Very Strong, Low–Temperature Bainite

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Background and Context

During the course of our research on the quantitative design of steels [1,2], an exciting discovery was made, in which carbide–free bainite was obtained by transformation at incredibly low temperatures, as low as 125 °C [3]. To put this into context, the random jump distance of an iron atom at that temperature is only 10^{-17} m over a period of three weeks. The consequence of the low transformation–temperature was to reduce the scale of the microstructure to such an extent, that it became possible to achieve a strength of 2300 MPa with signs of considerable ductility. The work described in what follows was carried out to understand and design this extraordinary bainite, which is incredibly strong, tough and cheap. The combination of properties achieved has never before been reported for bainite.

Essential Results from the Research

Hard Bainite

It is possible, using our theory based on the mechanisms of transformation, to calculate the bainite–start (B_S) and martensite–start (M_S) temperatures as a function of steel composition [4,5]. A set of these calculations for a steel with sufficient hardenability to avoid other transformations is illustrated in Fig. 1a. From a thermodynamic point of view, it clearly is possible to obtain bainite at very low temperatures. To estimate whether this is a reasonable statement from a kinetic point of view, time–temperature–transformation (TTT) diagrams were calculated as described elsewhere [5]. The time required to initiate transformation just below B_S is plotted in Fig. 1b as a function of the carbon concentration; it takes approximately a year to begin forming bainite when the carbon concentration of the Fe–2Si–3Mn alloy reaches 1 wt%, and at somewhat higher concentrations reaches 10 years. A systematic investigation showed that the calculated transformation times were in good agreement with measurements (time periods $\leq$ 3 months), even though such low transformation temperatures have not been used in previous work. Therefore, there is a severe kinetic limitation to producing bainite in such a steel for temperatures below about 400 K. It was our aim to form bainite at a low temperature in a steel designed for a specific structural application.

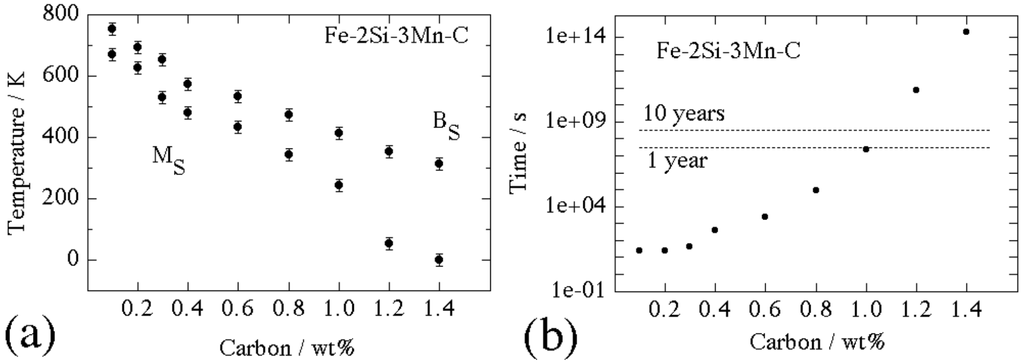

Fig. 1: Calculated transformation temperatures and times to initiate transformation at B_S as a function of the carbon concentration.

The alloy selected by calculation is described in Table 1 (alloy 1); it contains manganese, vanadium and chromium for hardenability, silicon to prevent the precipitation of cementite during upper bainite formation and molybdenum to prevent temper embrittlement due to phosphorus. The carbon concentration was selected using calculations of the type illustrated in Fig. 1, to suppress B_S whilst at the same time have realistic transformation times. It was first demonstrated that in a high–carbon steel where carbide precipitation is suppressed, bainite can be obtained by isothermal transformation at a temperatures as low as 125 °C. The time taken for nucleation at this temperature can be many days, but the transformation results in the growth of extremely thin platelets (Fig. 2) of bainite, so thin that the hardness of the resulting steel can be greater than 600 HV. The work has been published in [6,7].

Alloy	C	Si	Mn	Mo	Cr	V	Co	Al
1	0.98	1.46	1.89	0.26	1.26	0.09		
2	0.83	1.57	1.98	0.24	1.02		1.54	
3	0.78	1.49	1.95	0.24	0.97		1.60	0.99

