VERY STRONG BAINITIC STEELS

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ABSTRACT

A combination of thermodynamics and kinetics theory describing the atomic mechanism of displacive transformation, was used to develop steels which transform to bainite at temperatures as low as 125 ºC. This has had the effect of greatly refining the microstructure, which is found to have a strength in excess of 2500 MPa together with an ability to flow plastically before fracture. The toughness is in excess of 30-40 MPa $m^{1/2}$.

In this work we report metallographic details of the very fine bainitic microstructure associated with the incredibly low transformation temperature. X-ray diffraction analysis of the retained austenite has shown that it is enriched in carbon to a concentration close to T_o boundary, as expected from the incomplete reaction phenomenon. The X-ray analysis also revealed higher ferrite carbon concentrations than the expected paraequilibrium solubility levels. Atom probe microanalysis results on the carbon concentration bainitic ferrite confirmed the X-ray data and revealed that a substantial quantity of carbon was trapped at dislocation in the vicinity of the ferrite/austenite interface.

KEYWORDS

Bainite, high carbon, high silicon, low transformation temperature

INTRODUCTION

The addition of about 2 wt-% of silicon to steel enables the production of a distinctive microstructure consisting of a mixture of bainitic ferrite and carbon-enriched retained austenite. 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 [1-4]. This leaves large regions of untransformed retained 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 [5,6]. With careful design, impressive combinations of strength and toughness have been reported for high-silicon bainitic steels [7-9]. 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 [10,11]. 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 ninety 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 125 ºC. 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

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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 MPm$^{1/2}$). Such properties have never been achieved before with bainite. This article is intended to provide a brief description of the characteristics and significance of this remarkable microstructure in the context of the mechanism of transformation.

1. ALLOY DESIGN

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

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

where $G_{SB} \cong 400$ J mol^{-1} is the stored energy of bainite [12]; $\Delta G^{\gamma\rightarrow\alpha}$ 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 [12-15]. 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.

Table 1 Actual Chemical Composition of Designed Alloys, wt-%

Steel	C	Si	Mn	Cr	Mo	V	Co	Al
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	-	-
C	0.83	1.57	1.98	1.02	0.24	-	1.54	-
D	0.78	1.49	1.95	0.97	0.24	-	1.60	0.99

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 [4] 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.

Our aim here was to use the combination of the models described above, to produce the finest possible bainitic microstructure by transformation at the lowest possible temperature. Using the models together with some background knowledge, alloys 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 alloys contains 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. 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.

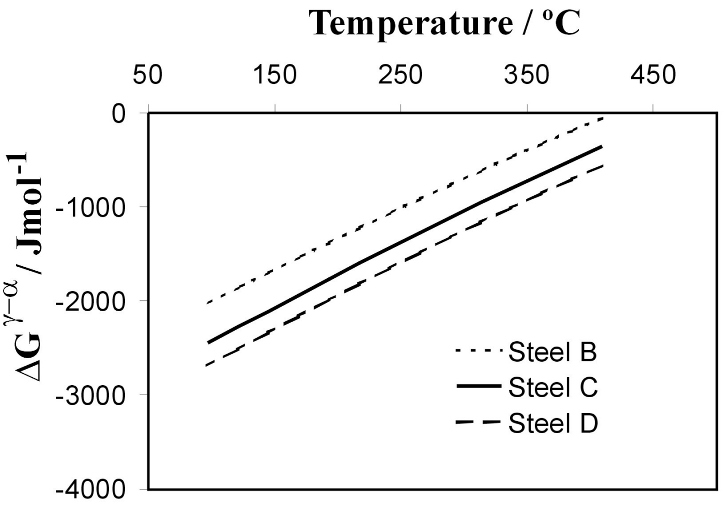

Fig. 1.- Free energy change $\Delta G^{\gamma\rightarrow\alpha}$ as a function of temperature for alloys listed in Table 1

In steels A and B (See Table 1), bainite can take between 2 to some 60 days to complete transformation with in the temperature range 125-325 ºC [16,17]. Therefore, it may be useful for industrial purposes to be able to accelerate transformation without losing the ability to transform at a low temperature. In this sense, elements such as Co and Al were added to the alloys. Calculations of the driving force for the transformation $\Delta G^{\gamma\rightarrow\alpha}$ confirm the expected effect of cobalt and aluminium on the relative stabilities of austenite and ferrite (Fig. 1).

