Effect of Morphology of Copper Precipitation Particles on Hydrogen Embrittlement Behavior in Cu-Added Ultra Low Carbon Steel

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Changes in fracture and hydrogen evolution behaviors in Cu-added ultra low carbon steels due to hydrogen charging were examined by small punch (SP) tests and thermal desorption spectroscopic (TDS) analyses, respectively, to understand effect of morphology of copper precipitation particles on susceptibility to hydrogen embrittlement. The SP tests and TDS analyses were applied to the hydrogen-charged steels, which had been thermally aged at 500°C for duration ranging from $2 \times 10^3$ to $5 \times 10^6$ s and provided with various kinds of fine particles. Experimental results revealed that the higher strength steel has a larger reduction in strength due to hydrogen charging. This degradation of the strength due to hydrogen charging was strongly dependent on the morphology of copper precipitation particles although, basically, the degradation had a tendency to be more pronounced with increasing hydrogen content. More hydrogen can be allowed in the steel in which the $\epsilon$-copper exists. The grown copper particles, such as an $\epsilon$-copper, are preferable to the copper clusters and/or the twinned 9R structures as trapping site for hydrogen and contribute the suppression of the reduction in strength caused by hydrogen.

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1. Introduction

Ultra low carbon steel of Cu-added precipitation hardening type with interstitial free matrix has recently received particular attention as structural steels ranging from thin sheets to thick plates. This Cu-added ultra low carbon steel is commonly used as cold rolled steel sheets for automobile body because of its excellent strength/ductility balance.1, 2) This balance derives from nanoscale fine copper precipitation particles, which are formed during aging subsequent to the solution heat treatment and are dispersed uniformly in the interstitial free matrix. Needless to say, the mechanical properties of the Cu-added low carbon steel, such as a tensile strength and fatigue strength are closely associated with the size of the copper particles, namely, the interparticle spacing. Additionally, it is also known that fine copper particles play an important role in the embrittlement of irradiated ferritic alloys.3)

It is well known that susceptibility to hydrogen embrittlement (delayed fracture) in structural steels increases with increasing strength level. Considering that thin sheets will be increasingly required higher strength and more excellent formability, it is essential to understand size effect of copper particles on not only the tensile and fatigue properties but also the susceptibility to hydrogen embrittlement in the Cu-added ultra low carbon steels.

In this study, in order to understand an effect of morphology of copper precipitation particles on susceptibility to hydrogen embrittlement, changes in fracture and hydrogen evolution behaviors due to hydrogen charging were examined by small punch (SP) tests and thermal desorption spectroscopic (TDS) analyses, respectively. The SP tests and TDS analyses were applied to the hydrogen-charged Cu-added ultra low carbon steels, which had been thermally aged at 500°C for duration ranging from $2 \times 10^3$ to $5 \times 10^6$ s and provided with various kinds of fine copper precipitation particles.

2. Experimental Procedure

2.1 Material and heat treatments

The material used in this study was a Cu-added ultra low carbon steel. The chemical composition of the steel is given in Table 1. The steel was solution treated at 1100°C for $1.8 \times 10^3$ s and subsequently quenched in water. Next, the steel was isothermally aged at 500°C for a duration ranging from $2 \times 10^3$ to $5 \times 10^6$ s.

After the thermal aging, the steels were subjected to Vickers hardness measurement under a load of 4.9 N at room temperature. The microstructure of the aged steels was observed using a high resolution transmission electron microscope (Hitachi H-8000, 200 kV).

2.2 Small punch tests and hydrogen desorption analyses

Hydrogen charging into the steels was conducted by means of cathodic electrolysis in 3 mass%NaCl + 3 kg/m³ NH₄SCN aqueous solution under a current density of 100 A/m² for 24 h, prior to the small punch (SP) tests and the thermal desorption spectroscopic (TDS) analyses.

The SP disk specimens with a dimension of $\phi 3 \times t 0.25$ mm were taken from the heat treated rod-shaped steels. The specimen surface was mechanically polished up to 2000 emery paper. The SP test was carried out on an Instron testing machine at room temperature using the hydrogen-charged and non-charged steels. The cross-head speed of the Instron was fixed at 3.3 $\times 10^{-3}$ mm/s throughout the test. The deflection measurements at the center of specimens were obtained from the displacement of the cross-head. Details of the SP testing technique and the data analysis are given in Refs. 4), 5).

The TDS analyses6, 7) of hydrogen were carried out from room temperature to 800°C to investigate hydrogen contents in the steels and hydrogen release behavior from trapping sites. The heating rate used in this study was 100°C/h and 200°C/h. The desorbed hydrogen carried with high purity ar-
Table 1  Chemical composition (mass%) of Cu-added ultra low carbon steel.

