The effects of chemical composition variations on microstructure and mechanical properties of nanostructured, low temperature bainitic steels

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Abstract
Bainitic transformation at low transformation temperatures leads to a microstructure involving fine plates of bainitic ferrite and thin films of retained austenite. This microstructure has shown ultimate tensile strength of about 2.2 GPa, noticeable uniform elongation in the range of 5 to 30%, hardness values of about 600 to 670 HV and impact toughness in the range of 30 to 40 MPa m$^{1/2}$. With careful design of the chemical composition of steel, suitable mechanical properties with lower cost production could be achieved. In the current work, the microstructure and mechanical properties of two steels with different chemical compositions have been evaluated using XRD, SEM, TEM, tensile and Charpy impact tests. The results of this study suggest that without trial and error, it is possible to design a new steel with unique microstructure and mechanical properties. The achieved mechanical properties are due to the microstructural characteristics which evolved during isothermal transformation.

Keywords: Bainitic transformation, Retained austenite, Bainitic ferrite, Isothermal transformation, Nanostructured.

1. Introduction
High strength bainitic steels have not been as successful as quenched and tempered martensitic steels due to the presence of coarse cementite phases within bainite, which results in deterioration in toughness. The precipitation of cementite during bainite formation could be suppressed by addition of Si in the range of 1.5 to 2 wt.%. Therefore, the carbon is rejected from the bainitic ferrite, enriches the retained austenite, which results in an austenite with higher thermal and mechanical stability. Therefore, austenite films remain unchanged during cooling to ambient temperature and transform in a progressive manner into the martensite upon deformation leading to strengthening by delaying the necking phenomenon. This is partly because of their higher carbon concentration, but also because of the constraint to transformation exerted by the surrounding plates of ferrite. However, the full benefit of this carbide-free bainitic microstructure has frequently not been realized. 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 $T_n$ curve, beyond which diffusionless growth is prevented. The $T_n$ curve is the locus of points where austenite and ferrite of the same chemical composition have identical free energies. This leaves large regions of untransformed austenite that tend to transform to high carbon, untempered martensite during the loading of small stress and consequently have an embrittling effect. According to the phase transformation theory, there are three ways to avoid this difficulty: By modifying substitutional solute content to shift the $T_n$ to higher $X_{tr}$ and by minimizing transformation temperature and controlling the mean carbon concentration of the steel 1-3).

Using phase transformation theory in carbide-free bainitic steels has led to a new series of steels composed of carbide-free bainitic ferrite and carbon enriched austenite in the microstructure. Evaluation of mechanical properties of novel bainitic steels shows a good combination of ultimate tensile strength (UTS) of about 2.2 GPa, hardness values in the range of 600 to 670 HV, a noticeable uniform elongation in the range of 5 to 30% and toughness in excess of 30 to 40 MPa m$^{1/2}$. Such properties have never before been achieved with bainite. These mechanical properties have been obtained without using any expensive alloying elements and without the need for rapid heat treatment or mechanical processing. Furthermore, these bainitic steels can be manufactured in bulk form 2-7).

Careful design of the bainitic steels has an undeniable role in the cost of production, mechanical properties and microstructure. Typical chemical compositions of the previous novel bainitic steels are listed in Table 1 2-8). In steels A and B, good combinations of mechanical properties have been reported. Because a long time is needed for the completion of bainite transformation in steel A and the presence of Co as an expensive alloying element in steel B, the steels are not efficient
from commercial point of view. In the current work, with the aim of fast bainitic transformation and lower cost in production, a new chemical composition has been designed using MUCG83™ thermodynamic model. This model which has been developed in Cambridge University based on thermodynamic relations and empirical results, is a powerful software for modeling of the thermodynamics and kinetics of solid state transformations in steels, and predicts TTT and TTT diagrams, martensite and bainite start temperatures and nucleation and growth driving force from the chemical composition ⁹. The effects of chemical composition variations on microstructure and mechanical properties have been investigated.

Table 1. Typical chemical compositions of the previous novel bainitic steels (wt.%) ⁸⁻⁹.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Co</th>
<th>Al</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1.5</td>
<td>1.9</td>
<td>1.25</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>B</td>
<td>0.8</td>
<td>1.5</td>
<td>2</td>
<td>1</td>
<td>0.25</td>
<td>1.5</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

2. Experimental Procedure

Steel 1 with chemical composition (0.65-0.85)C, (1.5-2)Si, (2.1-2.3)Mn, (0.9-1.1)Cr, (0.2-0.3)Mo, (1.2-1.4)Co and (0.7-1)Al (wt.%) was selected from the previous work ²⁻⁸. A new bainitic steel with chemical composition (0.65-0.85)C, (1.5-2)Si, (1.3-1.5)Mn, (1.3-1.5)Cr, (0.2-0.3)Mo, (≤0.15)Co and (0.7-1)Al (wt.%) was designed. The chemical composition was designed so that two alloys have a similar T₈ and TTT diagrams. This similarity in curves can guarantee similar hardenability, volume fraction of bainitic ferrite and carbon content in retained austenite for both steels.

