Acceleration of Low-temperature Bainite

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Recent work has shown that bainitic ferrite plates produced by transformation at low temperatures can be as thin as 20 nm with a hardness in excess of 650 HV. However, it may take several days in order to achieve the required degree of transformation at low temperatures. In this work we report methods for accelerating the rate of reaction without compromising strength.

KEY WORDS: bainite; retained austenite; phase transformations; kinetics.

1. Introduction

It has been discovered that bainite with an ultimate tensile strength in excess of 2.3 GPa and a toughness of some 30 MPa m$^{1/2}$ can be obtained in high-carbon, silicon-rich steels by transformation at homologous temperatures which can be as low as $T/T_m = 0.25$, where $T_m$ is the absolute melting temperature.1–3) The reported combination of mechanical properties is a consequence of the very thin bainite plates (20–40 nm thickness) and the fine-scale dispersion of austenite between the plates, obtained by transformation at the low temperature. Carbides are avoided in the microstructure by a judicious use of silicon as an alloying element.

In the steel studied, bainite can take between 2 to some 60 d to complete transformation within the temperature range 125–325°C, Table 1. A slow transformation at a low temperature (e.g., 200°C, 9 d) 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. It was the aim of the present work to design alloys which accelerate the formation of bainite at low temperatures.

2. Method

Transformation can be accelerated by increasing the free energy change accompanying the austenite ($\gamma$) to ferrite ($\alpha$) transformation. This has to be done without compromising the hardenability of the system if other high-temperature phases are to be avoided. It is well known that both cobalt and aluminium increase the free energy change.4) The basic alloy composition stated in Table 1 was therefore modified to create two further alloys, one containing cobalt and the other a combination of cobalt and aluminium.

It is worth noting that an increase in the driving force at constant temperature may be beneficial in further refining the microstructure in two ways, by promoting the formation of a greater quantity of bainitic ferrite, thereby eliminating islands of retained austenite, which are known to be detrimental to mechanical properties.5,6) It is the films of austenite between the plates of bainitic ferrite which are desirable. A second advantage could be a refinement of the size of the bainitic ferrite plates themselves, because an increase in the driving force stimulates a greater number density of plates.7)

Another common method of accelerating transformation is to refine the austenite grain size by using a lower austenitisation temperature or time. This can lead to contradictory effects in the case of the bainite reaction8); the reaction can be retarded if the austenite grain boundaries rapidly become saturated with bainite plates, before the sheafs have had a chance to penetrate the grains. This scenario does not apply to the present context where the transformation rate is slow.

3. Experimental Details

The chemical compositions of the alloys, measured after
Table 2. Chemical compositions of experimental alloys, wt%.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
<th>Cr</th>
<th>V</th>
<th>Co</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.98</td>
<td>1.46</td>
<td>1.89</td>
<td>0.26</td>
<td>1.26</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.83</td>
<td>1.57</td>
<td>1.98</td>
<td>0.24</td>
<td>1.02</td>
<td>1.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.78</td>
<td>1.40</td>
<td>1.95</td>
<td>0.24</td>
<td>0.97</td>
<td>1.60</td>
<td>0.99</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Measured transformation-start temperatures and austenite grain size, expressed as a mean lineal intercept \( L_t \) following the stated heat treatment. The uncertainties represent \( \pm 1.0 \).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_S/°C )</td>
<td>125</td>
<td>120</td>
<td>155</td>
</tr>
<tr>
<td>( B_S/°C )</td>
<td>335</td>
<td>360</td>
<td>385</td>
</tr>
<tr>
<td>( L_t/\mu m, 1000°C 15 \text{ min} )</td>
<td>49 ( \pm ) 2</td>
<td>58 ( \pm ) 4</td>
<td>44 ( \pm ) 2</td>
</tr>
<tr>
<td>( L_t/\mu m, 900°C 30 \text{ min} )</td>
<td>29 ( \pm ) 2</td>
<td>28 ( \pm ) 2</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. The free energy change \( \Delta G^w \) as a function of temperature for the alloys listed in Table 2.

Isothermal experiments to measure the bainite-start temperature (\( B_S \)) were conducted at 25°C intervals beginning with 250°C and raising the temperature until bainite was not observed over a 24 h period. In some cases, smaller temperature intervals (10°C) were used close to \( B_S \). The highest temperature at which bainite was observed using optical microscopy was designated \( B_S \).

The martensite-start temperatures \( M_S \) were determined using 2 mm diameter samples in a high-resolution dilatometer. The samples were heated to 1000°C and then force cooled using helium at 100 or 200°C s\(^{-1}\) to measure the \( M_S \) temperature. The results are listed in Table 3.

The austenite grain sizes are also presented in Table 3, for two sets of heat treatments. The size was measured by austenitising metallographically polished specimens in a Thermecmaster thermomechanical simulator in a vacuum environment; the resulting thermal grooves revealed the austenite grain structure. Between 60–96 measurements were conducted on optical micrographs taken from the thermally etched samples. Thermodynamic calculations using MTDATA, allowing for the possible existence of cementite, vanadium carbide, austenite and ferrite, confirmed that all the elements are in solid solution in austenite at the austenitising temperatures listed in Table 3.

4. Scale of Microstructure

The general microstructure, consisting of plates of bainite ferrite and retained austenite, has been reported elsewhere for alloy 1\(^{1,2,3}\); that of the two new alloys is not different other than in scale and phase fractions, as reported here.

