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The 37th John Player Memorial Lecture

THE DESIGN OF STRONG TOUGH AND AFFORDABLE ENGINEERING ALLOYS

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Strong, Tough & Affordable Steels

Introduction

Some 70% of the all the steel manufactured today is the result of developments over the past 10 years. Indeed, new and useful alloys are being invented with notorious regularity. There are many reasons for this success, including the versatility of steel and its low cost. But steel also inspires creativity because it is an incredibly complex and convoluted material with seemingly endless possibilities.

This lecture is about strong, tough and affordable steels that are invented using theory based on the atomic motions that lead to creation of crystals in the solid–state, combined with simple ideas about mechanical behaviour. Strength is taken to be the ability of the material to support a stress without permanent deformation. Toughness is related to the energy absorbed during the course of fracture. These two properties are difficult to reconcile because strength relies on avoiding plastic deformation whereas toughness depends on energy dissipated during plastic flow.

It is useful to note at the outset that toughness can be improved by refining the scale of the microstructure, by eliminating hard particles which fracture easily, by introducing ductile barriers to the propagation of cracks, and by mechanisms which damp the motion of cracks.

The State of Iron

What do we see when we look at a piece of metal? Not only its colour, shape and expression, but there is also a hint of what lies beneath the surface. Metals are, for the most part, made up of space–filling aggregates of crystals. The crystals can vary in size from a few hundreds of atoms to dimensions visible to the naked eye. The layman associates crystals with beauty and perfection, but in practice, they are littered with defects. It is these imperfections which make metals so useful as engineering materials [1]. Most of the elements in the periodic table are metallic, and some of the others can in principle be made metallic in extreme environments. But we shall see that iron has a unique combination of attributes which makes it more exploitable than all the other metallic and non–metallic materials put together (with the exception of concrete) [2].

Pure iron exists in many crystalline forms, each of which can be described in terms of a pattern of atoms: hexagonal close–packed, double hexagonal close–packed, trigonal, tetragonal, body–centred cubic and face–centred cubic. Most iron alloys when heated to temperatures above 900 °C have the face–centred cubic crystal structure which is more commonly known as *austenite* (Fig. 1). The austenite on cooling undergoes a solid–state transformation into the body–centred cubic crystal structure known as *ferrite*. Ferrite is the basis of more than 750 million tonnes of steels produced annually. It owes its existence to the detailed magnetic structure of iron, but that is another story.

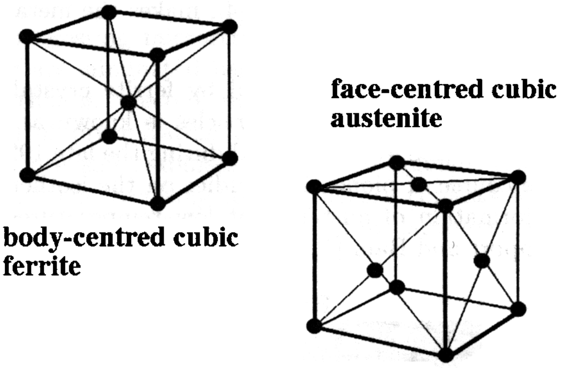


Fig. 1: The two common crystal structures of iron; for clarity, only three of the six face–centring atoms of austenite are shown.

The transformation from austenite to ferrite can occur by a variety of atomic mechanisms [3]. The pattern in which the atoms are arranged can be altered either by breaking all the bonds and rearranging the atoms into an alternative pattern (*reconstructive* transformation), or by homogeneously deforming the original pattern into a new crystal structure (*displacive* transformation), Fig. 2.

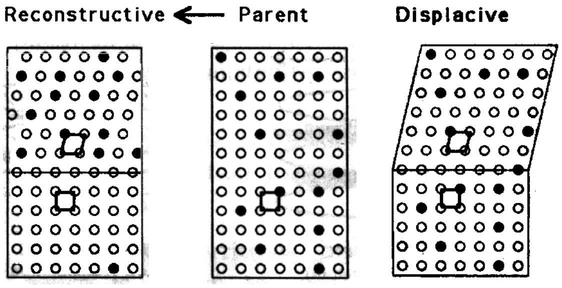


Fig. 2: The reconstructive and displacive atomic–mechanisms of transformation.

