Short Communication

Nucleation of Widmanstätten ferrite

Recently published experimental data on the variation of the highest temperature at which Widmanstätten ferrite can be seen to form at a detectable rate, as a function of steel chemistry, are analysed theoretically. It is found that the data can be predicted to a fair accuracy if it is assumed that the nucleation of Widmanstätten ferrite occurs by a mechanism similar to that of martensitic nucleation, but with the diffusion of carbon during nucleation, and if it is additionally assumed that the growth of Widmanstätten ferrite can only be sustained when the chemical driving force exceeds a specific stored energy term. *MST/1210*

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Introduction

Widmanstätten ferrite can sometimes be detrimental[1,2] to the mechanical properties of steels, because the ferrite plates often grow in parallel formations which permit cleavage cracks to propagate without much deviation.[3,4] The problem is particularly acute in steel weld deposits, where it is impractical to modify the microstructure which evolves during solidification and during subsequent cooling to ambient temperature, by the type of thermomechanical processing usually used to refine the microstructure in wrought alloys. Consequently, alloy design is the main route available for the minimisation of the quantity of Widmanstätten ferrite, and this in turn requires a good knowledge of the factors controlling its nucleation and growth.

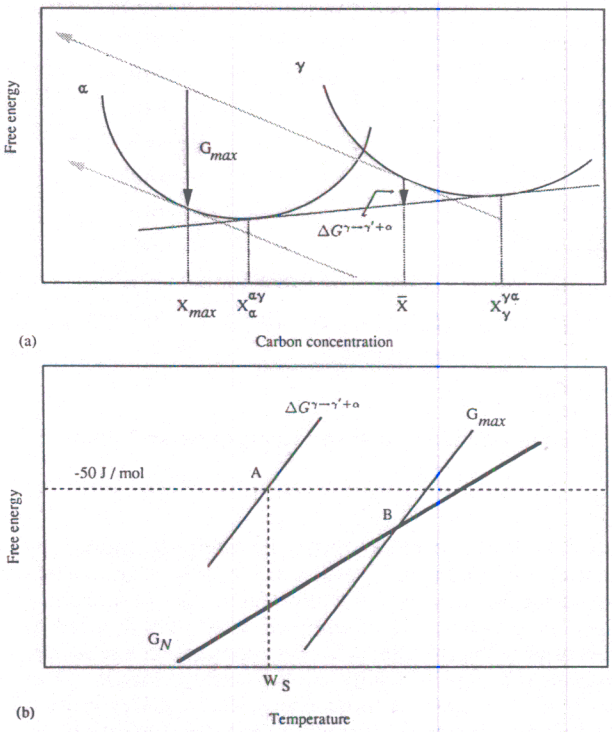
The purpose of this communication is to show that some recently published data[5] on the Widmanstätten start temperature, as a function of alloy chemistry, can be predicted using a model already available for the nucleation and growth of Widmanstätten ferrite. The data were originally[5] interpreted by considering the transition from allotriomorphic to plate-like ferrite to be determined by changes in the relative proportions of 'partially coherent' and 'disordered' regions of interface surrounding the ferrite particles. Whatever the details of the model,[5] that theory is indeterminate, since the proportion was found not to be constant and could not be predicted as a function of alloy chemistry.

Results and discussion

The growth of Widmanstätten ferrite is reasonably well understood.[6–8] The lengthening rate of an individual plate can be predicted to a fair degree of accuracy, as a function of alloy chemistry and transformation temperature, if it is assumed that growth occurs under paraequilibrium conditions at a rate controlled by the diffusion of carbon in the austenite ahead of the plate tip. The tip radius must be taken to be that which gives the maximum lengthening rate, when capillarity effects are taken into account. In calculating the carbon concentration at the plate tip, allowance must also be made for the stored energy term (~ 50 J mol^{-1}) arising from the displacive mode of growth.

