ADVANCED ULTRA HIGH STRENGTH BAINITIC STEELS

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Abstract: The addition of about 2 wt-% of silicon to steel enables the production of a distinctive microstructure consisting of a mixture of bainitic ferrite, carbon-enriched retained austenite and some martensite. The silicon suppresses the precipitation of brittle cementite, and hence should lead to an improvement in toughness. However, the full benefit of this carbide-free bainitic microstructure has frequently not been realised. This is because the bainite reaction stops well before equilibrium is reached. This leaves large regions of untransformed austenite which under stress decompose to hard, brittle martensite.

The essential principles governing the optimisation of such microstructures are well established, particularly that an increase in the amount of bainitic ferrite in the microstructure is needed in order to consume the blocks of austenite. With careful design, impressive combinations of strength and toughness have been reported for high-silicon bainitic steels. More recently, it has been demonstrated experimentally that models based on phase transformation theory can be applied successfully to the design of carbide free bainitic steels. Toughness values of nearly 130 MPa m^{1/2} were obtained for strength in the range of 1600-1700 MPa. This compares well with maraging steels, which are at least thirty times more expensive.

However, the concepts of bainite transformation theory can be exploited even further to design steels that transform to bainite at temperatures as low as 150 °C. Low transformation temperatures are achieved by the use of a high average carbon concentration and to some extent, substitutional solutes such as manganese. The aim of alloy design is to make austenite stronger by suppressing the bainite transformation to low temperatures in order to obtain extremely thin platelets of bainite (~40 nm). Microstructure obtained is so refined that it is possible to achieve a strength in excess of 2.5 GPa in a material which has considerable toughness (30 MPa m^{1/2}). Such properties have never been achieved before with bainite. It is intended to provide a description of the characteristics and significance of this remarkable microstructure in the context of the mechanism of transformation.

INTRODUCTION

The thermomechanical control processed bainitic steels have not been in practice as successful as those quenched and tempered, because the presence of coarse cementite particles in the bainitic microstructure. The formation of cementite has a detrimental effect in the microstructure since cementite particles are responsible for damage initiation in modern high-strength steels. However, the precipitation of cementite during bainitic transformation can be suppressed by alloying the steel with about 1.5 wt-% of silicon, which has very low solubility in cementite and greatly retards its growth from austenite. The carbon that is rejected from the bainitic ferrite enriches the residual austenite, thereby stabilising it down to ambient temperature. The resulting microstructure consists of fine plates of bainitic ferrite separated by carbon-enriched regions of austenite. There may also be some martensite present.

This mixed microstructure is in principle an ideal combination from many points of view. In particular, the steel has a high resistance to cleavage fracture and void formation due to the absence of fine carbides. There is then a possibility of improving simultaneously the strength and toughness

because of the ultrafine grain size of the bainitic ferrite plates, and of further enhancing the toughness by a transformation-induced plasticity effect.

In spite of all these potential advantages, the carbide-free bainitic microstructure has on some occasions failed to live up to its promise. This is primarily because of the instability of relatively large or blocky regions of austenite which become trapped between sheaves of bainite. Therefore, every effort has to be made to reduce the fraction of blocky austenite present in the microstructure and increase its stability to martensitic transformation. The aim of alloy design should then be to increase the maximum permitted degree of transformation to bainitic ferrite. There may be other constraints, for example, the need to ensure that the hardenability of the steel is sufficient for avoiding proeutectoid ferrite formation during cooling.

The bainite transformation progresses by the diffusionless growth of tiny platelets known as "sub-units". The excess carbon in these platelets partitions into the residual austenite soon after the growth event. Diffusionless growth of this kind can only occur if the carbon concentration of the residual austenite is below that given by the T'_o curve. The T_o curve is the locus of all points, on a temperature versus carbon concentration plot, where austenite and ferrite of the same chemical composition have the same free energy. The T'_o curve is defined similarly but taking into account the stored energy of the ferrite due to the displacive mechanism of transformation. It follows that the maximum amount of bainite that can be obtained at any temperature is limited by the fact that the carbon content of the residual austenite must not exceed the T'_o curve on the phase diagram. The design procedure avoids this difficulty in three ways: by adjusting the T'_o curve to greater carbon concentrations using substitutional solutes, by controlling the mean carbon concentration, and by minimising the transformation temperature.