It is the displacive mechanism which is of interest here. The deformation which carries the parent into the product phase also changes the overall shape of the sample (Fig. 2). This shape change is constrained by the surrounding crystals, so the product phase grows in the form of thin plates to minimise the strain energy. The atoms are displaced into their new positions in a coordinated motion. Displacive transformations can therefore occur at temperatures where diffusion is impossible over the time scale of the experiment. Some solutes may be forced into the product phase, a phenomenon known as solute trapping. Both the trapping of atoms and the strains make displacive transformations less favourable from a thermodynamic point of view.

The crystals can take many shapes and chemical compositions; their structures can be manipulated using thermomechanical processing or externally applied fields. It is easy in this context to understand the widespread use of iron alloys; the versatility and the fact that iron is 10,000 times cheaper than an equivalent weight of potato crisps [4], makes the metal incredibly useful.

One particular shape adopted by ferrite crystals in combination with carbide particles is known as *bainite.* The phase was discovered during the late 1920's, in the course of pioneering studies on the isothermal transformation of austenite at low temperatures by Davenport and Bain [5].

Bainite

Bainite is a non–lamellar aggregate of carbides and plate–shaped ferrite ([6], Fig. 3). The ferrite plates are each about 10×10^{-6} m long and about 0.2×10^{-6} m thick, making the individual plates invisible in the optical microscope. The fine scale of the microstructure is beneficial to both the strength and toughness. Within the broad classification of bainite, there are two particular forms.

Upper bainite consists of clusters of platelets of ferrite which are in identical crystallographic orientation and intimately connected to the austenite in which it grows. Elongated cementite particles decorate the boundaries of these platelets, the amount and continuity of the cementite layers depending on the carbon concentration of the steel.

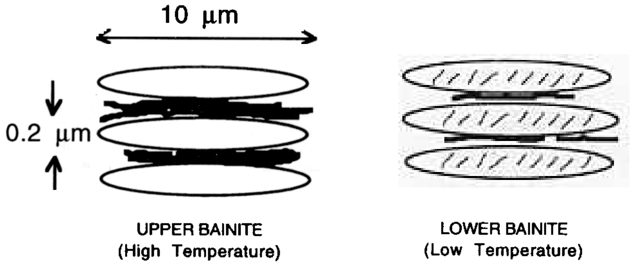


Fig. 3: Schematic illustration of the microstructure of upper and lower bainite.

As the transformation temperature is reduced, some of the carbon is encouraged to precipitate inside the ferrite plates, leading to the lower bainite microstructure. The clusters of ferrite plates in both upper and lower bainite are also known as 'sheaves' (Fig. 4) each of which has an overall shape akin to that of a thin wedge.

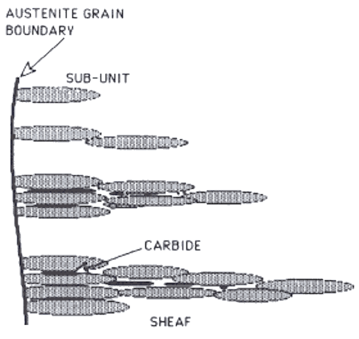


Fig. 4: Evolution of a bainite sheaf as a function of time.

Shape Deformation

Atoms move in a highly disciplined manner during the change from the austenite to the bainite crystal structure, so the transformation is often described as a *military* transformation; the atoms do not break rank as they cross the boundary between the parent and product crystals. By contrast, *civilian* transformations involve random movements of atoms [7].

Since the atoms move in a disciplined manner during the growth of bainite, the shape of the transforming crystal changes to reflect the atomic displacements ([8], Fig. 5). The resulting deformation is formally an invariant–plane strain with a shear component of about 0.26 and a dilatational strain normal to the habit plane of about 0.03. By comparison, a typical elastic strain in a metal is about 10^{-3} so the formation of bainite causes enormous strain in the surrounding material. One way to minimise the strain energy is to adopt a thin–plate shape. This is why the microstructure on a fine scale consists of platelets; this shape, which is a natural consequence of the transformation mechanism, is particularly beneficial to the mechanical properties.

