Hatfield Memorial Lecture

Bulk nanocrystalline steel

H. K. D. H. Bhadeshia*

Most new materials are introduced by selectively comparing their properties against those of steels. Steels set this standard because iron and its alloys have so much potential that new concepts are discovered and implemented with notorious regularity. In this 52nd Hatfield Memorial Lecture, a remarkably beautiful microstructure consisting of slender crystals of ferrite, whose controlling scale compares well with that of carbon nanotubes, is described. 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 that 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.

It is possible to think of many ways of creating extremely strong materials. Polycrystalline metals can be strengthened by reducing the scale of the microstructure whereas single crystals benefit from perfection. Carbon-based materials can in principle become incredibly strong if the only mode of deformation involves the stretching of carbon–carbon covalent bonds. These and many other mechanisms of strengthening unfortunately have limitations. In particular, it is difficult to make strong, isotropic materials which can be used to manufacture large components of arbitrary shape, whilst maintaining an attractive combination of properties at a reasonable cost. Such a material would be commercially viable over a broad range of applications.

Imagine in this context, 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. Before describing this novel material, it is important to review the meaning of strength, for there are many promises in the modern scientific and popular literature of materials which possess strength beyond our dreams. Appropriate comparisons will be made to show how steels feature in this scenario.

Theoretical strength

The strength of a crystal increases sharply as it is made smaller because the probability of avoiding defects increases. Brenner was able in 1956 to achieve a tensile strength greater than 13 GPa in an iron whisker about 1·5 μm in length Fig. 1.[1] It should in theory be possible to achieve a tensile strength of 21 GPa in ideal crystals of iron.

It is in this context that we now proceed to examine claims that large scale engineering structures can be designed using long carbon-nanotubes.[2,3]

Gigatubes

Single-walled carbon tubes can be imagined to be constructed from sheets of graphene consisting of sp^2 carbon arranged in a two-dimensional hexagonal lattice (Fig. 2). The sheets, when rolled up and with the butting edges appropriately bonded, are the nanotubes, which may or may not be capped by fullerene hemispheres.

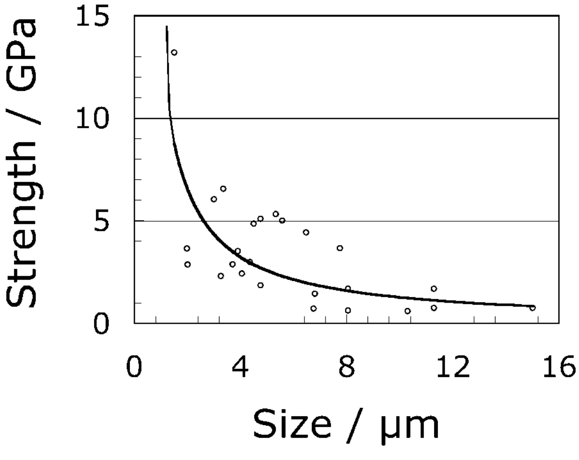
The carbon–carbon chemical bond in a graphene layer may be the strongest bond in an extended system;[5] carbon is also light, so it is not surprising that numerous papers extol the potential of long carbon-nanotubes as engineering materials to rival steel. The modulus of these tubes along the axis is about $1{\cdot}28 \pm 0{\cdot}59$ TPa.[5]

The calculated breaking strength of such a tube has been estimated to be 130 GPa; this number is so astonishing that it has led to exaggerated statements which are frequently repeated and hence have taken the form of 'truth' in the published literature. For example, the tubes are said to be 100 times stronger than steel; we have seen that whiskers of iron which are much bigger than carbon nanotubes, achieve a strength which is 14 GPa, with the potential of reaching 21 GPa. What all of this ignores is that materials *will* contain defects in their unstressed condition. Some of these defects will be there at equilibrium, i.e. they *cannot* be avoided. The concentration x of equilibrium defects is given by

$$x \approx \exp\{-\Delta h/kT\} \qquad (1)$$

where Δh is the enthalpy of formation of the defect and the other terms have their usual meanings.