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>N</th>
<th>Ti</th>
<th>Cu</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0027</td>
<td>0.01</td>
<td>0.09</td>
<td>0.01</td>
<td>0.005</td>
<td>0.02</td>
<td>0.0018</td>
<td>0.05</td>
<td>1.35</td>
<td>0.69</td>
</tr>
</tbody>
</table>

gon gas was detected by a gas chromatograph at intervals of 5 minutes. The flow rate of the argon carrier gas was fixed at $1.2 \times 10^{-5}$ m$^3$/min throughout the analysis. The hydrogen evolution rate was defined as the amount of hydrogen desorbed in one minute per one gram of specimen.

### 3. Results and Discussion

#### 3.1 Changes in hardness and microstructure with aging

The Vickers hardness measured is plotted as a function of aging time in Fig. 1. The maximum hardness is reached after the aging of $2 \times 10^4$ s, and the subsequent hardness decreases monotonously with aging time. Hereafter, the steel, which was thermally aged for $2 \times 10^4$ s and has maximum hardness, is defined as the “peak aged steel (PA)”. The steels aged for less and more than $2 \times 10^4$ s are also termed the “underaged steel (UA)” and “overaged steel (OA)”, respectively. Figure 2 shows the tensile strength of the aged steels plotted against the Vickers hardness. The strength increases with aging time until the maximum hardness is reached, and there is a well-known linear correlation between the strength and the Vickers hardness with slope of 3 in the Cu precipitation hardening steel.

A high resolution transmission electron microscope (HRTEM) observation has revealed that, copper-rich clusters, 2–4 nm in diameter, which were coherent with an α-iron matrix, predominantly existed in the peak aged steel. Figure 3(a) shows an example of the copper-rich cluster observed. It is apparent that the maximum hardness is attributable to these nanoscopic fine copper-rich clusters. Additionally, as shown in Fig. 3(b), copper particles, 10–15 nm in diameter were observed to be homogeneously distributed in the matrix of the overaged steel ($9 \times 10^4$ s). These particles seemed to be transitional phases represented by twinned 9R structures, which
could be transformed to ε-copper (fcc) due to an additional aging.

These behaviors of age-hardening and copper precipitation observed in the present study are in good agreement with those reported in earlier studies.1, 2)

3.2 Change in small punch properties with aging

Figure 4 shows typical examples of applied load versus central deflection curves measured on the peak aged (PA) steels. The load increases as the central deflection increases and then drops suddenly at a certain load level. The maximum load and the corresponding deflection measured on the hydrogen-charged specimen are much smaller than those on the non-charged specimen. All of the thermally aged steels exhibited the similar characteristics. However, the magnitude of the decrease in maximum load and in corresponding deflection varied, depending on the type of steel, namely, the aging condition. The specimen surfaces and the fracture surfaces of the peak aged steels after the SP tests are given in Fig. 5. It can be seen that the fracture mode of the non-charged specimen is typical ductile transgranular, while the fracture occurs in a brittle manner in the hydrogen-charged specimen. The fracture surface of the hydrogen-charged specimen exhibits a quasi-cleavage fracture characterizing hydrogen embrittlement. The similar fracture characteristics were also observed in the other aged steels.

The SP energy $E_{SP}$ was determined by calculating the total area under the load-deflection curve up to the maximum load. Figure 6 shows the SP energy measured plotted as a function of aging time. The variation in SP energy measured on the non-charged specimen with thermal aging is quite similar to that in Vickers hardness. The maximum fracture energy is attained at the peak aged stage. On the other hand, the SP energy of the hydrogen-charged specimen shows almost no variation with aging time, when compared with the non-charged specimen. In general, in proportion as the strength level of steels increases the delayed fracture properties, i.e., toughness in hydrogen atmosphere tend to deteriorate.7) Nevertheless, the peak aged steel, which has maximum strength level among the steels used in this study, retains comparatively large SP energy, and its energy is almost as same as the energies of the other aged steels. This result may indicate that in comparison with general high strength steels the present Cu-added ultra low carbon steel has relatively excellent resistance to susceptibility to hydrogen em-
brittlement. The peak aging condition steel is most desirable from the standpoint of both of the strength/ductility balance and the resistance to hydrogen embrittlement susceptibility.

3.3 Change in hydrogen evolution behavior with aging

Figure 7 shows examples of hydrogen evolution curves measured on the hydrogen-charged steels using the heating rate of 200°C/h, where the hydrogen evolution rate is plotted against temperature. The peak of evolution rate, which was not observed at all in the non-charged steels, appears at around 120°C in the solution treated steel. The peak value of the solution treated steel is smaller than those of the thermally aged steels and the value increases with aging time. Furthermore, it can be clearly seen that the peak temperature shifts only slightly toward higher temperature according to the increase in aging time.

