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Martensite and Bainite in Steels: Transformation Mechanism & Mechanical Properties

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Abstract: Many essential properties of iron alloys depend on what actually happens when one allotropic form gives way to another, *i.e.* on the mechanism of phase change. The dependence of the mechanical properties on the atomic mechanism by which bainite and martensite grow is the focus of this paper. The discussion is illustrated in the context of some common engineering design parameters, and with a brief example of the inverse problem in which the mechanism may be a function of the mechanical properties.

1. INTRODUCTION

More than 70% of all the steel that is used in modern economies has been invented within the last ten years. Novel iron alloys are being conceived, manufactured and marketed with a regularity which has confounded many prophecies. There is also elation in academia, because a few of the interesting alloys have come about from a basic understanding of steels.

The science is usually in the form of the detailed mechanisms of phase transformations, but this alone cannot lead to better steels. It is the mechanical properties which are important to engineers, who generally do not have a passion for transformations. To them, design does not consist simply of some theoretical calculations which produce an alloy with the required properties. The manufacture of any new material must be at a competitive cost, and it ought to be possible to fabricate it without difficulty. The new development may necessitate additional or novel manufacturing equipment. The best steel companies only permit capital investment if the profit is improved sufficiently to pay off that investment within two years. This is because the steel industry has in the past focussed too heavily on fixed assets with large burdens of debt servicing. On the other hand, the discovery may, in rare circumstances, be of sufficient importance to warrant longer term strategic investment.

It is worth emphasizing that good design usually emerges from a problem which does not have a unique solution. Creativity is therefore as important as scientific design in the commercial success of an alloy. It is frequently useful to design more than one alloy (or microstructure or heat treatment) for the same purpose. It is in this light that we shall consider the relationship between the mechanism and mechanical properties of two microstructures rather than one. For the sake of economy, we shall assume that the basic experimental features of both bainite and martensite are well known, for example, the plate shape, the shape deformation, the role of the alloying elements *etc.*

2. MECHANISM OF DISPLACIVE TRANSFORMATION

The Bain strain converts the structure of the parent phase into that of the product phase. When combined with an appropriate rigid body rotation, the net homogeneous lattice deformation **RB** is an invariant–line strain (Fig. 1), giving good fit only along a single line common to the two crystals. However, the observed shape deformation indicates a larger degree of fit. The shape change is in fact an invariant–plane strain (IPS) $\mathbf{P_1}$, but this gives the wrong crystal structure. If, however, a second homogeneous shear $\mathbf{P_2}$ is combined with $\mathbf{P_1}$, then the correct structure is obtained but the wrong shape since

$$\mathbf{P_1 P_2} = \mathbf{RB} \tag{1}$$

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These discrepancies are all resolved if the shape changing effect of $\mathbf{P_2}$ is canceled macroscopically by an inhomogeneous lattice–invariant deformation, which may be slip or twinning as illustrated in Fig. 1.

The theory illustrated explains all the essential features of martensite or bainite crystallography [1,2]. It is easy to predict the orientation relationship, by deducing the Bain strain and adding a rigid body rotation which makes the net lattice deformation an invariant–line strain. The habit plane does not have rational indices because the amount of lattice–invariant deformation needed to recover the correct macroscopic shape is not usually rational. The theory predicts a substructure in plates of martensite (either twins or slip steps) as is observed experimentally. The transformation goes to all the trouble of ensuring that the shape deformation is macroscopically an invariant–plane strain because this reduces the strain energy when compared with the case where the shape deformation might be an invariant–line strain.

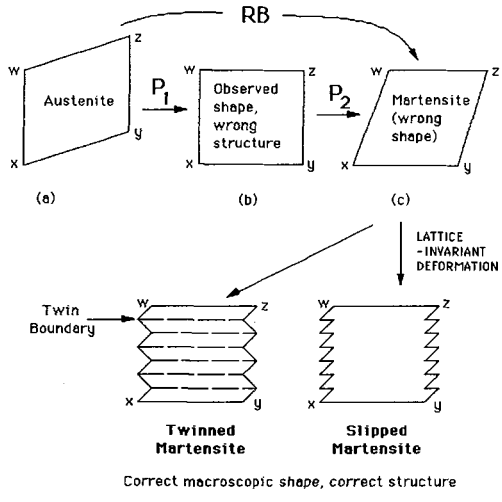

Fig. 1: Illustration of the phenomenological theory of martensite crystallography [3].