Edwards[2] has estimated that 120 000 km gigatubes grown with the properties of carbon nanotubes are needed to construct a space elevator such as that shown in Fig. 3. He further



1 **Tensile strength of whiskers of iron**

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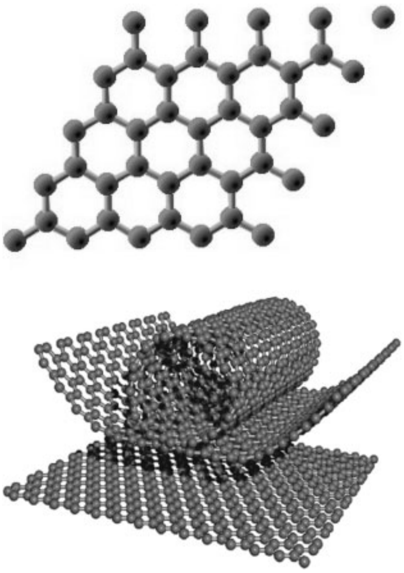
*University of Cambridge, Materials Science and Metallurgy, Pembroke Street, Cambridge CB2 3QZ, UK, www.msm.cam.ac.uk/phase-trans

DOI 10.1179/174328105X71308

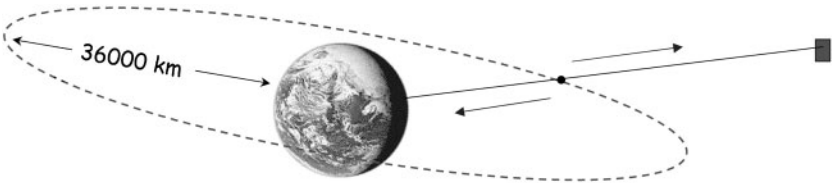


2 **Sheet of graphene and schematic diagram showing how sheet of graphene might be rolled to form tube.**[4]

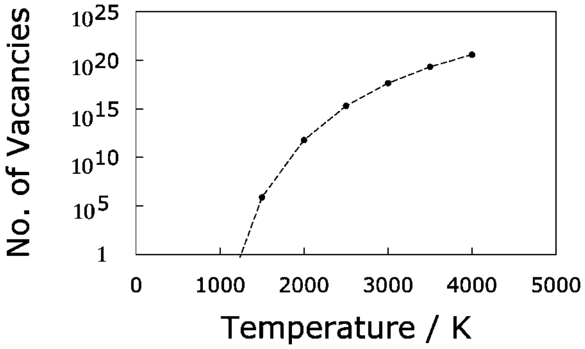
estimates that such a cable would weigh around 5000 kg. Based on this, assuming an upper limit of Δh of $\sim$7 eV,[6] and neglecting dimensionality differences, equation (1) can be used to calculate the equilibrium number of monovacancies expected as a function of temperature (Fig. 4). Here, the temperature of interest is that at which the carbon is assembled; this is typically 2000–4000 K, giving a large number of equilibrium defects. Given that the actual value of Δh is much smaller than 7 eV for a flat graphene sheet,[6] it cannot ever be assumed that defect-free gigatubes can be made with properties approaching tubes which are some 18 orders of magnitude smaller.

> Systems which rely on perfection in order to achieve strength necessarily fail on scaling to engineering dimensions. Indeed, there is no carbon tube which can match the strength of iron beyond a scale of 2 mm.

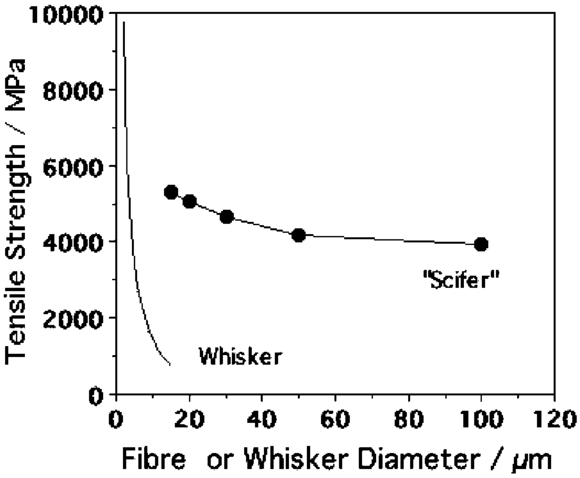
A gigatube rope would not be safe to use at a stress of 130 GPa in an engineering structure. The stored energy density in a tube stressed to 130 GPa, given an elastic modulus along its length of E=1·2 TPa, is in excess of that associated with dynamite, and the energy would be released at a speed greater than the detonation front in dynamite.