Table 1: Chemical compositions of experimental alloys, wt%

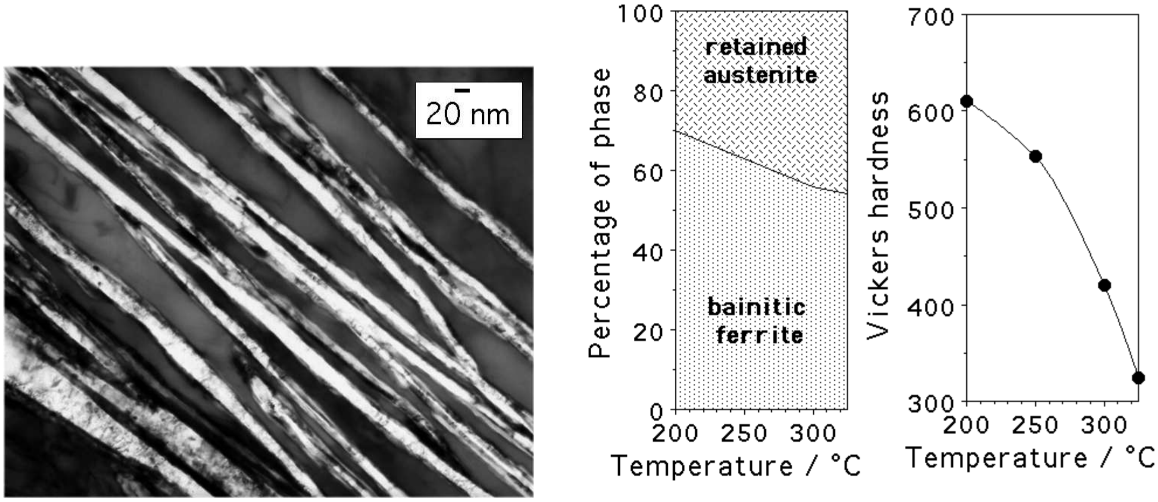

Fig. 2: The fine microstructure and other properties.

Acceleration of Transformation

Slow transformation at a low temperature (*e.g.* 200 °C, 9 days) is not necessarily a disadvantage since there is no need to cool the sample rapidly to the isothermal transformation temperature. Even a large steel component can therefore reach a homogeneous temperature prior to the onset of transformation, thereby mitigating residual stresses. And a low–temperature heat treatment is not in itself expensive since the energy requirements decrease as the temperature is reduced, and because there is no need to protect the steel against oxidation.

It may nevertheless be useful for small components to be able to accelerate transformation without losing the ability to transform at a low temperature and whilst retaining the fine microstructure which gives the desirable properties. This has been achieved by increasing the free energy change $\Delta G^{\gamma\alpha}$ through additions of cobalt aluminium on the basis of thermodynamic phase stability calculations (alloys 2,3, Table 1). In addition, the austenite grain size has been refined by using lower austenitisation temperatures, thereby increasing the number density of bainite nucleation sites.

The modified alloys show a more refined microstructure, a greater limiting volume fraction of bainitic ferrite and an increased hardness without any loss in toughness, results which are consistent with the theory of the bainite reaction in steels as reviewed in [8,9,10,11]. The work has been published in [12].

Detailed Mechanical Properties

The mechanical properties (tensile, K_{IC}) have been characterised in detail for all the steels studied; this work is in the process of publication, but can be summarised as follows.

In tension, the samples exhibit gradual yielding and an ultimate tensile strength which is in the range 2.0–2.3 GPa with a hardness up to 700 HV, for initial microstructures which consist only of bainitic ferrite and carbon–enriched retained austenite. The 0.2% proof strength is in the range 1.2–1.5 GPa, with rapid strain hardening; for example, the corresponding 1% proof strength is in the range 1.5–1.8 GPa. This gradual yielding is anticipated to be beneficial to the fatigue properties [11], which have yet to be investigated. The tensile elongation ranges from about 5-30%, the larger values corresponding to samples transformed at higher temperatures. The observed elongation is mostly uniform, with very little reduction of area in the fractured sample.

The very high strength values obtained are largely a consequence of the fine scale of the bainite plates. We have demonstrated quantitatively that almost 1700 MPa of the total strength of samples transformed at 200 °C, comes from the fact that the bainite plates are only tens of nanometers in thickness. The model predicts that the hardness can be related more accurately to the ratio $\overline{L}^{-1} \propto V_B/t$, where $\overline{L}$ is the mean lineal intercept defining the bainite plate size and V_B is the fraction of bainite; this relationship has been verified experimentally [12].

Measured fracture toughness values fall in the range $K_{IC} = 27 - 40\,\mathrm{MPa\,m}^{1/2}$. These values are impressive given that the alloys studied are all conventionally cast, *i.e.* they have not been vacuum arc refined as would normally be the case for ultra–high–strength steels. From experience, this implies that even higher values should be achievable.

The retained austenite does partly transform into martensite during the course of plastic deformation. However, the transformation is found to occur at plastic strains as small as 3% elongation. Much better properties are expected if the transformation can be delayed until the sample accumulates damage. We have proved this by stabilising the austenite, in which case the elongation increased from only 5% to more than 25%, without any loss of strength. This work needs to be pursued further.

The idea of achieving better mechanical properties by making the austenite more resistant to transformation during plastic deformation is contrary to popular opinion. A cursory examination of the published literature shows that the good mechanical properties of steels containing retained austenite are frequently attributed to transformation plasticity (TRIP). We have shown using crystallographic modelling that this is misleading [13], and that the TRIP effect *per se* has only a minor role in determining the uniform elongation. The major effect comes from the composite deformation behaviour of both the initial, and the mixed microstructure that develops during the course of deformation [13].

