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Bainitic Bulk–Nanocrystalline Steel

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Abstract. A remarkably beautiful microstructure consisting of slender crystals of ferrite, whose controlling scale compares well with that of carbon nanotubes, has recently been discovered. The crystals are generated by the partial transformation of austenite, resulting in an extraordinary combination of strength, hardness and toughness. All this in bulk steel without the use of expensive alloying elements. We now have a strong alloy of iron, which can be used for making items which are large in all three dimensions, which can be made without the need for mechanical processing or rapid cooling and which is cheap to produce and apply.

1. INTRODUCTION

Imagine a steel which is exceedingly strong, that can be made in large chunks, one which is easy to manufacture, and has a cost which is affordable. The novel steel which satisfies these criteria relies on achoreography of atoms during the course of the bainite transformation. In particular, the scale and extent of the structure is dependent directly on the fact that the atoms move in a disciplined fashion. This information can be exploited to develop unconventional alloys – for example, rail steels which do not rely on carbides for their properties, and the hardest ever bainite which can be manufactured in bulk form, without the need for rapid heat treatment or mechanical processing [1, 2, 3, 4, 5, 6, 7]. The purpose of this paper is to describe this novel hard bainite.

2. DESIGN CRITERIA

The following conditions are required to achieve a strong, cheap and reliable material [8]:

- The material must not rely on perfection to achieve its properties. Strength can be generated by incorporating a large number density of defects such as grain boundaries and dislocations, but the defects must not be introduced by deformation if the shape of the material is not to be limited.

- Defects can be introduced by phase transformation, but to disperse them on a sufficiently fine scale requires the phase change to occur at large undercoolings (large free energy changes).

- A strong material must be able to fail in a safe manner. It should be tough.

- Recalescence limits the undercooling that can be achieved. Therefore, the product phase must be such that it has a small latent heat of formation and grows at a rate which allows the ready dissipation of heat.

3. HARD BAINITE

Steel transformed into carbide–free bainite can satisfy these criteria. Bainite and martensite are generated from austenite without diffusion by a displacive mechanism. Not only does this lead to solute–trapping but also a huge strain energy term, both of which reduce the heat of transformation [9]. The growth of individual plates in both of these transformations is fast, but unlike martensite, the *overall rate* of reaction is much smaller for bainite. This is because the transformation propagates by a sub–unit mechanism in which the rate is controlled by nucleation rather than growth [10]. This mitigates recalescence.

Suppose we now attempt to calculate the lowest temperature at which bainite can be induced to grow. We have the theory to address this proposition [9, 11]. 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?
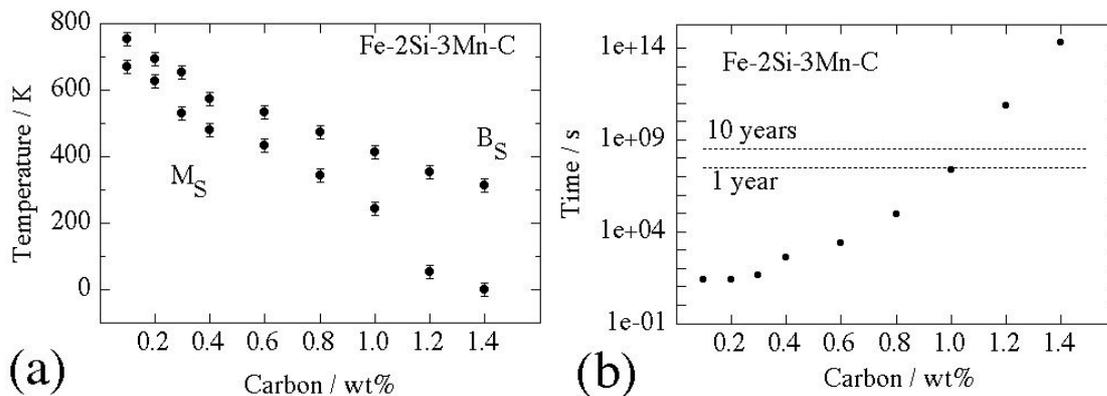

Fig. 1: (a) Calculated transformation start temperatures in Fe-2Si-3Mn steel as a function of the carbon concentration. (b) The calculated time required to initiate bainite at the B_S temperature.