The mechanism of transformation outlined above is valid for both martensitic and bainitic transformations, though there are subtle differences. It is not appropriate here to discuss these in detail, but some of important characteristics are highlighted in Table 1. We shall now proceed to relate mechanical properties to the mechanism of transformation.

	α'	α_b		α'	α_b
Nucleation & growth reaction	√	√	Large shear	√	√
Plate shape	√	√	IPS shape deformation	√	√
Diffusionless nucleation	√	×	Diffusionless growth	√	√
Carbon diffusion during nucleation	×	√	Carbon diffusion during growth	×	×
Substitutional diffusion during nucleation	×	×	Substitutional diffusion during growth	×	×
Confined to austenite grain	√	√	Glissile interface	√	√

Table 1: Transformation characteristics for bainite (α_b) and martensite (α') [4].

3. TEMPER EMBRITTLEMENT

The observed IPS shape deformation during displacive transformation in steel proves that there is a synchronized motion of atoms. Such a coordinated motion of atoms cannot be sustained across austenite

grain boundaries. Bainite and martensite plates are therefore confined within the grain in which they nucleate. This is not the case for reconstructive transformations in which *all* the atoms diffuse. Thus, allotriomorphic ferrite and pearlite can grow freely across austenite grain boundaries, thereby removing them from the microstructure.

On the other hand, with displacive transformations, a vestige of the austenite grain boundary remains even in a fully transformed microstructure. The misfit present at the original austenite grain boundaries can evidently be inherited in a fully transformed specimen. This is because the displacive transformation of austenite involves a minimal movement of atoms. The Bain Strain, which is the pure component of the deformation which converts the austenite lattice into that of ferrite, does not rotate any plane or direction by more than about 11° [5]. And the change in volume during transformation is a mere few percent.

The prior austenite grain boundaries in martensitic or bainitic steels therefore represent regions of atomic disorder in the original γ/γ boundaries, which are highly susceptible to the segregation of impurity atoms such as phosphorus [6].

Martensitic and bainitic steels are therefore particularly prone to temper embrittlement phenomena [7], to embrittlement by liquid zinc [8] and to failure by creep defects at the prior boundaries [9].

4. QUANTITATIVE FRACTURE TOUGHNESS

Much of the literature about toughness tends to focus on micromechanisms, test methodology or procedures for using experimental data in design excercises. By contrast, there is very little work on the *prediction* of the energy absorbed during fracture. This difficulty is illustrated by some basic concepts of fracture mechanics. The critical value K_{IC} of the stress intensity which must be exceeded to induce rapid crack propagation is the product of two terms

$$K_{IC} = \text{stress} \times \text{distance}^{\frac{1}{2}} \tag{2}$$

where the stress is a fracture stress σ_F which can measured independently using notched tensile specimens. It can be related to the microstructure via [10,11]:

$$\sigma_F \propto \left[\frac{E\gamma_p}{\pi(1-\nu^2)c}\right]^{\frac{1}{2}} \tag{3}$$

where E is the Young's modulus and ν is the Poisson's ratio. γ_p is the effective work done in creating a unit area of crack plane, estimated to be about $14\,\mathrm{J\,m^{-2}}$ for many iron–base microstructures [12]; it is much larger than a surface energy (typically $1\,\mathrm{J\,m^{-2}}$) because of the plastic zone which moves with the crack tip. This value of $14\,\mathrm{J\,m^{-2}}$ seems to apply to a wide variety of steel microstructures [12], which is surprising given that they often have quite different deformation characteristics. In any event, there is no obvious way of relating γ_p to the details of the microstructure. By contrast, the dimension c is usually attributed to the size of a sharp crack created by the fracture of a brittle microstructural constituent such as a cementite particle or a non–metallic inclusion.

