Effect of Cu Addition on Delayed Fracture Resistance of Low Carbon Steel for 1470 MPa Grade Electric Resistance Welded Tube

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The effect of chemical composition on delayed fracture resistance, taking into consideration the application of a 1470 MPa grade thin-wall as-rolled electric resistance welded (ERW) tube to automotive structural parts, was investigated. Chemical composition of the base steel alloy was 0.18%C–0.4%Si–1.8%Mn–0.015%Nb–0.01%P–0.001%S. Cu, Ni, Cr, B and Mo were individually added to the base steel. A 4-point bending test in 1 N-hydrochloric acid was conducted for quench and tempered specimens. Cu added steel showed the best delayed fracture resistance. After the immersion, a metallic Cu layer was formed on the steel surface. Based on the results of the 4-point bending test, several kinds of 1470 MPa grade ERW steel tubes were prepared and evaluated for their delayed fracture resistance. Cu added steel tubes showed excellent delayed fracture resistance in a cyclic corrosion condition with salt water spray, as well as in hydrochloric acid. Cu accumulation on the rust-steel interface was observed by electron probe microanalysis (EPMA). An atmospheric corrosion test lasting 12 years was also conducted. Delayed fracture resistance as evaluated by (a) an immersion test in hydrochloric acid, (b) a cyclic corrosion test with salt water spray, and (c) an atmospheric corrosion test, showed good correlation with each other. Based on the results above, two models are proposed for the mechanism of delayed fracture suppression by Cu addition: (1) Cu suppressed cathodic reaction and hydrogen entry at sulfide inclusion, and (2) Cu suppressed hydrogen entry by stabilization of sulfuric-ions as an insoluble compound.

KEY WORDS: steel; martensite; tube; hydrogen embrittlement; delayed fracture; corrosion; residual stress.

1. Introduction

In an effort to reduce the weight of automotive structural parts, high strength steels are currently used. In addition to tensile strength, knowledge of many of the practical properties, such as formability, low temperature toughness, and hydrogen embrittlement susceptibility, are required prior to real application.

Hydrogen embrittlement has been intensively studied and its basic kinetics have been considerably clarified recent years.1–10) Based on these studies, hydrogen embrittlement can be considered as a localized deformation induced by the concentrated diffusive hydrogen in front of a crack tip.

To improve hydrogen embrittlement susceptibility, the effects of chemical composition and microstructure have been investigated.11–35) Nagataki et al.11–13) showed that the lower carbon equivalent and the suppression of coarse cementite precipitation are beneficial for improvement of the delayed fracture resistance in low carbon martensite steel. The effects of titanium and vanadium carbide on delayed fracture resistance were evaluated as a function of hydrogen trap site.16–20) Whether this function enhances or suppresses the delayed fracture depends on the condition. For example, vanadium carbide increases the critical hydrogen content,20,24) but it also increases the absorbed hydrogen.24,25) The effects of the substitutional solute atom have also been examined.29–34) Siraga et al.31,32) clarified that the concentrated Ni on surface suppresses diffusible hydrogen permeation from FIP solution and improves the delayed fracture property. They also clarified the effects of Si on delayed fracture property through microstructure morphology.

These studies on the effects of additional elements mainly focused on the application of high strength steel bolts or prestressed concrete steel bars.16–35) Compared with high strength bolts, high strength thin-wall as-rolled ERW tubes have a different precondition: lower carbon equivalent, lower applied stress, smaller stress concentration, and different exposed environment. As the result, there might be differences in the limits for practical application of bolts versus thin-wall tubes. For example, it is important to prevent grain inter-granular fracture by optimization of chemical composition and microstructure for high strength bolts.26,37) On the other hand, suppression of trans-granular...
fracture is the main goal for further development of high strength thin-wall as-rolled ER W tubes.

In this study, the effect of chemical composition on delayed fracture resistance of sheets, in relationship to the application of 1470 MPa grade thin-wall as-rolled ER W tube to automotive structural parts such as door beams, was investigated using the 4-point bending test in hydrochloric acid. An immersion test of high tensile strength as-rolled ER W tubes in hydrochloric acid was also conducted and the results were compared with those from the cyclic corrosion test with salt water spray, as well as the weathering test under atmospheric corrosion conditions over the course of 12 years. Formability and low temperature toughness were also examined. On the basis of these experimental results, the mechanism of delayed fracture suppression by Cu addition, which has rarely reported before, was discussed.