It is well known that the scale of the microstructure, *i.e.,* the thickness of the bainite plates, decreases as the transformation temperature is reduced [9, 12]. 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 can be greater at larger undercoolings. 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 (detailed composition in Table 1), bainite can be generated at a temperature as low at 125°C [3], which is so low that the diffusion distance of an iron atom is an inconceivable 10^{-17} m over the time scale of the experiment!

What is even more remarkable is that the plates of bainite are only 20–40 nm 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 Fig. 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. There is no redistribution of substitutional atoms on the finest conceivable scale [13].

Ultimate tensile strengths of 2500 MPa in tension have routinely been obtained, ductilities in the range 5-30% and toughness in excess of 30-40 MPa m$^{1/2}$. All this in a dirty steel which has been prepared ordinarily and hence contains inclusions and pores which would not be there when the steel is made by any respectable process. The bainite is also the hardest ever achieved, 700 HV [3]. The simple heat treatment involves the austenitisation of a chunk of steel (at say 950°C), gently transferring into an oven at the low temperature (at say 200°C) and holding there for ten days or so to generate the microstructure. There is no rapid cooling – residual stresses are avoided. 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. Our tests indicate uniform microstructure in 80 mm thick samples – thicker samples were not available but calculations indicate that dimensions greater than 200 mm will show similar results. This is a major commercial advantage [14].

It is cheap to heat–treat something at temperatures where pizzas are normally cooked. But suppose there is a need for a more rapid process. The transformation can easily be accelerated to occur within hours, by adding solutes which decrease the stability of austenite. Aluminium and cobalt, in concentrations less than 2 wt%, have been shown to accelerate the transformation in the manner described. Both are effective, either on their own or in combination [15].

C	Si	Mn	Mo	Cr	V	Co	Al	Reference
0.98	1.46	1.89	0.26	1.26	0.09			[3]
0.83	1.57	1.98	0.24	1.02		1.54		[15]
0.78	1.49	1.95	0.24	0.97		1.60	0.99	[15]

Table 1: Typical chemical compositions of hard bainite. The silicon is added to prevent cementite formation during the growth of bainite, the molybdenum to counter embrittlement due to impurities such as phosphorus, the manganese and chromium for hardneability and the cobalt and aluminium to accelerate the transformation. The substitutional solute also contribute to hardenability and determine the T_0 curve which is vital in the design of carbide–free bainitic steels [16, 17].