The steels were cast using a high frequency induction furnace under argon gas atmosphere in the form of cylinder bar with a diameter of 50mm and a length of 600mm. The cast cylinders were electro slag remelted (ESR) for obtaining clean steel. The chemical compositions of the steels after ESR are given in Table 2. T₈ and TTT diagrams parameters are listed in Tables 3 and 4 for steels. It is evident that the two steels have similar T₈ and TTT diagram parameters. To reduce the thickness and to change the cast structure to a wrought structure, hot rolling was carried out after ESR.

Table 2. Chemical compositions of the steels (wt%) ¹⁰.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Co</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.8</td>
<td>1.84</td>
<td>2.18</td>
<td>1.04</td>
<td>0.30</td>
<td>1.31</td>
<td>0.85</td>
<td>Bal</td>
</tr>
<tr>
<td>B</td>
<td>0.69</td>
<td>1.92</td>
<td>1.38</td>
<td>1.39</td>
<td>0.24</td>
<td>0.14</td>
<td>0.75</td>
<td>Bal</td>
</tr>
</tbody>
</table>

To evaluate the microstructure and mechanical properties, samples were prepared from the hot rolled ingots and transformed isothermally at the temperature range of 200 to 300°C at bainite transformation completion time after austenitising at 950°C for 30 minutes, and finally quenched into water at room temperature. According to the previous work ¹¹, bainite transformation completion times for steels 1 and 2, are 6, 16 and 72 hours at transformation temperatures of 300, 250 and 200°C, respectively.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to examine the microstructure. SEM and XRD samples were ground to ensure the removal of the decarburized layer, then mechanically polished and chemically etched using nital 2%. TEM foils were sliced into 0.5mm thickness by wire electro discharge machining, ground down to 30µm thicknesses using SiC abrasive paper, and then thinned to perforation using a Gatan 691™ precision ion polishing system. The tensile tests were carried out at a cross head speed of 0.1mm/s according to ASTM E08 standard. Charpy impact tests were conducted at room temperature according to E23 standard. Fracture surfaces examination was carried out by a CamScan MV-2300™ scanning electron microscope.

3. Results and Discussion

3.1. The evaluation of phases in the microstructure

Microstructures of the samples transformed at 200°C have been shown in Fig. 2. In bainitic transformation, the carbon supersaturated bainitic ferrite grows by a displacive mechanism at the first stage of transformation. Then, the plate's excess carbon is partitioned into the retained austenite. At the bainite transformation completion time, the austenite is sufficiently enriched with carbon and will be retained at the ambient temperature during cooling to room temperature. Therefore, the microstructure is a mixture of a large amount of bainitic ferrite, retained austenite
and little martensite. The volume fraction of phases as a function of transformation temperature is shown in Fig. 2. Fig. 2a shows the volume fraction of bainitic ferrite estimated by MUCG83 thermodynamic model. Evidently, bainitic ferrite volume decreases with transformation temperature which is easily justified by the lever rule. Lower content of alloying elements especially Mn in steel 2, has led to higher bainitic transformation rate and less delay time before bainite transformation start. Therefore, volume fraction of bainitic ferrite in steel 2 has shown a higher value compared to that of steel 1. According to Fig. 2b, due to higher tendency to martensite formation at lower temperature, the volume fraction of martensite has been increased at low temperatures. According to the model results, retained austenite in steel 2 has shown a lower $M_S$, which leads to lower volume fraction of martensite in steel 2 compared to that of steel 1.

The volume fraction of retained austenite determined by XRD is shown in Fig. 2c. It is obvious that the austenite content gradually increases with isothermal temperature. This is consistent with lower bainitic ferrite content at higher temperature. The higher volume fraction of bainitic ferrite; and consequently, lower volume fraction of retrained austenite at lower temperature is due to large supercooling which leads to nucleation of a large number of bainitic ferrite plates. The higher volume fraction of retained austenite in steel 1 compared to that of steel 2 is also justified.

**Fig. 1.** SEM micrograph of steel 1 (a) and steel 2 (b) transformed at 200°C for 72 h.

**Fig. 2.** Variation of volume fraction of phases present in the microstructure with temperature, (a) bainitic ferrite, (b) retained austenite and (c) martensite.

The volume fraction of retained austenite determined by XRD is shown in Fig. 2c. It is obvious that the austenite content gradually increases with isothermal temperature. This is consistent with lower bainitic ferrite content at higher temperature. The higher volume fraction of bainitic ferrite; and consequently, lower volume fraction of retrained austenite at lower temperature is due to large supercooling which leads to nucleation of a large number of bainitic ferrite plates. The higher volume fraction of retained austenite in steel 1 compared to that of steel 2 is also justified.
the lower bainitic ferrite volume. The carbon content of retained austenite has a determining effect on mechanical stability of the retained austenite during deformation loading. The carbon content of retained austenite as a function of transformation temperature is shown in Fig. 3. It is obvious that maximum carbon content in retained austenite is related to samples transformed at 250°C. The results are not in agreement with the predicted results from thermodynamic model as given in Tables 3 and 4. The maximum carbon in retained austenite should be observed in samples transformed at 200°C. This difference could be as a result of large amount of carbon entrapment in bainitic ferrite at 200°C rather than higher transformation temperatures. Similar behavior has been reported by Caballero 11).

