Ultra-fine Bainite Structure in Hypo-eutectoid Steels

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Ultra-fine, carbide-free bainitic structure of plate thickness between 34 and 116 nm has been obtained by low temperature austempering process of two hypo-eutectoid steels with 0.42 and 0.57 % C. Decreasing the carbon content results in accelerating the bainite transformation reaction together with decreasing the retained austenite content, which is known to be detrimental to the mechanical properties. Furthermore, lowering the carbon content below the eutectoid composition allowed intercritical annealing of the material which resulted in a wider window for heat treatment parameters and consequently in a spread field for mechanical properties. Dilatometric measurements were used to design the suitable heat-treatment parameters including an estimation of the required time frames for the cessation of the bainitic reaction. The structure was characterized using light optical microscopy (LOM), scanning electron microscopy (SEM) and X-ray diffractometry. In order to investigate the effect of the microstructure parameters on the materials mechanical properties, compression tests had been conducted at room temperature.

KEY WORDS: fine bainite; heat-treatment design; dilatometry; phase transformation; intercritical annealing.

1. Introduction

In early 1965 Deliry reported that silicon strongly retards the precipitation of cementite during the bainite reaction.\(^1\) Consequently, in silicon-alloyed steel the martensite start, Ms, temperature of carbon-enriched austenite may, after a certain transformation time, decrease to the level where the martensite formation during cooling from the transformation temperature is avoided. Using this feature in combination with high carbon content and low bainitic transformation temperature ultra-high strength bainitic steels had been developed.\(^2\)–\(^6\)

The high strength of these steels is due to their very fine structure. The observed refinement is a consequence mainly of the ability of high carbon content and low transformation temperature to enhance the strength of the austenite. It is expected that the bainite-plates would become thinner as the yield strength of the austenite, from which they are formed, increases.\(^7\),\(^8\) Thus, the high carbon directly refines the structure by strengthening the austenite and indirectly by lowering the Ms temperature and thus allowing performing the bainitic transformation process at lower temperature.

However, the high carbon content results in the existence of large regions of untransformed austenite in the microstructure, which is known to be detrimental to the mechanical properties. The incomplete transformation phenomenon, which limits the amount of bainite that can be formed at any temperature, is the reason for the existence of these large regions of untransformed austenite.\(^7\),\(^8\)

This paper is concerned with a further development of the ultra-fine bainitic steel by decreasing its carbon content and accelerating the bainite transformation reaction. The consequence of lowering the carbon content below the eutectoid composition provides the possibility of intercritical annealing of the alloy which results in a wider window for designing mechanical properties.

A systematic method consisting of three steps was developed. In the first step the appropriate heat-treatment parameters, using the results of dilatometric measurements, were located. In the second step the obtained parameters were reapplied using salt-bath treatment and in third one the final structure was characterised. Throughout the present work the reliability of different thermodynamic and kinetic models based on phase transformation had been reviewed.

2. Experimental Procedure

2.1. Materials

Two steel alloys with different amounts of carbon had been induction melted in vacuum. A water-cooled suction-mould is used for the suction of cylindrical samples having dimensions of \(33 \text{ mm} \times 140 \text{ mm}\) from the melt. The samples were cooled down to the ambient temperature and then hot pressed to a thickness of 12 mm. The material was homogenised in a protection atmosphere for 48 h at 1200°C, then slowly cooled down to room temperature in the furnace simply by switching off the power. The chemical compositions of the materials are shown in Table 1. Manganese and chromium had been added for hardenability, molybde-

| Table 1. Chemical composition (wt%). |
|---|---|---|---|---|---|---|---|---|---|---|
| Alloy | C  | Si  | Mn  | Al  | Co  | Cr  | Mo  | P   | S   |
| A1   | 0.420 | 1.50 | 2.37 | 0.820 | 1.40 | 1.41 | 0.250 | 0.044 | 0.013 |
| A2   | 0.565 | 1.52 | 2.02 | 0.654 | 1.59 | 1.21 | 0.239 | 0.042 | 0.014 |
num to prevent temper embrittlement due to phosphorus and silicon to prevent the precipitation of cementite during bainite formation. Note that cementite is a cleavage and void-initiating phase which is best eliminated from strong steels. Aluminium and cobalt had been added to accelerate the bainite transformation process.