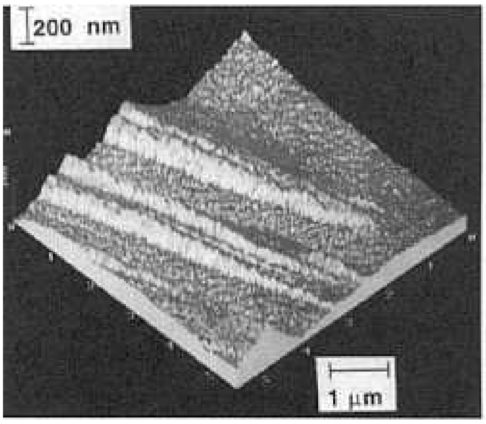
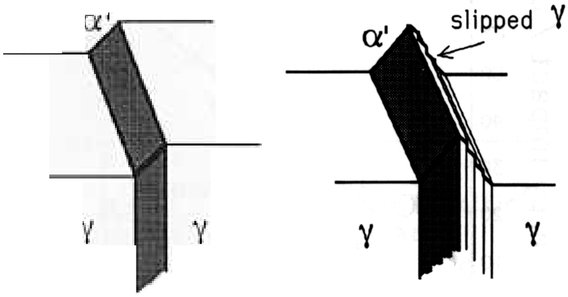


Fig. 5: Displacements caused on a polished surface of austenite by the growth of bainite.

Another consequence of the shape deformation is that it induces plastic strain in the surrounding parent phase. This creates a high density of defects in the region surrounding the growing bainite crystal, defects which eventually stifle its growth. By preventing the continued growth of each bainite plate, the plastic accommodation of the shape deformation leads to a great refinement of the overall microstructure.

Substitutional Alloying Elements

One final consequence of the military mechanism of transformation is that atoms do not redistribute during the growth of bainite; this has been verified using the highest conceivable atomic and chemical resolution ([9], Fig. 6). However, carbon, which can move rapidly within solid iron, prefers to reside in austenite and hence escapes into the austenite shortly after transformation.



(a) (b)

Fig. 5: (a) A perfect invariant–plane strain (α refers to bainite, γ to austenite). (b) One where the adjacent matrix has relaxed by plastic deformation.

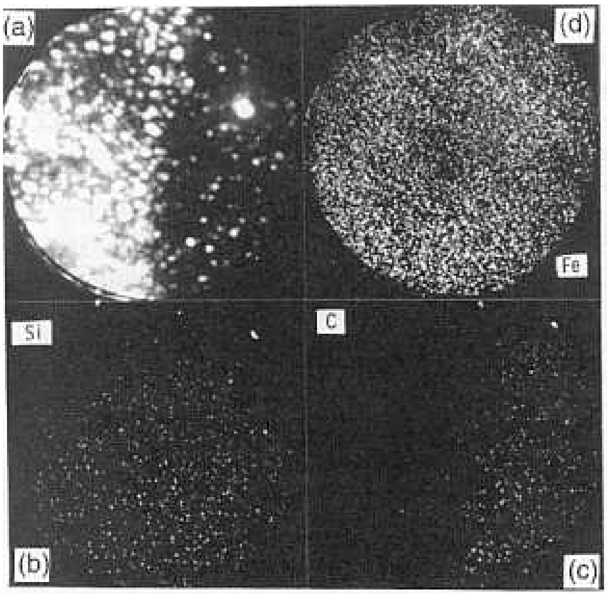


Fig. 6: Imaging atom–probe micrographs, taken across an austenite–bainitic ferrite interface in a Fe–C–Si–Mn alloy. The experiments confirm the absence of any substitutional atom diffusion during transformation. (a) Field–ion image; (b) corresponding silicon map; (c) corresponding carbon map; (d) corresponding iron map.

Brittle Carbides

All the indications are that following the growth of bainite, the carbon partitions into the parent phase and precipitates there as cementite (Fig. 4). This cementite occurs as rather coarse particles which initiate void formation or stimulate cleavage at low temperatures. They are undesirable consequences of the bainite reaction. This is why bainitic steels have not been as successful as the quenched and tempered martensitic alloys.

It has been known for a long time that the cementite can be eliminated from the microstructure by alloying with silicon, which has a very low solubility in the cementite [10].

Idyllic, Carbide–Free Microstructure

An interesting microstructure results when the carbides are eliminated using silicon in steel. The carbon that is rejected into the residual austenite, instead of precipitating as cementite, remains in the austenite and stabilises it down to ambient temperature. The resulting microstructure consists of fine plates of bainitic ferrite separated by carbon–enriched regions of austenite (Fig. 7).

