Formation of Nanostructured Steels
by Phase Transformation

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Introduction

The purpose of this paper is to develop thermodynamic criteria which define the finest grain structures that can be achieved in steels, and to see how far current technology is from achieving the minimum possible grain size.

In a pure material, a grain boundary is a region where the adjacent crystals do not match perfectly and hence is associated with an excess free energy per unit area (σ). In alloys, there may also be a difference in chemical composition of the abutting crystals and that of the boundary may in turn differ from that of the bulk crystals. These differences contribute a chemical component to σ.

For an equiaxed polycrystalline grain structure, the grain boundary surface per unit volume (S_V) is related to the grain size $\overline{L}$ (mean lineal intercept) by the equation $S_V = 2/\overline{L}$. The stored energy per unit volume due to the grain boundaries is then

$$\Delta G_V = \sigma S_V = 2\sigma/\overline{L} \tag{1}$$

Grain size refinement is an important method for improving both the strength and toughness of engineering alloys. In the context of steels, the stable phase at ambient temperature is generally ferrite (α), which is generated by transformation from austenite (γ). If $\Delta G_V^{\gamma\alpha}$ is the free energy change per unit volume when austenite transforms into ferrite, then

$$|\Delta G_V^{\gamma\alpha}| \geq \sigma S_V^{\alpha} - \sigma S_V^{\gamma} \tag{2}$$

which for equiaxed austenite–grains becomes

$$|\Delta G_V^{\gamma\alpha}| \geq \frac{2\sigma_\alpha}{\overline{L}_\alpha} - \frac{2\sigma_\gamma}{\overline{L}_\gamma} \tag{3}$$

It follows that the smallest ferrite grain size that can be achieved is when all of $G_V^{\gamma\alpha}$ is used up in creating α/α grain boundaries, so that

$$\overline{L}_\alpha^{min} = \frac{2\sigma_\alpha}{|\Delta G_V^{\gamma\alpha}| + 2\sigma_\gamma/\overline{L}_\gamma} \tag{4}$$

The term $2\sigma_\gamma/\overline{L}_\gamma$ arises when the formation of ferrite destroys the austenite grain boundaries, thus providing a thermodynamic gain which adds to the driving force for transformation. There are a number of interesting insights to be gained from this equation. A reduction in the austenite grain size should always lead to a corresponding reduction in the ferrite grain size; however, the magnitude of the change depends also on $|\Delta G_V^{\gamma\alpha}|$, *i.e.* on the undercooling at which the $\gamma \rightarrow \alpha$ transformation occurs. The austenite grain size becomes less important at large undercoolings. Equation 4 is not correct when dealing with anisotropic austenite

grains because of their greater surface to volume ratios [1,2,3]; the relationship between S_V and $\overline{L}$ is then different from the one assumed above [4]. Mechanical deformation prior to phase transformation therefore enables smaller values of $\overline{L}_\alpha^{min}$.

It has been assumed here that σ_γ is constant, but crystallographic texture may lead to a reduction in stored energy if low Σ orientations are introduced by thermomechanical processing. Random, high–energy austenite grain boundaries are ideal for the achievement of the smallest ferrite grains.

As shown below, these elementary equations can be used to study the grain sizes achieved in industrial steels.

Allotriomorphic Ferrite

Most engineering steels have a microstructure dominated by allotriomorphic ferrite; the steels are produced under conditions of continuous cooling transformation. A large variety of data exist in the published literature [5–25], for steels in roughly composition categories: Fe–0.15C–0.2Si–0.7Mn and Fe–0.15C–0.2Si–1.5Mn wt%. However, the published data are in general incomplete. Thus, the transformation temperature $\mathrm{Ar_3}$ was in each case calculated empirically [24,25]:

$$\mathrm{Ar_3} \simeq 910 - 80x_{\mathrm{Mn}} - 20x_{\mathrm{Cu}} - 15x_{\mathrm{Cr}} - 55x_{\mathrm{Ni}} - 80x_{\mathrm{Mo}} - 40\log\{\dot{T}\} \qquad (5)$$

where x is the concentration in wt% and $\dot{T}$ the cooling rate in $\mathrm{K\,s^{-1}}$. The equation is based on steels which have been deformed by rolling to greater than 50% reduction in a temperature regime where the austenite does not recrystallise, with cooling rates in the range 1–10 $\mathrm{K\,s^{-1}}$.