2.2. Dilatometry and Heat-treatment

Dilatometric measurements were conducted on a Baehr dilatometer “DIL 805A/D”, which has a resolution of 0.05 μm/0.05 K, using samples with 5 mm diameter and 10 mm length prepared from the homogenised material. The test specimens had been degreased with an acetone solvent. Sheathed type S “Pt/Pt–10% Rh” thermocouples with a nominal diameter of 0.1 mm have been individually spot welded to the specimen’s surface in central position to monitor temperature. Each sample was held between two quartz rods, with one of the rods fixed and the other one connected to a linear variable differential transducer (LVDT). A reference rod is also connected to the LVDT. The dimension variations of the specimens during the thermal cycle are transmitted via the moving quartz pushrod to the LVDT sensor. After placing the sample between the pushrods, the insulating sheaths on the thermocouple wires had been moved along the thermocouple wires until they contacted the specimen surface. The thermal cycles had been performed under vacuum of 5 × 10⁻⁷ mbar. Helium was used for cooling. The dilatometric curves had been recorded along the thermal cycle with the help of a computer-data acquisition system. The dilatometric results had been used for designing the appropriate heat treatment of the two alloys as will be described later.

Using salt baths, the designed heat-treatment had been repeated on further mechanical testing and on samples for micro-constituents investigations. This had been done by austenitising in Durferrit GS 540/R2® and austempering in Durferrit AS 140® salt baths. The inertor R2 had been added to prevent any oxidation or decarburisation during the autenitisation process.

2.3. Materials Characterization

Quasi static-compression tests were performed at a cross head speed of 1 mm/min. All the samples had been machined after homogenisation and before the heat-treatment because of the softest condition at this stage. For micro-constituents investigation, the samples were ground and polished using the normal metallographic preparation procedure.

Microstructure had been examined by an optical microscope after etching using LePera® or nital etchant. The samples for the X-ray diffraction analysis were lightly etched with nital to remove the distorted thin layer resulting from the metallographic preparation procedure, whereas those for the scanning electron microscope (SEM) investigations had been deep nital etched.

The volume fraction of retained austenite, \( V_a \), and its carbon content, \( C_g \), were measured using X-ray diffraction analysis, as described in. The experiments were conducted using a Siemens D5000 diffractometer with Fe-filtered Co-Kα radiation at 40 kV and 40 mA. The peak intensities of the whole patterns were collected by the step scanning technique utilising small step size of \( \Delta 2\theta = 0.025^\circ \) and a period of 3 s at each fixed value of \( 2\theta \) in the range between 48°–130°. The \( V_a \) was measured using the integrated intensity from (111), (200), (220) and (311) austenite diffraction peaks and from (110), (200), (211) and (220) ferrite diffraction peaks.

The precise austenite lattice parameter, \( a_g \), had been calculated with Nelson–Riley extrapolation method. From the measured value the carbon concentration in the retained austenite (\( C_g \)) was calculated using the Equation:

\[
C_g = (a_g - 0.3555)/0.0044
\]

where \( a_g \) is given in nm and \( C_g \) in mass%.

3. Results and Discussion

3.1. Design of the Heat-treatment Process

In order to define the intercritical region, dilatometric measurements had been applied by heating specimens up to 1100°C. For better tracing the equilibrium points, a heating rate of 0.05 K/s had been used. The variation of the relative change in length as a function of temperature had been measured from which the transformed austenite fraction was calculated employing the lever rule. The results for both steels are shown in Fig. 1(a). Figure 1(b) compares the measured transformed-fraction and the predicted one obtained using the Thermo-Calc TCW3 software employing the TCFE3 database.

As can be seen from Fig. 1(b) the austenite starts to form at a high rate with the formation of austenite in the carbide rich areas for both, the experimental and the predicted transformation kinetics. Once the cementite rich region disappeared (corresponding to the point \( T_C \)), the austenite formation continues at much slower rate.