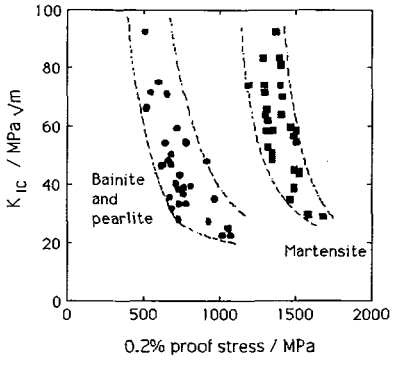

Fig. 2: Fracture toughness K_{IC} as a function of the strength [13]

The other parameter in equation 2, distance$^{\frac{1}{2}}$, refers to a length ahead of the crack tip, within which the stress is large enough to cause the fracture of brittle crack–initiators.

We can now examine the observed fracture toughness behaviour for engineering steels with bainitic or martensitic microstructures. It is evident from Fig. 2 that bainitic steels are far more brittle than martensitic steels. Microscopic cleavage fracture stress σ_F for the bainitic steels is between 1100–2200 MPa whereas that of martensite is about 3100–4000 MPa, approximately independent of temperature [12]. This can be explained if the distance c in equation 3 is equated to the cementite particle size. The latter is much coarser in bainite than in martensite [13]:

Microstructure	Mean cementite size / nm	Coarsest particle / nm
Auto–tempered martensite	14	36
Tempered martensite	38	110
Severely tempered martensite	230	600
Upper bainite	220	1000
Mixed upper & lower bainite	230	720

The reason for the coarser cementite in bainite is its mechanism of transformation (Fig. 3). Growth is initially diffusionless. For upper bainite the excess carbon is then rapidly partitioned into the austenite from which it precipitates as coarse cementite during the progress of the transformation. For lower bainite, the partitioning of carbon is somewhat slower because of the lower temperature so that there is an opportunity to precipitate some fine carbides within the ferrite. There is nevertheless some precipitation of cementite from carbon–enriched austenite. For martensite, the carbon remains within the supersaturated plate until a tempering heat treatment can be given to precipitate fine carbides.

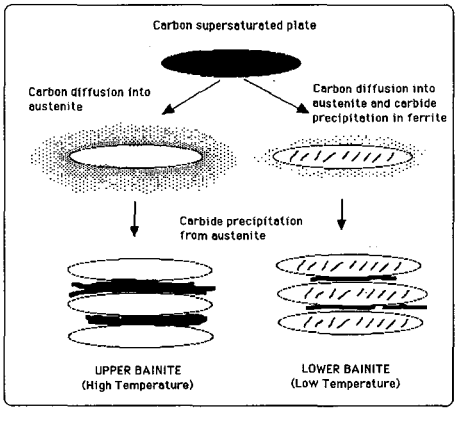

Fig. 3: The stages in the development of a bainitic microstructure.

5. BETTER BAINITE

Because of the difference in the mechanism of transformation, bainitic steels have always been second–best when compared with tempered martensite. The lack of toughness can in principle be eliminated by using steels with a high silicon concentration (*e.g.* 1.5 wt%). Silicon has a negligible solubility in cementite and hence greatly retards its precipitation.

The transformation stops before the final stage illustrated in Fig. 3 is reached, leaving at the isothermal transformation temperature, plates of bainitic ferrite separated by films of carbon–enriched austenite (Fig. 4a). There are no cementite particles to nucleate cleavage cracks or voids; the bainitic ferrite has a low concentration of dissolved carbon; strengthening and toughening is achieved by the very fine ferrite plates (a natural consequence of the transformation mechanism); there are intimately–mixed ductile films of austenite to blunt any cracks and perhaps to toughen via a TRIP effect; the austenite also impedes penetration of the steel by hydrogen. Evidently, a dream microstructure.