2. Experimental Procedures

The chemical compositions of steels used are listed in Table 1. The chemical composition of the base steel alloy was 0.18% C–0.4% Si–1.8% Mn–0.015% Nb–0.01% P–0.001% S. The effects of Cu, Ni, Cr, B, and Mo addition on delayed fracture resistance were investigated by comparison with other steels. The Mn content of 1.3Mn–Cr, 1.3Mn–B, and 1.3Mn–Mo was reduced to compensate for increased hardenability with Cr, B, and Mo addition. Nb addition suppressed austenite grain coarsening in the heat treatment after cold rolling.

Figure 1 shows the heat and mechanical treatment of the specimens. Laboratory vacuum-fused and hot-rolled 50 mm thick plates were hot-rolled into 4 mm thick sheets after reheating at 1200°C for 1 h. Finishing temperature was controlled at 890°C and the sheets were air-cooled to room temperature. After surface grinding for scale removal, the sheets were cold-rolled into 2 mm thick sheets. Cold rolled sheets were heat-treated at 870°C for 5 min in a salt bath and immediately water quenched and tempered at 200°C for 5 min. The sheets were cold-rolled with 10% reduction corresponding to the plastic strain in tube forming, followed by tempering at 200°C for 5 min as a simulation of the paint-baking process.

The tensile test was conducted using a half size JIS No. 13B specimen with 6.25 mm width and 25 mm gauge length. The microstructure of the quenched and tempered specimen was observed using a scanning electron microscope (SEM) after etched by 2% Nital. For evaluation of delayed fracture resistance, coupon specimens with a size of 5 mm×80 mm×1.8 mm were prepared from the sheets in transverse direction as a specimen of 4-point bending test. The specimens were immersed in 1N hydrochloric acid with a loading stress of 1370 MPa, as schematically illustrated in Fig. 2. The applied stress, \( \sigma \) was calculated using the following equation, without considering stress relaxation by plastic deformation:

\[
\sigma = \frac{12E \cdot t \cdot \delta}{(3H^2 - (H-h)^2)}
\]

where \( t \) and \( \delta \) are respectively the specimen thickness and the deflection of specimen center, \( H \) and \( h \) are the fulcrum distances shown in Fig. 2, and \( E \) is Young's modulus of the steel.

The effects of the corrosion rate in 1N hydrochloric acid on the increase of the time to fracture were also evaluated. A Charpy impact test was conducted using a 1.8 mm thick sub-size 2 mm V-notched specimen.

3. Results

3.1. The effects of Cu, Ni, Cr, B, and Mo Addition on Delayed Fracture Resistance

Table 2 shows the tensile properties of heat and mechanically treated specimens. Tensile strength of 4-point bending test specimen ranges from 1552 to 1602 MPa. Figure 3 shows SEM microstructures of water quenched and tempered specimens. All the specimens showed a lath martensite structure and finely dispersed cementite (white dot) in
the martensite lath. Microstructure morphology was almost the same regardless of additional alloy elements, except the steel containing B, which showed a slightly larger martensite packet size.

**Table 2.** Tensile properties of specimens.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Quench and tempered</th>
<th>10% cold-rolled and tempered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YS (MPa)</td>
<td>TS (MPa)</td>
</tr>
<tr>
<td>1.8Mn (Base)</td>
<td>1314</td>
<td>1485</td>
</tr>
<tr>
<td>1.8Mn–Cu</td>
<td>1323</td>
<td>1507</td>
</tr>
<tr>
<td>1.8Mn–Ni</td>
<td>1325</td>
<td>1542</td>
</tr>
<tr>
<td>1.3Mn–Cr</td>
<td>1281</td>
<td>1490</td>
</tr>
<tr>
<td>1.3Mn–B</td>
<td>1239</td>
<td>1457</td>
</tr>
<tr>
<td>1.3Mn–Mo</td>
<td>1316</td>
<td>1501</td>
</tr>
</tbody>
</table>