Fig. 1. (a) Dilatation versus temperature curves observed during continuous heating together with the calculated transformed austenite fraction (\( f_g \)) and (b) comparison of the calculated (\( f_g \)) and the predicted one using Thermo-Calc.
Table 2. Calculated (using Thermo-Calc) versus measured critical temperatures.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>(\Delta S_1 (^\circ C))</th>
<th>(T_f (^\circ C))</th>
<th>(\Delta S_2 (^\circ C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Measured 787.4</td>
<td>836.9</td>
<td>894.7</td>
</tr>
<tr>
<td>A2</td>
<td>Calculated 747.2</td>
<td>829.9</td>
<td>840.8</td>
</tr>
</tbody>
</table>

Table 3. Percentages of ferrite–ferrite+pearlite obtained using different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>870</th>
<th>850</th>
<th>830</th>
<th>815</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microstructure</td>
<td>8.1</td>
<td>17.2</td>
<td>23.4</td>
<td>36.1</td>
</tr>
<tr>
<td>Thermo-Calc</td>
<td>5.82</td>
<td>11.4</td>
<td>17.2</td>
<td>23.2</td>
</tr>
<tr>
<td>Dilatometric</td>
<td>10.5</td>
<td>20.4</td>
<td>28.2</td>
<td>40.4</td>
</tr>
</tbody>
</table>

Fig. 2. Microstructure observed after quenching from (a) 870°C, (b) 850°C, (c) 830°C and (d) 815°C.

Fig. 3. Dilatation versus temperature curves observed during continuous cooling from the prescribed temperatures.

tercritical annealing stage. Determination of the temperature range of pearlite dissolution process allows the selection of the most suitable intercritical temperature for obtaining microstructures which gives optimum combination of mechanical properties. During the current investigation it was important to show that the austenitising temperature used in the experiments is higher than the austenite+ferrite–pearlite temperature range.

On the other hand, in order to locate the martensite start temperatures, the dilatometer was used to quench both alloys A1 and A2 from different temperatures with a cooling rate of 10 K/s. The dilatation curves during quenching are shown in Fig. 3, where the decrease of the Ms temperature with decreasing intercritical annealing temperature is observed and can be explained by the austenite enrichment with carbon during the intercritical annealing.

According to the investigations of the intercritical trans-
formation and the Ms temperatures of the two alloys, the heat treatment temperatures have been selected as shown in Table 4. Not to be mentioned that the selected bainite transformation temperature ($T_B$) should be above Ms temperature and that of the autenitisation temperature ($T_A$) should be above $T_c$ temperature.

The dilatometer was also used to perform the heat treatments at different temperatures. The samples were heated at a rate of 10 K/s up to the prescribed austenitising temperature, held there for 15 min and then cooled down to the austempering temperature with a cooling rate of 10 K/s. This cooling rate was sufficient to avoid any allotriomorphic ferrite and pearlite formation during cooling to the prescribed bainitic holding temperature. This could be detected from the linearity of the temperature-relative change-in-length curve, being recorded during cooling. Similar linearity had been obtained during cooling to RT after the austempering process at the prescribed bainitic holding temperature. The latter linearity indicates that the autenitisation process has stabilised the retained austenite and moved the Ms temperature well below RT. So the final microstructure is free of martensite.

Representative results from the real-time monitoring of the extend of the bainite reaction “in terms of dimensional changes” are shown in Figs. 4(a)–4(c). It is assumed that the point, where dimensions cease to change, represents 100% of transformation. In all cases the samples had been quenched after reaching this point. Horizontal lines have been drawn nearby these points to aid in estimating them.

The reason for this termination of the reaction, which limits the amount of bainite that can be obtained at any temperature, is explained by the incomplete-reaction phenomenon. The reaction is said to be incomplete since transformation stops before the phases achieve their equilibrium compositions. The current dilatometric results demonstrate that the alloy with lower carbon content proceeds to higher amounts of bainitic ferrite in shorter time frames compared with that of higher carbon. The holding times required for cessation of the bainite reaction for the investigated heat treatment conditions are illustrated in Fig. 5. It should be mentioned that the holding time required for termination of the bainite reaction is shorter than that reported in Refs. 4, 5 and 17. This is due to the lower carbon content used during the current research. Furthermore, much longer time-frames are required for alloys with higher carbon content and without addition of the bainite-reaction accelerating elements, i.e. Al and Co.

The bainite transformation is therefore accelerated by both, lowering the carbon content of the alloy and the addition of the Al and Co elements. Calculations of the driving force for the transformation of austenite into ferrite ($\Delta G^{\text{trans}}$) for alloys A1 and A2 (see Fig. 6) confirm the thermal dilatation results. Thus, the dilatometric results demonstrate that

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_A$ (°C)</th>
<th>$T_B$ (°C)</th>
<th>$T_{c}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>920</td>
<td>290</td>
<td>230</td>
</tr>
<tr>
<td>A2</td>
<td>850</td>
<td>290</td>
<td>230</td>
</tr>
</tbody>
</table>

Table 4. Used heat-treatment parameters (annealing temperature “$T_A$” and austempering temperature “$T_B$”) together with the martensite start observed for each $T_A$. 