Much of the strength and hardness of the microstructure comes from the very small thickness of the bainite plates. Of the total strength of 2500 MPa, some 1600 MPa can
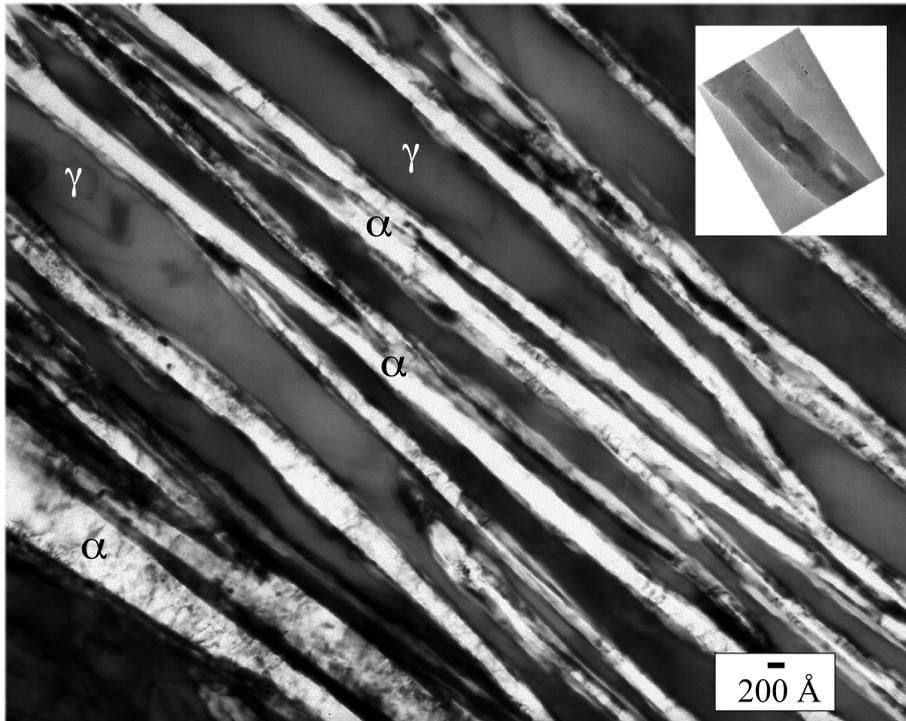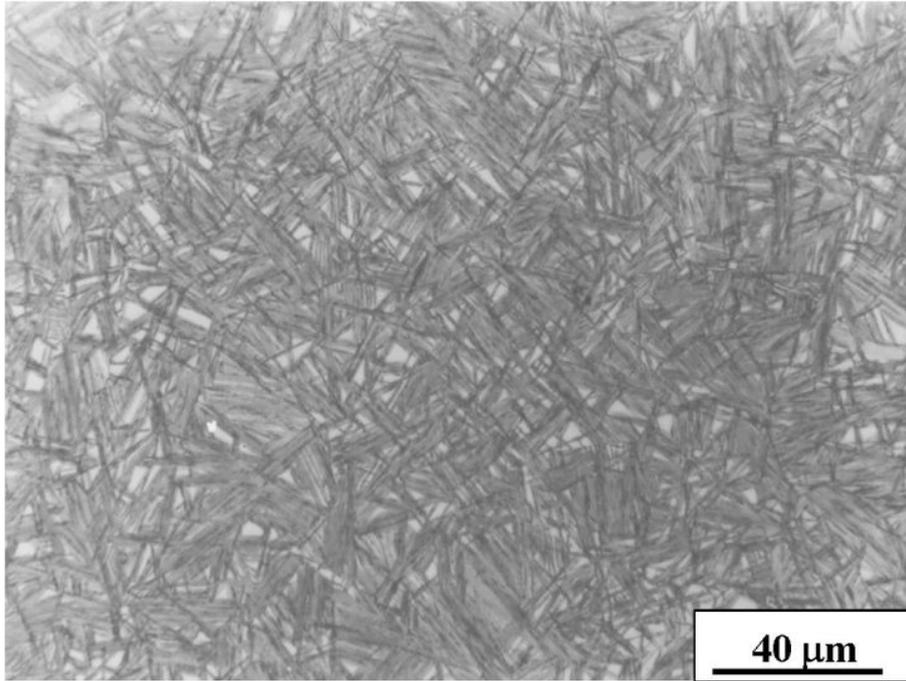
Fig. 2: Fe-0.98C-1.46Si-1.89Mn-0.26Mo-1.26Cr-0.09V wt%, transformed at 200°C for 5 days. (a) Optical micrograph. (b) Transmission electron micrograph [1, 2, 3]. The inset is an image of a carbon nanotube at the same magnification, courtesy of Ian Kinloch.

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. Because there are many defects created during the growth of the bainite [9], a large concentration of carbon remains trapped in the bainitic ferrite and does not precipitate, probably because it is trapped at defects [18].

