Unraveling the Effect of Martensite Volume Fraction on the Mechanical and Corrosion Properties of Low-Carbon Dual-Phase Steel

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The effect of martensite volume fraction on the mechanical and corrosion properties of low-carbon dual-phase steel is studied based on both step quenching (SQ) and intercritical annealing (IA) routes. For SQ samples, hardness and ultimate tensile strength decrease with increasing holding time at the intercritical temperature and reach a plateau, which is related to the decrease in the amount of martensite during annealing. Conversely, for the IA samples, hardness increases during holding at the intercritical temperature due to austenitization and reaches the same plateau. At a same martensite volume fraction, the work-hardening behavior of SQ samples is better than IA samples, which is related to both the finer grain size and smaller martensite islands in the former. At low martensite fractions, the corrosion properties are comparable with the as-received ferritic–pearlitic sample. It is revealed that by decreasing the volume fraction of martensite in SQ samples, the corrosion current density ($i_{corr}$) decreases almost linearly, and at martensite content of zero, it reaches the $i_{corr}$ of the fully ferritic microstructure. The latter is found to be lower than the $i_{corr}$ of the as-received sample. Therefore, the real effect of martensite on corrosion properties is unraveled for the first time.

1. Introduction

Low-carbon dual-phase (DP) steels have microstructures composed of a ferritic matrix and a hard phase (normally martensite), and thanks to their excellent mechanical properties, they are suitable materials for industrial applications, especially in the automotive industry. Accordingly, research on this subject is still under way to improve their strength–ductility balance. In contrast, corrosion has been also an important factor affecting the durability and reliability of cars and should be taken into account.

The volume fraction and morphology of martensite phase as well as the grain size of ferritic matrix are the main parameters that control the mechanical properties. It has been reported that increasing the volume fraction of martensite enhances the hardness. In DP steel, the yield stress (YS) increases, the ultimate tensile strength (UTS) remains approximately constant, the uniform elongation decreases, and the total elongation remains constant. These results are related to high martensite contents (more than 45 vol%), and hence, this subject needs more attention by consideration of usual martensite contents of ≈20 vol%.

Bhagavathi et al. studied the corrosion resistance of 0.04C-0.03Si-0.6Mn DP steels with martensite volume fractions up to 28%. They reported that the corrosion rate of DP steels was lower than the steel with ferrite–pearlite microstructure and the volume fraction of martensite had a little effect on the increase in the corrosion rate. They explained these results based on the weaker galvanic couple formed between ferrite and martensite compared with the galvanic couple formed between ferrite and pearlite. This was also verified by D Trejo et al. and Ismail et al. where this enhanced galvanic corrosion resistance was related to the absence of eutectoid carbides in DP steel.

For 0.15C-0.17Si-0.73Mn steel, Kayali and Anaturk reported that an increase in intercritical temperature led to an increase in the amount of martensite, and hence, the corrosion rate was increased. Moreover, the corrosion rates of the DP steels were higher than that of the steel with ferrite–pearlite microstructure. Allam and Abbas reported similar findings for the

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/srin.201900327.

DOI: 10.1002/srin.201900327
0.06C-0.40Si-0.43Mn steel. Salamci et al.\cite{29} also reported an increase in corrosion rate with increasing martensite content. Keleştemur and Yıldız\cite{30} and Sarkar et al.\cite{31} showed that both amount and morphology of the martensite have definite effects on the corrosion rate of DP steel, and by increasing martensite content, the corrosion rate increases. Keleştemur et al.\cite{32} showed that the corrosion rates of DP steels were higher than that of the steel with the ferrite–pearlite microstructure. Sarkar et al.\cite{31} also showed that the refinement of phase constituents increases the tendency of corrosion due to an increase in interphase area. Osório et al.\cite{33} showed the deleterious effect of DP microstructure on the corrosion resistance due to the residual stress from martensite formation but acknowledged its good mechanical properties.

It can be seen that the reported corrosion results are contradictory, and hence, more systematic works are required. Moreover, most of the reported works have studied the effect of martensite volume fraction based on the IA of ferrite–pearlite microstructures, which complicates microstructure formation during IA (transformation of pearlite, austenite formation at grain boundaries, etc.\cite{34,35}). Conversely, as only ferrite and austenite (martensite after quenching) are present during processing, SQ from the austenitic region to the IA range is an optimum approach to study the effect of martensite volume fraction on the properties of DP steel. Moreover, the problem of Mn partitioning is much less pronounced in DP steel processed via the SQ route.\cite{36}

Therefore, the present work is dedicated to unravel the effect of martensite volume fraction on the mechanical and corrosion behavior of low-carbon DP steel. Accordingly, the SQ technique was used for processing, and it was compared with the conventional IA. Moreover, the martensitic and ferritic–pearlitic microstructures were also considered.