The free energy change ΔG_V at the calculated transformation temperature $\mathrm{Ar_3}$ was estimated using MTDATA in combination with the SGTE database [26], for the reaction $\gamma \rightarrow \gamma' + \alpha$, assuming paraequilibrium. The symbol γ' stands for carbon–enriched austenite.

Fig. 1 shows the variation in the ferrite grain size ($\overline{L}_\alpha^{min}$) as a function of ΔG_V, calculated using equation 3 with $\sigma_\alpha = 0.6\,\mathrm{J\,m^2}$; given the absence of data the $2\sigma_\gamma/\overline{L}_\gamma$ term in equation 3 was set to zero. These calculations are presented as the 'ideal' curve in Fig. 1. The curve indicates that at large grain sizes, $\overline{L}_\alpha^{min}$ is very sensitive to ΔG_V, i.e. the undercooling below the equilibrium transformation temperature. However, reductions in grain size in the submicrometer range require huge values of ΔG_V, meaning that the transformations would have to be suppressed to large undercoolings to achieve fine grain size.

Also plotted on Fig. 1 are points corresponding to measured ferrite grain sizes from the low and high–Mn steels as described earlier; the ΔG_V values are calculated for the appropriate transformation temperatures. It is evident that except at the lowest undercoolings, $\overline{L}_\alpha \gg \overline{L}_\alpha^{min}$.

The experimental data all represent continuously cooled steels; during transformation, the enthalpy change leads to recalescence. The maximum temperature rise due to recalescence can be estimated using:

$$\Delta T^{max} \simeq \Delta H/C_\gamma \qquad (6)$$

where ΔH is the change in enthalpy associated with the phase transformation (calculated using MTDATA for $\mathrm{Ar_3}$) and C_γ the appropriate heat capacity. The value of ΔG_V was then recalculated for the temperature $\mathrm{Ar_3} + \Delta T$, assuming that all the enthalpy change is used up in instantaneously heating the sample. The curves marked low and high–Mn on Fig. 1 represent these recalescence corrected curves corresponding to the ideal case where there an enthalpy change is dissipated isothermally at $\mathrm{Ar_3}$. It is seen that the recalescence corrected curves show better agreement with the experimental data, indicating that at large undercoolings,
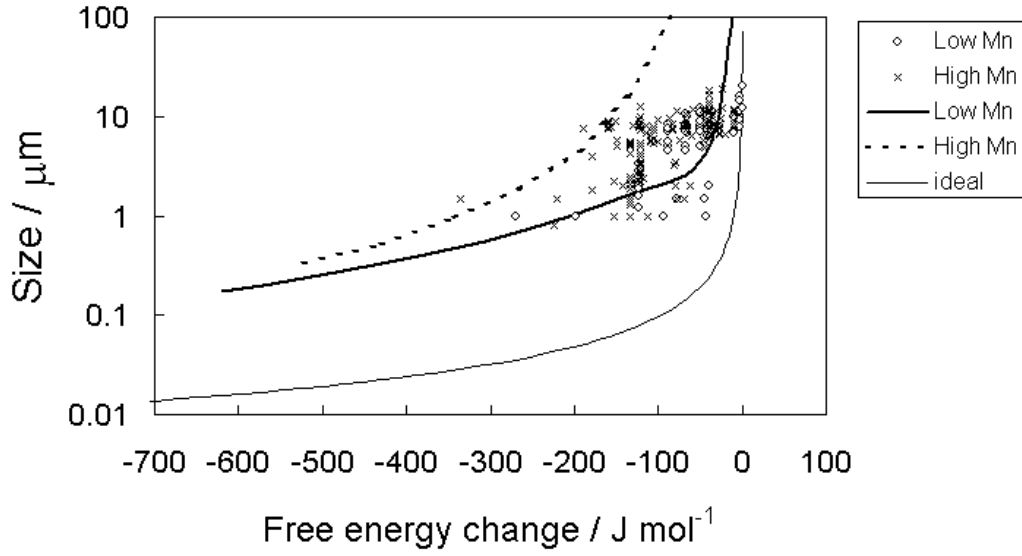
Fig. 1: Plot of the logarithm of ferrite grain size versus the free energy change at Ar_3. The ideal curve represents the values of $\overline{L}_\alpha^{min}$. The points are experimental data. The curves marked low and high–Mn represent calculated values of $\overline{L}_\alpha^{min}$ after allowing for recalescence.

the achievement of fine grain size is limited by the need to dissipate enthalpy during rapid transformation.