Figure 4 shows the time to fracture and the corrosion rate in 1 N-hydrochloric acid of each specimen. Corrosion rate was evaluated after immersion test in 1 N-hydrochloric acid without loading stress for 400 h. 1.8Mn–Cu showed a much higher delayed fracture resistance compared to 1.8Mn (Base); it also showed lower corrosion rate. 1.3Mn–Cr also showed higher delayed fracture resistance and a lower corrosion rate than 1.8Mn (Base). Replacement of Mn by B slightly improves the delayed fracture resistance. 1.3Mn–Mo and 1.8Mn–Ni showed a much higher corrosion rate than 1.8Mn (Base). Replacement of Mn by Mo slightly improves the delayed fracture resistance. 1.3Mn–Mo and 1.8Mn–Ni showed almost the same time to fracture. There formed spherical concaves on the surface of 1.3Mn–Mo and 1.8Mn–Ni specimens as shown Fig. 5. So, their relatively higher corrosion rate may well be due to occurrence of pitting corrosion possibly caused by micro segregation of Mo and Ni. It could be said that even 1.8Mn (Base) has an excellent delayed fracture resistance, because it was able to endure over 200 h in 1 N-hydrochloric acid. Figure 6 shows SEM fractographs after the 4-point bending test. The fractographs consist of trans-granular fracture.

Figure 4. Time to fracture and corrosion rate in 1 N-hydrochloric acid.

**Figure 5.** Appearance after 4-point bending test in 1 N-hydrochloric acid: (a) 1.8Mn (Base), (b) 1.8Mn–Cu, (c) 1.8Mn–Ni, (d) 1.3Mn–Cr, (e) 1.3Mn–B and (f) 1.3Mn–Mo.
0.15% Cu containing steel has the same excellent delayed fracture resistance as the 0.5% Cu containing steel. Moreover, with 0.15% Cu, it is not necessary to add Ni to avoid surface scratches.

3.2. Low Temperature Toughness

Figure 8 shows fracture appearance transition temperature and the absorbed energy from the Charpy impact test. Although there is a slight dependence of the impact properties on the alloy element content, all of the specimens have fairly good low-temperature toughness. Compared to 1.8Mn (Base), 1.3Mn–B and 1.8Mn–Ni have slightly higher \( vTrs \) and smaller absorbed energy. A slightly larger martensite packet size is probably the reason for 1.3Mn–B. The lowered transformation starting temperature due to Ni,\(^{44}\) which suppresses auto-tempering in quenching process, could be the reason for 1.8Mn–Ni.

3.3. Delayed Fracture Resistance of Cu added 1 470 MPa Grade ERW Tube

ERW steel tubes are made from a hoop strip by way of sequential roll forming. As the result of the circumferential bending and the ensuing sizing process, there remains some level of residual stress. Figure 9 shows an example of residual stress in a 1 470 MPa grade ERW steel tube. Tensile stresses in the circumferential and longitudinal directions gradually decrease from the outer-surface to the inner-surface.

Table 3 shows the chemical composition and tensile strength of 1 470 MPa grade steel tubes prepared for delayed fracture resistance evaluation. CuLC and LC have lower than 0.50% carbon equivalents, and have finely dispersed carbide in the martensite lath, which is effective to prevent hydrogen-induced intergranular cracking.\(^{11-13}\) HCCP has a greater than 0.50% carbon equivalent and coarsely precipitated carbides in the grain boundary, which is obtained by a tempering temperature that is much higher than 200°C. HCNP has a greater than 0.50% carbon equivalent and its carbides are not precipitated. HCNP is obtained with a tempering temperature that is much lower than 200°C.

Table 4 shows the test conditions for delayed fracture resistance: (a) an immersion test in 0.1 N-hydrochloric acid, (b) a cyclic corrosion test with 5% NaCl water spray, and (c) an atmospheric corrosion test.\(^{45}\) The pH of the immersion solution was kept 1.0.

Table 5 shows the time to delayed fracture of 1 470 MPa grade steel tubes. The duration in 0.1 N-hydrochloric acid.
Table 3. Chemical composition, tensile strength, and carbide morphology of 1470 MPa grade ERW steel tubes.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Chemical composition (mass%)</th>
<th>TS (MPa)</th>
<th>Carbine morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuLC</td>
<td>C 0.18 Si 0.4 Mn 1.5 P 0.01 S 0.01 Cu 0.15 Others 0.45</td>
<td>1490~1560</td>
<td>Finely dispersed in martensite lath</td>
</tr>
<tr>
<td>LC</td>
<td>C 0.17 Si 0.4 Mn 1.8 P 0.01 S 0.01 Cu 0.15 Others 0.49</td>
<td>1520~1560</td>
<td>Coarsly precipitated in grain boundary</td>
</tr>
<tr>
<td>HCCP</td>
<td>C 0.21 Si 0.4 Mn 1.8 P 0.01 S 0.01 Cu 0.15 Others 0.52</td>
<td>1490~1580</td>
<td>Not precipitated</td>
</tr>
<tr>
<td>HCNP</td>
<td>C 0.21 Si 0.4 Mn 1.8 P 0.01 S 0.01 Cu 0.15 Others 0.52</td>
<td>1660~1710</td>
<td>Not precipitated</td>
</tr>
</tbody>
</table>