2. Experimental Section

2.1. Processing

0.12C-1.11Mn-0.16Si (wt%) steel was received in the fully annealed condition. A cylindrical specimen (2 diameter \times 10 length mm$^2$) was heated up to 1000°C at the rate of 2°C s$^{-1}$ in a dilatometer, which resulted in the dilatometric curve and the corresponding derivative curve shown in Figure 1a. Accordingly, the $A_1$ and $A_3$ temperatures were estimated as 730 and 904°C, respectively.

For the processing of SQ samples, the as-received steel was austenitized at 950°C in the first furnace, followed by quick transferring (less than 3 s) to the second furnace at IA temperature of 850°C for holding times up to 120 min and subsequent water quenching (WQ). The as-received steel was also intercritically annealed at 850°C for holding times up to 120 min, followed by WQ (IA samples). The applied processing routes for important samples are shown in Figure 1b. It should be noted

![Figure 1. a) Dilatometric analysis of the as-received steel. b) Applied processing routes. c) Schematic of the tensile test specimen (all dimensions are expressed in mm).](image-url)
that a fully annealed 0.035C-0.27Mn-0.035Si (wt\%) steel with a low carbon content of 0.035 wt\% resulting in a nearly fully ferritic microstructure was also considered in this work, as will be explained later.

2.2. Microstructural Characterization

Microstructural features were revealed by pre-etching in LePera’s reagent (1 g Na2S2O5 in 100 mL H2O + 4 g C6H3N3O7 in 100 mL ethanol), followed by etching in the 2% Nital solution. Afterward, an Olympus Vanox optical microscope was used for microstructural characterization.

2.3. Evaluation of Mechanical Properties

Vickers hardness test with a load of 5 kg was used for studying the effects of IA time (decreasing hardness via increasing the amount of the ferrite phase during holding at the IA temperature). Tensile test specimens were prepared according to the sub-size ASTM E8 standard with the gauge length of 25 mm (Figure 1c). Tensile testing was conducted at room temperature by a computerized testing machine at the constant cross-head speed of 1 mm min\(^{-1}\). These tests were repeated once to insure the reproducibility of the results. The YS was measured based on the 0.2% offset method, and the total elongation was determined by putting together the fractured pieces of the tensile samples.

2.4. Potentiodynamic Polarization Test

A Solartron potentiostat (Model SI 1287) was used for corrosion tests using the three-electrode configuration in a 3.5 wt\% NaCl solution (providing Cl\(^{-}\) ions) at room temperature. A saturated calomel electrode (SCE) and a platinum electrode were used as the counter and the reference electrodes, respectively. Polarization potentials were in the range from \(-1\) to \(-0.6\) V, and the scanning speed was 2 mV s\(^{-1}\). The ground and polished surfaces of the samples were used for corrosion analysis. Based on the obtained polarization curves, the corrosion current density (\(i_{\text{corr}}\)) was obtained by the Tafel extrapolation method\(^{[37]}\) as shown in Figure 2. This figure also shows the repetition of the test resulted in the same \(i_{\text{corr}}\), and hence, the reproducibility of the results was in a valid range.

3. Results and Discussion

3.1. Microstructures and Mechanical Properties

The hardness versus holding time at 850 °C is shown in Figure 3. For the SQ samples, by increasing holding time, hardness decreases and finally reaches a plateau at \(\approx 120\) min. Figure 4b–g shows the representative microstructures, where it is shown that by increasing the holding time, the amount of martensite (austenite at 850 °C) in the SQ samples decreases. The measured amount of martensite is also shown in Figure 3, where the martensite content decreases from 100 to \(\approx 20\) vol\% at 120 min (SQ 120 sample). Therefore, a decrease in hardness with the increasing holding time is related to a decrease in the amount of martensite. Conversely, as shown in Figure 3, for the IA samples, hardness increases during holding at the IA temperature due to partial austenitization (formation of austenite from pearlite and then from the surrounding ferrite phase\(^{[38]}\)), and the resulting increase in the martensite fraction after quenching can be deduced by comparing Figure 4h,i. The hardness reaches the same plateau at \(\approx 5\) min. Image analysis of Figure 4i revealed that at this plateau (IA 5 sample), the equilibrium amount of martensite (\(\approx 20\) vol\%) was achieved, which is similar to the equilibrium amount of martensite for the SQ 120 sample.