3 **Space-elevator concept (originally due to Arthur C. Clark), requiring a cable 120 000 km in length.**[2] **Cable would be launched in both directions from geosynchronous orbit at a height of 36 000 km**



4 **Calculated number of single-atom vacancies in 5000 kg of carbon nanotubes**



5 **Comparison of size-sensitivity of single-crystals whiskers of iron and *Scifer***

> Structures in tension which reversibly store energy far in excess of their ability to do work during fracture must be regarded as unsafe.

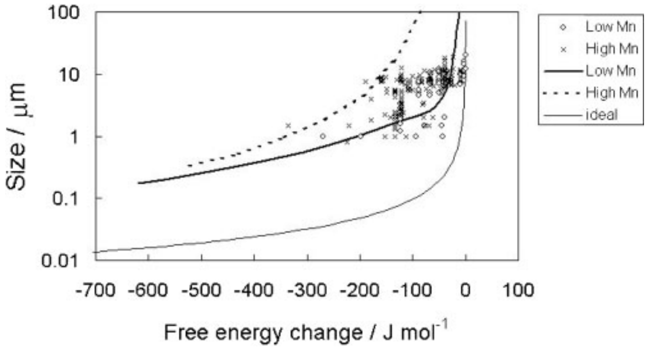
Strengthening by deformation

It has been possible for some time to obtain commercially, steel wire which has an ultimate tensile strength of 5·5 GPa and yet is very ductile in fracture.[7,8] *Scifer,* as the wire is known, is made by drawing a dual-phase microstructure of martensite and ferrite in Fe–0·2C–0·8Si–1Mn (wt-%) steel in the form of 10 mm diameter rods, into strands which individually have a diameter of about 8 μm. This amounts to a huge deformation with a true strain in excess of 9. The dislocation cell size in the material becomes about 10–15 nm, from which much of the strength of *Scifer* is derived.[8] A similar stainless steel thread is also available commercially.[9]

The fact that the properties are here achieved by introducing defects, also means that the strength of *Scifer* is insensitive to its size (Fig. 5).

A denier is the weight in grams of 9 km of fibre or yarn. A 50 denier thread is typically used in making socks, whereas stockings are made from 10 denier fibre. *Scifer* is just 9 denier in this classification; this highlights one of the difficulties in using deformation to increase strength. The deformation necessary to accumulate a large number density of defects limits the size and form of the product, in the case of *Scifer* to that of a textile thread. Deformation processes such as equi-channel angular processing and accumulative roll-bonding maintain the overall dimensions but the range of shapes that can be achieved is limited.

> The properties of severely deformed materials are insensitive to size but the forms that can be produced are limited.



6 **Plot of logarithm of ferrite grain size versus free energy change at Ar_3. Ideal curve represents values of $\bar{L}_\alpha^{\min}$: points are experimental data; in some cases it is assumed that grain size quoted in literature corresponds to mean lineal intercept; curves marked low and high-Mn represent calculated values of $\bar{L}_\alpha^{\min}$ after allowing for recalescence[10]**

Undeformed, fine, polycrystalline steel

High-strength low-alloy steels have contributed so much to the quality of engineered products that tens of billions of tonnes of such alloys now permeate all aspects of life. During the processing, fine austenite (γ) grains are generated by a combination of deformation and recrystallisation; the austenite finally transforms into fine grains of ferrite (α), with a size typically of 10 μm. The recent search has been for processes which reduce the grain size dramatically to less than 1 μm . Fine grains represent one of the few mechanisms available to increase both strength and toughness. What then is the theoretical minimum grain size that can be achieved using this technology?

The smallest ferrite grain size $\bar{L}_\alpha^{\min}$ is achieved when all the free energy change associated with the austenite to ferrite transformation ($\Delta G_V^{\gamma\alpha}$) is used up in creating α/α grain boundaries[10]

$$\bar{L}_\alpha^{\min} = \frac{2\sigma_\alpha}{|\Delta G_V^{\gamma\alpha}| + 2\sigma_\gamma / \bar{L}_\gamma} \qquad (2)$$

where σ is the interfacial energy per unit area and $\bar{L}_\gamma$ is the austenite grain size. Figure 6 shows the variation in the limiting ferrite grain size ($\bar{L}_\alpha^{\min}$) as a function of ΔG_V (details in Ref. 10). These calculations are presented as the 'ideal' curve, which indicates that at large grain sizes, $\bar{L}_\alpha^{\min}$ is sensitive to ΔG_V and hence to the undercooling below the equilibrium transformation temperature. However, reductions in grain size in the submicrometre 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. 6 are points corresponding to measured ferrite grain sizes from low and high-Mn steels.[10] It is evident that except at the lowest undercoolings, $\bar{L}_\alpha \gg \bar{L}_\alpha^{\min}$. The data indicate that, in spite of tremendous efforts, the smallest ferrite grain size obtained commercially using thermomechanical processing is stuck at about 1 μm.