A higher carbon content in retained austenite leads to a more stable austenite. This austenite transforms in a progressive manner into martensite upon deformation, leading to strengthening by delaying the necking. Mn lowers the activity coefficient of carbon in ferrite and austenite and increases the C solubility in ferrite 12). If only the contribution of Mn on carbon content of retained austenite is considered, retained austenite in the steel 2 should show a higher carbon content. In practice, two steels have shown similar carbon contents as it is shown in Fig. 3. This is as a result of the effects of other alloying elements which act in opposite manner compared to Mn.

\[ \text{Fig. 3. Variation of carbon content of the retained austenite with temperature for steel 1 and 2.} \]

3.2. The thickness of the bainitic ferrite plates

Much of the strength of the microstructure comes from the very small thickness of the bainite plates.

\[ \text{Fig. 4. TEM micrograph of steel 1 and 2 transformed at: (a,b) 300°C for 6 h and (c,d) 250°C for 16 h. F and A denote to the bainitic ferrite and retained austenite, respectively.} \]
Of the total strength of 2500 MPa, some 1600 MPa can be attributed solely to the fineness of the plates.

The TEM micrographs in Fig. 4 show a microstructure involving long and very fine carbide-free bainitic ferrite plates and retained austenite. Size of the plates, measured from the TEM micrographs and peak broadening in diffraction patterns due to the presence of fine crystallites, is given in Table 5. It is obvious that by decreasing the transformation temperature, the bainite plate thickness decreases. This is because the yield strength of the austenite becomes greater at lower temperature and presumably the nucleation rate can be greater at larger supercooling.

Austenite with higher yield strength and presence of larger nucleation driving force leads to finer plates, firstly, because there is a larger resistance to interface motion and secondly, because an increased nucleation rate leads to microstructural refinement. The variation of yield strength of austenite as a function of transformation temperature based on an empirical model is shown in Fig. 5. From the figure, the austenite strength decreases with temperature for both steels. The nucleation driving force (chemical free energy change) calculated by MUCG83 thermodynamic model is also shown in Fig. 6 which decreases by increasing the temperature. Consequently, the finest plates are observed in the transformation temperature of 200°C.

According to Fig. 5, austenite in steel 1 shows higher yield strength compared to that of steel 2, while the steels nucleation driving force is vice versa. Finally, the combined effects of these factors have led to a similar bainite plate thickness in both steels as shown in Table 5.

Table 5. Bainite plate thickness measured from the TEM micrographs and XRD patterns.

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>Bainitic ferrite thickness by TEM (nm)</th>
<th>Bainite ferrite thickness by XRD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Steel 1</td>
<td>Steel 2</td>
</tr>
<tr>
<td>300</td>
<td>26-117</td>
<td>23-154</td>
</tr>
<tr>
<td>250</td>
<td>13-134</td>
<td>21-136</td>
</tr>
<tr>
<td>200</td>
<td>12-96</td>
<td>10-83</td>
</tr>
</tbody>
</table>

Fig. 5. Variation of austenite yield strength with temperature.

Fig. 6. Variation of nucleation driving force with temperature plotted using MUCG83 model.

### 3.3. Mechanical properties

The variation of ultimate tensile strength (UTS) and impact toughness of samples with isothermal transformation temperature are shown in Figs. 7 and 8. It can be seen that as the transformation temperature increases, the UTS decreases and the impact toughness increases.

As mentioned earlier, most of the strength comes from the very small thickness of the bainite plates. Due to the similar bainite plate thickness in the studied steels, it seems reasonable that both steels show approximate similarity in UTS values. Minor difference in UTS is as a result of different volume fraction of phases in the microstructure and dislocation density.

The unique microstructure of the steel is responsible for high Charpy impact toughness as shown in Fig. 8, especially for the samples transformed at 300 and 250°C. The results are well comparable with maraging steels, which are more expensive. The microstructure characteristics including the volume fraction of phases and their morphology influence the Charpy impact toughness changes. From the figure, it is evident that steel 2 has shown higher impact toughness compared to that of steel 1, which could be as a result of a lower martensite volume in steel 2.

Fig. 7. Variation of UTS with temperature for steels 1 and 2.
4. Conclusion

With careful design, it is possible to produce bainitic steels with lower cost production, suitable mechanical properties and unique microstructure. In the designed new steel, a unique microstructure composed of carbide-free bainitic ferrite and carbon enriched austenite has been obtained. Also, the suitable mechanical properties involving UTS of about 1983 MPa and impact toughness of about 35 J have been achieved. The achieved good combination of microstructure and mechanical properties not only are comparable with expensive steels, but also show better impact toughness values.

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References