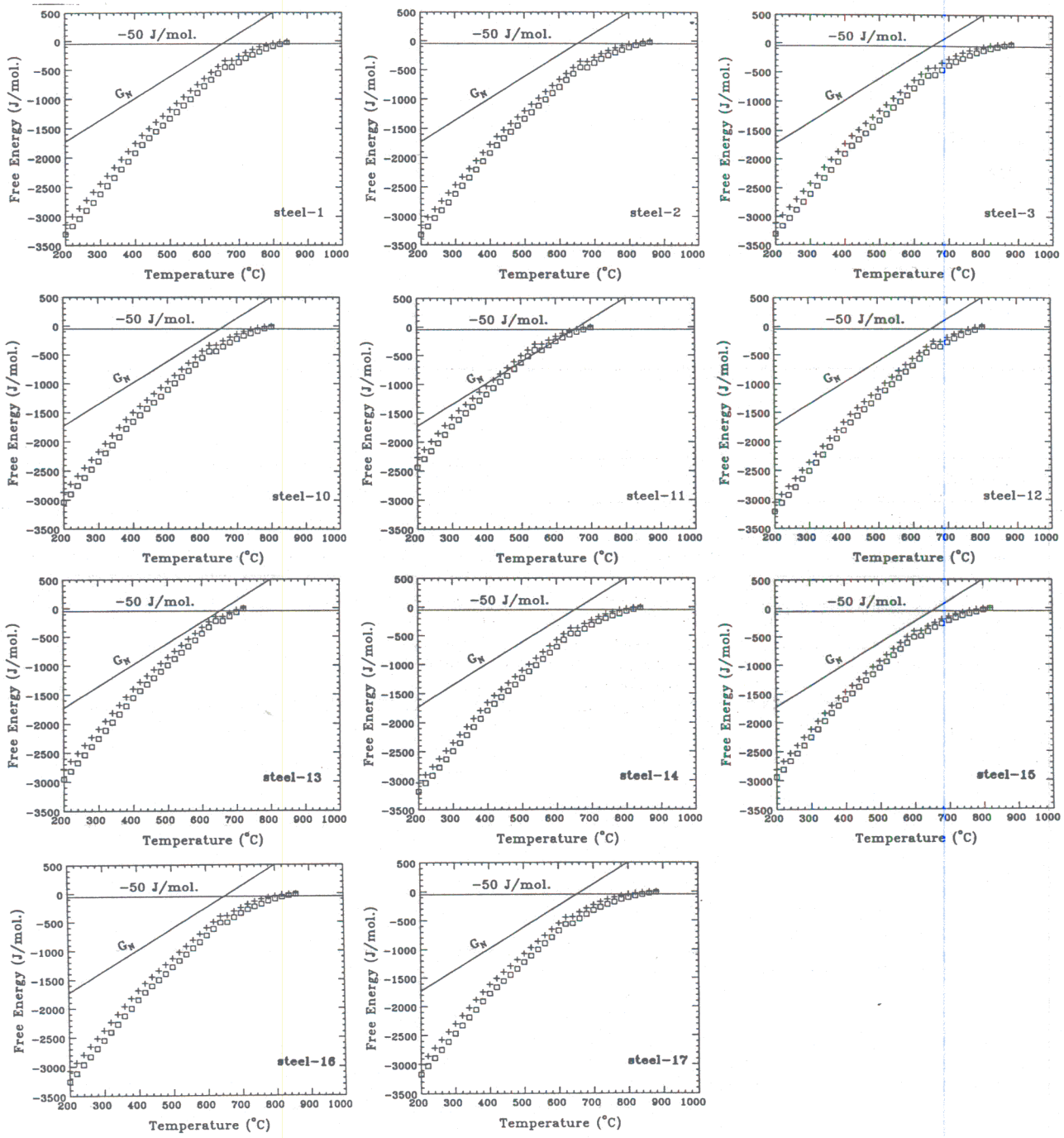
By contrast, the nucleation of Widmanstätten ferrite is not understood in detail. The Widmanstätten start temperature W_s can be identified as the highest isothermal transformation temperature at which Widmanstätten ferrite is found to form in detectable quantities. An interesting feature of the W_s temperature is that it is more sensitive to alloy chemistry than the Ae_3 temperature, which is the highest temperature at which α ferrite and austenite can coexist in equilibrium.[6,9] The W_s temperature is often found to decrease more rapidly with suitable solute additions than the Ae_3 temperature, indicating that the effect of alloying elements on Widmanstätten ferrite is in many cases more than just thermodynamic.