There are therefore two significant conclusions from this work. The first is that from the form of equation 3, it is necessary to achieve very large undercoolings before submicrometer grain sizes can be achieved. The difficulty when these large undercoolings are attained is that the enthalpy of transformation is likely to lead to recalescence, so that the actual grain size obtained is more than an order of magnitude greater than can be obtained in principle. It is necessary to design some industrial process which enables isothermal transformation at large undercoolings.

Bainite and Martensite

Strain energy dominates displacive transformations and this is reflected in their characteristically fine and plate–like microstructures. In what follows, the microstructure is discussed primarily in terms of the plate thickness, since for a plate–shape, the mean lineal intercept is twice the thickness, almost independent of the plate length.

The elastic strain energy per unit volume (G_V^e) of a transformed region with the same shear modulus (μ) and Poisson's ratio (ν) as the isotropic constraining matrix is given by [27]:

$$\frac{1-\nu}{\mu}G_V^e = \overbrace{\frac{2}{9}(1+\nu)\Delta^2 + \frac{\pi t}{4l}\delta^2 + \frac{\pi t}{3l}(1+\nu)\Delta\delta}^{\text{due to volume change}} + \underbrace{\frac{\pi}{8}(2-\nu)\frac{t}{l}s^2}_{\text{due to shear}} \tag{7}$$

$$\text{or} \qquad G_V^e \simeq \frac{t}{l}\mu(s^2+\delta^2)$$

where Δ is the uniform dilatation strain which is now known to be zero and the other strains s and δ are illustrated in Fig. 1. t and l are the thickness and diameter respectively of the oblate spheroid shape used to represent the martensite plate. For typical values of the parameters in equation 7, with $t/l = 0.05$, $G_V^e \simeq 600$ J mol^{-1}, which is large, and the reason why the plates tend to be thin.

Assuming that a martensite plate can grow unhindered across an austenite grain of size $\overline{L}_\gamma$, the mean lineal intercept. The maximum thickness of the plate is obtained by balancing the chemical free energy change accompanying transformation $\Delta G^{\gamma\alpha}$ against G_V^e, *i.e.*

$$t \simeq \frac{|\Delta G^{\gamma\alpha}| \times \overline{L}}{\mu(s^2 + \delta^2)} \tag{8}$$

The plate thickness defines the mean free slip distance which is about $2t$ [4] and hence is the effective grain size. With these assumptions, the size of elastically accommodated martensite plates is related directly to the austenite grain size and the driving force for transformation. The mean size of the plates within a single austenite grain will be somewhat smaller than predicted because of the way in which the plates geometrically partition the parent phase. Notice how the shape deformation plays a vital role in determining the scale of the microstructure, with the shear strain dominating the equation.

Plastically Accommodated Plates

A displacive transformation is accomplished by the translation of a glissile interface, whose motion can be halted by defects in the austenite. Dislocations are created when the shape deformation is accommodated by plastic relaxation of the surrounding austenite [28,29]. The growing plate then brings itself to a halt before it collides with a hard obstacle such as an austenite grain surface. This is vividly illustrated by the sub–unit mechanism of bainite [30,31], in which an individual sheaf consists of a myriad of much smaller plates, each of which grows to a limited size which can be much smaller than that of the austenite grain.