Transmission electron microscopy was conducted to determine the true plate-thicknesses \( t \), by measuring the mean lineal intercept \( L_t = \pi t/2 \) in a direction normal to the plate length. The thickness \( t \) is related to the mean lineal intercept measured using randomly oriented test lines by the relation \( L_t = 2t_{12,13} \) but \( L_t \) is easier to measure since it is rare in transmission electron micrographs that entire plates of bainite can be imaged. The measured plate thickness \( t \) is plotted as a function of transformation temperature in Fig. 2; the detailed data are presented in Table 4.

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.\(^7\) Aluminium does not significantly affect the strength of austenite, causing only a 3 MPa change at ambient temperature, due to 1 wt% of aluminium.\(^{16,19}\) Cobalt causes a much smaller change in the lattice parameter of austenite when
compared with aluminium, and has a correspondingly smaller (negligible) effect on the proof strength of austenite.\textsuperscript{15,16} Therefore, it is concluded that the observed refinement is a consequence mainly of the effect of cobalt and aluminium, on increasing $|\Delta G^{\text{ref}}|$.\textsuperscript{7}

It is a feature of any refinement process that the reduction of scale is most difficult when the scale is small—this is because parameters such as the amount of surface per unit volume vary with the inverse of the scale. In alloy 2, which starts off with a coarse plate size following transformation at 300°C, a reduction in the austenite grain size causes $t$ to decrease, presumably because of the greater number density of nucleation sites.

Consistent with the increased driving force in the cobalt and aluminium alloyed steels, the total volume fraction of bainite obtained following prolonged holding at any given temperature has increased (Table 4).

5. Hardness

The contribution to strength due to the size of the plates is given by $\Delta \sigma = 115(\bar{L})^{-1}$ MPa where $\bar{L}$ is in micrometers.\textsuperscript{17–19} From this equation, and given the very fine scale of the bainitic ferrite plate, it is easily shown that much of the strength of low-temperature bainite is due to the fine scale; for example, in alloy 1, $\Delta \sigma = 463$ MPa for plates of thickness $124$ nm obtained by transformation at 300°C, whereas $\Delta \sigma = 1642$ MPa for plates of thickness $35$ nm obtained by transformation at 200°C.

Since the major strengthening effect is due to the fine plate size, it is expected that the hardness will vary linearly with the reciprocal of the plate thickness, even when other contributions are neglected. The latter include contributions such as solid solution strengthening, variation in the fraction of bainite within the observed range (Table 4) are neglected. The observed trend is consistent with theory, with a correlation coefficient of 0.85 (Fig. 3(a)).

In practice, the mean lineal intercept $\bar{L}$ should depend on the fraction of bainite, since the ferrite plates are dispersed in the austenite matrix. Suppose that plates are square with dimensions $t \times a \times a$. The volume per plate would then be $V_p \times a^2$, the number of plates per unit volume $N_c = V_p/ta^2$, where $V_p$ is the fraction of bainite. The surface area per unit volume would thus become

$$S_{V} = V_p/ta^2 = V_p/t$$

Since $S_{V} = 2/\bar{L}$, it follows that the hardness can be related more accurately to the ratio $\bar{L}^{-1} \times V_p/t$. The hardness is plotted against $V_p/t$ in Fig. 3(b); a slightly higher correlation coefficient of 0.88 is obtained (compared with 0.85, Fig. 3(a)).

6. Rate of Transformation

The two-phase microstructures (austenite and bainitic ferrite) studied here are relatively easy to characterise quantitatively using X-ray diffraction after interrupting isothermal transformation. In particular, martensite (the plates of which are easy to resolve) was never observed after the

![Fig. 2. Plate thickness $t$ as a function of transformation temperature.](image)

<table>
<thead>
<tr>
<th>Table 4. Summary of quantitative experimental data. $V_p$ designates the fraction of bainitic ferrite, the remainder of the microstructure being retained austenite. The thickness refers to $t$, the stereologically corrected value. The error is $\pm 1\sigma$ on the thickness. The term ‘fine’ refers to alloys in which the austenite grain size was refined by austenitising at 900°C for 30 min.</th>
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</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>Alloy 1</td>
</tr>
<tr>
<td>Alloy 1</td>
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<tr>
<td>Alloy 1</td>
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<tr>
<td>Alloy 2 (fine)</td>
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<td>Alloy 2 (fine)</td>
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<tr>
<td>Alloy 2 (fine)</td>
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<td>Alloy 2</td>
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<tr>
<td>Alloy 3</td>
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<td>Alloy 3</td>
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</tbody>
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onset of the bainite reaction, in any of the samples described below.

The results of an extensive set of experiments like these are illustrated in Fig. 4, for alloys 1, 2 and 3, using the high austenitisation temperature. It is clear that there is a significant increase in the rate of transformation due to the cobalt, and an even greater effect with the combined addition of cobalt and aluminium.

A further increase in the rate of reaction is achieved by refining the austenite grain size, as seen from Fig. 5.

The data are represented differently in Fig. 6 in order to allow an easier comparison, focussing only on the start and finish times; the start time corresponds to the first stage at which bainite could be detected using optical microscopy (estimated fraction 0.01), whereas the finish time is when the fraction ceases to change.

7. Conclusions

It has been possible to accelerate the bainite transformation at low-temperatures, by adding cobalt and aluminium.
to a high-carbon steel in which the transformation time was originally measured in days. A further acceleration has been obtained by refining the austenite grain size.

The observed effects are attributed to the increase in the free energy change during the transformation of austenite, caused by the alloying additions, and to the increase in the number density of austenite grain surface nucleation sites due to grain refinement.

The modified alloys in general show a more refined microstructure, a greater limiting volume fraction of bainitic ferrite and an increased hardness. All of these effects have been interpreted using the theory of the bainite reaction in steels.

Work is now in progress to characterise the important mechanical properties, including tensile strength, ductility and toughness of these alloys.

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REFERENCES