The reason for this is recalescence, which is the heating of the sample caused by release of the latent heat of transformation at a rate so high that it cannot easily be dissipated by diffusion. This recalescence reduces the effective undercooling and hence the driving force for transformation.[10] It is seen from Fig. 6 that the recalescence-corrected curves show better agreement with the experimental data, indicating that at large undercoolings, the achievement of fine grain size is limited by the need to dissipate enthalpy during rapid transformation.

> To achieve submicrometre grain sizes it is necessary to transform at large undercoolings, but the rate of transformation then increases, leading to recalescence, which defeats the objective. Large scale thermomechanical processing is therefore limited by recalescence and is unlikely to lead to grain sizes which are uniformly less than about 1 μm.

Martensite

Very strong martensitic steels with strength greater than 3 GPa already exist. This kind of martensite is produced in fairly large steel samples by rapid cooling from the austenitic condition. However, the dimensions can be limited by the need to achieve a uniform microstructure, a fact implicit in the original concept of hardenability. To increase hardenability requires the addition of expensive alloying elements. The rapid cooling can lead to undesirable residual stresses which can ruin critical components and which have to be accounted for in component-life assessments.

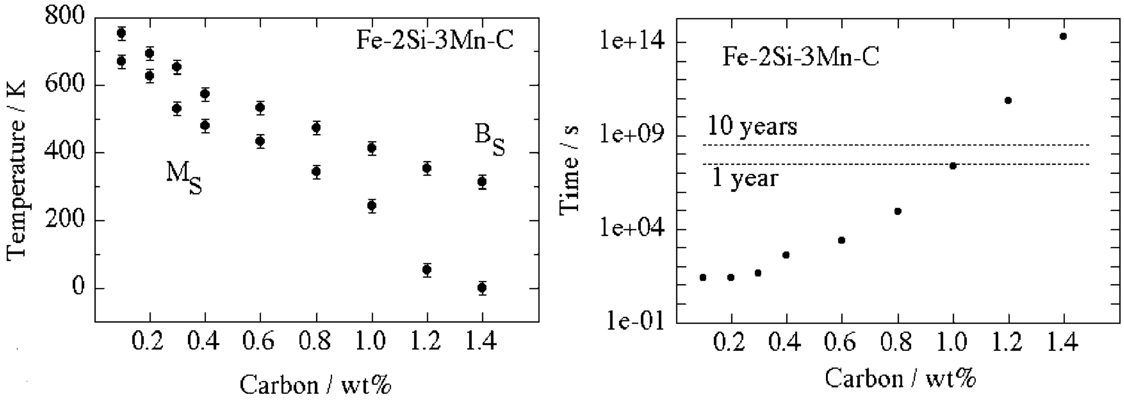
Design criteria

It would be nice to have a strong material for making components which are large in all their dimensions, and which does not require mechanical processing or rapid cooling to reach the desired properties. It has been shown that the following conditions are required to achieve this:

- 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 that allows the ready dissipation of heat.

Hard bainite

Steel transformed into carbide-free bainite can satisfy these criteria. Bainite and martensite are generated from austenite without diffusion by a



7 Calculated transformation start temperatures in Fe–2Si–3Mn steel as function of carbon concentration and calculated time required to initiate bainite at B_S temperature.

displacive mechanism. This leads to solute-trapping and also a huge strain energy term, both of which reduce the heat of transformation. The growth of individual plates in both 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.[11] 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. Such calculations are illustrated in the left part of Fig. 7, 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 the right plot of Fig. 7. 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, i.e. 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 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 Fig. 7 demonstrated that in a 1C–1·5Si–2Mn steel (detailed composition in Table 1), bainite can be generated at a temperature as low at 125°C,[12] 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 shown in Fig. 8 not only have metallurgical significance in that they confirm calculations, but also are elegant. 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.[12] 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 10 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.