In order to show quantitatively the variation in the peak profile with aging, the differences in the evolution rate between the solution treated and thermally aged steels were plotted in Fig. 8. Two peaks of the hydrogen evolution rate exist at about 60–80°C and 160–190°C in the curves. The peak height in the lower temperature region seems to show almost no variation with aging time, while the peak height in the higher temperature region is enhanced by increasing aging time. In addition, the peak temperature at the higher temperature region shows a tendency to move toward higher temperature with aging time. This increase in the hydrogen evolution rate in the higher temperature region seems to reflect the increase in hydrogen trapped by the iron matrix/copper particle interfaces and/or copper particles themselves, because microstructures other than the copper particles, i.e. grain size and dislocation density show no significant changes during aging. It is considered that due to the loss of coherency of the copper particles the interfacial energy increases in this aging order: the copper clusters, the twinned 9R structures and the ε-copper, resulting in the increase of hydrogen trapped by the interface. It is likely that the lower temperature peak corresponds to hydrogen released from the trapping sites, such as a grain boundary and point and line defects.9)

The total hydrogen content in the steel was determined by the peak area of each evolution curve in Fig. 7. The result obtained is plotted against aging time in Fig. 9, along with the hydrogen content measured using the heating rate of 100°C/h. The results obtained from the heating rate of 100°C/h are in relatively good agreement with those of 200°C/h. The hydrogen content tends to increase gradually early in the aging and the increase seems to be more distinguished through the overaged region (OA I ~ OA III). This increase in hydrogen content with aging time coincides with the above-mentioned increase in the hydrogen evolution rate in the higher temperature region of 160–190°C, that is, the increase in hydrogen released from the interface and/or copper particles.

3.4 Effect of morphology of copper particles on degradation of strength

The ratio of the $E_{SP}$ measured on the hydrogen-charged specimen to that of the non-charged one was termed the "normalized SP energy". The normalized SP energy is plotted as a function of aging time in Fig. 10. In contrast to the change in Vickers hardness, the normalized SP energy decreases early in the aging process and attains to the minimum value after the aging of $6 \times 10^3$ to $2 \times 10^4$ s. That is, the higher strength steel has a larger reduction in strength due to hydrogen charging.

Figure 11 shows the relationship between the normalized SP energy and the total hydrogen content calculated from Fig. 7. The results obtained from the steels aged at 650°C are also included in this figure. The two different relations classified as the "copper clusters/twinned 9R structures region" and the "ε-copper region" can be clearly observed to lie in this plot. The copper clusters and/or the twinned 9R structures are precipitated in the steel of the former region.
content. The grown copper particles, such as an precipitation particles although, basically, the degradation has hydrogen is strongly dependent on the morphology of copper particles. 

The response to the amount of hydrogen trapped by the copper particles plays an important role in the reduction in strength due to hydrogen charging, because, as mentioned above, the amount of hydrogen released from the trapping sites, such as a grain boundary and point and line defects shows almost no variation with aging. It is worthy of note that the normalized SP energy in the ε-copper region is much larger than that in the copper cluster/twinned 9R structures region even though the hydrogen content is the same. That is, more hydrogen can be allowed in the steel in which the ε-copper exists. The quite similar correlation was also observed in the relationship between the normalized SP energy and the hydrogen content, which was determined by the peak area in the higher temperature region in Fig. 8 and corresponds to the amount of hydrogen trapped by the copper particles.

In this way, the degradation of strength attributable to hydrogen is strongly dependent on the morphology of copper precipitation particles although, basically, the degradation has a tendency to be more pronounced with increasing hydrogen content. The grown copper particles, such as an ε-copper, are preferable to the copper clusters and/or the twinned 9R structures as trapping site for hydrogen and contribute the suppression of the reduction in strength caused by hydrogen. However, the cause of the above particle dependence and the exact role of hydrogen trapped by the copper particles during the process of deformation and/or fracture have not been thoroughly clarified as yet. Further detailed research is required to make clear the interaction between the copper particles and hydrogen, such as an examination of variation in diffusion coefficient of hydrogen in the steel under loading condition with the growth of copper particles.

4. Conclusions

In order to understand an effect of morphology of copper precipitation particles on susceptibility to hydrogen embrittlement, changes in fracture and hydrogen evolution behaviors due to thermal aging were examined by small punch (SP) tests and thermal desorption spectroscopic (TDS) analyses, respectively, using the hydrogen-charged specimens. From the present investigation the following conclusions can be drawn.

(1) There is almost no variation in the SP energy measured on the hydrogen-charged specimen with thermal aging. In comparison with general high strength steels the present Cu-added ultra low carbon steel has a relatively excellent resistance to susceptibility to hydrogen embrittlement. However, the higher strength steel has a larger reduction in strength due to hydrogen charging.

(2) Two peaks of the hydrogen evolution rate exist at about 60–80°C and 160–190°C, and the peak height in the higher temperature region has a tendency to increase with increasing aging time. This increase seems to reflect the increase in hydrogen trapped by the iron matrix/copper particle interfaces and/or copper particles themselves.

(3) The degradation of strength attributable to hydrogen is strongly dependent on the morphology of copper particles although, basically, the degradation has a tendency to be more pronounced with increasing hydrogen content. More hydrogen can be allowed in the steel in which the ε-copper exists. The grown copper particles, such as an ε-copper, are preferable to the copper clusters and/or the twinned 9R structures as trapping site for hydrogen and contribute the suppression of the reduction in strength caused by hydrogen.

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REFERENCES