In further work [14,15], we have also developed a quantitative model for the strain–induced transformation of austenite in mixed microstructures and have validated it against a vast array of experimental data available in the published literature. We have a feeling that the progress that has been made within this project, on understanding the role of the retained austenite, could lead to major improvements in toughness. The work has already been cited in the context of low–strength steels of the kind used in automobiles.

Tempering Resistance

As pointed our earlier, much of the strength (1700 MPa out of 2300 MPa) of the virgin microstructure comes from the fine size of the bainite plates in the alloy studied here. This microstructure has been found to be incredibly resistant to tempering, the hardness behaviour replicating that of richly–alloyed secondary–hardening steels. This is in spite of the absence of secondary hardening in the steels used during the tempering experiments. The resistance of this microstructure to tempering has been shown to originate from the fact that it is very difficult for the plate microstructure to coarsen due to the intense precipitation of cementite. These carbides form from the carbon–enriched austenite between the bainitic ferrite plates in the virgin microstructure, and hence are ideally located to prevent the plate–coarsening process.

The carbides themselves lead to some precipitation strengthening as indicated by an initial rise in hardness during the early stages of tempering. It is not surprising therefore, that the decomposition of austenite itself does not lead to any overall softening. The work has been submitted for publication [16].

Excess Carbon

We have conducted a large number of experiments, using X–ray analysis [16], Mössbauer spectroscopy and atom–probe analysis to show that the bainitic ferrite in the steels studied contains a huge excess of carbon in solid solution. The concentrations can be as large as 0.3 wt%. Whereas this is far less than the average carbon concentration of the steel (about 1 wt%), it is orders of magnitude larger than expected from equilibrium or paraequilibrium considerations. The observations are of crucial importance in proving the mechanism of the bainite transformation and papers are currently being prepared for publication. The excess carbon in the ferrite is largely located at defects; it does not precipitate until there is a substantial recovery in the microstructure. This is expected from theory found in the published literature.

Nucleation Theory

To make comprehensive calculations requires a reliable nucleation model for bainite. The first such model was developed by us in 1981 [11] based on a dislocation mechanism and was validated on a large amount of published data on low–carbon steels. The new experimental data on the present high–carbon steels have been shown quantitatively to agree remarkably well with the early work [17].

Research Impact: Scientific and Technological Relevance

Substitutional solutes are often used to suppress transformation temperatures. Here we have achieved this using a high carbon concentration, with bainite forming at temperatures where substitutional atom diffusion is impossible over very long time scales. If proof were ever needed of the displacive mechanism of transformation, then this is powerful evidence. The large carbon supersaturation found in the ferrite adds to the body of evidence that the initial concentration in bainitic ferrite is far in excess of equilibrium.

The theory used throughout this work to develop the alloys has all been associated with the displacive mechanism. There is no alternative theory available to make such predictions. Thus, all the new alloys manufactured in this work have been predicted, rather than arrived at by trial and error. The details of the theories have been published.

From a technological point of view, the main achievement is that it is now possible to obtain ultra–high strength steel, in bulk form, without rapid cooling or severe plastic deformation, without the use of expensive alloying.

Benefits to Society

The work has already led to a major defence development programme within QinetiQ, research programmes at Volvo and SKF on gears, and has stimulated a number of basic research programmes in academic institutes (Cavendish Laboratory in Cambridge, CENIM, Spain) and US Government laboratories (Oak Ridge). The QinetiQ work is particularly advanced; although we are not permitted to reveal details, it is clear that the steel outperforms, by a factor of about four, conventional alloys used to protect humans and equipment from high–velocity projectiles. The performance compares with ceramic protection, but has the additional advantages of cost and being able to take multiple impacts.

Dissemination and Exploitation

Much of the work has been published. The papers, data and micrographs have been archived on our web site (www.msm.cam.ac.uk/phase–trans) for free access. Samples of the steel have been provided to academic organisations via Cambridge University, whereas much larger quantities have been supplied to commercial organisations via QinetiQ. Discussions are in progress with Rolls-Royce.

The work has been presented in colloquia and invited lectures at: Materials Science and Metallurgy (Cambridge); Cavendish Laboratory (Cambridge); Nippon Steel Corporation (Japan); Osaka University (Japan); John Player Lecture of the Institution of Mechanical Engineers (London); Oak Ridge National Laboratory (USA); QinetiQ (UK); U.S. Naval Research Laboratory (Washington); Tata Steel (India); IIT Kharagpur (Calcutta); IIT Bombay (Tendolkar Memorial Lecture); Indian Institute of Science (Birla Chair Lecture, Bangalore); Birmingham University (UK).

Lectures, some of which were invited, have been presented at international conferences: ICOMAT (Finland); JWRI Meeting (Japan); ESOMAT (UK).

Project Plan Review and Expenditure

There have been no substantive changes to the original project plan or proposed expenditure.

Further Research

The essential ideas for further research have been outlined above, but two detailed proposals are being prepared for EPSRC/Industry funding for developing an understanding of the fatigue and hydrogen resistance of the novel steel.

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