Bainite is formed below the T'_o temperature when

$$\Delta G^{\gamma \rightarrow \alpha} < -G_{SB} \text{ and } \Delta G_m < G_N \quad (1)$$

where $G_{SB} \cong 400 \text{ J mol}^{-1}$ is the stored energy of bainite [1]; $\Delta G^{\gamma \rightarrow \alpha}$ is the free energy change accompanying the transformation of austenite without any change in chemical composition. The first condition therefore describes the limit to growth. The second condition refers to nucleation; thus, ΔG_m is the maximum molar Gibbs free energy change accompanying the nucleation of bainite. G_N is a universal nucleation function based on a dislocation mechanism of the kind associated with martensite [1-4]. The temperature dependence of G_N is independent of chemical composition; together with the growth condition, the function allows the calculation of the bainite start temperature, B_s , from a knowledge of thermodynamics alone.

Apart from controlling the T'_o curve and B_s temperature, substitutional solutes also affect hardenability which is an important design parameter to avoid transformations such as proeutectoid ferrite and pearlite. For this purpose, we use a thermodynamic method [5] developed to allow the estimation of isothermal transformation diagrams, from a knowledge of the chemical composition of the steel concerned. Calculated time-temperature-transformation (TTT) diagrams also give us an idea of the time required to initiate transformation.

Alloy design

The aim of this work was to design bainitic alloys with the following engineering requirements: a Charpy impact energy of 40 J at -40 °C, 1100 MPa tensile and 1000 MPa proof strength. A minimum ductility of 12% elongation and 50% reduction of area were also required. Previous research, carried out by Bhadeshia and Edmonds [6,7] and Miihkinen and Edmonds [8-10], on two silicon-containing steels, nominally, Fe-0.2C-2Si-3Mn wt-% and Fe-0.4C-2Si-4Ni wt-% showed that these alloys hold promise. The Fe-0.2C-2Si-3Mn wt-% alloy exhibited excellent fracture toughness (K_{Ic} =160 MPa $\sqrt{m}$) in a strength range of 1375-1440 MPa as isothermally heat-treated at 250 °C. This fracture toughness is better or equal than that of quenched and tempered AISI 300M and AISI 4340 steels at equivalent strength levels and approaches that of the 18 wt-% Ni maraging steel [10]. Because of the increased carbon content, higher strength levels 1500-1840 MPa were obtained in the Fe-0.4C-2Si-4Ni wt-% alloy, with lower fracture toughness values, but this still exceeded those of commercial high strength martensitic steels. These original experiments [6,7] were carried out in order to demonstrate the role of the T_o curve in greatly influencing the mechanical properties of carbide-free bainitic steels. The experimental alloys developed for this purpose are not necessarily the optimum alloys from the point of view of mechanical properties. Our aim here was to use the combination of the models mentioned above, to produce the best possible alloys, with microstructures produced by continuous cooling transformation, building on the previous work [6,7].

TABLE 1: Actual chemical composition of designed bainitic steels, wt-%

Steel	C	Si	Mn	Ni	Cr	Mo	V
Mn	0.32	1.45	1.97	<0.02	1.26	0.26	0.10
Ni1	0.31	1.51	<0.01	3.52	1.44	0.25	0.10
Ni2	0.30	1.51	<0.01	3.53	1.42	0.25	<0.005
A	0.79	1.59	1.94	-	1.33	0.30	0.11
B	0.98	1.46	1.89	-	1.26	0.26	0.09

The alloys (Mn, Ni1 and Ni2) that were proposed following a very large number of theoretical investigations, are listed in **Table 1**. The alloys contain manganese, vanadium and chromium for hardenability, silicon to prevent the precipitation of cementite during bainite formation, and molybdenum to prevent temper embrittlement due to phosphorus. In order to increase the strength of the Fe-0.2C-2Si-3Mn wt-% alloy and the toughness of the Fe-0.4C-2Si-4Ni wt-% alloy, the amount of carbon was selected to be 0.3 wt-% C in the three designed alloys. **Figure 1** shows the calculated TTT diagrams representing the initiation of transformation. Also plotted are representative cooling curves [11] simply as an indication of hardenability. The curves should really be plotted on continuous cooling transformation diagrams, where the transformation curves would be displaced to longer times. The calculated microstructures listed in **Figure 1** are, on the other hand, rigorous, using the methods described in Ref. [12].

