Very Strong, Low-Temperature Bainite

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Bainite has been obtained by heat treatment at temperatures as low as 125 ºC in a high-carbon high-silicon steel. This has had the effect of greatly refining the microstructure, which is found to have a strength in excess of 2.5 GPa together with an ability to flow plastically before fracture. Such properties have never before been achieved with bainite. In this paper we report metallographic details of the very fine bainitic microstructure associated with the incredibly low transformation temperature, where during the time scale of the experiments, an iron atom cannot diffuse over a distance greater than about 10^{-17} m. And yet, the microstructure has a scale in the micrometer range, consistent **only** with a displacive mechanism of transformation.

1 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, carbon-enriched retained austenite and some martensite.[1-5] 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, *i.e.* when the carbon concentration of the residual austenite reaches a point given by the T_o curve, beyond which diffusionless growth is prevented. This leaves large regions of untransformed austenite which under stress decompose to hard, brittle martensite.[6]

There is, however, a design procedure[6,7] which 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. Steels were designed on this basis and when tested, revealed a reduction in the impact transition temperature of more than 100 K.[6,7] Fracture toughness measurements confirmed the remarkable levels of toughness that could be achieved, in some cases matching the much more expensive marageing steels.[8-10] Other aspects of the theory have been verified using a variety of advanced research techniques.[11]

The first major commercial exploitation came with the development of a kinetic theory[12] to complement the three thermodynamic criteria, so that continuous cooling transformation which is typical in industry, could be dealt with. More recently, it has been demonstrated experimentally that models based on phase transformation theory can be applied successfully to the design of novel strong and tough steels.[13,14] These alloys were designed to ensure that the hardenability is consistent with specific industrial specifications and have achieved the highest ever combinations of strength and toughness for bainitic steels. Toughness values of nearly 130 MPa $m^{1/2}$ have been obtained for strength in the range of 1600-1700 MPa. This compares well with marageing steels, which are at least ninety times more expensive.

During the course of this research on the design of bainitic steels,[13,14] a discovery was made, that very fine bainite can be obtained by transformation at temperatures, as low as 125 ºC during heat treatment for many days. To put this into context, an iron atom diffuses a distance of just 10^{-17} m during the course of the transformation, even though the resulting bainite has a scale of many micrometers. The aim of this work presented here was to characterise and understand this fine bainitic microstructure in the context of the mechanism of transformation.

2 Experimental Procedures

The chemical composition of the steel studied is given in Table 1. The alloy was supplied as a cast ingot, samples of which were then homogenised at 1200 °C for 2 days whilst sealed in partially evacuated quartz capsules flushed with argon. The sealed samples were cooled in air following the homogenisation heat treatment.

The homogenised specimens were 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.

Optical and scanning electron microscopy (SEM) were used to examine the etched microstructures. Specimens were ground and polished using standard techniques 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.[15] A grid superimposed on the microstructure provides, after a suitable number of placements, an unbiased statistical estimate of V_b. Stereological errors for V_b values correspond to the standard deviation of the measurement.

Quantitative X-ray analysis was used to determine the volume fraction of retained austenite. After grinding and final polishing using 0.25 μm diamond paste, the samples were etched to obtain an undeformed surface. They were then step-scanned in a Philips - PW 1730 X-ray diffractometer using unfiltered Cu K_α radiation The 2θ scan rate was 1 degree min^{-1}. The machine was operated at 40 kV and 40 mA.

The retained austenite content was calculated from the integrated intensities of (200), (220) and (311) austenite peaks, and those of (002), (112) and (022) planes of ferrite.[16] Using three peaks from each phase avoids biasing the results due to any crystallographic texture in the samples.[17] The carbon concentration in the austenite and ferrite was estimated using the measured lattice parameters.[18]

Specimens for transmission electron microscopy (TEM) were machined down to 3 mm diameter rods. The rods were sliced into 100 μm thick discs and subsequently ground down to foils of 50 μm thickness on wet 800 grit silicon carbide paper. These foils were finally 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. Carbon replicas were extracted in 5 % hydrochloric acid and 95 % methanol. Foils and replicas were examined in a JEOL JEM-200 CX transmission electron microscope at an operating voltage of 200 kV.

The martensite-start temperature of the steel was measured using a Thermecmaster-Z thermomechanical simulator. Cylindrical specimens 12 mm in height and 8 mm in diameter were heated at a rate of 5 ^{o}C s^{-1} to 1000 ^{o}C and then cooled at two different rates (40 and 100 ^{o}C s^{-1}). The formation of martensite during cooling was detected by monitoring the fractional change in dilatation with temperature.

Austenite formation begins during heating at the Ac_1 temperature and is completed when the Ac_3 temperature is reached. Tempering must be carried out below the Ac_1 temperature to avoid the accidental formation of austenite. The austenite formation temperatures were determined using a Thermecmastor-Z simulator. Dilatometric specimens were heated at a rate of 5 ^{o}C s^{-1} to 1000 ^{o}C and then cooled at 40 ^{o}C s^{-1}. The formation of austenite during heating was detected by monitoring the fractional change in dilatation with temperature. An Ac_1 temperature of 805 ºC and an Ac_3 temperature of 840 ºC were determined from the heating experiment. Specimens were tempered at temperatures ranging from 400 to 700 ^{o}C for 30 min and an hour.