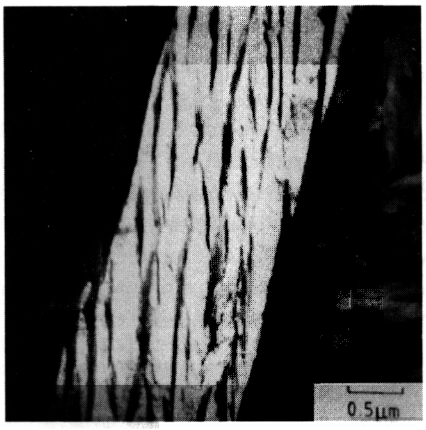


Fig. 7: Transmission electron micrograph of a mixture of bainitic ferrite and stable austenite.

The potential advantages of the mixed microstructure of bainitic ferrite and austenite can be listed as follows:

(a) Brittle cementite is eliminated, making the steel more resistant to cleavage fracture and void formation.

(b) The bainitic ferrite is depleted in carbon, which is known to embrittle ferritic microstructures.

(c) The microstructure, which is generated by a simple heat treatment, derives its strength from ultrafine ferrite plates, which are much less than one millionth of a meter in thickness. This cannot be achieved by any other commercially viable process. Furthermore, refinement is the only mechanism for simultaneously improving the strength and toughness of steels.

(d) The ductile films of austenite which are intimately dispersed between the plates of ferrite have a crack blunting effect. They may also undergo stress–induced transformation, thereby adding to the work of fracture.

(e) The diffusion of hydrogen in austenite is slower than in ferrite. Austenite can therefore lead to an improved stress corrosion resistance.

(f) Steels with this microstructure are cheap. All that is required is that the silicon concentration should be large enough to suppress cementite.

Incomplete Reaction & Disappointment

In spite of all these appealing features, it turns out that steels with this microstructure have an appalling resistance to fracture.

The reason for the poor toughness lies in thermodynamics [11,12]. The diffusionless growth of bainite is prevented before equilibrium is reached, once the carbon concentration of austenite reaches a limiting concentration x_{T_0}, when the free energies of austenite and ferrite of the same chemical composition become equal.

This leaves considerable amounts of carbon–enriched austenite untransformed (Fig. 8). Thus, islands of austenite as large as ten micrometers are left in the otherwise fine microstructure. This austenite can change and become brittle under stress, effectively introducing large, hard particles in the steel. And all this because the thermodynamic limit prevents the large regions of austenite from being consumed by bainite, no matter how long the heat treatment!

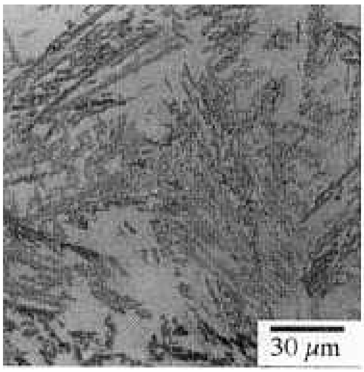


Fig. 8: Optical micrograph of upper bainite in a silicon–rich steel showing the blocks of retained austenite between sheaves of bainite.

Thermodynamic Cure to Toughness

It is the simultaneous realisation of the cause of brittleness and an understanding of the atomic mechanisms of transformation [13], that led to a disarmingly easy solution [11,12]. It clearly is necessary to increase the amount of bainitic ferrite to eliminate the islands of austenite, without violating the thermodynamic limit. It was discovered that this can be done in three ways. First, the free energies of the parent and product phases can be modified by using solutes which increase x_{T_0}. Secondly the average carbon concentration of the steel can be reduced without sacrificing the strength since this leads to a greater fraction of bainite. Thirdly, the transformation temperature can be reduced (to increase x_{T_0}), without going so low as to trigger martensite.

These theoretical concepts were expressed quantitatively and led to the spectacular improvement in toughness illustrated in Fig. 9.