On the other hand, combination of the models described above was used to produce the finest possible bainitic microstructure by transformation at the lowest possible temperature. Using the models together with some background knowledge, Steels A and B listed in **Table 1** were proposed to decrease bainite transformation temperatures, increase the maximum volume fraction of bainite in the final microstructure and to improve the hardenability of the steels. The carbon concentration was

selected using calculations to suppress B_s temperature and to make austenite stronger with the aim of obtaining extremely thin platelets of bainite.

FIGURE 1: Calculated TTT diagram for the initiation of transformation of a) Mn alloy, b) Ni1 alloy and c) Ni2 alloy.

15 min at 1000 °C, and then isothermally transformed at temperatures ranging from 125 to 500 °C for different times before quenching into water.

Specimens were polished in the usual way and etched in 2% Nital solution, and examined using a JEOL JXA-820 scanning electron microscope operated at 10-15 kV. The volume fraction of bainite (V_b) was estimated by a systematic manual point-counting procedure on scanning electron micrographs. Specimens for transmission electron microscopy were electropolished at room temperature until perforation occurred, using a twin-jet electropolisher set at a voltage of 40 V. The electrolyte consisted of 5 % perchloric acid, 15 % glycerol and 80 % methanol. The foils were examined in a JEOL JEM-200 CX transmission electron microscope at an operating voltage of 200 kV. Quantitative X-ray analysis was used to determine the fraction of retained austenite. The carbon concentration in the austenite was estimated by using the lattice parameters of the retained austenite. Finally, atom probe specimens were cut from bulk material and electropolished with the standard double layer and micropolishing methods. Atom probe analyses were performed in a local electrode atom probe operating with a specimen temperature of 60K, a pulse repetition rate of 200 kHz, and a pulse fraction of 20%.

Tensile testing was carried out in accordance with BS EN 10 002-1: 1990 at room temperature on a 100 kN Instron-6025 machine at a crosshead speed of 2 mm min⁻¹. Two specimens were tested for each alloy. Impact toughness was measured at temperatures between 20 and -120 °C using a 300 J

EXPERIMENTAL

Steels Mn, Ni1 and Ni2 in **Table 1** were prepared as 35 kg vacuum induction melts using high purity base materials. After casting and cropping, the ingots were hot forged down to a thickness of 65 mm. These were then homogenised at 1200 °C for 2 days and cut into smaller 65 mm thick samples which were then forged down to 50 mm thickness. These samples were then held at 900 °C for 2 hours, removed from the furnace and immediately hot-pressed to a thickness of 25 mm before their temperature fell below 750 °C. Finally they were allowed to cool in air. On the other hand, Steels A and B in **Table 1** were supplied as cast ingot. They were firstly homogenised at 1200 °C for 2 days whilst sealed in partially evacuated quartz capsules flushed with argon. Afterwards the sealed samples were cooled in air. The homogenised specimens were then austenitised for

Charpy testing machine. Specimens were tested in accordance with BS EN 10 045-1: 1990. Six specimens were tested at each temperature for every alloy.

RESULTS AND DISCUSSION

Experimental data of the designed steel microstructures are presented in **Table 2**. These data reveal that Ni1 and Ni2 have the desired microstructure consisting of mainly bainitic ferrite and retained austenite. Because of the high carbon content in austenite (x_γ) for these alloys, the majority of residual austenite present after bainite is formed, is retained on cooling to room temperature.