2. LOW TEMPERATURE BAINITE

Alloys in Table 1 were supplied as a cast ingot. They were firstly homogenised at 1200 ºC 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 15 min at 1000 ºC, and then isothermally transformed at temperatures ranging from 125 to 500 ºC for different times before quenching into water. Isothermal transformation in the temperature range 125-325 ºC led to the formation of bainite, as illustrated in Fig. 2 for Steel A. The early stage of transformation is shown in Fig. 2a for a sample isothermally heat treated for 25 days at 125 ºC. As Fig. 2.b suggests, only a small fraction of bainite (~0.10) is formed after 30 days of holding time at 150 ºC. Very long heat treatments are required (more than 2 months) to obtain substantial transformation when the temperature is as low as 125 ºC or 150 ºC. The rate of transformation is faster when the temperature exceeds 150 °C. Thus, it is found that the fraction of bainite is 0.6 for transformation at 200 ºC for 7 days (Fig. 2c). A almost fully bainitic microstructure (~90 % bainite) is obtained at 190 ºC after 9 days of transformation. At 300 ºC, the maximum volume fraction of bainite formed was 0.6 and 4 days are needed to complete the transformation.

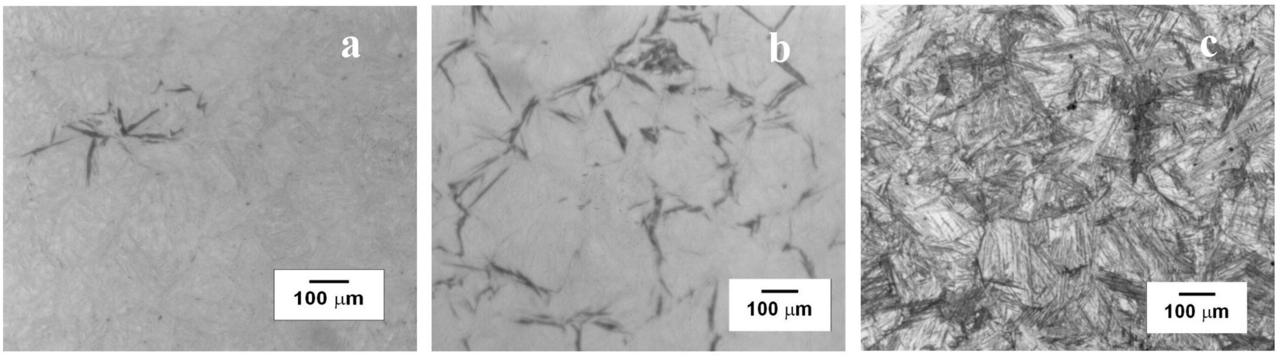

Fig. 2.- Optical micrographs of isothermal decomposition of austenite in Steel A: (a) 125 ºC for 25 days; (b) 150 ºC for 30 days; and (c) 200 ºC for 7 days.

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 Fig. 3a. 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.

As mentioned above, 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. Thus, the completion of transformation leaves carbon enriched residual austenite which can no longer transform into bainite. The carbon concentrations of austenite and bainite, determined using X-ray analysis in Steels A and B are presented in Fig. 3b.

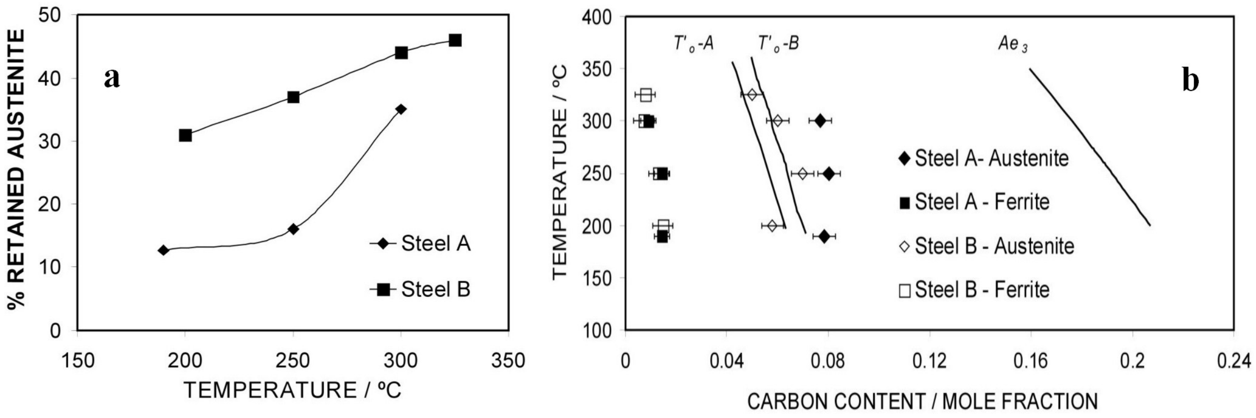

Fig. 3.- X-ray experimental data on: a) volume fractions of retained austenite; b) carbon in bainitic ferrite and austenite.

