Reverse Transformation-induced Hydrogen Desorption and Mn Effect on Hydrogen Uptake in Fe–Mn Binary Alloys

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The effects of ε-martensite and Mn on hydrogen uptake and desorption were investigated through cryogenic thermal desorption analysis. Increasing Mn content promoted hydrogen uptake, and reverse transformation from ε to γ phases induced hydrogen desorption.

KEY WORDS: cryogenic thermal desorption analysis; ε-martensite; hydrogen; austenitic steel.

1. Introduction

Hydrogen embrittlement has been a critical issue in the practical use of structural materials. Over the last decade, there has been an increasing need for developing a new class of usable high strength alloys for hydrogen-related infrastructure. Fe–Cr–Ni-based stable austenitic stainless steel has been tentatively accepted as one of such materials. The hydrogen embrittlement susceptibility of austenitic steels has therefore been the focus of considerable research interest in the hydrogen-energy-related research field.1–4)

High Mn austenitic alloys containing ε-martensite exhibit good potential in the development of new high strength materials with low hydrogen embrittlement susceptibility. The addition of ε-martensite is considered to improve hydrogen embrittlement resistance because of the following reasons.

1) Since ε-martensite has a hexagonal closed-pack structure, the diffusivity of hydrogen is at least lower than that in body-centered cubic structure (α-phase or α’,martensite).5) 2) ε-martensite transformation enhances work hardening capacity,6–8) effectively improving elongation and strength.7,9,10)

3) Owing to deformation-induced reversible transformation from γ→ε,11,12) fatigue properties are also expected to be greater than those of other high strength steels.

In contrast, the negative effect of ε-martensite on hydrogen embrittlement susceptibility has also been reported.13,14) For instance, γ↔ε interfaces can be an initiation site for hydrogen-assisted cracking.13) Therefore, to mitigate these drawbacks, it is very important to understand the effects of ε-martensite on hydrogen-related issues.

Despite of the abovementioned importance of ε-martensite, its hydrogen uptake and desorption behavior has not yet been investigated. Further, Mn is one of the most important elements in ε-martensitic transformation. In this work, we aim to clarify the effects of ε-martensite and Mn on hydrogen uptake and desorption by utilizing cryogenic thermal desorption analysis (C-TDA).

2. Experimental

Fe-20Mn, Fe-24Mn, and Fe-40Mn austenitic alloys were prepared by vacuum induction melting. Their chemical compositions are detailed in Table 1. The ingots were forged and rolled at 1 000°C. Subsequently, the sheets were solution-treated at 1 000°C for 1 h followed by water quenching to suppress uncontrolled precipitation and segregation. The samples were cut by spark machining, and their thickness was reduced by mechanical gliding. The specimens used in this study were chemically polished with a mixed solution of 10%HF and 90%H2O2 in Vol. before the experiments in order to eliminate surface damage caused by the mechanical polishing.

Fe-20Mn and Fe-24Mn alloys are known to exhibit thermally induced ε-martensite at ambient temperature.15) In contrast, austenite of Fe-40Mn alloys is fully stable even after cooling to −269°C.16) In order to thermally induce a high amount of ε-martensite, the three alloys were cooled to −196°C using liquid nitrogen before the following experiments.

X-ray diffraction (XRD) measurements were conducted at 40 kV at a scanning rate of 0.05° s−1 to identify ε-martensite formation. The specimens for the XRD measurements were 5 mm wide, 10 mm long, and 1 mm thick. Reverse transformation temperatures of the cooling-induced ε-martensite were determined by differential scanning calorimeter (DSC) operated at 10°C min−1 using 1-mm-thick specimens of diameter 3 mm.