TABLE 2: Quantitative Data on Microstructure and Hardness

Steel	V_b	V_γ	$V_{\alpha'}$	x_γ wt-%	Hardness, HV30
Mn	0.26±0.01	0.07±0.01	0.67±0.02	0.55	597±2
Ni1	0.62±0.05	0.12±0.01	0.26±0.04	0.92	493±5
Ni2	0.81±0.06	0.11±0.01	0.08±0.05	1.03	536±6

V_b bainitic ferrite volume fraction; V_γ retained austenite volume fraction; $V_{\alpha'}$ martensite volume fraction; x_γ carbon content in austenite. Hardness values are averaged over 10 tests

FIGURE 2.- Bright field images of microstructures obtained in a) Ni1 alloy and b) Ni2 alloy

Due to the high volume fraction of bainitic ferrite in Ni1 and Ni2 alloys, 0.62 and 0.81 respectively, the retained austenite was largely present as films between the subunits of bainitic ferrite. **Figure 2** shows typical bright-field images of carbide-free upper bainite in Ni1 and Ni2 with interlath retained austenite films. These films have a typical wavy morphology characteristic of the bainite in high-silicon steels. By contrast, the small amount of bainite in the Mn alloy causes much of the residual austenite to transform to martensite during cooling because of lower carbon-enrichment of the austenite (0.55 wt-%).

Tensile test results are presented in **Table 3**. Plates of bainitic ferrite are typically 10 μm in length and about 0.2 μm in thickness. This gives a rather small mean free path for dislocation glide. Thus, the main microstructural contribution to the strength of bainite is from the extremely fine grain size of bainitic ferrite. On the other hand, tensile elongation is controlled by the volume fraction of retained austenite. Retained austenite is a ductile phase compared to the bainitic ferrite and would be expected to enhance ductility as far as the austenite is homogeneously distributed along plate boundaries (film austenite). From **Table 3**, it is clear that the steels present a combination of high strength and good ductility.

TABLE 3: Tensile, Impact Toughness and Fracture Toughness Properties

Steel	YS, MPa	UTS, MPa	Elong, %	RA, %	CV _{-40 °C} , J
Mn	1167	1790	13	44	31±1
Ni1	1150	1725	14	55	46±1
Ni2	1100	1625	14	59	43±1

YS yield strength; UTS ultimate tensile strength; Elong elongation; RA reduction of area; CV impact energy.

Charpy impact test results at $-40\text{ }^{\circ}\text{C}$ are also listed in **Table 3** for all the alloys. A considerable improvement in toughness is obtained when the volume fraction of bainite increases in the microstructure. This improvement occurs despite the fact that the strength of the microstructures involved remains almost unchanged. The volume fraction of bainite, V_b and thus the carbon content of the retained austenite, x_γ explains the improvement in toughness observed in Ni1 and Ni2 alloys as compared with the Mn alloy. The results are consistent with the enhancement of toughness expected when the amount of blocky austenite and martensite are reduced and, in general, when the stability of residual austenite is increased.

FIGURE 3.- Optical micrographs of isothermal decomposition of austenite in Steel A: (a) $125\text{ }^{\circ}\text{C}$ for 25 days; (b) $150\text{ }^{\circ}\text{C}$ for 30 days; (c) $190\text{ }^{\circ}\text{C}$ for 7 days; and (d) $250\text{ }^{\circ}\text{C}$ for 24 hours.

temperature is as low as $125\text{ }^{\circ}\text{C}$ or $150\text{ }^{\circ}\text{C}$. The rate of transformation is faster when the temperature exceeds $150\text{ }^{\circ}\text{C}$. Thus, it is found that the fraction of bainite is 0.6 for transformation at 190 and $250\text{ }^{\circ}\text{C}$ for 7 days and 24 hours, respectively (**Figures 3c and 3d**). An almost fully bainitic microstructure ($\sim 90\%$ bainite) is obtained at $190\text{ }^{\circ}\text{C}$ after 9 days of transformation. At $300\text{ }^{\circ}\text{C}$, the maximum volume fraction of bainite formed was 0.6 and 4 days were needed to complete the transformation.