Compression tests were carried out at room temperature on samples transformed isothermally at 190 ºC for 2 weeks. The compression specimens of 5 mm in diameter and 15 mm in length were tested in accordance with ASTM E9-89a :1995 standard test method on a 100 kN *Mayes* servohydraulic machine at a crosshead speed of 1 mm min^{-1}. Two specimens were tested in compression. Reliable tensile tests could not be conducted because of extensive casting defects in the form of porosity.

3 Results and discussion

3.1 MICROSTRUCTURE OF ISOTHERMALLY TRANSFORMED SAMPLES

Isothermal transformation in the temperature range 125-300 °C led to the formation of bainite, as illustrated in the optical micrographs presented in Figures 1a-d. The early stages of transformation are shown in Figs 1a,b for samples isothermally heat treated for 29 days at 125 and 150 ºC respectively. Transformation remains incomplete even after 60 days of holding time at 125 ºC. Transformation at temperatures much in excess of 300 °C did not lead to the formation of bainite, suggesting that the bainite-start temperature is between 300-350 °C; experiments were conducted up to 500 °C which revealed only eutectoid decomposition.

Figure 2 shows the evolution of hardness and the fraction of bainite as a function of the isothermal transformation temperature and time. The rate of transformation is fastest when the temperature exceeds 150 °C. For example, it is estimated that the fraction of bainite is 0.8 for transformation at 190 and 250 ºC for 9 and 2 days, respectively. However, a very long heat treatment is required (more than 2 months) to obtain substantial transformation when the temperature is as low as 125 ºC. At 300 ºC, the maximum volume fraction of bainite formed was 0.6 and 4 days are needed to complete the transformation.

X-ray analysis was used to estimate the quantities of retained austenite present in the microstructure, and its carbon concentration, following two weeks at different temperatures. The experimental results are **shown** in Table 2 and Figs. 3 and 4. The retained austenite fraction is expected to increase for the higher transformation temperature. This is because less bainite forms at 300 °C, 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.

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.[19-22]

The variation of the carbon content of austenite, x_γ as a function of the average carbon content of the alloy, x_o, and the volume fraction of bainitic ferrite V_b is given by,[23]

$$x_\gamma = \bar{x} + V_b \frac{(x_o - x_\alpha)}{(1 - V_b)} \tag{1}$$

where x_α is the amount of carbon trapped in the bainitic ferrite.

The fact that the measured carbon concentrations of the retained austenite in Fig. 4 lie between the T_0 and the paraequilibrium Ae_3 phase boundaries 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.[24] The fact that the measured carbon concentrations of the austenite exceed the T_o concentration is a consequence of the fact that the isolated films of austenite between the bainite plates can accumulate carbon, beyond T_o.[25] They **cannot, of course,** transform to bainite **once** the T_o curve is exceeded.

According to the experimental data in Table 2, 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. Experimental results in Table 2 reveal this carbon in solid solution in the ferrite and Fig. 5 confirms the presence of some cementite in the bainitic ferrite, in the sample isothermally transformed at 190 ºC for 2 weeks. The carbides are extremely fine, approximately 20 nm wide and 175 nm long. These observations explain the small extent of carbon enrichment detected in the residual austenite.

Using all these experimental data, the time-temperature-transformation diagram of the steel was calculated[24] and compared against the experimental data (Fig. 6). The curves represent the initiation of transformation whereas the points all represent a finite amount of bainite (about a volume fraction of 0.05); in the circumstances, the agreement between the measured data and the calculated TTT curve is considered reasonable.

3.2 MECHANICAL PROPERTIES

As mentioned earlier, the bainite that forms has a very fine microstructure because of the low transformation temperatures. This is illustrated in the transmission electron micrographs shown in Fig. 7. Quite remarkably, the bainite plates formed at 190 °C have a width which is less than 50 nm, with each plate separated by an even finer film of retained austenite. Not surprisingly, the fine microstructure leads to a very high strength.

Figure 8 shows the compression curve of the microstructure formed by transformation at 190 ^{o}C for 2 weeks; a view of the sample after testing is shown in Fig. 9. The sample clearly has considerable plasticity for deformation at room temperature even though the yield strength in compression is about 2000 MPa.

3.3 TEMPERING EXPERIMENTS

Experiments were carried out to study the stability of the microstructure to tempering heat treatments. Figure 10 shows the hardness as a function of the tempering temperature. The experiments were conducted on the bainitic microstructure formed at 190 ^{o}C for 2 weeks. Tempering that microstructure at temperatures lower than 500 ^{o}C for 30 min did not result in any significant loss of hardness.