4. STRONG BAINITE: ARMOUR

Whereas the ordinary tensile strength of the strong bainite is about 2.5 GPa, the strength has been reported to be as high as 10 GPa at the very high strain rates ($10^7\,\mathrm{s}^{-1}$) associated with ballistic tests illustrated in Fig. 3 [19]. The strong bainite has therefore found application in armour [20, 21]. Fig. 4 shows a series of tests conducted using projectiles which are said to involve "the more serious battlefield tests" (the details are proprietary). Figs. 4a,b show experiments in which an armour *system* is tested. A 12 mm thick sample of the bainitic steel is sandwiched between vehicle steel, the whole contained in glass–reinforced plastic. In ordinary armour the projectile would have penetrated completely whereas the bainite has prevented this; the steel did however crack. By reducing the hardness (transforming at a higher temperature), it was possible for the armour to support multiple hits (Fig. 4c) without being incorporated in an armour–system.
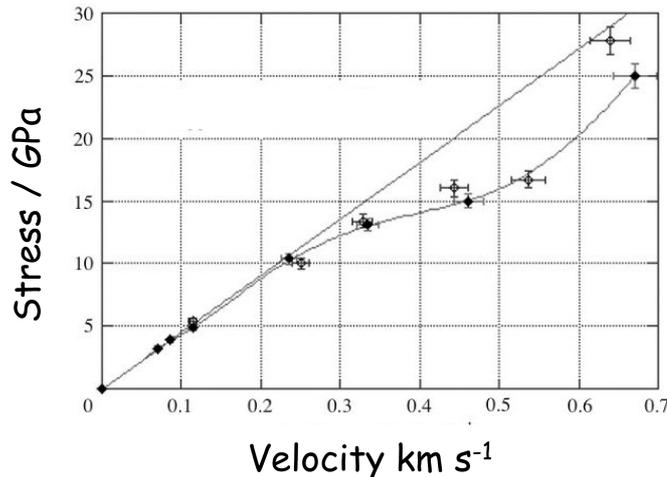

Fig. 3: Ballistic test on the bainitic armour alloys [19]. Departure from the straight line indicates plasticity and the horizontal axis represents projectile velocity.

The ballistic mass efficiency *BME* of an armour is defined as

$$BME = \frac{\text{mass of ordinary armour to defeat a given threat}}{\text{mass of test armour to defeat same threat}} \tag{1}$$

Fig. 4d shows that the *BME* of the strong bainite exceeds titanium armour and compares with the alumina [20].

Low–Carbon Hard Bainite?

