Large chunks of very strong steel

Steel with an ultimate tensile strength of 2500MPa, a hardness of 600–670HV and toughness in excess of 30–40MPa m$^{1/2}$ is the result of exciting new developments with bainite. The simple process route avoids rapid cooling so that residual stresses are avoided, even in large pieces.

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Strength is a term that is much used and abused in materials science. It is common to claim that a novel material is as strong as steel, without specifying the nature of the steel against which the comparison is made. The claimants are either ignorant of the fact that it is possible to commercially make polycrystalline iron with a strength as low as 50MPa or as high as 5.5GPa, or neglect it to impress a fickle audience. In an academic context, single crystals of iron have been made which behave elastically to a stress of 14GPa, taking them into a range of recoverable strain where Hooke's law does not apply.

The giga-pascal steels rely for their strength on martensitic microstructures or on pearlite containing closely spaced lamellae of cementite. Each of these microstructures may be cold deformed in order to enhance strength. This article describes an imaginative microstructure that is neither martensite, nor pearlite, does not contain carbides, is extremely strong in the undeformed state, is cheap to achieve, does not require thermo-mechanical processing, and can be produced in large samples. Before revealing its mysteries, it is appropriate to set martensitic and pearlitic strong-steels in context.

Martensite grows without diffusion; the change in lattice during the transformation of austenite is therefore achieved by the deformation of the parent phase. The associated displacements are large, with the shear component approaching 0.25.

The accommodation of the transformation strains causes the martensite to grow in the form of thin plates which minimise the strain energy. Since the mean free slip distance in a plate shape is about twice the plate-thickness, the effective grain size associated with a martensitic microstructure is less than 0.5μm. All the efforts in the steel industry to achieve a ferrite grain size in this range have yet to match the ease with which martensite achieves its structure. There are of course other strengthening mechanisms associated with martensite, but grain size refinement is unique in that it also leads to an improvement in toughness.

Martensite is produced in commercial steels by relatively rapid cooling. This limits the size of samples which can be uniformly martensitic, a fact implicit in the concept of hardenability. To increase hardenability requires the addition of expensive alloying elements. The rapid cooling also means that undesirable residual stresses frequently are induced in critical components and have to be accounted for in component-life assessments.

A colony of pearlite forms by the simultaneous growth of lamella of cementite and ferrite at a common front with the austenite. There is an energy penalty associated with the cementite/ferrite interfaces that are locked into the pearlite; fine microstructures are therefore generated by transforming at large undercooling. On its own this is not sufficient to produce strong steel so the pearlitic wire is deformed by drawing until strengths in the range 2-2.5GPa are obtained. Both the required undercooling and the deformation limit the cross-section of the wire. Kobe Steel's Scifer with a strength of 5.5GPa can only be produced in wires whose diameters are measured in micrometers.
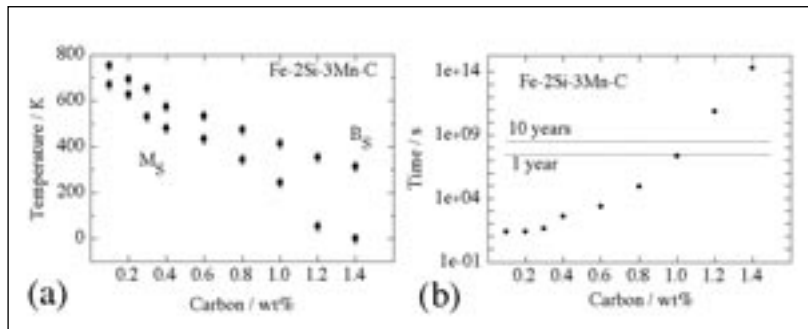
● **Figure 1** *(a) Calculated transformation start temperatures in Fe-2Si-3Mn steel as a function of the carbon concentration; (b) the calculated time required to initiate bainite*
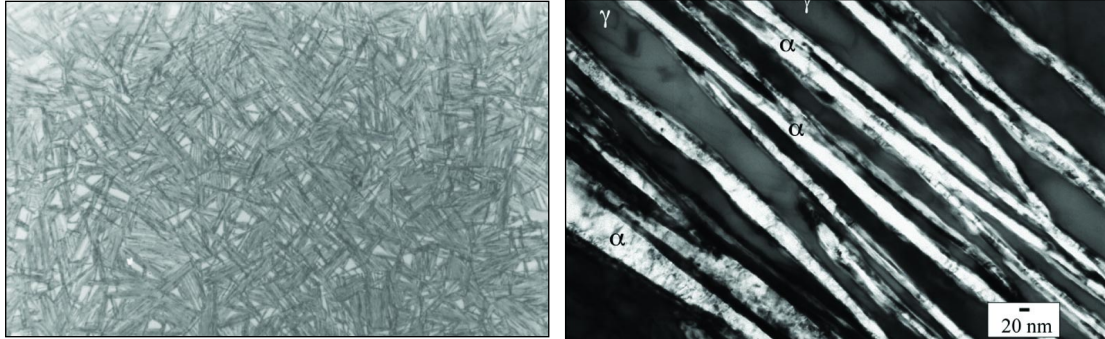
● **Figure 2** *Fe-0.98C-1.46Si-1.89Mn-0.26Mo-1.26Cr-0.09V wt%, transformed at 200°C for 5 days.*
(a) Optical micrograph; (b) transmission electron micrograph

Wouldn't it be good to have a strong steel that can be used for making large components and which does not require mechanical processing or rapid cooling to reach the desired properties? Pearlite and martensite do not in general fit this description, and ordinary bainite is simply not strong enough because of the tempering that occurs simultaneously with transformation.