Tensile stress–strain curves are shown in Figure 5a. The as-received ferritic–pearlitic sample shows discontinuous yielding at the onset of plastic flow, where the presence of distinct yield point is evident. In low-carbon steel, this phenomenon is well known to be related to the Cottrell atmospheres of interstitials around dislocations.\(^{[39]}\) In contrast, for the IA 5 DP steel, due to the presence of geometrically necessary dislocations (GNDs) at the interphases between ferrite and martensite,\(^{[40]}\) the continuous yielding behavior can be seen. Moreover, the work-hardening rate (\(\frac{d\sigma}{d\varepsilon}\), i.e., the slope of the true stress–true strain curve in Figure 5b) at each strain is much higher. This resulted in the high UTS of this sample compared with its YS. In fact, the yield ratio (YS/UTS) for the IA 5 sample is 0.41 compared with 0.65 for
1) It has been shown that \( \frac{d\sigma}{de} \propto \sqrt{V_M/D_M} \) \(^{[42,43]} \) where \( V_M \) is the volume fraction of martensite and \( D_M \) is the average diameter of martensite islands. The measured values are also reported in Table 1. It is shown that at the same \( V_M \), the value of \( D_M \) for the SQ 120 sample is much lower compared with that obtained for the IA 5 sample, which is related to the transformation of large pearlite colonies (Figure 4a) to martensite (Figure 4i) in the latter. Therefore, based on \( \frac{d\sigma}{de} \propto \sqrt{V_M/D_M} \), a better work-hardening behavior is expected for SQ 120 sample.

2) The average ferrite grain size of SQ 120 sample is much finer compared with that of the IA 5 sample (19 vs 31.7 \( \mu \text{m} \)). This is mainly related to the large grain size of the as-received sample (Figure 4a). Now, austenite (or martensite after quenching) forms instead of pearlite at the IA temperature and grows into the surrounding ferrite grains, and hence, the IA 5 sample inherits the large ferrite grains of the as-received sample (Figure 4i). The enhancement of the work-hardening rate of DP steel with ferrite grain refinement (contrary to the trend seen in conventional steels) has been reported in several research works.\(^{[44,45]}\)

### 3.2. Corrosion Resistance

Polarization curves are shown in Figure 6, and the obtained values of corrosion current density \( (i_{corr}) \) are summarized in Figure 7 as a plot of \( i_{corr} \) versus martensite content. It is shown that by decreasing the volume fraction of martensite in the SQ samples, \( i_{corr} \) decreases almost linearly. A straight line was fitted to the data obtained from SQ samples as shown in Figure 7. Extrapolation of this line to martensite volume percent of zero results in the \( i_{corr} \) of 0.417 \( \mu \text{A cm}^{-2} \). This is slightly lower than \( i_{corr} \) of 0.456 \( \mu \text{A cm}^{-2} \) for the as-received sample. The latter can be related to the presence of pearlite in the as-received sample, whereas \( i_{corr} \) of 0.417 \( \mu \text{A cm}^{-2} \) was estimated for a fully ferritic microstructure. To further support this argument, a fully annealed 0.035C-0.27Mn-0.035Si (wt%) steel was also subjected to the corrosion test, as described in Section 2.4. The carbon content of this steel is very low and it has a ferritic microstructure with very low pearlite content, as shown in Figure 4j. The polarization curve of this sample is shown in Figure 6 as the “ferrite” sample. The \( i_{corr} \) of 0.413 \( \mu \text{A cm}^{-2} \) was obtained for this sample, as shown in Figure 7, which is close to the estimated value of 0.417 \( \mu \text{A cm}^{-2} \). Therefore, it seems that the real effect of martensite is revealed.