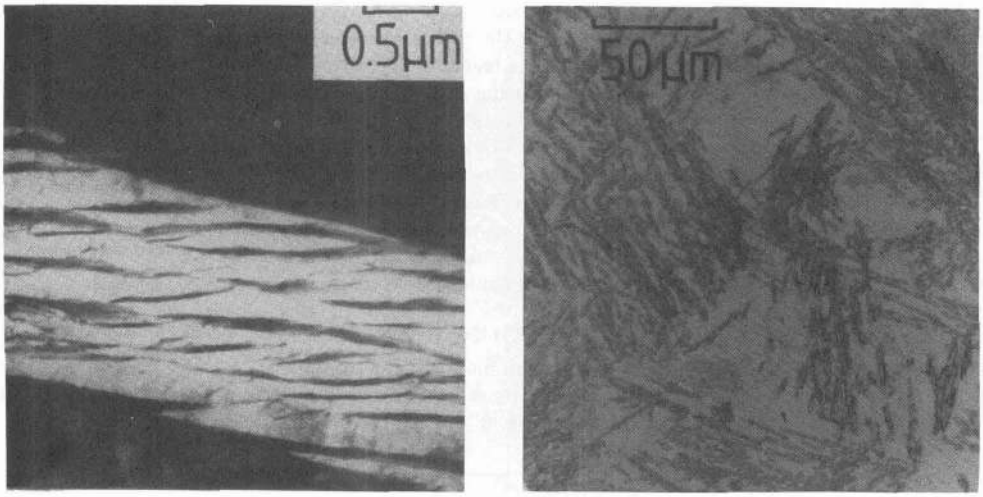

Fig. 4: (a) Transmission electron micrograph of a mixture of bainitic ferrite and stable austenite. (b) Optical micrograph of upper bainite in an Fe–0.43C–3Mn–2.02Si wt% showing the blocks of retained austenite between sheaves of bainite.

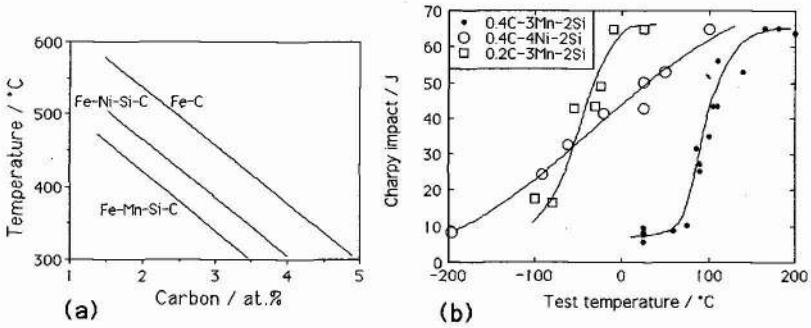

Fig. 5: (a) Calculated T_0' curves for the Fe–C, Fe–Mn–Si–C and Fe–Ni–Si–C steels. (b) Experimentally determined impact transition curves showing how the toughness improves as the amount of blocky austenite is reduced. The chemical compositions stated are approximate [15,16,17].

Unfortunately, this seemingly ideal microstructure does not live up to expectations. There are, in addition to the films of austenite, some large "blocky" regions of austenite in the microstructure (Fig. 4b). The blocks are relatively unstable and transform into high–carbon, untempered, brittle–martensite under the influence of stress. These large "inclusions" render the steel brittle. They are a direct consequence of the mechanism of transformation. We have noted earlier that bainite grows without diffusion (although the excess carbon is then redistributed). The transformation therefore becomes thermodynamically impossible once the austenite composition reaches the T_0' curve of the phase diagram. At this point, austenite and supersaturated bainitic ferrite of the same chemical composition have the same free energy. If, on the other hand, the bainite formed with its equilibrium composition, then the transformation could continue until the austenite achieves its equilibrium composition given by the usual $Ae3$ curve of the phase diagram, and the blocky regions of high carbon austenite would be consumed, giving a tough steel.