It has been demonstrated[9] that the behaviour described above can be rationalised if it is assumed that the nucleation of Widmanstätten ferrite is similar to that of martensite, i.e. the activation energy G^* for nucleation varies directly with the magnitude of the chemical driving force ΔG,



intersections at A and B determine temperatures where growth and nucleation conditions are satisfied; in example illustrated, it is growth which limits W_S temperature

1 ***a*** **Schematic illustration of terms G_{max} for nucleation and $\Delta G^{\gamma\rightarrow\gamma'+\alpha}$ for growth and** ***b*** **schematic illustration of conditions determining Widmanstätten start temperature**



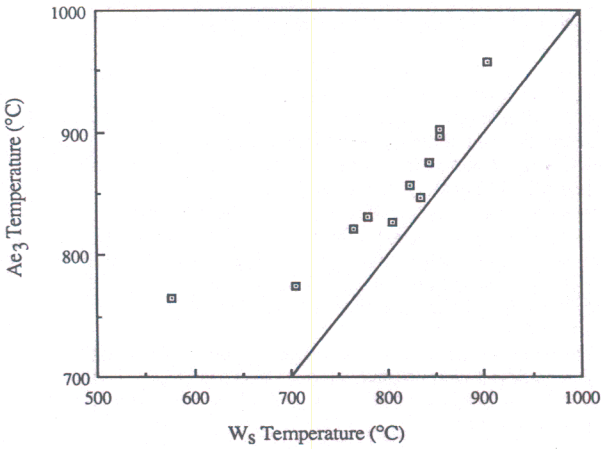
2 Driving forces for specific steels given in Table 1

rather than the inverse square relationship implied by classical nucleation theory where $G^* \propto (\Delta G)^{-2}$. In martensite nucleation theory,[10] this dependence is interpreted to imply the pre-existence of embryos, which simply need to grow rapidly to give what is in effect operational nucleation, controlled by the mobility of the embryo/matrix interface.[11,12] It is the activation energy for interface motion which is detected experimentally as that for nucleation. An analysis of kinetic data for a large number of steels[6,9] was found to indicate that, owing to the lower driving force available at the higher temperatures where Widmanstätten ferrite forms, it is necessary for its nucleation to occur by a paraequilibrium mechanism involving the partitioning of carbon, whereas that of martensite is diffusionless.

The implication of this is that it becomes more difficult (i.e. requires a larger driving force) to obtain a detectable degree of nucleation as transformation is suppressed to lower temperatures by solute additions, so that the W_s temperature decreases more rapidly than the Ae_3 temperature with change in alloy chemistry. In fact, the free energy G_N necessary to obtain a detectable degree of transformation is found to be an approximately linear function of temperature[9]

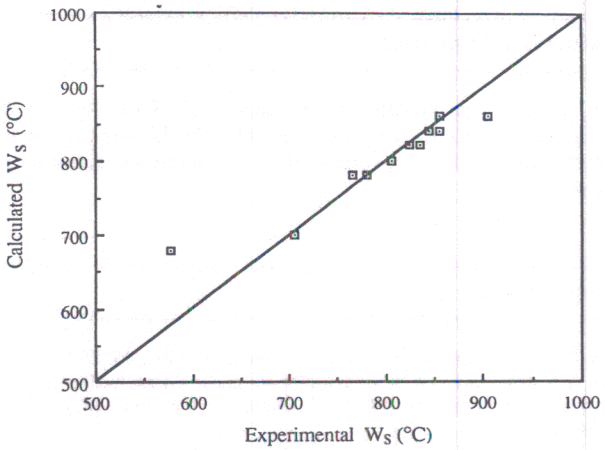
$$G_N = A + B(T - 273{\cdot}18) \quad \ldots\ldots\ldots \quad (1)$$

and this is a universal function which can be applied to any low alloy steel. The constant $A = -2540$ J mol^{-1} and $B = 3{\cdot}637$ J mol^{-1} K^{-1} (Ref. 6). The driving force G_{max} that



full line is line of unit slope and zero intercept; deviations from this line therefore represent cases where Ae_3 and W_s temperatures are not identical

3 Ae_3 temperatures versus measured W_s temperatures for steels studied in Ref. 5



4 Comparison of calculated and experimentally determined[5] Widmanstätten start temperatures

is available for nucleation in any given steel, must exceed G_N, giving the condition

$$G_{max} \leqslant G_N \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where G_{max} represents the maximum free energy change possible during nucleation, assuming that the nucleus adopts the chemical composition consistent with the maximum change in free energy[6] (Fig. 1).

