1. INTRODUCTION

Present day trends in the metal industry are towards improving the surface properties (e.g. corrosion and wear resistance) of materials. Alloying and heat treatment are very useful tools to improve the matrix properties against corrosion or wear. Besides, many coating methods are used to enhance the surface properties to protect materials from corrosive and wear effects [1–5].

It is inevitable that the industrial performance of a given metal will significantly decrease by exhibiting anodic dissolution or oxidation, when an electrochemical reaction occurs [6]. The corrosion behavior of the steels, which are the most widely used metallic materials, differs depending on their matrix and corrosive media [7, 8]. Austenitic, ferritic, pearlitic, bainitic and martensitic steels, formed as a function of transformation conditions such as alloying and cooling rate, show different anodic dissolution in the same media. Ferritic steels having a softer matrix can be easily and rapidly corroded by corrosion reactions depending on the time. On the other hand, hardness of the steel matrix provides good chemical and mechanical properties. Bainitic and martensitic steels having ceramic based hard precipitates, having lath or plate shapes, are resistant to corrosion. Stainless steels are very resistant to corrosion due to high chromium alloying which results in the formation of a passive chromium oxide layer on the surface [9–15].

Many studies on the corrosion behavior of heat treated steels having different carbon and other alloying element contents concluded that the composition and heat treatment conditions in addition to corrosion media are very effective on their corrosion resistance [16–20].

Ibrahim et al. studied the corrosion behavior of some austenitic stainless steels by using potentiodynamic polarization technique in 2.5 M NaCl solution and reported that the increase in Mo and Cr content in the alloys of the stainless steels improved their corrosion resistance [16].

Wang et al. reported that the homogenous microstructure and lower carbon content had an important effect on the corrosion behavior of ultra low carbon bainitic steel, produced by thermomechanical controlled processing and relaxation precipitation controlled phase transformation techniques, under accelerated weathering testing conditions. In their study, the precipitation mechanism resulting from the applied thermo-mechanical treatments determines the final microstructure and lath type bainitic steel has a close corrosion resistance to a weathering steel 09CuPCrNi [17].

Guo et al. studied the corrosion behavior of low alloy steels having different carbon contents and compared to 09CuPCrNi under salt fog and outdoor testing. Their results reveal that (i) selective corrosion of large pearlite produces stress in films of initial corrosion products, (ii) films of uniform corrosion products that contain few cracks tend to form on homogeneous microstructures such as ferrite and bainite and this is advantageous for the formation of compact rust layers during initial corrosion, (iii) homogenous microstruc-
Zhao et al. reported that corrosion resistance of a low alloy Mo–Nb–Cu–B microalloyed steel under wet-dry cycle corrosion test was higher than 09CuPCrNi weathering steel due to suppression of the formation of pearlite. The corrosion takes place in low carbon microalloyed steel they studied by local nucleation of the corrosion pits, which spread with exposure time up to completely covering the surface. The preferred sites for such nucleation are associated with the presence of different phases. Pearlite has bad effect on the corrosion behavior of the steel. The cementite lamella of pearlite are large and act as cathode while the ferrite acts as anode, and the local corrosion takes place during the initial stage of accelerated corrosion test [19].

Chen et al. studied on different low alloy steels having ferritic and ferritic-bainitic matrices, AISI 1018 with ferritic-pearlitic matrix and Acr-Ten A weathering steel having ferritic-pearlitic matrix to determine the corrosion behavior by using cyclic wet/dry conditions in a chloride environment. Their results show that the steels having ferritic and ferritic-pearlitic matrices are very sensitive to corrosion than the one having ferritic-bainitic matrix based on their weight loss after corrosion test [20].

In the present study, variation of microstructure and hardness in a quenched and tempered steel and its effect on the formation-progression of corrosion for a given period of time were investigated as a function of the tempering temperature.

2. MATERIALS AND METHODS

2.1. Materials

Table 1 shows the chemical composition of the steel used in this study. Austenization, quenching in water and then tempering as conventional techniques were applied on the sheet steel to form a tempered martensitic matrix. The heat treatment conditions are listed in Table 2. Vickers microhardness measurements were carried out with 0.1 kg load and Table 3 shows the mean microhardness values of 5 measurements.

2.2. Metallographic Preparation

Metallographic samples were prepared using the standard procedure including grinding, polishing and etching by 3% nital. Zeiss Axiotech 100 model light microscope (LM) was used in microstructural characterization.

2.3. Corrosion Test

All the surfaces of steel samples, 22 × 5 × 5 mm in size, were polished and they were immersed into 3.5% NaCl (wt %) solution up to 7 days. Weight losses of the samples were determined after every 24 hours of immersion and surfaces were characterized by light microscope to observe the formation and progress of corrosion. After the completion of the test, the surfaces of the seventh day samples were examined by using Jeol JSM 8040A scanning electron microscope (SEM).

Potentiodynamic measurements were also carried out to understand anodic behaviour of the steels and to determine pitting potentials and corrosion rates. Electrochemical measurements were carried out by using classical three electrode technique. Working electrode was the tempered steel sample with a surface area of 0.25 cm², calomel electrode was the reference electrode and platinium was selected as opposite electrode. Polished electrodes were immersed into 3.5% NaCl (wt %) solution for 1 hour to reach equilibrium and potentiodynamic measurements were done in the range of −1.8 V/+0.2 V using 5 mV/s scanning velocity. Corrosion rates of the steels determined by potentiodynamic measurements were compared with the weight loss data.

3. RESULTS AND DISCUSSIONS

3.1. Microstructural Characterization of the Steels

The efficiency of quenching has a strong effect on the decomposition of austenite and as the cooling rate increases, martensitic transformation which is a type of non-equilibrium reaction can easily occur. Consequently, the transformation from austenite to fer-

### Table 1. The chemical composition (wt %) of the steel used in this study

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Nb</th>
<th>V</th>
<th>Ti</th>
<th>B</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt %</td>
<td>0.23</td>
<td>0.19</td>
<td>0.19</td>
<td>0.04</td>
<td>2.35</td>
<td>1.40</td>
<td>0.50</td>
<td>0.08</td>
<td>0.08</td>
<td>0.002</td>
<td>0.002</td>
<td>0.01</td>
<td>0.01</td>
<td>balance</td>
</tr>
</tbody>
</table>

### Table 2. The heat treatment conditions applied on the steels

<table>
<thead>
<tr>
<th>Steel</th>
<th>Austenization temperature–time</th>
<th>Cooling</th>
<th>Tempering temperature–time</th>
</tr>
</thead>
<tbody>
<tr>
<td>QT1</td>
<td>1000°C – ½ h</td>
<td>quenching in water</td>
<td>200°C – ½ h</td>
</tr>
<tr>
<td>QT2</td>
<td>1000°C – ½ h</td>
<td></td>
<td>540°C – ½ h</td>
</tr>
<tr>
<td>QT3</td>
<td>1000°C – ½ h</td>
<td></td>
<td>600°C – ½ h</td>
</tr>
</tbody>
</table>
rite/pearlite is hindered and the transformations such as martensite/bainite having higher strength appear. In this condition, the transformation occurs due to athermal reactions including shear or twinning mechanism as a function of carbon content instead of thermal reaction consisting of diffusion mechanism. Martensite phase, which is unyielding, hard and brittle, is formed. In the initial stage of tempering, relief of stresses due to transformation under rapid cooling and the immigration of carbon atoms to lattice defects, dislocations and lath intersurface are realized. In low carbon steels, tempering at 150–200°C only causes the immigration of carbon atoms. During tempering, carbon concentration decreases due to migration of atoms and cementite (Fe3C), which is known as equilibrium precipitate, is formed [21–24].

Figure 1, 2 and 3 show LM micrographs of etched steels. Stress relief annealing was carried out by tempering at 200°C and a typical tempered lath martensitic matrix is observed in Fig. 1. The prior austenite grain boundaries play an important role in starting the transformation to martensite. In both low and high alloyed steels, secondary hardening is obtained depending on the chemical composition and especially tempering temperature. In this case, the steel has a tougher matrix which is also harder than the original matrix due to the formation of more stable nano-sized alloy carbides compared to cementite. These alloy carbides provide high hardness to the steel

![Fig. 1. The microstructure of etched QT1 steel. The matrix consists of lath type martensite and there is no degradation of the martensite morphology due to low tempering temperature, 200°C.](image1)

![Fig. 2. The microstructure of etched QT2 steel. The matrix consists of tempered martensite. Lath type cementite precipitates start to decompose due to the migration of carbon atoms with tempering effect at 540°C.](image2)

### 3.2. Microstructural Characterization of the Steels after Immersion into NaCl Solution

The formation and progression of corrosion in QT1 steel immersed into NaCl are illustrated in Fig. 4. Martensitic transformation is a structure that occurs due to rapid cooling of austenite which is a single phase. The transformation begins from austenite grain boundaries and continues until all austenite grains are transformed to martensite. Tempering affects the morphologies of laths but has no effect on the original grain boundaries. Metallic loss due to anodic dissolution is an important factor in ferrous based materials. In a metal, anodic dissolution starts at the grain boundaries since they are amorphous regions and have high defect energy. Thus, the grain boundaries anodically dissolve as a function of time in an aggressive media having Cl− ions, and corrosion proceeds along the grain boundaries leaving the steel surface covered with corrosion products such as metallic oxides. In this case, it is inevitable that the original matrix loses weight. The prior austenite grain boundaries in QT1 steel corroded according to the concepts mentioned above (Fig. 4a). Figure 4b shows the progression of corrosion along the grain boundaries of the matrix.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Hardness, HV0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>QT1</td>
<td>382</td>
</tr>
<tr>
<td>QT2</td>
<td>387</td>
</tr>
<tr>
<td>QT3</td>
<td>372</td>
</tr>
</tbody>
</table>

In the experimental study, tempering at 540°C gives a similar effect on the steel and Fig. 2 shows the steel matrix having massive precipitates after tempering at this temperature. Lath type cementite precipitates start to decompose due to the migration of carbon atoms with tempering effect at 540°C. At higher temperature like 600°C, it is inevitable that the toughness of matrix increases due to the decomposition of original martensite in addition to coarsening of precipitates as a function of distribution of carbon atoms (Fig. 3). Tempered martensitic matrix consists of coarsened ferrite laths with cementite phases as massive precipitates.

**Table 3. Microhardness values of the steels after heat treatments**
After a certain period, corrosion selects another path and anodic dissolution starts along the laths within the martensitic matrix. The laths are very narrow so it is difficult to observe the corroded interfaces by light microscope (Figs. 4c and 4d). Finally, the rust layer on the surface appears in dark contrast or reddish contrast due to high oxygen content.

Figure 5 represents the microstructural variations in polished QT2 steel immersed into salt water solution as a function of time. As seen from Fig. 5a, the grain boundaries promote corrosion and anodically dissolve due to their high energies after a period of 24 hours. It is observed that the corrosion rapidly progresses along the grain boundaries in QT2 steel and a homogenous corroded surface after 72 hours is shown in Fig. 5b. The grain boundaries rapidly react with aggressive Cl⁻ ions and form pits, therefore, they are observed as dark contrast areas due to the low reflection index of cavities under light microscope. As time progresses, the amount of grain boundaries for anodic dissolution decrease and lath interfaces preferentially become new regions to be corroded (Fig. 5c). The system runs as an anode-cathode setup with the electron transportations. Ferrite phase which is an allotrope of iron having a lower hardness behaves like an anode and cementite phase which is a kind of ceramic component behaves like cathode in corrosive media. Tempered martensitic steels consist of ferrite laths and mainly micron-sized iron carbides and commonly nano-sized alloy carbides at the boundaries of laths or within the laths. Alloy carbides mostly have coherent or semi-coherent interfaces with the matrix and they increase the hardness of the steel. The precipitates coarsen due to heat effect during tempering and the coherence of the precipitates to matrix decreases [21–24]. This effect may promote the formation of corrosion along the precipitate boundary. After 168 hours, corroded surface of QT2 steel has a similar microstructure like etched steel showing original laths (Fig. 5d).

The formation of corrosion and its progression by time in QT3 steel is illustrated in Fig. 6. Pitting areas are clearly seen in QT3 that has a softer matrix than QT1 and QT2 (Figs. 6a and 6b). It is observed that corrosion progresses along the grain boundaries and laths similar to QT1 and QT2 (Fig. 6c). Massive precipitates like decomposed cementite laths within the matrix promote the progression of corrosion. The coarsening of these massive precipitates and also their tendency to have incoherent interfaces are higher than the ones in
QT2 because of the higher tempering temperature (Fig. 6d).

Figure 7 shows SEM micrographs of the steel after seven days of immersion. It is observed that the corrosion preferentially proceeds along the grain boundaries and interfaces of laths.

3.3. Potentiodynamic Polarization Measurements

The cathodic reaction is given below for iron and its alloys in neutral ventilation solution.

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-.$$  \hspace{1cm} (1)

The anodic reaction as passivation reaction is the followings [25]:

$$Fe + 2H_2O \rightarrow Fe(H_2O)_{ads} + H^+_ads + OH^-_{ads},$$ \hspace{1cm} (2)

$$Fe(H_2O)_{ads} \rightarrow Fe(OH)_{ads} + H^+ + e^-,$$ \hspace{1cm} (3)

$$Fe(OH)_{ads} + OH^- \rightarrow FeO + H_2O + e^-,$$ \hspace{1cm} (4)

$$Fe(OH)_{ads} + H_2O_{ads} \rightarrow [Fe(OH)_{2ads}]_{ads} + H^+ + e^-,$$ \hspace{1cm} (5)

$$Fe(OH)_{ads} + OH^- \rightarrow Fe(OH)_{2ads} + e^-,$$ \hspace{1cm} (6)

$$3Fe(OH)_{2ads} \rightarrow Fe_3O_4 + 2H_2O + 2H^+ + 2e^-,$$ \hspace{1cm} (7)

$$2Fe_3O_4 + H_2O \rightarrow 3Fe_2O_3 + 2H^+ + 2e^-.$$ \hspace{1cm} (8)

In chloride solutions, Cl$^-$ ions preferentially adsorbed instead of OH$^-$ anions in the solution react with iron ions, the metallic matrix is easily dissolved and these effects provide the formation of soluble complex [26–28]. Figure 8 shows the potentiodynamic polarization curves of all tempered steels. The electrochemical parameters obtained from the potentiodynamic polarization curves are listed in Table 4. The corrosion current density of QT2 steel is lower than those of QT1 and QT3 steels. This indicates that the oxide layer formed on the surface of QT2 steel provides a higher protection characteristic by passivation effect on the metal.

3.4. Relationship between Matrix Hardness and Corrosion Rate

As it is well known, the increase in matrix hardness increases both physical and chemical properties of a given metallic material. In steels, the matrix hardness can be increased by alloying and heat treatments as they both affect the final microstructure. The variation of microstructure and hardness as a function of tempering temperature and its effect on corrosion behav-
EFFECT OF TEMPERING TEMPERATURE AND MICROSTRUCTURE

The total weight loss per unit area for each tempered steel increases linearly with immersion period in NaCl solution. The slopes of the fitted lines in Fig. 9 indicate that the corrosion rate increases by decreasing hardness. The corrosion rates determined from these slopes for the steels tempered at 200, 540 and 600°C are 0.692, 0.665 and 0.826 mg/dm²h, respectively. On the other hand, the corrosion rates (I_corr) determined from potentiodynamic measurements are 20.99, 10.03 and 26.03 µA/cm² for QT1, QT2 and QT3, respectively. Both of these measurements indicate that as the hardness of matrix increases due to the microstructure, the corrosion rate decreases. QT3 steel is the softest one due to having coarse ferritic matrix at high tempering temperature. It is inevitable that the steel having a soft matrix anodically dissolves with the interaction of Cl⁻ ions as a function of time. QT2 steel tempered at lower temperature has a higher corrosion resistance compared to QT3 steel. Lath type ferrite and cementite phases within QT2 steel are responsible for the low corrosion rate. Massive precipitates can occur in the steel matrix due to tempering at 540°C in which secondary hardness provides a higher hardness value to the matrix.

The alloy carbides re-precipitated by tempering at 540°C are more stable than cementite and these hard carbides cause the matrix to be more resistant to corrosion. Obtained results display the relationship between the hardness variation as function of tempering temperature and corrosion behavior of the experimental steel. As the hardness of the experimental steel increases, the corrosion rate decreases (Fig. 10).

Fig. 9. Loss in weight in the experimental steel as a function of immersion time.

Fig. 10. Change of corrosion rate in the steels as a function of matrix hardness.
ration. QT1 steel, tempered at 200 °C, was investigated by light microscope examinations after metallographic preparation. The microstructures were investigated by light microscopy. Tempering effect and microstructure on the corrosion behavior of a tempered steel were investigated. The following results were obtained:

(i) Austenization, quenching and tempering were selected as heat treatment scheme. Tempering effect on the microstructures was investigated by light microscope examinations after metallographic preparation. QT1 steel, tempered at 200 °C, exhibits typical decomposed martensite due to stress relief annealing. Lath type ferrite and cementite are the dominant phases. QT2 steel, tempered at 540 °C, has tempered martensitic matrix with massive cementite precipitation. Secondary hardening leads to an increase in the hardness of this steel due to the presence of more stable alloy carbides than cementite. A higher tempering temperature like 600 °C causes a softer QT3 steel.

(ii) Weight loss of the steels is determined as a function of immersion period in 3.5 NaCl solution. The results show that the microstructure and microhardness of the steels tempered at different temperatures directly affect the corrosion rate and as the microhardness of steel matrix increases, the corrosion rate decreases. The corrosion rates for tempered steel at 200, 540 and 600 °C are 0.692, 0.665 and 0.826 mg/dm²h, respectively. According to the data, QT2 steel has the lowest corrosion rate and its corrosion rate is close to that of QT1. Tempering at 600 °C causes softening and as a result QT3 steel is the most corroded one.

(iii) The corrosion rates (I_corr) determined from potentiodynamic measurements are 20.99, 10.03 and 26.03 μA/cm² for QT1, QT2 and QT3, respectively. The potentiodynamic polarization measurements showed that the corrosion current density of QT2 steel is lower than those of QT1 and QT3 steels. This indicates that oxide layer formed on the surface of QT2 steel provides a higher protection characteristic by passivation effect on the metal.

(iv) The microstructural characterization of the steel after immersion into NaCl solution as a function of immersion period showed that the grain boundaries are the regions where corrosion initiates and propagates preferentially, due to their high energy potential for a given reaction. Lath boundaries play a similar role as the grain boundaries. It is inevitable that corrosion propagates on both grain boundaries and lath boundaries due to their atomic irregularities.

### Table 4. The electrochemical parameters for tempered steels in 3.5 NaCl solution

<table>
<thead>
<tr>
<th>Steel</th>
<th>E_corr, mV</th>
<th>I_corr, μA/cm²</th>
<th>β_A, mV</th>
<th>β_C, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>QT1</td>
<td>−1541.38</td>
<td>20.99</td>
<td>137.94</td>
<td>227.19</td>
</tr>
<tr>
<td>QT2</td>
<td>−1028.77</td>
<td>10.03</td>
<td>81.460</td>
<td>146.42</td>
</tr>
<tr>
<td>QT3</td>
<td>−825.01</td>
<td>26.03</td>
<td>140.32</td>
<td>244.67</td>
</tr>
</tbody>
</table>

### 4. CONCLUSIONS

In this study, the effects of tempering temperature and microstructure on the corrosion behavior of a tempered steel were investigated. The following results were obtained:

(i) Austenization, quenching and tempering were selected as heat treatment scheme. Tempering effect on the microstructures was investigated by light microscope examinations after metallographic preparation. QT1 steel, tempered at 200 °C, exhibits typical decomposed martensite due to stress relief annealing. Lath type ferrite and cementite are the dominant phases. QT2 steel, tempered at 540 °C, has tempered martensitic matrix with massive cementite precipitation. Secondary hardening leads to an increase in the hardness of this steel due to the presence of more stable alloy carbides than cementite. A higher tempering temperature like 600 °C causes a softer QT3 steel.

(ii) Weight loss of the steels is determined as a function of immersion period in 3.5 NaCl solution. The results show that the microstructure and microhardness of the steels tempered at different temperatures directly affect the corrosion rate and as the microhardness of steel matrix increases, the corrosion rate decreases. The corrosion rates for tempered steel at 200, 540 and 600 °C are 0.692, 0.665 and 0.826 mg/dm²h, respectively. According to the data, QT2 steel has the lowest corrosion rate and its corrosion rate is close to that of QT1. Tempering at 600 °C causes softening and as a result QT3 steel is the most corroded one.

(iii) The corrosion rates (I_corr) determined from potentiodynamic measurements are 20.99, 10.03 and 26.03 μA/cm² for QT1, QT2 and QT3, respectively. The potentiodynamic polarization measurements showed that the corrosion current density of QT2 steel is lower than those of QT1 and QT3 steels. This indicates that oxide layer formed on the surface of QT2 steel provides a higher protection characteristic by passivation effect on the metal.

(iv) The microstructural characterization of the steel after immersion into NaCl solution as a function of immersion period showed that the grain boundaries are the regions where corrosion initiates and propagates preferentially, due to their high energy potential for a given reaction. Lath boundaries play a similar role as the grain boundaries. It is inevitable that corrosion propagates on both grain boundaries and lath boundaries due to their atomic irregularities.

### REFERENCES