The fact that bainite growth is without diffusion causes large regions of austenite to remain untransformed, no matter how long the sample is held at the transformation temperature. The blocky regions of austenite can be eliminated by promoting further transformation to bainite, either by displacing the T_0' curve to larger carbon concentrations, or by reducing the average carbon concentration. The former can be accomplished by modifying the susbtitutional solute content of the steel (*i.e.* the phase stabilities).

Fig. 5b shows the impact transition curves of three steels, the first (Fe–0.4C–3Mn–2Si wt%) has large quantities of blocky austenite (Fig. 4a) and very poor impact toughness at room temperature. The nickel–containing steel has a T_0' curve which is at larger carbon concentrations (Fig. 5a); the Fe–0.2C–3Mn–2Si steel has half the carbon concentration of the bad steel. Both of these new steels have much better impact properties because the modifications allow more bainitic ferrite to form at the expense of blocky austenite [15,16]. The better toughness is achieved without any sacrifice to strength.

6. EXPLOITATION OF TRANSFORMATION MECHANISM

It was demonstrated above that a strong and tough bainitic steel can be designed using the T_0' curve. This has led to the development of novel ultra–high strength steels with strength and toughness combinations which match or exceed more expensive alloys, Fig. 6 [15–21].

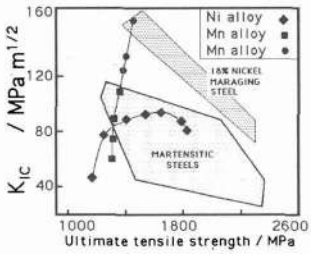

Fig. 6: New, cheap bainitic steels (points) which match the properties of expensive alloys [18–20]

A recent application has been in rail steels which are tough and at the same time exceptionally resistant to fatigue and wear [21]. The microstructure of conventional rails is based on a mixture of cementite and ferrite in the form of pearlite. The cementite is hard and therefore provides wear resistance, but is at the same time brittle. The new bainitic rail steel is completely free of carbides; it has a much higher toughness but is harder due to the fine grain size and residues of martensite and retained austenite (Fig. 7).

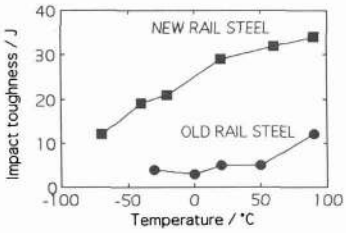

Fig. 7: Toughness of new rail steel against conventional rail steels

7. MECHANISM & STRENGTH

The equilibrium shape of ferrite in austenite is that of an equiaxed idiomorph. Many varieties of ferrite nevertheless grow in the form of plates. These all grow by the displacive mechanism described above, so

that their growth causes the shape of the transformed region to change, the change being an invariant–plane strain (IPS) with a large shear (Table 2). This is not the case when the ferrite grows in any other shape. A small aspect ratio (plate thickness/plate length) leads to a better accommodation of the plate and hence to a minimisation of the elastic strains in the austenite.

Transformation	s	δ	Morphology	Ref.
Widmanstätten ferrite	0.36	0.03	Thin plates	[22]
Bainite	0.22	0.03	Thin plates	[23,24]
Martensite	0.24	0.03	Thin plates	[25,26]
Allotriomorphic α	0	0.03	irregular	
Idiomorphic α	0	0.03	equiaxed	

Table 2: Approximate values of shear (s) and dilatational (δ) strains accompanying the formation of for a variety of transformation products in steels.

Processes of plastic deformation absorb a lot more energy than when cleavage occurs. Therefore, most mechanisms of strengthening lead to a decrease in toughness. The exception is grain size strengthening, where a refinement of the microstructure simultaneously improves the strength and toughness. In this respect, a plate shape is better than an equiaxed grain structure. The mean free slip distance through a plate is only about twice its thickness [27], which for bainite is typically far less than a micrometer in size. The accelerated cooled thermomechanically processed steels with bainitic microstructures rely on this. Quantitative details about the strengths of bainite and martensite can be found in [4,17].

