur. $\Delta G_{\mathrm{CHEM}} = G_V^{\alpha} - G_V^{\gamma}$, G_V is the Gibbs free energy per unit volume of α and G_{STRAIN} is the strain energy per unit volume of α; σ is the α/γ interfacial energy per unit area. The minimum force per unit length required to move the partial-dislocation array is $n\tau_0 b$ where τ_0 is the intrinsic resistance to their motion and b is the magnitude of the Burger's vector. The fault becomes unstable when

$$G_{\mathrm{F}} = -n\tau_0 b \tag{2}$$

and nucleation is said to occur.

Like all dislocations, the partials have to mount barriers G_0^* in order to move. However, the actual activation energy G^* is dependent on the applied stress τ [20,21]: this has the effect of reducing the height of this barrier:

$$G^* = G_0^* - (\tau - \tau_\mu)v^* \tag{3}$$

where v^* is an activation volume and τ_μ the temperature independent resistance to dislocation motion. In the context of nucleation, the stress τ is not externally applied but comes from the chemical driving force. On combining the last three equations we obtain

$$G^* = G_0^* + \left[\tau_\mu + \frac{\rho}{b}G_{\mathrm{STRAIN}} + \frac{2\sigma}{nb}\right]v^* + \frac{\rho v^*}{b}\Delta G_{\mathrm{CHEM}} \tag{4}$$

It follows that with this model of nucleation the activation energy G^* will decrease *linearly* as the magnitude of the driving force ΔG_{CHEM} increases. This direct proportionality contrasts with the inverse square relationship of classical theory.

3. Bainitic nucleation

The time–temperature-transformation diagram for a steel can be represented as in Fig. 1, where the temperature T_{h} represents the highest temperature at which displacive transformation to Widmanstätten ferrite or bainite is observed.

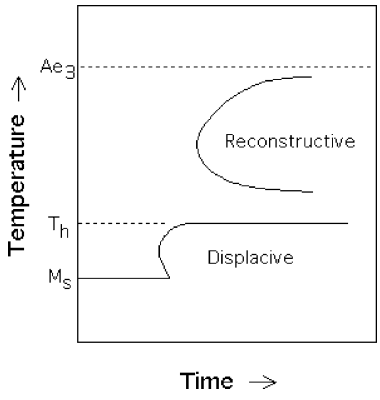

Fig. 1. Schematic time temperature transformation diagram illustrating the two C-curves and the temperature T_{h}.

It has been shown in previous work [14] that bainite and Widmanstätten ferrite nucleate by the same mechanism as martensite, but it is necessary for the carbon to partition because there isn't sufficient driving force for partitionless nucleation at the temperature T_{h} at which the transformations start. The nucleus then develops into bainite if diffusionless *growth* is possible.

Bhadeshia [14] found that if a large number of different steels are examined, and the critical value of the chemical free energy change $G_N = \Delta G_{\mathrm{CHEM}}\{T_{\mathrm{h}}\}$ at T_{h} is calculated, then a plot of G_N versus T_{h} is a straight line. This G_N function then defines the minimum free energy change necessary in any steel, in order to nucleate bainite; i.e. it is a universal nucleation function which can be used to accurately calculate transformation-start temperatures. He then went on to demonstrate that the straight line can be justified theoretically as follows.

The nucleation rate is given by

$$I_V \propto \nu \exp\left\{-\frac{G^*}{RT}\right\} \tag{5}$$

where ν is an attempt frequency. It follows that

$$-G^* \propto \beta T \quad \text{where } \beta = R \ln\left\{\frac{I_V}{\nu}\right\} \tag{6}$$

If it is assumed that there is a specific nucleation rate at T_{h}, irrespective of the type of steel, in which case β is a constant, negative in value since the attempt frequency should be larger than the actual rate. This gives the interesting result that

$$G_N \propto \beta T \tag{7}$$

which is precisely the relationship observed experimentally. This is evidence for nucleation by the dissociation of dislocations with the activation energy proportional to the driving force, as opposed to the inverse square relationship predicted by classical theory. The activation energy G^* in this model comes from the resistance of the lattice to the motion of dislocations.

4. Experiments

Our concern in this work was to establish that the same methodology that has been developed for low-carbon steels [14,15] can be used to describe the nucleation of bainite in high-carbon steels, without the need to define a new nucleation function. The steels listed in Table 1 were therefore studied experimentally to measure their bainite-start (B_{S}) temperatures; the alloys form a part of a programme of research on high-strength steels. The alloys were made as vacuum melts and the ingots were homogenised in vacuum at 1200 °C for 2 days. Rods of 3 mm diameter were then machined and sealed in quartz capsules containing pure argon,

Table 1
Chemical compositions of experimental alloys (wt.%)

Alloy	C	Si	Mn	Mo	Cr	V	Co	Cu	Al	W
1	0.79	1.59	1.94	0.30	1.33	0.11				
2	0.98	1.46	1.89	0.26	1.26	0.09				
3	0.76	1.60	1.04	0.29	1.31	0.10				
4	0.73	1.39	3.76	0.25	1.06		1.01			
5	0.85	1.49	3.40	0.25	1.01		0.93	0.20		
6	0.80	1.67	3.52	0.24	1.01		1.44	0.20		0.99
7	0.83	1.57	1.98	0.24	1.02		1.54			
8	0.78	1.49	1.95	0.24	0.97		1.60		0.99	

Table 2
Measured transformation-start temperatures

Alloy	1	2	3	4	5	6	7	8
M_S (°C)	125	125	173	105	135	136	120	155
B_S (°C)	310	335	415	275	335	335	360	385

austenitised at 1000 °C for 15 min followed by isothermal transformation to bainite. The isothermal experiments were conducted at 25 °C intervals beginning with 250 °C and raising the temperature until bainite was not observed over a 24 h period. In some cases (alloys 3, 7, 8), smaller temperature intervals (20 °C) were used close to B_S. The highest temperature at which bainite was observed using optical microscopy was designated B_S.

The martensite-start temperatures M_S were determined using 2 mm diameter samples in a high-resolution dilatometer. The samples were heated to 1000 °C and then force cooled using helium at 100 or 200 °C s^{-1} to measure the M_S temperature. The results are listed in Table 2.

5. Analysis

The B_S data presented in Table 2 were together with the data of Steven and Haynes [22] used in the original analysis [14], and some new data found in the literature [23].

The chemical free energy change which must be substituted into Eq. (7) is that for the paraequilibrium transformation of austenite into a mixture of ferrite and carbon-enriched austenite ($\Delta G^{\gamma\rightarrow\gamma'+\alpha}$). Even this has to be modified to account for the fact that although the ferrite is practically carbon-free, the austenite is hardly enriched given that only a minute quantity of ferrite formed during nucleation [15]; the change appropriate during nucleation is usually designated ΔG_m. However, we shall neglect this latter complication and assume that $\Delta G^{\gamma\rightarrow\gamma'+\alpha} \propto \Delta G_m$ in order to avoid complications in the use of MTDATA [25] to do the calculations; there is some justification for this approximation [15].

Fig. 2 shows a plot of G_N versus T_h for all the steels. It is evident that they can all be represented rather well by a single straight line with the equation:

$$G_N = 3.5463T_h - 3499.4\,\text{J mol}^{-1} \quad (8)$$

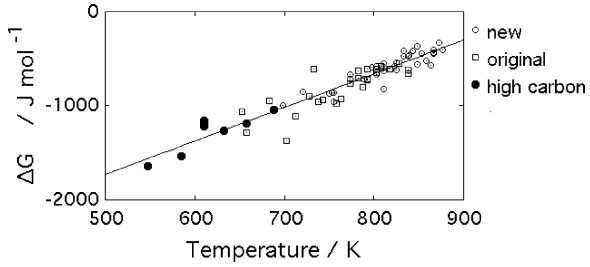

Fig. 2. Plot of the free energy change $\Delta G^{\gamma\rightarrow\gamma'+\alpha}$ (calculated using MTDATA) vs. T_h. The "original" data refer to Steven and Haynes [22], the "new" data to Chang [24] and Zhao et al. [23] and the "high-carbon" data are from Table 2.

where the units of T_h are in Kelvin and the correlation coefficient is 0.94. The high-carbon steels behave in the same way as the others, which means that the same theory can be used in the design of austempered ductile cast irons and very high-strength steels.

Eq. (8) defines the G_N function which can henceforth be used in conjunction with MTDATA to calculate the B_S temperature of any steel, simply by finding the temperature by satisfying two conditions [15]. Bainite is expected below the T'_0 temperature when:

$$\Delta G^{\gamma\rightarrow\alpha} < -G_{SB} \quad (9)$$

$$\Delta G_m < G_N \quad (10)$$

where G_{SB} is the stored energy of bainite (about 400 J mol^{-1}). $\Delta G^{\gamma\rightarrow\alpha}$ is the free energy change for diffusionless growth. The calculation procedure is illustrated in Fig. 3.

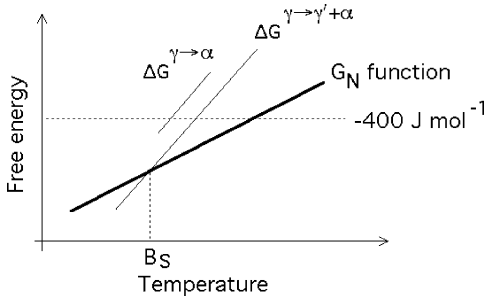

Fig. 3. Calculation of B_S temperature using the G_N function.

6. Conclusions

It has been demonstrated that within the limits of experimental error, the same nucleation theory can be used for high and low carbon steels, for the calculation of the bainite-start temperature.

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