Equation 8 indicates that during unhindered growth, thermoelastic equilibrium requires that the plates are coarser at low temperatures where $|\Delta G^{\gamma\alpha}|$ is largest. This trend contradicts observations because plastic relaxation prevents the bainite from achieving thermoelastic equilibrium. Since austenite is weaker and dynamic recovery more likely at high temperatures, the plates in fact become thicker at elevated transformation temperatures. It is found that an increase in the strength of austenite by 100 MPa leads to approximately a 0.2 μm decrease in the thickness of bainite plates [32,33]; the intrinsic effects of $\Delta G^{\gamma\alpha}$ and temperature are found to be much smaller in comparison (Fig. 2). By obtaining bainite in a strong austenitic steel at a large driving force, it has been possible to obtain plates which are between 20–40 nm thick, resulting is steels which are 2.5 GPa strong whilst at the same time exhibiting respectable toughness [34]. The reason why the thickness tends to level out beyond a strength of about 120 MPa in Fig. 2b is not understood, but investigations show that it is not because the plates become elastically accommodated.

Recrystallised Plates

When equiaxed grain structures are required, they can be generated by deformation followed by recrystallisation but in the context of current trends, this does not lead to a sufficiently fine grain structure. The extent of deformation needed also limits the form of the final product.

Tsuji and co–workers [37,38] have developed a process which avoids these difficulties by starting with a martensitic microstructure, which already has a high stored energy. Martensite can therefore be recrystallised without any additional deformation. However, Tsuji *et al.* discovered that a small amount of plastic strain ($\simeq 50\%$) applied to a martensitic microstructure
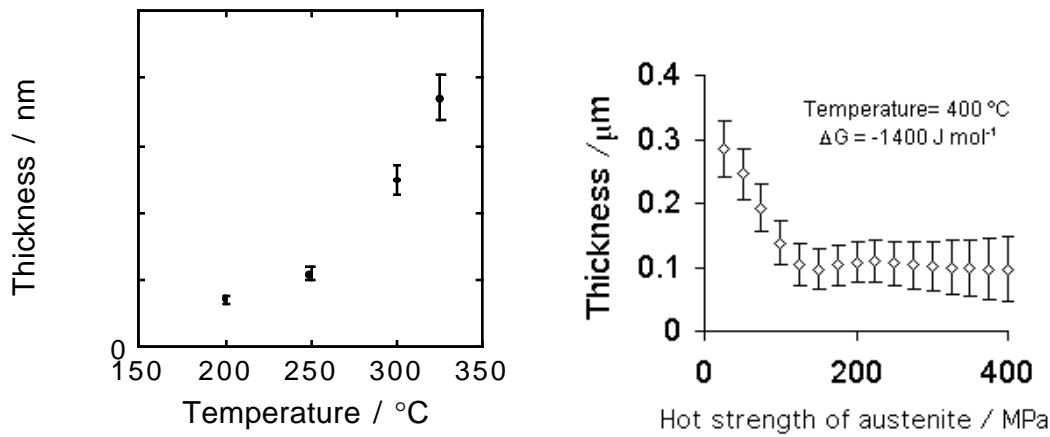
Fig. 2: (a) Stereologically corrected thickness of bainite plates as a function of the transformation temperature [35]. (b) An example of the variation in thickness as a function of austenite strength. The calculations represent the latest analysis using the method described in [36Singh].

introduces three kinds of heterogeneities in the martensite, which have the effect of subdividing it. These are fine dislocation cells, irregularly bent laths and kinked laths and in each case the defect results in large local–misorientation, thereby providing ideal sites for the generation of new grains during annealing.

Defining grain size in terms of regions with a critical level of misorientation, the original martensite was judged to have a grain size of 3.2 μm. Its subdivision by heterogeneous deformation, led by the same definition, to an equiaxed grain size of about 180 nm after annealing, a reduction in scale by a remarkable factor of 18.

SUMMARY

The challenge in nanostructured steels is to obtain very fine grain size, high strength and toughness, in bulk samples and at a cost which is reasonable. It appears, however, that recalescence is likely to limit the size of the allotriomorphic ferrite grains that can be obtained during continuous cooling transformation. On the other hand, displacive transformations lead to fine microstructures as a natural consequence of their atomic mechanisms. Commercially viable nanostructured–steels based on bainite and martensite are already at an advanced stage of exploitation. Nevertheless, a fundamental understanding of the role of plastic accommodation of the shape deformation, in limiting the scale of the microstructure, is lacking.

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