The second condition that must also be satisfied is that growth should be thermodynamically possible, so that the free energy change for growth (Fig. 1) should exceed the stored energy of Widmanstätten ferrite

$$\Delta G^{\gamma \rightarrow \gamma' + \alpha} < -50 \text{ J mol}^{-1} \quad \ldots\ldots\ldots \quad (3)$$

It is the simultaneous satisfaction of these two conditions which gives the highest temperature at which a detectable degree of reaction occurs. These concepts are illustrated schematically in Fig. 1.

The calculations for most of the steels (Table 1) studied by Aaronson *et al.*[5] are presented in Fig. 2. A few of the steels they studied contained substantial amounts of copper, cobalt, or aluminium, elements for which thermodynamic data compatible with the Lacher–Fowler–Guggenheim quasichemical solution model used here, are not available.[13] Consequently, those steels are not included in the analysis. Figure 3 is a plot of the Ae_3 temperatures versus the measured W_s temperatures. The full line on Fig. 3 is a line of unit slope and zero intercept; deviations from this line therefore represent cases where the Ae_3 and W_s temperatures are not identical. This figure shows that for almost all the steels given in Table 1, the W_s temperature is directly proportional to the Ae_3 temperature, a consequence of the fact that in most cases it is determined by equation (3). However, for steel 11, which is heavily alloyed with manganese, the W_s temperature is suppressed to a greater extent, when compared with the Ae_3 temperature, as is predicted by the present analysis, because for that steel the undercooling necessary to satisfy the nucleation condition (equation (2)) is larger than for the growth condition (equation (3)). The fact that most of the experimental data can be predicted using equation (3) implies that for the low alloy steels concerned, the W_s temperature is determined by the need to accumulate sufficient free energy to permit growth, rather than by an inability to achieve a detectable nucleation rate. It is evident (Fig. 4) that there is very good agreement between experiment and theory.

To summarise, it has been found possible to explain the large variations in the Widmanstätten ferrite start temperatures determined metallographically[5] for a series of ternary steels, using a previously published theory[6,9] on the nucleation and growth of Widmanstätten ferrite.

Table 1 Chemical composition of steels used in Ref. 5 and values of $W_{s(exp)}$, $W_{s(calc)}$, and Ae_3

Steel no.	Composition, wt-%									Temperature, °C		
	C	Si	Mn	Cr	Mo	Ni	Al	Co	Cu	$W_{s(exp)}$	$W_{s(calc)}$	Ae_3
1	0·110	...	...	...	...	...	...	...	...	825	820	857
2	0·096	0·51	...	...	...	...	...	...	...	855	840	897
3	0·120	1·47	...	...	...	...	...	...	...	905	860	957
4	0·098	...	...	...	...	...	...	1·02	...	835	...	872
5	0·140	...	...	...	...	...	...	3·20	...	855	...	872
6	0·089	...	...	...	...	...	0·52	...	...	875	...	932
7	0·270	...	...	...	...	...	1·40	...	...	905	...	957
8	0·096	...	...	...	...	...	...	...	1·02	815	...	842
9	0·120	...	...	...	...	...	...	3·20	2·98	755	...	807
10	0·110	...	1·01	...	...	...	...	...	...	765	780	822
11	0·120	...	3·08	...	...	...	...	...	...	577	680	765
12	0·093	...	...	...	...	1·06	...	...	...	780	780	832
13	0·110	...	...	...	...	3·28	...	...	...	705	700	775
14	0·092	...	...	0·94	...	...	...	...	...	835	820	847
15	0·092	...	...	2·64	...	...	...	...	...	805	800	827
16	0·110	...	...	...	0·90	...	...	...	...	845	840	876
17	0·110	...	...	...	1·95	...	...	...	...	855	860	902

Values of $W_{s(calc)}$ are from present work and those of $W_{s(exp)}$ are from Ref. 5.

Acknowledgments

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