*: Ceq = C + Si/24 + Mn/6

Table 4. Evaluation conditions of delayed fracture resistance of 1470 MPa grade ERW steel tubes.

<table>
<thead>
<tr>
<th>Evaluation method</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immersion test in hydrochloric acid</td>
<td>0.1N; room temp.</td>
</tr>
<tr>
<td>Cyclic corrosion test with salt water spray</td>
<td>5%NaCl-drying-wetting 1cycle:24h</td>
</tr>
<tr>
<td>Atmospheric corrosion test</td>
<td>Coastal industrial zone; NaCl=0.07mdd*</td>
</tr>
</tbody>
</table>

*: 1mdd=1mg/dm²/d

Table 5. Delayed fracture resistance of 1470 MPa grade ERW steel tubes.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Time to fracture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>TS (MPa)</td>
</tr>
<tr>
<td>CuLC</td>
<td>1490~1560</td>
</tr>
<tr>
<td>LC</td>
<td>1520~1560</td>
</tr>
<tr>
<td>HCCP</td>
<td>1490~1580</td>
</tr>
<tr>
<td>HCNP</td>
<td>1660~1710</td>
</tr>
</tbody>
</table>

*: 1: main size: Φ31.8~2.0t -150L (mm) *2: perforated corrosion without any delayed fracture

Fig. 10. Weight change of 1470 MPa grade tubes under atmospheric corrosion.

Fig. 11. Thickness change of 1470 MPa grade tubes under atmospheric corrosion (including rust layer). was CuLC > LC > HCCP > HCNP. This duration order is the same as the one for the cyclic and the atmospheric corrosion tests. With the exception of HCNP, delayed fracture did not occur by atmospheric corrosion over 12 years. Figure 10 shows the total weight change under atmospheric corrosion. The weight was increased by oxidation, and then decreased. An electro-deposition (ED) coated tube sample was also exposed for comparison. Weight loss was somewhat suppressed by the ED coating, although its surface turned brown only after 40 months of exposure. Figure 11...
shows total thickness change under atmospheric corrosion. The thickness also has a peak due to growth of the rust layer. The slope after the peak (about $-0.01$ mm/y) is the same level as that previously reported on mild carbon steel.\textsuperscript{46–48} An ED coated CuLC sample was also tested using a cyclic corrosion test with salt water along with a cross cut. It corroded inhomogeneously, but did not crack until perforated corrosion appeared as shown in Fig. 12.

4. Discussion

4.1. Mechanism of Delayed Fracture Suppression by Cu Addition

Figure 13 shows the electron probe micro-analysis (EPMA) results of the rust-steel interface of CuLC after a cyclic corrosion test with a 5$\%$ NaCl water spray. Cu was accumulated on the rust-steel interface. Cu may well dissolve and incorporate into the rust layer as Cu$^{2+}$ and deposit as metallic copper\textsuperscript{49–51} or an insoluble copper compound.\textsuperscript{52,53} Cu is accompanied by S. S initially exists as MnS in steel, so it should also dissolve and be deposited in the rust-steel interface. The mechanism of delayed fracture suppression by Cu may be explained by one or both of the following two models:

Model 1: Cu suppresses cathodic reaction and hydrogen entry at inclusion sulfide. Morita et al. have proposed that Cu deposition suppresses under-film corrosion by reduction of sulfide cathode activity.\textsuperscript{50} In this case, not only the corrosion reaction, but also hydrogen entry has been suppressed by Cu deposition at the sulfide cathode as schematically illustrated in Fig. 14.