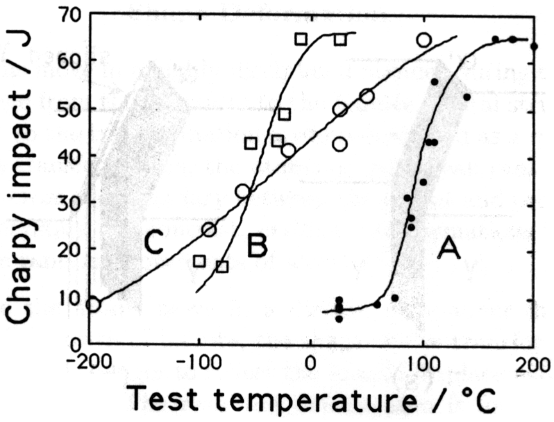


Fig. 9: (Experimentally determined impact transition curves for a variety of bainitic steels. Curve A represents the original, brittle steel, whereas B and C represent tough alloys designed using atomic theory [11,12].

A recent major application [6] has been in the development of rail steels which are tough and at the same time extremely resistant to wear and rolling–contact fatigue [14]. Producers of steel for railway tracks have had the long standing difficulty that the harder they make the rail, the longer it lasts but can increase the wear suffered by the rolling stock wheels. 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 while at the same time being harder due to the fine grain size and the presence of some martensite and retained austenite. Tests show that it has remarkable wear resistance, reduces wear on the wheels, is tough and weldable (Fig. 10). The steel is now commercialised.

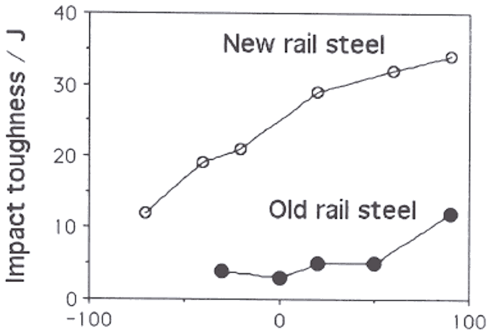


Fig. 10: Toughness of new rail steel against conventional rail steels.

In another application for the defence industry, cheap bainitic–steels have been designed, without doing experiments, with the highest ever combination of strength and toughness (1600 MPa, 130 $\mathrm{MPa\,m^{\frac{1}{2}}}$, Fig. 11) [14,15]. We are now working towards the design of novel bainitic steels with the remarkable strength of 2500 MPa and toughness beyond

30 $\mathrm{MPa\,m^{\frac{1}{2}}}$, by transforming at a temperature where the diffusion distance of an iron atom is just 10^{-17} m [16].

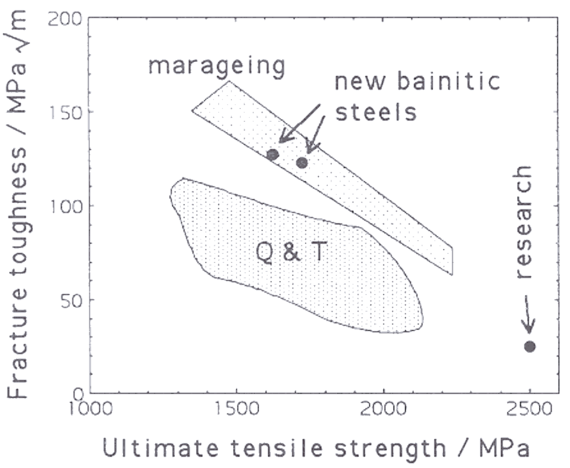


Fig. 11: Toughness versus strength. The two bainitic steels with a strength of 1600 MPa match the toughness of marageing steels at a cost which is 90 times cheaper. The bainitic steel illustrated at 2500 MPa is the subject of current research with potential for much improved toughness.

Summary

The examples of steel design that I have presented here are not the only ones. A variety of fundamental and empirical techniques have been used successfully in the design of novel creep–resistant steels of the type used in the energy industries [17]. The process has also worked in reverse, where investigations of commercial steel has inspired basic theory which defines the thermodynamic behaviour of nanomixtures [18]. Solution theory has always considered only mixtures of atoms, whereas this new theory of particulate solutions has demonstrated that nanomixtures also behave like solutions. Furthermore, the theory has identified that there is an important mathematical artefact in established thermodynamics, which vanishes in the new model [19]. And all this has emerged from studies of steel!

Apart from enthusing about steel, I hope I have illustrated that there is a rewarding new science, which from atomic mechanisms, attempts predictions capable of dealing with the most complex of industrial problems. There is no doubt in my mind that steels represent the most challenging of all the subjects covered in the materials sciences, with a complexity that truly fires the imagination.

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