8. FURTHER PLATE–REFINEMENT

Martensite and bainite plates sometimes stop growing before they impinge with a hard obstacle such as a grain boundary or another plate. Such tiny plates which are prematurely halted are called "sub–units" (Fig. 4) because they grow in clusters called sheaves. Within each sheaf the sub–units are parallel and of identical crystallographic orientation and habit plane. The sub–units are usually separated from each other either by carbide particles or residual austenite [28,29,30].

When transformation occurs at high temperatures, the shape deformation causes the relatively weak austenite to deform plastically. Fig. 8 illustrates the irreversible deformation caused in the adjacent austenite by the transformation. The resulting forest of dislocations blocks the progress of the glissile transformation interface, explaining why the sub–unit stops growing even though it may not have encountered an austenite grain surface. In fact, the size can be decreased further by causing the bainite to grow in plastically deformed austenite [31]; there is evidence to suggest that thermomechanically processed bainitic steels benefit from this *mechanical stabilisation.*

The plastic relaxation of the shape change causes an increase in the dislocation density of bainitic ferrite since any motion of the interface into the deformed austenite will cause the defect structure to be inherited. Thus, although there is considerable scatter in published data, the dislocation density generally decreases as the transformation temperature is increased (Fig. 8b).

9. EFFECT OF STRENGTH ON TRANSFORMATION

We now examine the inverse problem, *i.e.* the effect of mechanical properties on the mechanism of transformation.

In dilute steels, the transformation temperature (M_S or B_S) is found not to be sensitive to the austenite grain size or the austenitisation temperature as long as the temperature is high enough to dissolve residual phases such as carbides. This indicates that martensitic transformation might be triggered when the driving force for transformation without a change in the chemical composition, $\Delta G^{\gamma\alpha}$ reaches a critical value $\Delta G^{\gamma\alpha}_{Ms}$ as illustrated in Fig. 9, the only effect of alloying elements being to modify the relative thermodynamic stabilities of the austenite and martensite phases.

For dilute steels, the critical value of the driving force is found to be about -1100 J mol^{-1}, varying a little with the carbon concentration [33].

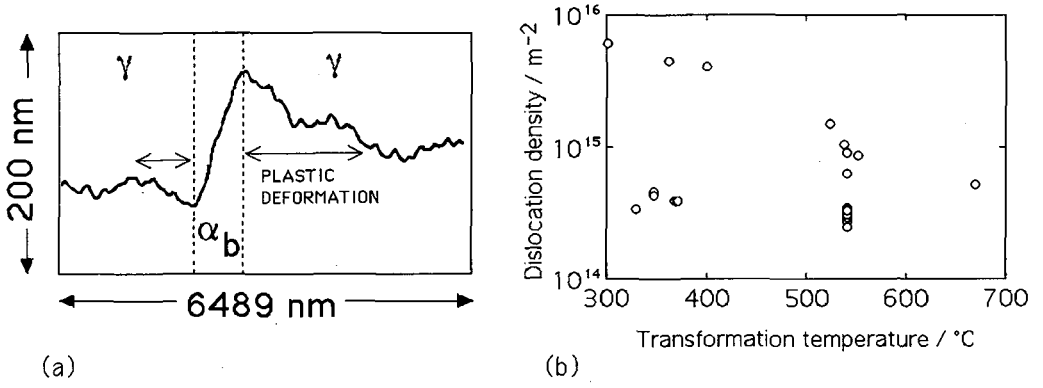

Fig. 8: (a) High–resolution atomic–force microscope plot of the displacements caused by the formation of a single sub–unit of bainite. The surface was flat before transformation. Note the plastic deformation caused in the adjacent austenite [24]. (b) Dislocation density of martensite, bainite and Widmanstätten ferrite as a function of the transformation temperature [32]