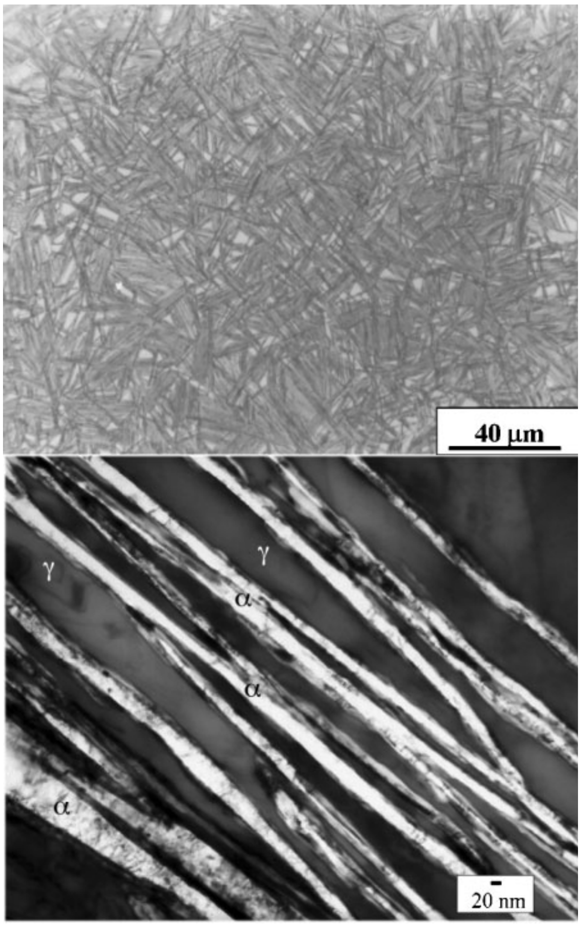
It is cheap to heat-treat something at temperatures at which pizzas are normally cooked. But suppose there is a need for a more rapid process. The

Table 1 Typical chemical compositions of hard bainite: silicon is added to prevent cementite formation during growth of bainite; molybdenum to counter embrittlement due to impurities such as phosphorus; manganese and chromium for hardenability; and cobalt and aluminium to accelerate transformation. Substitutional solutes also contribute to hardenability and determine T_0 curve which is vital in design of carbide-free bainitic steels

C	Si	Mn	Mo	Cr	V	Co	Al	Ref.
0·98	1·46	1·89	0·26	1·26	0·09	…	…	12
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

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]

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 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 many defects are created during the growth of the bainite, a large concentration of carbon remains trapped in the bainitic ferrite and does not precipitate, probably because it is trapped at defects.[16,17]



8 **Optical and transmission electron micrographs of Fe–0·98C–1·46Si–1·89Mn–0·26Mo–1·26Cr–0·09V transformed at 200°C for 5 days[12,14]**

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 ($10^7 s^{-1}$) associated with ballistic tests.[18] The strong bainite has therefore found application in armour.[19] Tests have been conducted using projectiles which are said to involve 'the more serious battlefield tests' (the details are proprietary). Figure 9 shows the result of a test on an armour *system*. A 12 mm thick sample of the bainitic steel is sandwiched between vehicle steel, the whole contained in glass-reinforced plastic. The projectile would have penetrated ordinary armour completely, whereas the bainite has prevented this; the steel did, however, crack.

The ballistic performance of the strong bainite exceeds that of titanium armour and approaches that of alumina.[19]

Summary

The ultimate aim above has been to emphasise the ability to make large chunks of strong and tough steel. But it has been necessary to place this in the wider context of strong materials to allow sensible comparisons to be made.

When claims are made about strong materials for structural applications, they seem frequently to neglect the elementary science of scale. Just because it is possible to produce a nanotube of carbon which has a calculated strength of 130 GPa and a measured strength approaching that value, it does not mean that this can be translated into a fibre of a length visible to the naked eye, let alone the 120 000 km needed to begin thinking about a space-elevator. Indeed, it may not be possible even in principle to scale the properties given the existence of entropy-stabilised equilibrium defects.

It is noticeable in the contemporary materials literature that *strength* is a

9 **Result of ballistic test on Fe–0·98C–1·46Si–1·89Mn–0·26Mo–1·26Cr–0·09V, transformed at 200°C for 5 days: rear view, showing lack of penetration (courtesy D. Crowther and P. Brown)**

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.

There remain, as is always the case, many parameters yet to be characterised, for example the fatigue and stress-corrosion properties.

> 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 in large chunks*!

Acknowledgement

This is an edited version of the 52nd Hatfield Memorial Lecture, presented in Sheffield, UK on 7 December 2004.

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