4 Conclusions

Bainite has been obtained by transformation at temperatures as low as 125 ºC in a high-carbon high-silicon steel. The bainite plates thus obtained are incredibly fine, with a width of some 50 nm, giving a very high strength in excess of 2.5 GPa and perceptible ductility. Such properties have never been achieved with bainite. It is the intention now to design new alloys using the theory of the bainite reaction, for creating a new class of ultrahigh-strength steels and then to conduct comprehensive mechanical and microstructural tests.

5 Acknowledgments

This work was carried out as part of Technology Group 4 (Materials and Structures) of the MoD Corporate Research Programme. The authors would like to **thank Professor** Alan Windle for the provision of laboratory facilities at the University of Cambridge.

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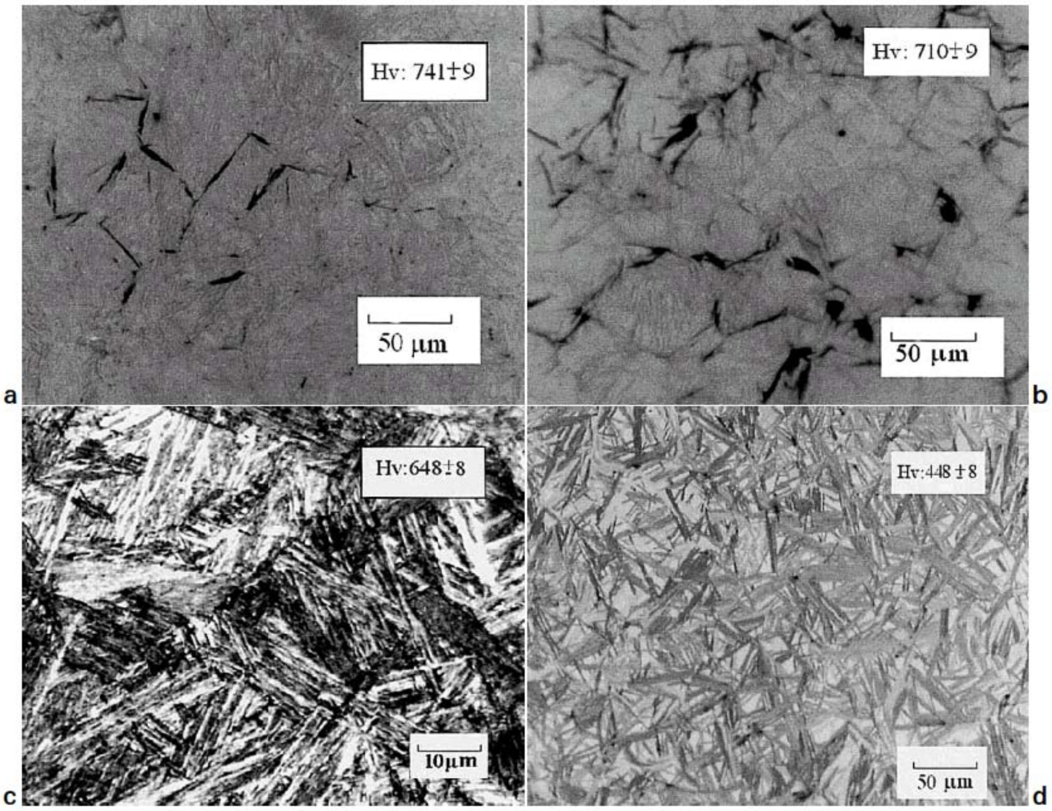
Table 1 Chemical Composition of the Steel, wt-%