Fig. 4. Dilatation versus time curves observed during isothermal holding at different temperatures of (a) A1 quenched from 920°C, (b) A1 quenched from 850°C, and (c) A2 quenched from 920°C.

Fig. 5. Estimated holding time required for the cessation of the bainitic reaction for alloys A1 and A2 quenched from different annealing temperatures austempering temperatures.

Fig. 6. Variation of the free energy change $\Delta G^{\text{trans}}$ with temperature for alloys A1 and A2.
both of rates of the bainite formation and its total amount would increase as a result of decreasing the carbon content. Of course, the reduction of the carbon content of the alloy is only as long useful as it does not lead to an unacceptable decrease in strength of the steel, i.e. by coarsening the structure.

Concerning the transformation times of alloy A1, it is to be mentioned that two contradicting factors are controlling them in the intercritical region. The formation of ferrite resulted in decreasing the total amount of bainite which consequently results in decreasing the transformation time, whereas increasing the ferrite amount results in enriching the austenite with carbon, (according to Thermo-Calc calculations: 0.420, 0.444, 0.470 and 0.501% C at 920, 870, 850, and 830 °C, respectively) the latter effect results in deceleration of the transformation process.

3.2. Microstructural Features

3.2.1. Observed Phases

The micrographs in Figs. 7 and 8 show the typical structure obtained after isothermal transformation of austenite into bainitic-ferrite. LePera etchant was used to differentiate the polygonal ferrite within the acicular ferrite aggregates (see Figs. 7(c) and 7(b)). As clearly seen in Figs. 7 and 8 it is not possible to distinguish individual ferrite plates within the thin aggregates using LOM. Therefore,
SEM investigations had been conducted. Figs. 9 and 10 show that the ferrite aggregates build up from many ferrite plates in the same crystallographic orientation. A decrease in the transformation temperature leads to a structure refinement, i.e., a reduction in the packet width and in the thickness of individual ferrite plates. Sandvik et al. reported that the thickness of individual ferrite plates at a certain temperature is relatively uniform, regardless of the transformation time, while acicular-ferrite aggregate width is affected by the transformation time.19)

The retained austenite is present in a form of homogeneously distributed films along ferrite plate boundaries as well as in a form of small isolated austenite colonies. The polygonal-ferrite phase is easily distinguishable within the intercritically-annealed structure.

For the intercritically annealed material, the frequent observation of the retained austenite islands in the neighbourhood of the polygonal ferrite (see Figs. 7(c), 7(d), 9(c) and 9(d)) can be justified by the stabilisation of the austenite particles as a result of the matrix constraints resulting from the partially coherent nature of the ferrite austenite interface.20)

The existence of retained austenite islands, which have lower mechanical stability, in the vicinity of the soft polygonal-ferrite phase (Fig. 9(c) and 9(d)) is of vital importance for the mechanical properties. In a recent publication21) the authors have revealed the importance of the effect of polygonal ferrite and the interaction between polygonal ferrite, retained austenite, and strain-induced martensite during straining on the structure–property relationship.

3.2.2. Structure Fineness

SEM investigations were conducted on alloy A1 annealed at two temperatures of 920°C and at 850°C and on alloy A2 annealed at 920°C to determine the true plate thickness $t$. This has been done by measuring the mean linear intercepts $L_t$ in a direction normal to the plate length. The thickness $t$ is related to $L_t$ by the relationship $t = 2L_t / \pi$.4)

Figure 11 compares the plate thicknesses for the investigated structures. The strength of the austenite from which the ferrite plates are formed is the main factor controlling the plate thickness.9) As expected, the plates become thinner for the alloy with higher carbon content and with decreasing the transformation temperature due to the effect of both factors on enhancing the strength of the austenite. The observed thinner plate for alloy A1 annealed at 850°C in comparison with that annealed at 920°C is due to the carbon enrichment of the austenite phase.