High–carbon steels are difficult to weld because of the formation of untempered, brittle martensite in the coarse–grained heat–affected zones of the joints. The martensite fractures easily, leading to a gross deterioration in the structural integrity of the joint. For
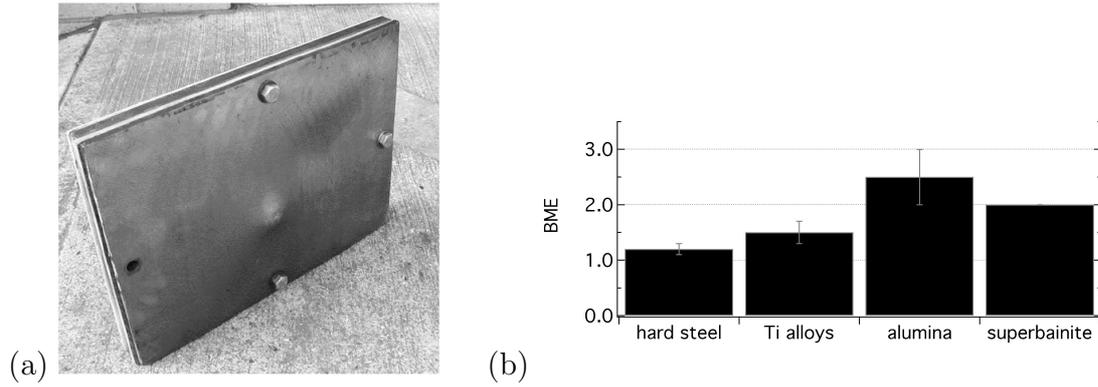
Fig. 4: Fe-0.98C-1.46Si-1.89Mn-0.26Mo-1.26Cr-0.09V wt%, transformed at 200°C for 5 days. (a) 12 mm thick sample of bainite between two plates of ordinary vehicle armour, with a layer of glass–reinforced plastic. Shows lack of penetration. (b) Comparison of armours. After D. Baxter and P. Brown.
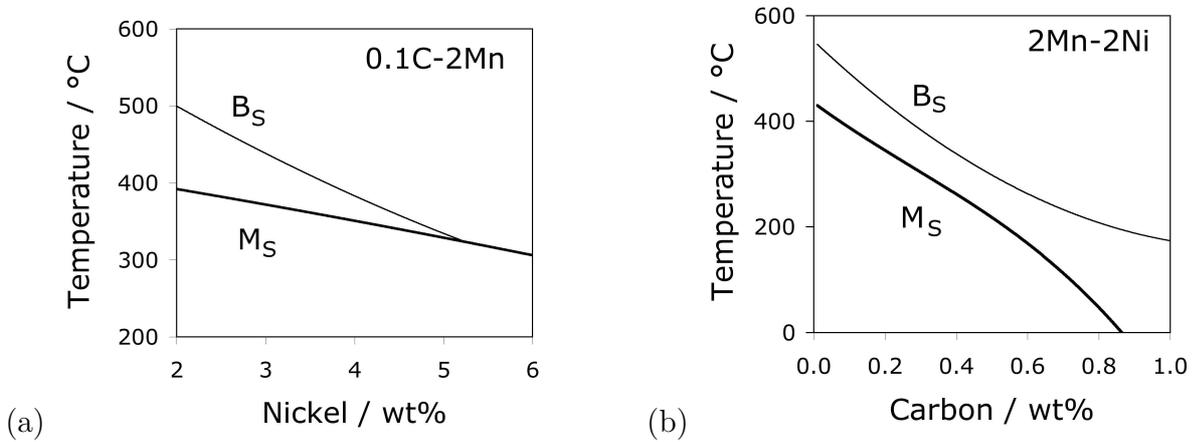

Fig. 5: Calculated bainite and martensite–start temperatures: (a) Fe–0.1C–2Mn wt%, with a variation in nickel concentration; (b) Fe–2Ni–2Mn with a variation in the carbon concentration [11].

this reason, the vast majority of weldable steels have low carbon concentrations. It would be desirable therefore to make the low–temperature bainite with a much reduced carbon concentration.

Calculations done using the scheme outlined elsewhere [11] indicate that carbon is much more effective in maintaining a difference between the M_S and B_S temperatures than are substitutional solutes which reduce $|\Delta G^{\gamma\alpha}|$ simultaneously for martensite and bainite, Fig. 5. Substitutional solutes do not partition during any stage in the formation of martensite or bainite; both transformations are therefore identically affected by the way in which the substitutional solute alters the thermodynamic driving force. It is the partitioning of carbon at the nucleation stage which is one of the distinguishing features of bainite when compared with martensite. This carbon partitioning allows bainite to form at a higher temperature than martensite. This advantage is diminished as the overall carbon concentration is reduced, as illustrated in Figure 5.

From these results, it must be concluded that it is not possible to design low–temperature bainite with a low carbon concentration.

5. SUMMARY

It is noticeable in the contemporary materials literature that *strength* is a term which is much abused. 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 50 MPa or as high as 5.5 GPa, 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 14 GPa, taking them into a range of recoverable strain where Hooke's law does not apply.

The bainite obtained by transformation at very low temperatures is the hardest ever, has considerable ductility (almost all of it uniform), does not require mechanical processing, does not require rapid cooling, the steel after heat–treatment therefore does not have long–range residual stresses, it is very cheap to produce and has uniform properties in very large sections. In effect, the hard bainite has achieved all of the essential objectives of structural nanomaterials which are the subject of so much research... but large in all its three dimensions.

ACKNOWLEDGMENTS

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