Extraordinary bainite
One of the undesirable features of bainite is the cementite, which in the context of high-strength steels helps nucleate cracks and voids. It has been known for a long time that cementite can be eliminated from the microstructure by alloying the steel with about 1.5wt% silicon. The resulting microstructure then consists of a mixture of only two phases: bainitic ferrite and carbon-enriched retained austenite. The absence of cementite along with certain other factors improves the toughness. It has in this way been possible to achieve a toughness of more than 130MPa m$^{1/2}$ at an ultimate tensile strength of 1,600MPa. This combination of properties matches those of the weaker maraging steels, at a cost some ninety times cheaper (maraging steels are rich in nickel and molybdenum). Although this is impressive, 1,600MPa is not man enough in the present context. There has been a discovery that is likely to radically change this scenario. It is now possible to produce very strong bainite which can easily be processed into very large components.

Suppose we attempt to calculate the lowest temperature at which bainite can be induced to grow. After all, there is good theory routinely available for addressing just such propositions. Such calculations are illustrated in *Figure 1a*, which shows for an example steel – how the bainite-start (B$_S$) and martensite-start (M$_S$) temperatures vary as a function of the carbon concentration. There is, in principle, no lower limit to the temperature at which bainite can be generated. On the other hand, the rate at which bainite forms slows down drastically as the

transformation temperature is reduced, as shown by the calculations in *Figure 1b*. It may take hundreds or thousands of years to generate bainite at room temperature. For practical purposes, a transformation time of tens of days is reasonable. But why bother to produce bainite at a low temperature? It is well known that the scale of the microstructure, that is, the thickness of the bainite plates, decreases as the transformation temperature is reduced. This is because the yield strength of the austenite becomes greater at lower temperatures, thereby affecting the plastic accommodation of the shape deformation accompanying bainite growth, and presumably because the nucleation rate is faster with greater under-cooling. The strength of the microstructure scales with the inverse of the plate thickness, thus providing a neat way of achieving strength without compromising toughness.

Experiments consistent with the calculations illustrated in *Figure 1* demonstrated that in a Fe-1.5Si-2Mn-1C wt% steel, bainite can be generated at a temperature as low at 125°C, which is so low that the diffusion distance of an iron is an inconceivable 10^{-17}m over the timescale of the experiment!

What is even more remarkable is that the plates of bainite are only 20–40nm thick. The slender plates of bainite are dispersed in stable carbon-enriched austenite which, with its face-centred cubic lattice, buffers the propagation of cracks. The optical and transmission electron microstructures are shown in *Figure 2*; they not only have metallurgical significance in that they confirm calculations, but also are elegant to look at. Indeed, the microstructure has now been characterised, both chemically and spatially to an atomic resolution; the pleasing aesthetic appearance is maintained at all resolutions, as depicted in *Figure 3*. This shows a three-dimensional volume element indicating the positions of carbon atoms. Each dot represents a carbon atom. The carbon-rich and carbon-poor regions correspond to austenite and bainitic ferrite. The latter phase has a relatively low carbon concentration

which is nevertheless much higher than the equilibrium solubility in ferrite[6].

Getting down to earth, it is the properties which have excited industry. Ultimate tensile strengths of 2500MPa in tension have been routinely obtained, with toughness in excess of 30–40MPa m$^{1/2}$, and this in a dirty steel that has been prepared by air melting and hence contains inclusions and pores which would not be there when the steel is made by any respectable manufacturer. And all this using a simple heat treatment in which a chunk of steel is removed from the austenitising furnace (say 950°C), gently transferred into an oven at the low temperature (say 200°C) and held there for ten days or so to generate the microstructure. There is no rapid cooling so that residual stresses are avoided and large samples can be generated. The size of the sample can be large because the time taken to reach 200°C from the austenitisation temperature is much less than that required to initiate bainite. This is a major commercial advantage.

The initial reaction from industry was that the transformation times are too slow. What this knee-jerk reaction shows is that it is not appreciated how cheap it is to heat treat something at temperatures at which pizzas are normally cooked, when compared with common commercial heat treatments. With a little imagination and flair it should be possible to set up a production line containing appropriate ovens so that the throughput is not limited by the transformation time.