Low temperature bainite

Isothermal transformation in the temperature range $125\text{--}325\text{ }^{\circ}\text{C}$ led to the formation of bainite, as illustrated in **Figure 3** for Steel A. Transformation at so low temperatures was possible in this steel because of its high carbon content. Carbon exerts an important influence on bainite transformation temperatures decreasing B_s and M_s transformation temperatures. The early stage of transformation is shown in **Figure 3a** for a sample isothermally heat treated for 25 days at $125\text{ }^{\circ}\text{C}$. As **Figure 3.b** suggests, only a small fraction of bainite (~ 0.10) is formed after 30 days of holding time at $150\text{ }^{\circ}\text{C}$. Very long heat treatments are required (more than 2 months) to obtain substantial transformation when the

X-ray analysis was used to estimate the quantities of retained austenite present in the microstructure when bainite transformation essentially ceases. The experimental results for Steels A and B are shown in **Figure 4a**. The retained austenite fraction is expected to increase for the higher transformation temperature. This is because less bainite forms, and by contrast to low-carbon bainitic steels, the residual austenite is stable to martensitic transformation on cooling to ambient temperature even at the higher bainite transformation temperatures.

FIGURE 4.- X-ray experimental data on: a) volume fractions of retained austenite; and b) carbon in bainitic ferrite and austenite.

diffusion, but with excess carbon partitioning into the austenite soon after transformation. It is for this reason that the bainite reaction remains *incomplete*, with the maximum fraction limited by a boundary well below the paraequilibrium Ae_3 phase boundary.

FIGURE 5.- Carbon concentration profile of selected volume showing austenite and ferrite regions in Steel B transformed at 200 °C for 7 days.

According to X-ray experimental data, despite the quite large fraction of bainite, austenite is not greatly enriched in carbon. This can only be possible if a substantial quantity of carbon is trapped in the bainitic ferrite as **Figure 4b** reveals. Similar supersaturation in bainitic ferrite were detected using a local electrode atom probe. **Figure 5** shows an austenite-ferrite interface in Steel B transformed at 200 °C for 7 days. The 5 at. % C isoconcentration surface and carbon concentration profile indicate that the average carbon concentrations of austenite and ferrite are 7.7 and 1.2 at. % C, respectively (i.e. 0.077 and 0.012

mole fraction). The estimated austenite carbon content is in agreement with X-ray results and calculated values presented in **Figure 4**. The atom probe results on carbon content of the ferrite are lower than those measured by X-ray. However, both techniques confirm that there is excess carbon in ferrite, well beyond that expected from paraequilibrium with austenite at 200 °C (0.02 at.% i.e. 0.0002 mole fraction).

Transmission electron micrograph of Steel B transformed at 200 °C for 15 days is presented in **Figure 6**. Some of the plates of bainite are incredibly thin and long, giving a most elegant fine scale structure consisting of an intimate mixture of austenite and ferrite. Dislocation debris is evident in both the bainitic ferrite and the surrounding austenite. Extensive transmission microscopy failed to

FIGURE 6.- Transmission electron micrographs of microstructure obtained at 200 °C for 15 days in Steel B.

reveal carbides in the microstructure, only a few extremely fine (20 nm wide and 175 nm long) cementite particles in the bainitic ferrite were found in Steel A transformed at 190 °C for 2 weeks. [13]. Quite remarkably, the bainite plates formed at 200 °C in Steel B (**Figure 6**) have a width that is less than 50 nm, with each plate separated by an even finer film of retained austenite. It is the very small thickness of bainitic ferrite plates in low temperature bainite which leads to hardness values in excess of 600 HV and strengths in excess of 2.5 GPa [13].

Theory indicates that the largest effect on bainite plate thickness is due to the strength of the austenite, the free energy change accompanying transformation and a small independent effect due to transformation temperature [14]. In the present case, the observed refinement is a consequence mainly of the effect of high carbon content and the low transformation temperature on increasing the strength of the austenite.

CONCLUSIONS

1. The alloys designed theoretically in this work present the highest strength/toughness combinations ever recorded in bainitic steels. These alloys show better mechanical properties of the quenched and tempered low-alloy martensitic steels and match the critical properties of maraging steels, which are at least thirty times more expensive.
2. Moreover, this work has revealed that it is possible to obtain bainite by transforming at very low temperatures where the diffusion of iron atoms is inconceivably low. This has the consequence that the plates of bainite are incredible fine, 20-40 nm thick, so that the material becomes very strong. When this feature is combined with the fact that the plates of ferrite are interspersed with austenite, it becomes possible to create strong and tough steels. Although this is itself exciting, the potential for commercial exploitation is large because the alloys are very cheap and easy to manufacture.

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