C	Si	Mn	Ni	Cr	Mo	V
0.79	1.59	1.94	0.02	1.33	0.30	0.11

Table 2 Experimental Quantitative Data on Microstructure

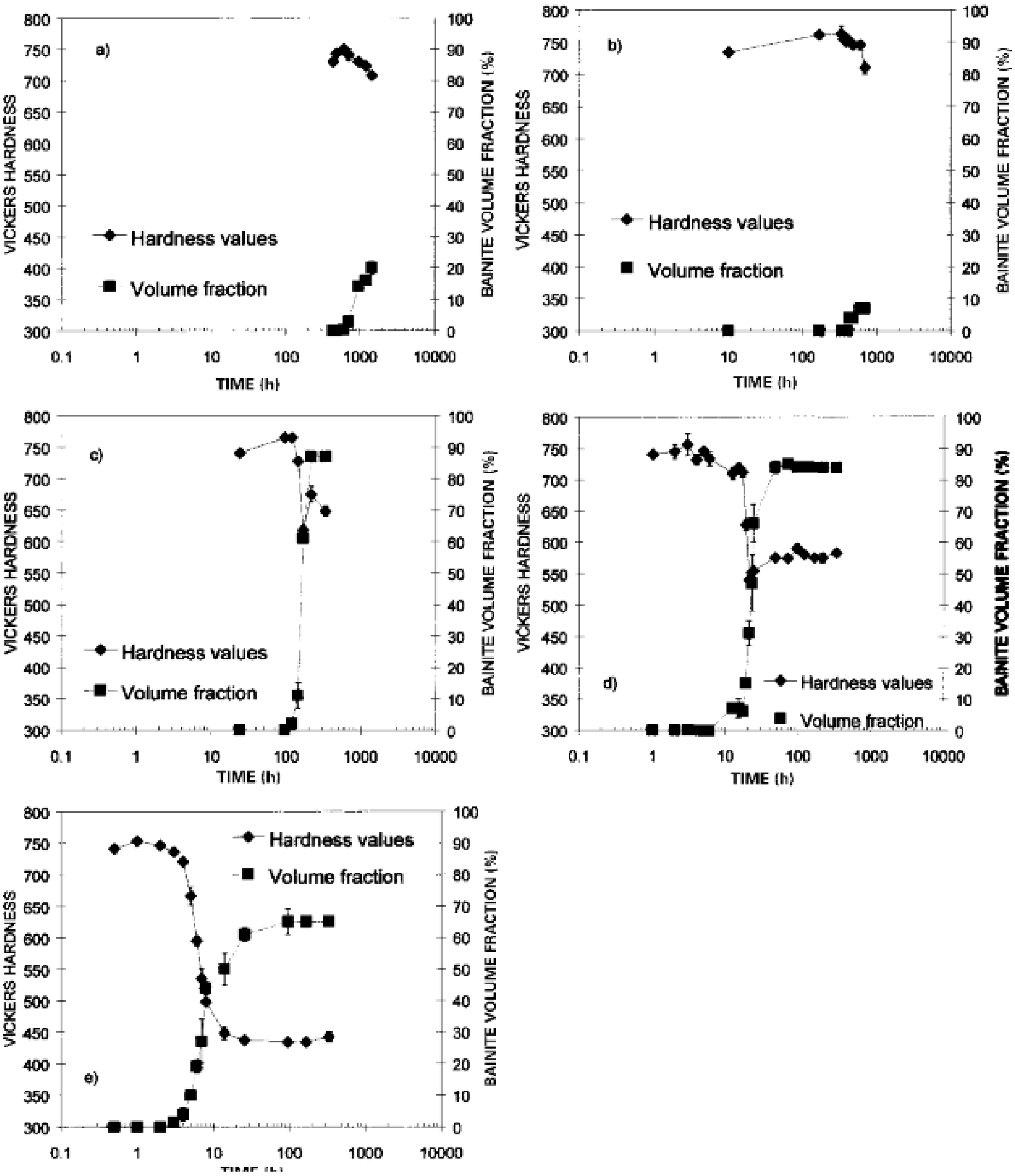
Bainite formation temperature, ^{o}C	V_γ	V_b	x_γ, wt-%	x_α, wt-%
300	0.35±0.01	0.65±0.01	1.69±0.10	0.20±0.07
250	0.16±0.01	0.84±0.01	1.76±0.10	0.32±0.07
190	0.13±0.01	0.87±0.01	1.72±0.10	0.32±0.07

V_γ retained austenite volume fraction; V_b bainitic ferrite volume fraction; x_γ carbon content in austenite; x_α carbon content in ferrite



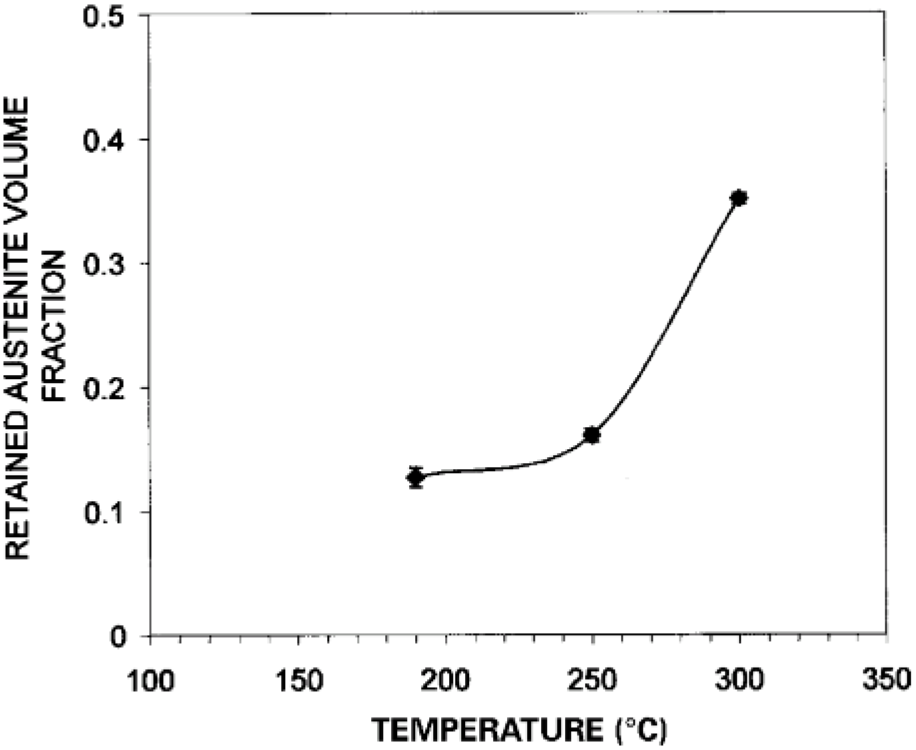
a 125 °C for 29 days; *b* 150 °C for 29 days; *c* 190 °C for 2 weeks; *d* 300 °C for 2weeks