But suppose there really is a need for more rapid heat-treatment? The transformation can easily be accelerated to complete the processing within hours (as opposed to days), by making controlled additions of small quantities of solutes to the steel, such that the free energy change as austenite changes into ferrite is enhanced. There are essentially two choices: aluminium and cobalt, which, in concentrations less than 2wt%, have been shown to accelerate the transformation in the manner described. Both are effective, either on their own or in combination.

Much of the strength of the microstructure comes from the very small thickness of the bainite plates. Of the total strength of 2,500MPa, some 1,600MPa can be attributed solely to the fineness of the plates. The residue of strength comes from dislocation forests, the strength of the iron lattice and the resistance to dislocation motion due to solute atoms. The latter aspect is quite interesting. Because there are many defects created during the growth of the bainite, a large concentration of carbon remains trapped in the bainitic ferrite. This concentration has, using atom-probe and X-ray techniques, been found to be about 0.3wt% which is many orders of magnitude greater than the equilibrium solubility of carbon in the ferrite at the transformation temperature. Furthermore, this
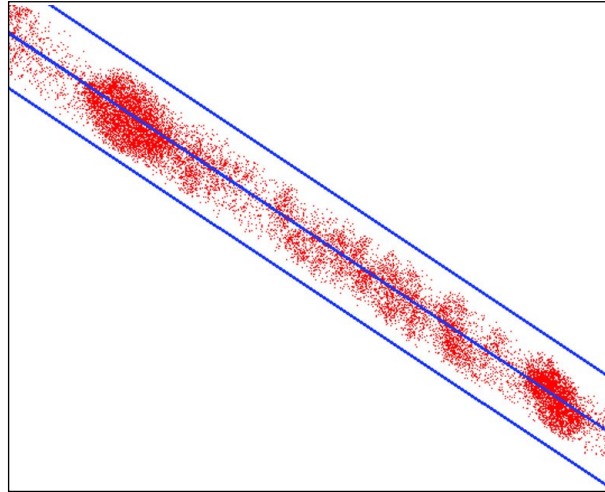
● **Figure 3** *A three dimensional volume element showing the positions of carbon atoms*

carbon refuses to precipitate even during prolonged tempering, because it is more favourable for it to remain trapped at defects than to form cementite.

Although the emphasis of this article has been on strength, it is worth pointing out that the hardness of the microstructure is the highest ever recorded for bainite, at 600–670HV. The hardness is also extremely stable to tempering at temperatures as high as 500°C for an hour, in spite of the fact that the high-carbon retained austenite decomposes into a mixture of ferrite and cementite. In fact, the tempering resistance of this extraordinary bainite is somewhat better than that of comparable secondary hardening steels or of martensitic steels with the same silicon concentration. *Figure 4* compares the temper resistance of the present alloy with that of an Fe-0.5C-1.3Siwt% quenched and tempered martensitic steel, and a secondary-hardening steel (Fe-0.34C-5.08Cr-1.43Mo-0.92V-0.4Mn-1.07Si wt%). For comparison purposes, the hardness is in each case normalised with respect to the difference in the maximum and minimum values.

This most unusual behaviour is a feature of the resistance of the fine plates of bainite to coarsening; indeed, the intense precipitation of cementite at the plate boundaries when the austenite decomposes, is another factor opposing the coarsening of the plates.

Summary
There are many adjectives that have been given to the bainitic microstructure described above:

■ Cold-bainite because of the low temperatures where it grows
■ Hard-bainite because the hardness of the microstructure (600-650HV) almost matches that of the hardest untempered martensite
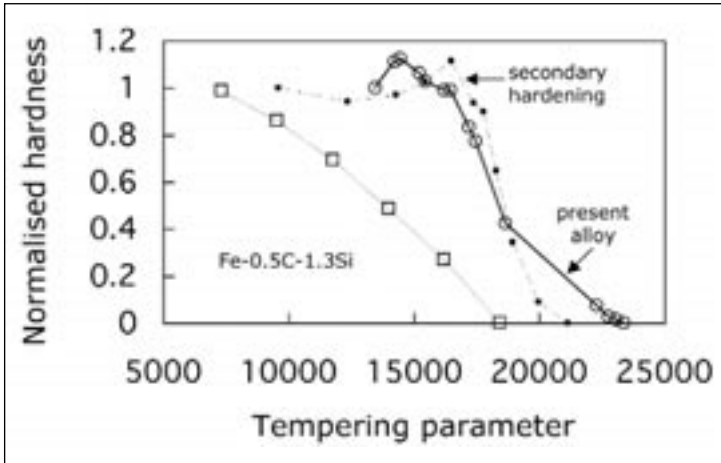
● Figure 4 *Comparison of temper resistances*

■ Strong-bainite because of the observed tensile strength (compressive strengths in excess of 4.5GPa have been recorded)

■ Fast-bainite for the faster transforming cobalt and aluminium containing variants

■ Super-bainite, an unfortunate term coined in industry

There remain, as is always the case, many parameters which have yet to be characterised, for example the fatigue and stress-corrosion properties. However, this has not held back one or two major applications which I am aware of but which remain, unfortunately, confidential. Keep on watching this space!

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