It is surprising that $\Delta G^{\gamma\alpha}_{M_S}$ is found to be insensitive to the chemical composition. Martensitic transformation occurs by the propagation of a glissile interface. Anything that impedes the glide of the interface dislocations must therefore depress the transformation temperature. Solute additions generally strengthen the austenite and there is considerable evidence that the ability of austenite to resist deformation is an important factor in its decomposition to martensite [34]. An appropriate solution strengthening model for austenite is that its strength should vary with the square root of the solute concentration (wt.%); therefore, Ghosh and Olson [35] were able to demonstrate that the critical driving force should vary with the concentration as follows:

$$\begin{aligned} -|\Delta G^{\gamma\alpha}_{M_S}|(\mathrm{J\,mol^{-1}}) =& 1010 + 4009 w_C^{0.5} + 1879 w_{Si}^{0.5} + 1980 w_{Mn}^{0.5} \\ &+ 172 w_{Ni}^{0.5} + 1418 w_{Mo}^{0.5} + 1868 w_{Cr}^{0.5} + 1618 w_V^{0.5} \\ &+ 752 w_{Cu}^{0.5} + 714 w_W^{0.5} + 1653 w_{Nb}^{0.5} + 3097 w_N^{0.5} - 352 w_{Co}^{0.5} \end{aligned} \tag{4}$$

This gives greatly improved predictions of the M_S temperature when the steel is richly alloyed, in which case $|\Delta G^{\gamma\alpha}_{M_S}|$ can be as large as 3000 J mol^{-1}.

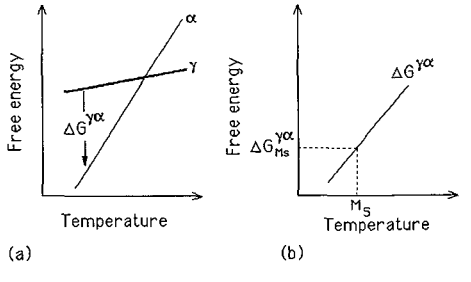

Fig. 9: (a) Difference in the free energies of austenite and martensite of the same chemical composition as a function of temperature. (b) Formation of martensite when the driving force achieves a critical value.

The elastic constants also feature in the mechanism of martensitic transformation. Austenite can in principle be deformed continuously into the structure of martensite. Zener pointed out in 1948 [36] that the elastic constant of the lattice can be used as a measure of its stability to shear deformation. In particular, for a cubic crystal, the two moduli characterising the resistance to shear deformation are C_{44} and $C' = \frac{1}{2}(C_{11} - C_{12})$. The former is a measure of the resistance to shear on the system (0 1 0)[0 0 1] whereas the latter the corresponding resistance on (1 1 0)[1 $\bar{1}$ 0]. C_{44} is larger than C' so that their ratio is a measure of the elastic anisotropy. C' sometimes softens as the transformation temperature is approached. If it actually approaches zero then the austenite becomes mechanically *unstable* and deforms spontaneously into the structure of martensite, passing through a continuous series of transition structures in the process.

However, calculations using electron theory [37] suggest that this mechanism of transformation is unlikely to be important in iron, except perhaps during the nucleation stage in the vicinity of a defect [38]. This is because the driving force necessary to induce the defect-free austenite to be mechanically unstable is about 14.5 kJ mol^{-1}, far less than the 1000 to 3000 kJ mol^{-1} observed for steels at their M_S temperatures.

10. CONCLUSIONS

Progress has obviously been made in relating the transformation mechanism to both the microstructure and the mechanical properties, and in using this knowledge towards the design of successful steels. This is particularly true in the calculation of strength, and a few aspects of toughness. However, there remain many areas where there is an appalling lack of quantitative understanding. Some of the least well researched from this perspective are listed in Table 3.

Property	Relevance
Yield strength	All structural applications
Ultimate tensile strength	All structural applications
YS/UTS ratio	Tolerance to plastic overload
Elongation	Resistance to brittle fracture
Uniform elongation	Related to YS and UTS
Non-uniform elongation	Related to inclusions
Toughness	Tolerance to defects
Fatigue	Cyclic loading, life assessments
Stress corrosion	Slow corrosion & cracking
Creep strength	High temperature service
Creep ductility	Safe design
Creep-fatigue	Fatigue at creep temperatures
Elastic modulus	Deflection, stored energy
Thermal expansivity	Thermal fatigue
Hardness	Tribological properties

Table 3: Mechanical properties that need to be related to transformation theory.

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