Model 2: Cu suppresses hydrogen entry by stabilize sulfur-ion as insoluble compound. Matsushima et al. reported that S is oxidized into SO$_4^{2-}$ by atmospheric corrosion and this would accelerate the corrosion rate through a reversible reaction\textsuperscript{54}: Cu$^{2+}$ would stabilize SO$_4^{2-}$ as insoluble CuSO$_4$\textsuperscript{55} and prevent a decrease in pH by the reaction shown in Fig. 15. It is also possible that Cu may directly stabilize the sulfuric-ion as CuS when MnS dissolves into the rust layer.\textsuperscript{52} CuS is known as the hydrogen entry barrier under light sour conditions.\textsuperscript{56,57}

Figure 16 shows the surface SEM appearance of 1.8Mn–Cu after immersion in 1N-hydorocrolic acid. Metallic Cu particles, whose diameter is about 1 or 2 $\mu$m were dispersed on the surface. To the naked eye, as immersion time progresses, the surface color turned copper brown. Coincidentally, the corrosion rate indicated by hydrogen bubbling at the surface has decreased. Figure 17 shows the EPMA cross-section analysis of 1.8Mn–Cu after immersion in 1N-hydorocrolic acid. Similar to what occurs after cyclic corrosion with the 5$\%$ NaCl water spray, a Cu layer was formed on the steel surface. Conversely, S is only discretely observed on the surface. Therefore, the mechanism of delayed fracture suppression by Cu addition in hydorocrolic acid may well be Model 1.
4.2. Absorbed Hydrogen in Cu Added Steel

Figure 18 shows hydrogen evolution profiles during continuous heating measured by thermal desorption analysis of copper containing CuLC and not containing S22CrTB (described in Table 7) after immersion in 1.6 N-hydrocrolic acid for 0.5 h. Table 6 shows the absorbed hydrogen calculated from Fig. 18. Diffusible hydrogen in CuLC is much lower than in S22CrTB. This indicates that the hydrogen entry might be ‘slowed down’ by the mechanism of Model 1 in hydorocric acid.

Table 8 shows the total hydrogen in the prescribed (Tables 1 and 2) steels after immersion in 1 N-hydrocrolic acid without loading for 168 h. Total hydrogen, including not-desorbed hydrogen below 600°C, was measured by the inert-gas fusion method. There is no significant difference in total hydrogen content with and without Cu. This data could be explained by tendency to stagnation of absorbed hydrogen.58)

Figure 19 shows the corrosion rate of CuLC and S22CrTB under JASO M609-91 (JIS H 8502) cyclic corrosion test with 5% NaCl water spray. There is no significant difference between those samples that contained Cu and those that did not. Therefore, Cu addition does not necessarily lead to corrosion rate suppression under cyclic corrosion, which may be due to the discontinuity of the Cu layer at the rust-steel interface. Despite this, hydrogen entry, and, consequently, the delayed fracture would be suppressed by Cu addition through ‘selective immunization’ of the stress-concentrated sulfide cathode in corrosion pit illustrated in Fig. 14.

As described above, Cu has the unique function of suppressing hydrogen-induced cracking fractures under static tensile stress conditions. However, its effects under changing stress conditions, is a topic that requires further investigation.

5. Conclusions

The effects of chemical composition on delayed fracture resistance, taking into consideration the application of
1470 MPa grade thin-wall as-rolled ERW tube to automotive structural parts, was investigated. The results and conclusions are summarized as follows:

(1) Cu-added steel showed excellent delayed fracture resistance in 1 N-hydrochloric acid. After the immersion, a metallic Cu layer was formed on the steel surface. Cu addition also lowered the corrosion rate in hydrochloric acid.

(2) Cu-added steel also showed excellent delayed fracture resistance under cyclic corrosion condition with salt water. Cu accumulation on the rust-steel interface was observed by EPMA analysis.

(3) Atmospheric corrosion test over 12 years of a 1470 MPa grade thin-wall as-rolled ERW tube to automotive structural parts, was investigated. The results and conclusions are summarized as follows:

(4) The results of delayed fracture resistance in (a) an immersion test using 0.1 N-hydrochloric acid, (b) a cyclic corrosion test with 5% NaCl water spray, and (c) an atmospheric corrosion test of 1470 MPa grade ERW tubes had good correlation with each other.

(5) For the explanation of delayed fracture suppression function of Cu, two models were proposed: (a) Cu suppresses cathodic reaction and hydrogen entry at inclusion sulfide and (b) Cu suppresses hydrogen entry by stabilizing sulfuric-ion as an insoluble compound.

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