1. **Optical micrographs of the isothermal decomposition of austenite**

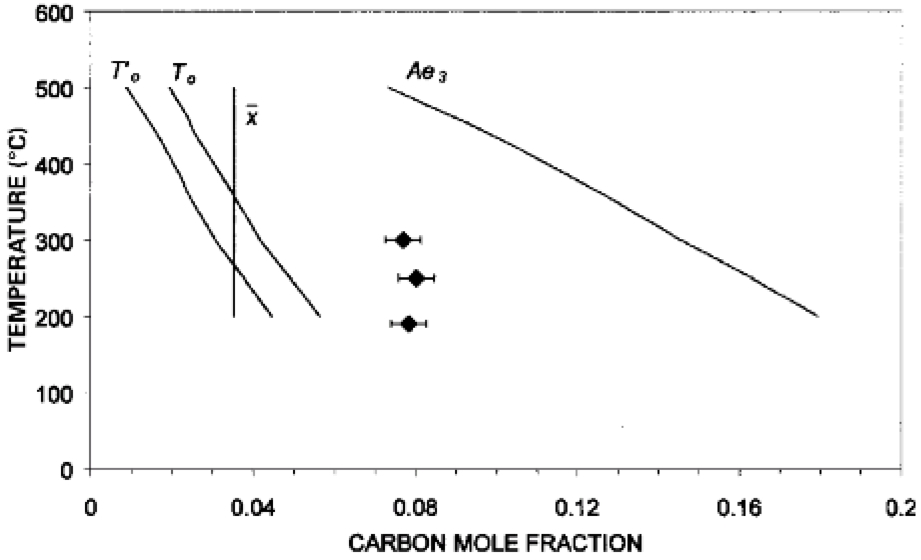


a 125 °C; *b* 150 °C; *c* 190 °C; *d* 250 °C; *e* 300 °C

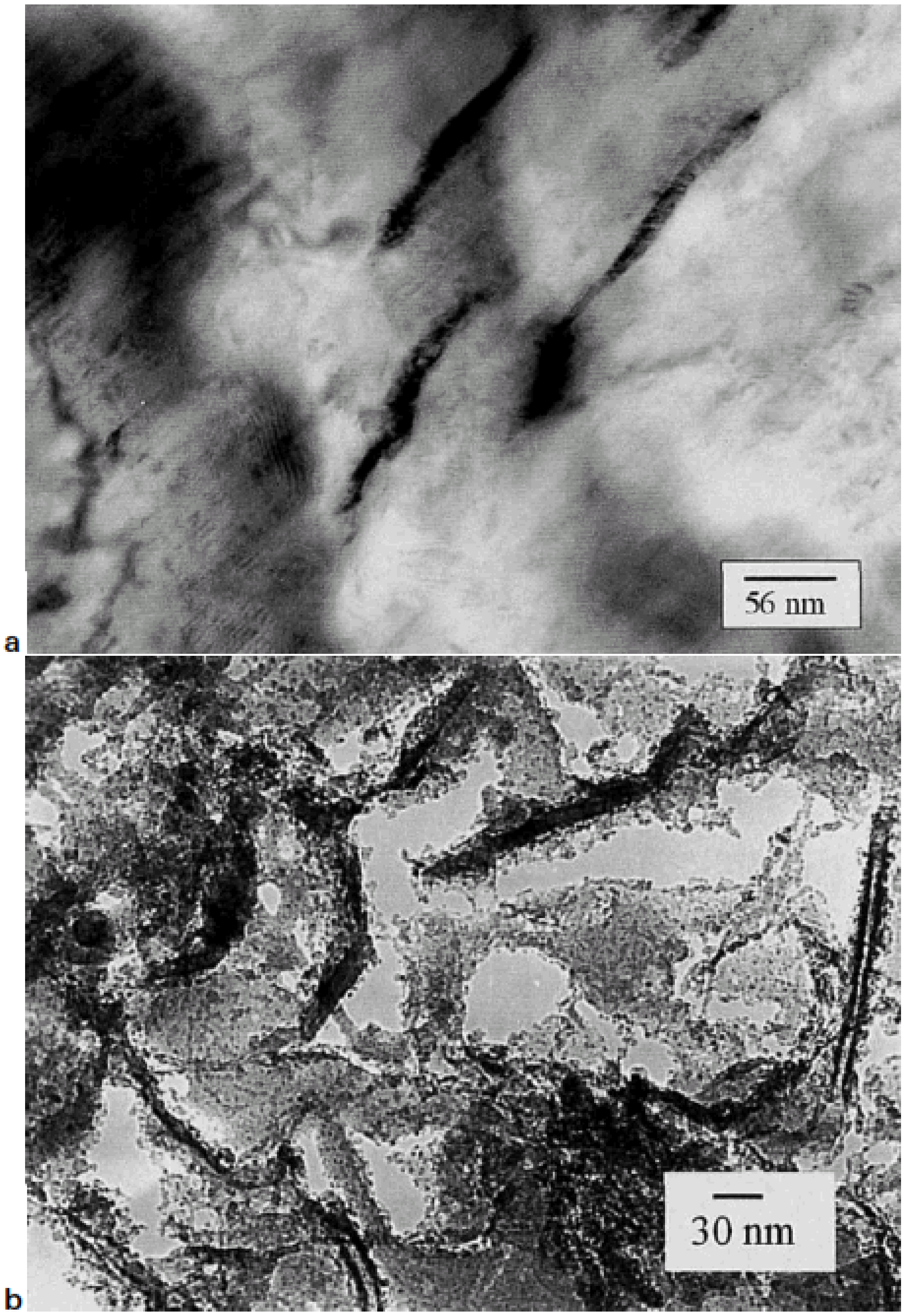
2. **Plot of the hardness values and bainite volume fraction as a function of time at different transformation temperatures**