The fact that the measured carbon concentrations of the retained austenite in Fig. 3b lie between the T_o' and the paraequilibrium Ae_3 phase boundaries for both steels is consistent with a mechanism in which the bainite grows without any 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 [18]. The fact that the measured carbon concentrations of the austenite exceed the T_o' concentration in

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Steel A is a consequence of the fact that the isolated films of austenite between the bainite plates can accumulate carbon, beyond T_o' [1]. They cannot, of course, transform to bainite once the T_o' curve is exceeded.

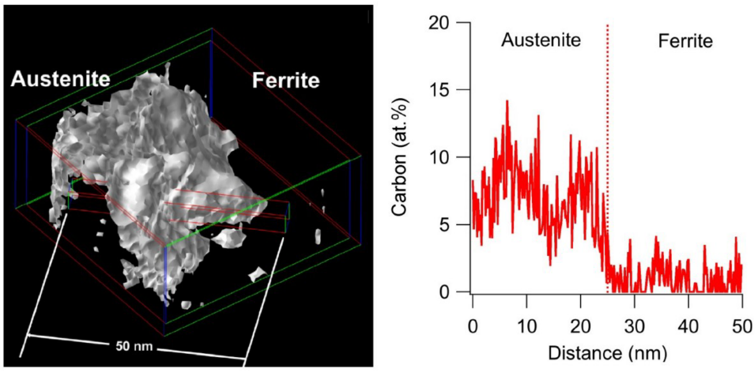

Fig. 4. 5 at. % carbon isoconcentration surface and carbon concentration profile of selected volume showing austenite and ferrite regions in Steel B transformed at 200 ºC for 7 days sample.

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 Fig. 3b reveals. Similar supersaturation in bainitic ferrite were detected using a local electrode atom probe. Fig. 4 shows an austenite-ferrite interface in Steel B transformed at 200 ºC 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 Fig. 3. 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 ºC (0.02 at.% i.e. 0.0002 mole fraction).

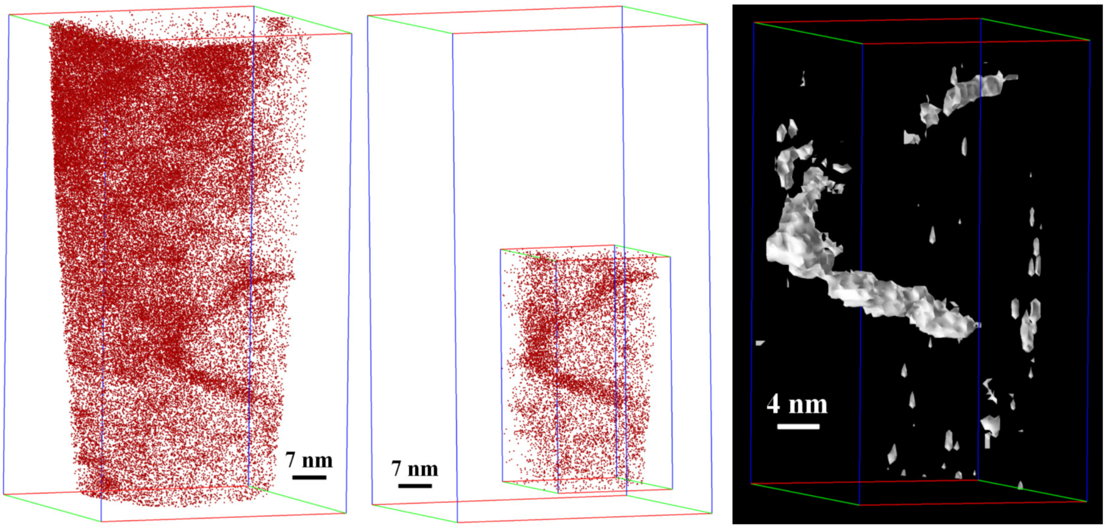

Fig. 5. Carbon atom map and 5 at. %-isoconcentration surface of dislocations in the vicinity of a ferrite/austenite interface obtained from the two days transformed sample.

On the other hand, a carbon atom map of a selected volume in Steel B transformed at 200 ºC for 5 days is shown in Fig. 5. The distribution of carbon atoms in the analysis volume is not uniform and

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carbon-rich and carbon-depleted regions are clearly distinguishable. Carbon enriched region at the top-left of the atom map represents a region of austenite since its carbon content is beyond the average carbon content of the steel. The regions with low carbon contents indicates the presence of ferrite phase. Finally, linear features with significant levels of solute in this carbon atom map are believed to be dislocations in the vicinity of a ferrite/austenite interface. The 5 at. % carbon isoconcentration surface outlines the carbon-enriched region around the dislocations located in the selected volume. These results indicate that carbon supersaturation in ferrite is due to the formation of carbon Cottrell atmospheres in the vicinity of the dislocations. This trapping prevents the carbon from partitioning into austenite and explains the small extent of carbon enrichment detected in the residual austenite.

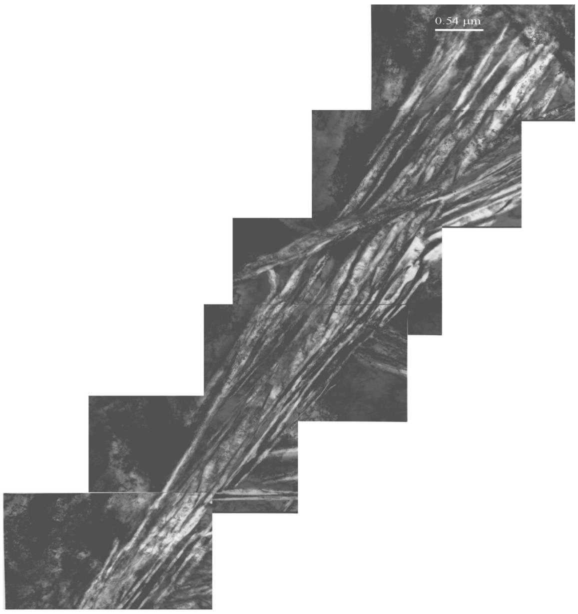

Fig. 6.- Transmission electron micrographs of microstructure obtained at 200 ºC for 15 days in Steel B.

Transmission electron micrograph of Steel B transformed at 200 ºC for 15 days is presented in Fig. 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 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 ºC for 2 weeks. [16]. Quite remarkably, the bainite plates formed at 200 ºC in Steel B (Fig. 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 [16].

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 [19]. 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.

3. ACCELERATION OF TRANSFORMATION

Steels C and D were designed with aim of accelerating bainite transformation by cobalt and aluminium additions. Both elements were found to increase the free energy change accompanying

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austenite to ferrite transformation (Fig. 1). Kinetics results in Fig. 7.a suggests that there is a slightly increase in the rate of transformation due to the cobalt, but a significant effect with the combined addition of cobalt and aluminium. A further increase in the rate of transformation is achieved by refining the austenite grain size as shown in Fig. 7.b.

On the other hand, the volume fraction of bainite obtained after prolonged holding at any given temperature has increased in steels C and D. Likewise, a refinement of the size of the bainitic ferrite plates is obtained in both steels. Those results are consistent with the higher driving force in the cobalt and aluminium alloyed steels [20].

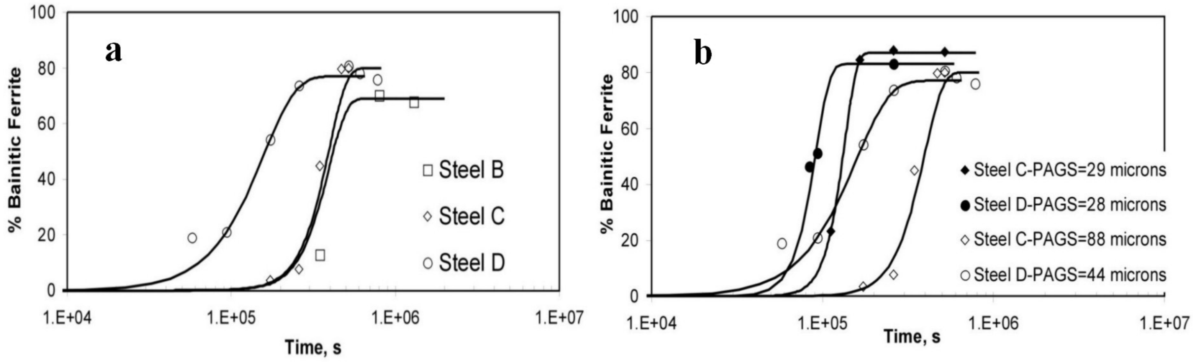

Fig. 7.- Isothermal Transformation curves at 200 ºC: (a) austenitisation at 1000 ºC for 15 min; (b) austenitisation at 900 ºC for 30 min. PAGS stands for prior austenite grain size.

4. CONCLUSIONS

All 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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