3.2.3. Retained Austenite

X-ray analysis was used to estimate the retained austenite volume fraction, $V_a$, and its carbon content, $C_a$. Figure 12 shows the influence of the bainitic holding temperature on the amount of the retained austenite observed for both alloys. A comparison between experimentally measured ($C_a$) and calculated $T_0$ curve is shown in Fig. 13. The $T_0$ 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 measured concentrations are close to the $T_0$ curve. During the course of the isothermal bainitic transformation austenite is enriched with carbon, which is rejected from the bainitic acicular-ferrite. This reaction can take place only until reaching the point at which the free energy of ferrite equals the free energy of austenite ($T_0$ curve). At this point no further transformation of austenite to ferrite can take place. For lower temperatures the reaction can proceed to higher carbon concentrations in austenite (Fig. 13), and consequently to higher amounts of bainite (Fig. 4) and lower amount of retained austenite (Fig. 12).

On the other hand, decreasing the carbon content does not result in a significant change in the $T_0$ curve position, indicating that there is no significant variation in the maximum amount of carbon that can enrich the austenite at different bainitic holding temperatures. One consequence of that is the increase of the bainite on the expense of the retained austenite by decreasing the alloy carbon content ($\bar{C}$) according to equation:

$$C_\gamma = \bar{C} + V_b \left( \frac{\bar{C} - s}{1 - V_b} \right)$$

where $s$ is the amount of carbon in the bainitic ferrite and $V_b$ is the bainite volume fraction.

The previous analysis explains why the alloy A1 has proceeded to higher final amount of bainite compared with alloy A2 considering the same transformation temperature (Figs. 4(a) and 4(c)).

For this type of steel a relatively higher dislocation density is reported due to the phase transformation which is attributed to the fact that the shape deformation accompanying displacive transformations is accommodated partially by plastic relaxation. As the transformation temperature decreases, the amount of the formed bainite and hence the dislocation density increases. Atomic probe analysis of the carbon distribution in the structure revealed that a substantial quantity of carbon is trapped at these dislocations. In the light of that, the departure of the measured $C_\gamma$ from the $T_0$ curve towards lower values as the temperature decreases (Fig. 13) can be explained. The dependence of the redistribution of carbon between the solid solution and dislocations on the dislocation density, which is getting higher by decreasing the temperature, could be the reason for such deviation.

3.3. Compression Properties

The mechanical properties for alloys A1 and A2 determined by the compression test are shown in Figs. 14 and 15. The very high strength of the materials corresponds to their very fine structure.

Lowering the transformation temperatures increases the ultimate compression strength which corresponds to a reduction in the ferrite-plates thickness together with a decrease in the volume fraction of the retained austenite. The results shown in Fig. 14 indicate that the compression strength is controlled by the work-hardening properties of the austenitic structure component. The important results which can be concluded from Fig. 14 is that the negative effect of the retained austenite content could be partially ab-
sorbed by the use of the strain hardening of a designed amount of ferrite in the structure. Together with the well-known strong work-hardening effects caused by transformation-induced plasticity (TRIP) effect, the existence of the retained austenite/transformed-martensite in the vicinity of the soft polygonal-ferrite (Fig. 9(c) and 9(d)) can remarkably reduce its detrimental effect.

During the current study, the axial compression testing has been used for comparing the ductile fracture limits of the material. This has been done by taking the advantage of the barrel formation and controlled stress and strain conditions at the equator of the barrelled surface when compression is carried out with friction. These stress and strain conditions lead to tensile stress around the circumference and compressive stress at the bulge equator. Eventually, the surface is cracked due to the tensile stress in the circumferential direction at the bulge surface.

The highest fracture strain values have been recorded for the highest transformation temperature and the highest amount of ferrite. Ferrite serves to enrich the austenite with carbon, which helps to strengthen the bainite but it decreases its amount. In addition, the presence of ferrite in the final microstructure provides good ductility, i.e., deformation to fracture.

4. Conclusions

Ultra fine bainite structure had been obtained in two hypo-eutectoid steels by isothermal transformation at low temperatures (210–290°C). The major conclusions drawn from the present investigation are as follows:

1. Using the dilatometric analysis, a clear differentiation between pearlitic dissolution process and $\alpha \rightarrow \gamma$ transformation was found in these steels. This allowed selecting the most appropriate intercritical temperature to obtain microstructures with optimum combination of mechanical properties.

2. The consequence of lowering the carbon content below the eutectoid composition provided the possibility of intercritical annealing of the alloy which resulted in a wider window of mechanical properties.

3. The redistribution of carbon between the retained austenite and dislocations was observed to be dependant on the dislocations density.

4. The negative effect of the retained austenite content could be partially accommodated by the use of the strain hardening of a designed amount of ferrite in the structure.

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REFERENCES


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