It can be deduced that the corrosion resistance of the developed ferrite–martensite DP samples is lower than that of the ferrite–pearlite as-received sample. This is consistent with the results of Keleştemur et al.\(^{[32]}\) and Osório et al.\(^{[33]}\) where the residual stress that resulted from the martensite formation was found to be responsible for the decreased corrosion resistance. In fact, \( i_{corr} \) of 0.472 \( \mu \text{A cm}^{-2} \) was obtained for the IA 5 sample with martensite volume percent of \( \approx 20\% \) (Figure 6 and Figure 7). This value is comparable with the \( i_{corr} \) of 0.456 \( \mu \text{A cm}^{-2} \) for the as-received sample. At the same martensite volume percent of \( \approx 20\% \), the SQ120 sample has an \( i_{corr} \) of 0.494 \( \mu \text{A cm}^{-2} \), which is relatively larger than \( i_{corr} \) of 0.456 \( \mu \text{A cm}^{-2} \) for the as-received sample. By applying the usual route (holding the ferrite–pearlite microstructure at the IA temperature), inferring the effect of DP microstructure formation on the corrosion behavior becomes hard, which is related to the
complications of microstructure formation during IA. This is common to most of the previous works on this subject. At a low martensite volume percent of \( \approx 20\% \), the \( i_{\text{corr}} \) of IA 5 and SQ 120 samples are near each other and close to that obtained for the as-received sample. In fact, the \( i_{\text{corr}} \) of IA 5 and SQ 120 samples should be compared with that of the ferrite sample to deduce the effect of the presence of martensite. This is a point that has not been addressed in previous works. At a higher martensite content, the \( i_{\text{corr}} \) of DP steels is much higher than that of both as-received and ferrite samples. Therefore, it is obvious that the presence of martensite can impair the corrosion resistance.

4. Conclusions

The effect of martensite volume fraction on the mechanical and corrosion properties of low-carbon DP steel was studied based on both SQ from the austenitic state (SQ) and IA of the ferrite–pearlite microstructure (IA). The following conclusions can be drawn:

1) For SQ samples, hardness and UTS decreased with increasing holding time at the IA temperature and reached a plateau, which was related to the decrease in the amount of martensite. Conversely, for the IA samples, hardness increased during holding at the IA temperature due to partial austenitization and reached the same plateau. 2) The effect of IA on the tensile properties and disappearance of discontinuous yielding was shown. Moreover, at the same martensite volume fraction, the work-hardening behavior of the SQ sample was found to be better than IA sample, which was related to both the finer grain size and smaller martensite islands in the former. 3) At low martensite fractions, the corrosion properties were comparable to the as-received ferritic–pearlitic sample. It was revealed that by decreasing the volume fraction of martensite in the SQ samples, the corrosion current density (\( i_{\text{corr}} \)) decreased almost linearly.

### Table 1. Summary of image analysis results and tensile properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>YS [MPa]</th>
<th>UTS [MPa]</th>
<th>Total elongation [%]</th>
<th>YS/UTS</th>
<th>Average ferrite grain size [( \mu \text{m} )]</th>
<th>Average island size of martensite [( \mu \text{m} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>222.2</td>
<td>343</td>
<td>48</td>
<td>0.65</td>
<td>31</td>
<td>--</td>
</tr>
<tr>
<td>IA 5</td>
<td>231</td>
<td>558</td>
<td>23</td>
<td>0.41</td>
<td>31.7</td>
<td>21.5</td>
</tr>
<tr>
<td>SQ 5</td>
<td>290</td>
<td>605.3</td>
<td>15.2</td>
<td>0.48</td>
<td>20.3</td>
<td>14.2</td>
</tr>
<tr>
<td>SQ 120</td>
<td>243</td>
<td>576.5</td>
<td>21</td>
<td>0.42</td>
<td>19</td>
<td>8.2</td>
</tr>
</tbody>
</table>

### Figure 5. a) Engineering stress versus engineering strain and b) true stress versus true strain curves.

### Figure 6. Obtained polarization curves.

### Figure 7. Corrosion current density versus martensite content.
and at the volume fraction of martensite of zero, it reached the $i_{corr}$ of the fully ferritic microstructure. The latter was found to be lower than the $i_{corr}$ of the as-received sample. Therefore, the real effect of martensite on corrosion properties was unraveled for the first time in this work.

**Acknowledgements**

The authors greatly thank the members of the “Advanced Steels and Thermomechanically Processed Engineering Materials Laboratory” and the “Coating and Corrosion Lab” for their help and support. Financial support by the University of Tehran is also gratefully acknowledged.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

corrosion resistances, dual-phase steels, martensite volume fractions, mechanical properties

Received: July 2, 2019
Revised: October 14, 2019
Published online: