A Study on Corrosion Behavior of DP-Type and TRIP-Type Cold Rolled Steel Sheet

Il-Jeong Park¹, Soon-Tae Kim¹,* , In-Sung Lee¹, Yong-Soo Park¹ and Man Been Moon²

¹Department of Metallurgical System Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749, Korea
²Technical Laboratories, Hyundai HYSKO, 313, Donggok-ri, Songuan-myeon, Danjin-gun, Chungnam 343-831, Korea

Corrosion behaviors of DP-type and TRIP-type cold rolled steel sheet have been investigated using cathodic Tafel extrapolation test and immersion test, measuring nano-scale hardness of various phases and the volume fraction of various phases, and analyzing inclusion and nitride. Based upon nano-scale hardness of various phases before and after potentiodynamic anodic polarization test in deaerated 5 mass% NaCl at 35 °C, the phase with the most inferior corrosion resistance in DP-type steel is martensite ($\alpha'$) and that in TRIP-type steel is bainite ($\sigma_B$). The reasons why corrosion rate of TRIP-type steel is lower than that of DP-type steel are first, the volume fraction (39.8 vol%) of bainite ($\sigma_B$) in TRIP-type steel is higher than that (15.9 vol%) of martensite ($\alpha'$) in DP-type steel and second, the corrosion resistance of oxide and nitride formed in TRIP-type steel is more than that of sulfide formed in DP-type steel. [doi:10.2320/matertrans.MRA2008252]

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1. Introduction

Numerous research developments have been attempted due to the need for lighter automobiles by employing high-strength steel products to improve fuel efficiency and reduce the amount of gas emissions. As a result, the demand for high-strength cold rolled steel with improved formability is increasing very rapidly.¹,² Dual phase steel (hereafter, DP Steel) with tensile strength of 60 Kg/mm² has been used to meet such necessity, but recent research is being carried out actively to replace it with transformation induced plasticity steel (hereafter, TRIP Steel), which has superior strength and elongation to that of DP steel.

Studies on TRIP-type cold rolled steel of the C-Si-Mn group³–⁶,¹⁷ have been carried out mostly on the steel that usually contains 0.2–0.4 mass% range of carbon under the conditions of forming the indispensable austenite retained through TRIP behavior. However, as the amount of carbon contained in TRIP steel is higher than that of the conventional cold rolled carbon steel, the problem of deteriorating weldability has been exposed. By establishing the optimum conditions of heat treatment in the two phase region and that of isothermal transformation for the low carbon cold rolled steel of 0.1–0.15%, high tensile strength over 700 MPa and elongation over 30% were acquired,⁵,⁷,⁸ and they showed an excellent formability during the actual pressing process.

The steels are composed of more than two different phases. Namely, DP steel consists of a soft ferrite phase as the base metal and a hard martensite phase, and TRIP steel is composed of a soft ferrite phase as the base metal, a hard bainite and a soft austenite phase less than 5%. The austenite phase that retained in the TRIP phase can be transformed into a martensite phase during the pressing process.

As those two and three phases have different corrosion resistances, it is thought that galvanic corrosion will be generated in the less corrosion-resistant phase (= phase with the lower open-circuit potential) and decrease the life-time of the product.

In this study, to elucidate the corrosion behavior of DP type and TRIP type cold rolled steel, an electrochemical polarization test and an immersion-corrosion test were carried out, the volume fraction of each phase were measured using an image analyzer and a XRD analyzer, and the inclusions were quantitatively analyzed through SEM-EDS. Moreover, this study clarified the phase with the weakest corrosion resistance before and after the anodic polarization test using a Nano-Indenter, and investigated the influence of phase fraction and inclusion on the corrosion mechanism.

2. Experimental

2.1 Specimens and analysis of microstructure characteristics

Figure 1 shows the heat treatment conditions of DP steel and TRIP steel. Table 1 shows the chemical compositions of the experimental specimens.

The specimens were polished with diamond paste (1 µm) after 2,000 grit polishing with a SiC sandpaper, and then were cleaned with acetone. Next, the DP steel was etched with 2% Nital, TRIP steel with 2% Nital + 10% Metabisulfate, and the volume fraction of each phase were measured using an image analyzer after acquiring the micrographs from an optical microscope, a back-scattered electron image (hereafter, BEI) and a secondary electron image (hereafter, SEI) from a scanning electron microscope (hereafter, SEM).

Meanwhile, the inclusion, carbo-nitride, and nitride were quantitatively analyzed using an energy dispersive spectroscope (hereafter, EDS).

2.2 Corrosion test

2.2.1 Polarization test

To evaluate the corrosion behavior, a polarization test was carried out. After cutting the specimen to a size of 10 mm W × 10 mm L, a copper rod coated with a rubber tube was connected using a solder on one side of the specimen. Afterwards, the specimen was fixed with polyester resin and the opposite side was polished with SiC paper of 600 grit. It was covered with resin so that only 0.5 cm² of the area would be exposed to the solution and kept in a desiccator before the test.

*Corresponding author, E-mail: stkim78@yonsei.ac.kr
Before carrying out the test, dissolved oxygen was eliminated injecting nitrogen gas at a rate of 150 mL/min for 30 min in 5 mass% NaCl solution of 35 °C, and the polarization test was conducted with a scanning rate of 1 mV/s using a potentiostat (EG & G, Model 263A). Here, the counter electrode was a high-density graphite rod and the reference electrode was saturated calomel electrode (hereafter, SCE). In addition, after applying cathodic potential of \(-500 \text{ mV (SCE)}\) for 10 minutes eliminating oxide layer, the corrosion potential was measured after maintaining an open circuit state for 10 minutes. Next, a polarization test was started at \(-250 \text{ mV (SCE)}\) which is a lower potential than the corrosion potential and polarization behaviors were studied.

Corrosion current density (Icorr) was calculated using the cathodic Tafel extrapolation method.\(^9\)  

\[ \text{mpy} = \frac{534 \times \Delta W}{A \times \rho \times H} \]  
\(1 \text{ mpy} = 0.001 \times 25.4 \text{ mm per year} = 0.0254 \text{ mm per year}\)

Here, A surface area, \(\Delta W\) indicates weight loss (mg), \(\rho\) density (g/cm\(^3\)), and \(H\) immersion time (hours).

### 2.3 Study on phases with the less corrosion resistance through Nano-indentation

To find the phase with the less corrosion resistance in DP steel and TRIP steel, the micro hardness of each phase was measured using the nano-indentation after completing the potentiodynamic anodic polarization test to about 100 mV\(_{SCE}\) towards the anodic direction from the corrosion potential. Diameter of the nano-indentation probe was about 1 \(\mu m\) and the material was diamond.

### 3. Results and Discussion

#### 3.1 Microstructure characteristics

Figure 2 (a1) to (a3) show the optical and SEM micrographs of DP steel. DP steel is composed of a ferrite (dark gray) as the base metal and a hard martensite (white) that is minutely distributed as observed through BEI and SEI. The volume fraction of martensite determines the strength of DP steel and the volume fraction of martensite phase is within the range of \(10\% \sim 15\%\).\(^{10,11}\) Furthermore, it is known that the mechanical characteristics of DP steel is obtained through the low temperature transformation forming lath-type martensite when heat treated in the inter-critical annealing region of ferrite and austenite.\(^{11,12}\)

Figure 2 (b1) to (b3) presents the optical and SEM micrographs of TRIP steel. TRIP steel consists of three-phases, i.e., ferrite (dark gray) as the base metal, bainite (black), and austenite (white). The microstructure of TRIP steels is achieved by carrying out a two-stage heat treatment after cold rolling. The first stage of heat treatment is carried out at slightly higher temperature in the ferrite + austenite two-phase region, leading to a microstructure of about 50% austenite and 50% ferrite. A fast cooling rate after annealing is employed to avoid any major ferrite formation and the final transformation is carried out isothermally in the bainite region (second stage heat treatment). During bainite formation, the carbon diffuses into the austenite islands. The enrichment of carbon in the austenite increases its thermal stability and, consequently, the austenite can be retained upon cooling to the room temperature.\(^5,13\)

Here, the generation of carbide (cementite; Fe\(_3\)C) that commonly accompanies the bainite transformation due to ferrite stabilizing elements, such as Si, Al, and P, is controlled. In addition, as the surplus C elements that are released at the point end of the transformation due to the production of ferrite lath are concentrated into austenite, they increase the stability of austenite, allowing the phase to be retained at room temperature. Therefore, the microstructure of cold rolled steel annealed in the dual phase region shows a three-phase structure composed of ferrite, bainite, and retained austenite.\(^{14,15}\)
Figure 3 shows the SEM micrographs of the each phase formed in DP steel after etched with 2% Nital and TRIP steel after color etched by the LePera method. The volume fraction of each phase measured through an image analyzer is as follows: the volume fraction of ferrite in DP steel is 84.1% and that of martensite is 15.9%. For TRIP steel, it is understood that the volume fraction of ferrite is 45%, bainite 39.8%, and that of retained austenite is about 15.2%.

3.2 Analysis of X-ray diffraction patterns

Figure 4 shows the X-ray diffraction patterns of DP and TRIP steels. The volume fraction of the retained austenite phase in the TRIP steel is obtained through the formula as follows:15)

$$V_\gamma = \frac{1.4I_\gamma}{(I_\alpha + 1.4I_\gamma)} = \frac{1.4[(I_\gamma^{220} + I_\gamma^{311})/2]}{I_{\alpha^{311}} + 1.4[(I_\gamma^{220} + I_\gamma^{311})/2]}$$ (2)

In eq. (2), $I_\gamma$ is the average integral intensity obtained at the {220}$\gamma$, {311}$\gamma$ peak and $I_\alpha$ is that obtained at the {211}$\alpha$ peak. Figure 5 presents the area fraction at the peaks that fall under the three plane indexes mentioned above. The volume fraction of retained austenite in TRIP steel is confirmed to be 15.4% using eq. (2). It can be understood that this numerical value is equivalent to the volume fraction of retained austenite through an image analyzer.

3.3 Corrosion characteristics

Figure 6 shows the corrosion rate of DP steel and TRIP steel after an immersion test in deaerated 5% NaCl solution at 35, 70, and 100°C. The corrosion rate of TRIP steel is found lower than that of DP steel.

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Figure 7(a) presents the potentiodynamic polarization curves in the deaerated 5% NaCl solution of 35°C, and the corrosion current density (Icorr) measured through cathodic Tafel extrapolation method shows that Icorr of TRIP steel is smaller than that of the DP steel.
<table>
<thead>
<tr>
<th>(a) DP-type</th>
<th>SEM &amp; optical image</th>
<th>Volume fraction of phases</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="SEM image" /></td>
<td>Ferrite ($\alpha$): 84.1vol.%&lt;br&gt;Martensite ($\alpha'$): 15.9vol.%</td>
<td></td>
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<table>
<thead>
<tr>
<th>(b) TRIP-type</th>
<th>SEM &amp; optical image</th>
<th>Volume fraction of phases</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image2.png" alt="Optical Microscopy image" /></td>
<td>Ferrite ($\alpha$): 45.0vol.%&lt;br&gt;Austenite ($\gamma$): 15.2vol.%&lt;br&gt;Bainite ($\delta_b$): 39.8vol.%</td>
<td></td>
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</table>

<table>
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<tr>
<th>(c) TRIP-type</th>
<th>SEM &amp; optical image</th>
<th>Volume fraction of phases</th>
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<tbody>
<tr>
<td><img src="image3.png" alt="Optical Microscopy image" /></td>
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**Fig. 3** Measurement of volume fraction of various phases using image analyzer: (a) martensite in DP-type steel, (b) austenite in TRIP-type steel, and (c) ferrite + austenite in TRIP-type steel.

**Fig. 4** X-ray diffraction patterns of cold rolled steel sheets: (a) DP-type steel and (b) TRIP-type steel.
3.4 Elucidation of phase with the less corrosion resistance

Figure 8 presents the micro hardness measured with a nano-indenter after potentiodynamic anodic polarization test up to about 100 mV SCE toward the anodic direction from the corrosion potential in deaerated 5% NaCl at 35 °C for DP and TRIP steel respectively to elucidate the phase with the less corrosion resistance out of the various phases formed in DP steel and TRIP steel. In addition, (a) and (c) of Fig. 8 present the pits formed in DP and TRIP steel respectively after the potentiodynamic anodic polarization test. Next, (b) and (d) of Fig. 8 show the micro hardness measured with the nano-indenter on the pits and the surrounding phases in DP steel and TRIP steel respectively.

Based upon the results of micro hardness measured with a nano-indenter on the pits formed in DP steel and TRIP steel, the phase with the corrosion resistance is judged to be a martensite (α') phase for DP steel and a hard bainite phase (αB) for TRIP steel. The reason is that the martensite phase showed hardness twice higher than that of the ferrite phase. Moreover, bainite phase showed a higher value than that of ferrite about 1.5 times, and that of austenite about 6.2 times.

3.5 Influence of phase volume fraction, inclusion, and nitride on corrosion mechanism

As already known about how area effect generally affects galvanic corrosion, it was reported that the galvanic corrosion resistance decreases when the area of anodic phase with the less corrosion resistance is much smaller than that of cathodic phase with the more corrosion resistance.17,18) As manifested above, the anodic phases with the less corrosion resistance measured with the nano-indenter on the pits and the surrounding phases in DP steel and TRIP steel respectively.

Based upon the results of micro hardness measured with a nano-indenter on the pits formed in DP steel and TRIP steel, the phase with the corrosion resistance is judged to be a martensite (α') phase for DP steel and a hard bainite phase (αB) for TRIP steel, and the volume fractions of these phases measured with an image analyzer are about 16 vol% α' for DP steel and 40 vol% αB for TRIP steel. Therefore, it is judged that corrosion rate of TRIP steel is superior to that of the DP steel because the volume fraction of the bainite (αB) phase is about 2.5 times bigger than that of the martensite (α') phase, based upon the theory of area effect affecting galvanic corrosion.
Meanwhile, Fig. 9 shows the results of SEM images and EDS analysis of various inclusions, carbonitride and nitride formed in DP and TRIP steel before the potentiodynamic anodic polarization test. It can be understood that most of (Fe, Mn) S sulfides formed in DP steel, and carbonitride of (Fe, Al, Ti, Zr) CN and nitride of (Fe, Al, Ti) N formed in TRIP steel. Figure 10 shows the effect of inclusions and precipitates on pitting corrosion resistance after the potentiodynamic anodic polarization test up to about 100 mV_{SCE} toward the anodic direction from the corrosion potential in deaerated 5% NaCl at 35°C. It seems that for the (Fe, Mn) S sulfide, pits is generated by the chloride ion (Cl^\text{−}), while for the (Fe, Mn, Mg, Al) O oxides and nitrides of (Mn, Al) N, pits are not generated by Cl^\text{−}.

Therefore, the reasons why corrosion rate of TRIP steel is lower than that of DP steel are first, the volume fraction (39.8 vol%) of bainite phase that is an anodic phase with the less corrosion resistance in TRIP steel is greater than that (16 vol%) of martensite phase that is an anodic phase with the weakest corrosion resistance in DP steel, based upon the area effect theory affecting galvanic corrosion, and second, the corrosion resistance of oxide and nitride formed in TRIP-type steel is more than that of sulfide formed in DP-type steel.

4. Conclusion

Corrosion behaviors of DP-type and TRIP-type cold rolled steel sheet have been investigated using cathodic Tafel
extrapolation test and immersion test, measuring nano-scale hardness of various phases through nano-indentor, and the volume fraction of various phases through a image analyzer, and analyzing inclusion and nitride through a SEM-EDS. The main conclusions are summarized as follows:

1. The results of measuring the volume fraction through using a image analyzer and X-ray diffraction (XRD) show that the ferrite volume fraction of DP-type steel is 84.1% and the fraction of martensite is 15.9%. For TRIP-type steel, ferrite volume fraction is 45%, bainite 39.8%, and retained austenite fraction is about 15.2%.
2. The results of immersion test and polarization test in deaerated 5% NaCl at 35°C show that corrosion rate of TRIP-type steel is lower than that of DP-type steel.

3. The measured results of micro hardness through the Nano Indenter before and after potentiodynamic anodic polarization test show that the most inferior corrosion resistance phase in DP-type steel is a martensite (α′) and that in TRIP steel is a bainite (α′).
4. The reasons why corrosion rate of TRIP-type steel is lower than that of DP-type steel is first, the volume fraction of bainite phase as an anodic phase with the less corrosion resistance in TRIP steel is higher than that of martensite phase as an anodic phase with the less corrosion resistance in DP steel, based upon the area effect theory affecting galvanic corrosion, and second, the corrosion resistance of oxide and nitride formed in TRIP-type steel is more than that of sulfide formed in DP-type steel.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Results of test</th>
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| DP-type | ![DP-type SEM](image)  
          | ![DP-type EDS](image) |
| TRIP-type | ![TRIP-type SEM](image)  
           | ![TRIP-type EDS](image) |

Fig. 9 (a) SEM image of sulfide in DP-type steel before anodic polarization test, (b) EDS analysis of sulfide in DP-type steel, (c) SEM image of carbo-nitride in TRIP-type steel before anodic polarization test, (d) EDS analysis of carbo-nitride in TRIP-type steel, (e) SEM image of nitride in TRIP-type steel before anodic polarization test, and (f) EDS analysis of nitride in TRIP-type steel.
Fig. 10 (a) & (c) SEM image of sulfide in DP-type steel after anodic polarization test, (b) & (d) EDS analysis of sulfide in DP-type steel, (e) SEM image of oxide and nitride in TRIP-type steel after anodic polarization test, and (f) EDS analysis of oxide and nitride in TRIP-type steel.

REFERENCES

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