3. Plot of volume fraction of retained austenite as a function of isothermal transformation temperature

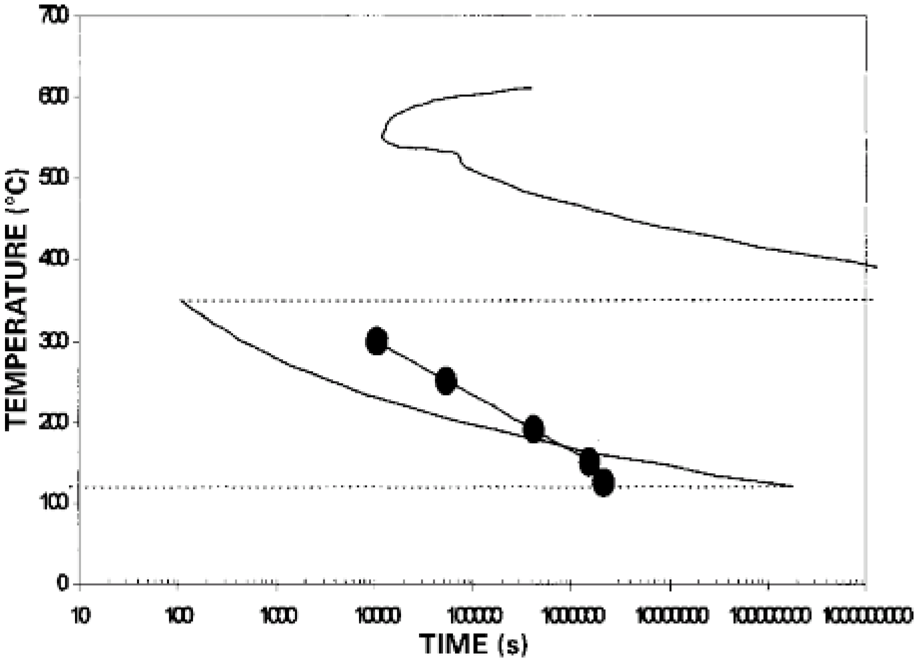


4. Calculated T_o', T_o and the paraequilibrium Ae_3 curves for the studied steel and experimental data for the carbon composition of retained austenite in samples heat treated for 2 weeks at different temperatures. $\bar{x}$ represents the overall carbon content of the steel. The phase boundaries were calculated as in Reference 24

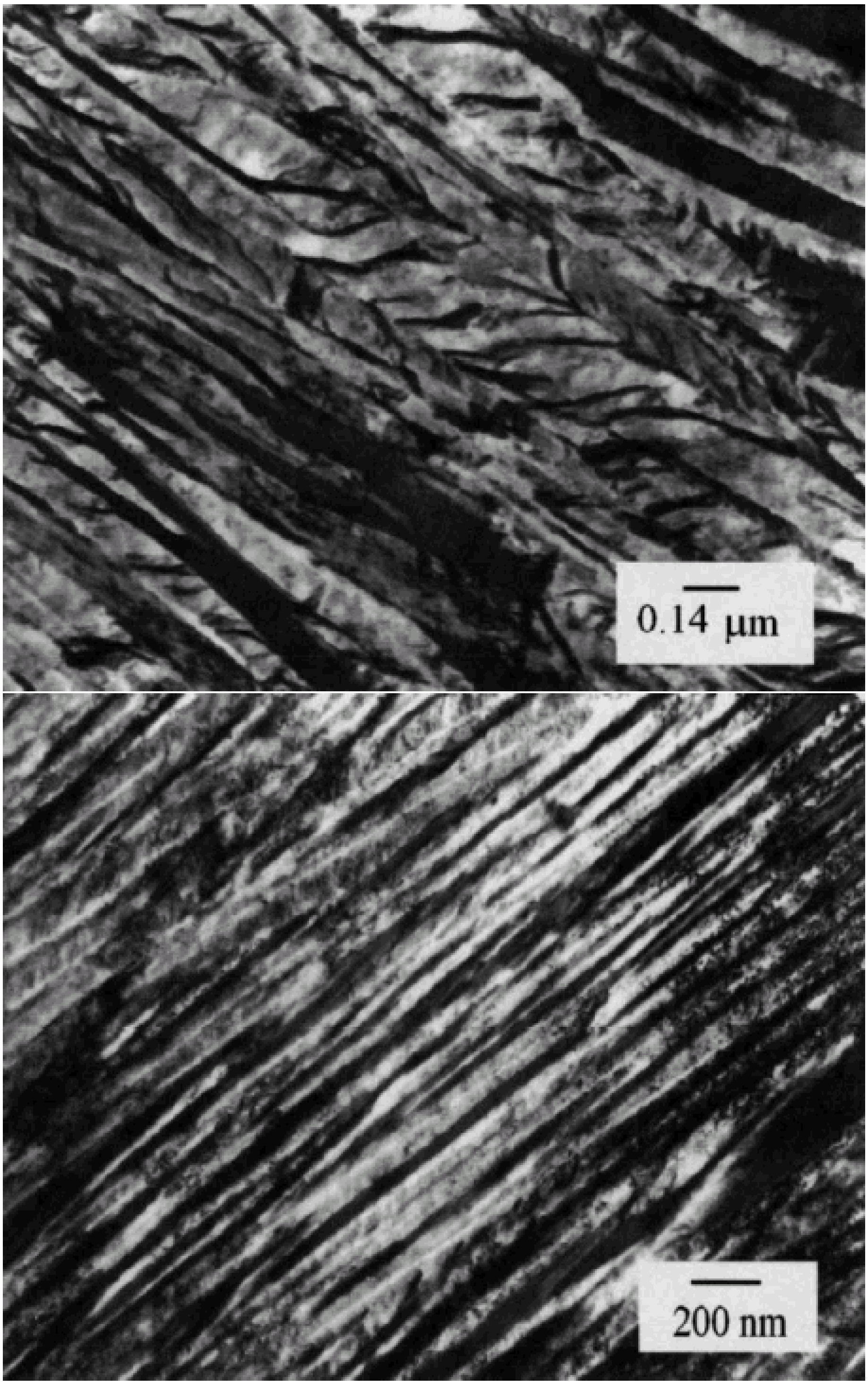


a Thin foil transmission electron micrograph; *b* carbon extraction replica transmission electron micrograph

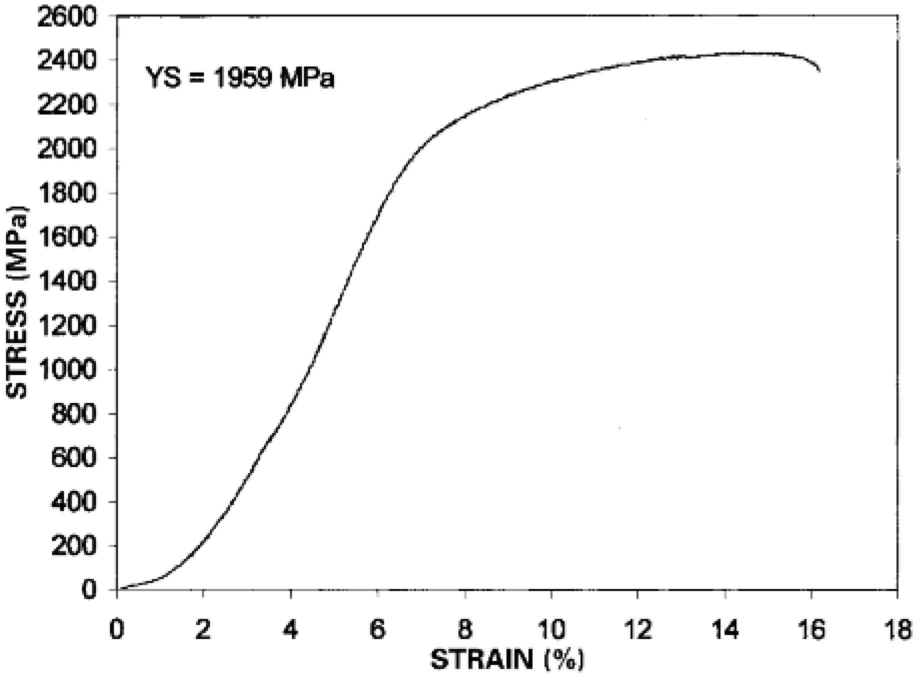
5. Transmission electron micrographs of some carbides precipitated in bainitic ferrite in a microstructure formed at 190 °C for 2 weeks



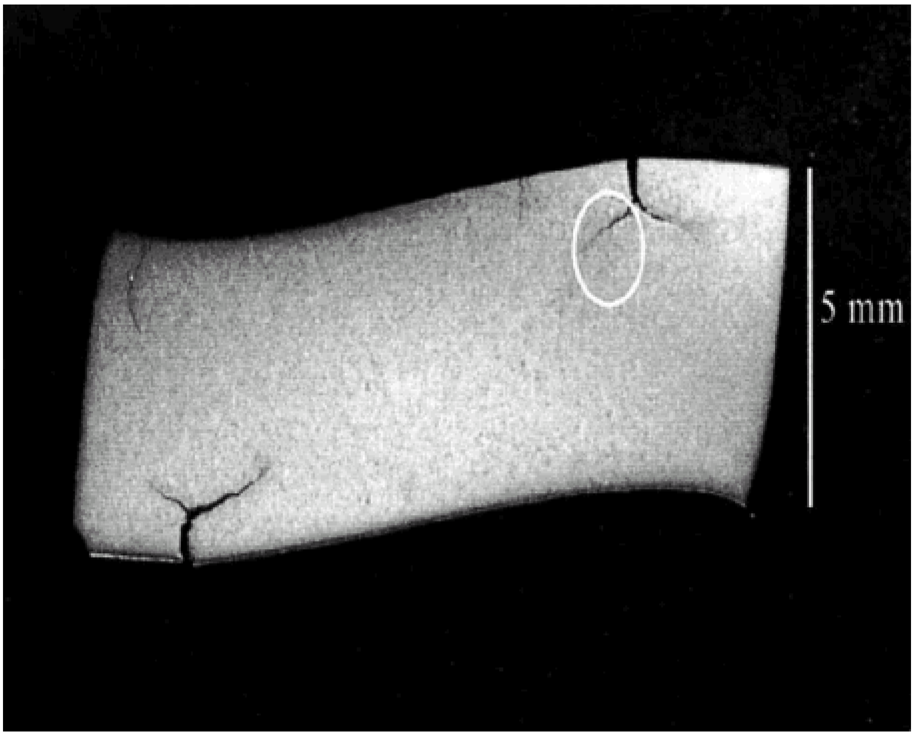
6. **Calculated time-temperature-transformation diagram of the steel. Points in the graphs represent the start and finish time for bainite transformation**



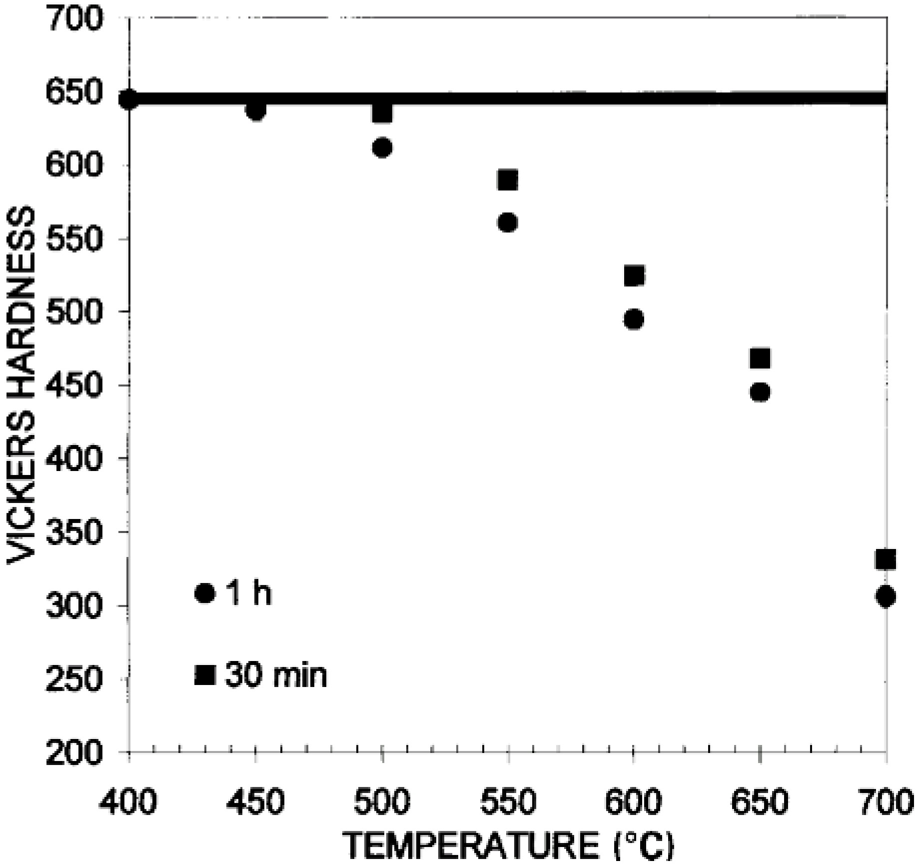
7. Thin foils transmission electron micrographs of the microstructure obtained at 190 ºC for 2 weeks



8. **Compression curve for the microstructure formed at 190 ºC for 2 weeks**



9. **Compression sample after being tested**



10. **Plot of hardness values as a function of tempering. The horizontal line represents the hardness of microstructure formed at 190 °C for 2 weeks.**