For C-TDA, specimens of width 10 mm, length 12 mm, and thickness 0.4 mm were hydrogen-charged at 10 A m−2 for 6 days in 3% NaCl aqueous solution with 3 g l−1 NH4SCN after the pre-cooling to −196°C. A platinum wire was used as the counter electrode for the hydrogen charging. The three specimens were connected to each other by spot welding during the hydrogen charging, thus implying the same conditions during charging for all specimens. The specimens were preserved in liquid nitrogen until the initiation of C-TDA in order to suppress hydrogen desorption before the measurements. C-TDA was performed using a quadrupole mass spectrometer from −50°C to 300°C at a constant heating rate of 3°C min−1.

Table 1. Chemical compositions (wt.%) of the alloys used.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mn</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>O</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-20Mn</td>
<td>19.8</td>
<td>&lt;0.001</td>
<td>&lt;0.003</td>
<td>0.0053</td>
<td>0.0046</td>
<td>0.0041</td>
<td>Bal.</td>
</tr>
<tr>
<td>Fe-24Mn</td>
<td>24.0</td>
<td>&lt;0.001</td>
<td>&lt;0.003</td>
<td>0.0081</td>
<td>0.0043</td>
<td>0.0046</td>
<td>Bal.</td>
</tr>
<tr>
<td>Fe-40Mn</td>
<td>39.7</td>
<td>0.002</td>
<td>&lt;0.003</td>
<td>0.012</td>
<td>0.0079</td>
<td>0.0064</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

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Note

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heating rate of 200°C·h⁻¹. The specimen temperature was maintained below −50°C, and the desorption behavior revealed no significant hydrogen desorption below −50°C.

3. Results and Discussion

Figure 1 shows the XRD patterns for the Fe-20Mn, Fe-24Mn, and Fe-40Mn alloys pre-cooled to 77 K. These results indicate that the pre-cooled Fe-20Mn and Fe-24Mn alloys have 91 and 94 vol.% of ε-martensite, respectively, whereas no ε-martensite formed in the pre-cooled Fe-40Mn alloy. As shown in Fig. 2, the thermally induced ε-martensite of the Fe-20Mn and Fe-24Mn alloys started to reversely transform at 182 and 157°C ($A_s$), respectively. The reverse transformations in the alloys completed at 216 and 197°C ($A_f$), respectively.

Figure 3 shows hydrogen desorption rate curves plotted against temperature for the three alloys. The hydrogen desorption was initiated below room temperature, which indicates that the cryogenic technique is effective for extremely precise experiments even in austenitic steels. The amount of hydrogen increases with increasing Mn content. The cumulative hydrogen amount from approximately −60 to 250°C for the Fe-20Mn, Fe-24Mn, Fe-40Mn alloys were 17.5, 30.9, and 45.4 wt.ppm, respectively. The second peak on the hydrogen desorption rate curves indicated by the red arrows shifted to the higher temperatures with increasing Mn content, and disappeared in the Fe-40Mn alloy.

The increase in the hydrogen amount with Mn content can be attributed to 1) a decrease in ε-martensite amount, which would change the solubility, and 2) increasing hydrogen entry rate due to surface-hydrogen reactions associated with an increase in hydrogen surface coverage.¹⁷,¹⁸ However, the increase in Mn content from 20 to 24 vol.% did not change the amount of ε-martensite in the pre-cooled specimens, indicating that the influence of ε-martensite formation is ruled out to explain the large difference in hydrogen amount among the alloys. In other words, the increase in hydrogen content is considered to stem from a change in the surface-hydrogen reaction owing to increasing Mn content.

The second peak indicated by the red arrows in Fig. 3 corresponds to the reverse transformation temperatures.
measured by the DSC. Namely, the reverse transformation from $\varepsilon$ to $\gamma$ induces hydrogen desorption in the present alloys. The disappearance of the peak in the Fe-40Mn alloy, which has no $\varepsilon$-martensite, supports the correlation between reverse transformation and hydrogen desorption. Here note that the hydrogen desorption associated with the $\varepsilon \rightarrow \gamma$ reverse transformation indicates that extra hydrogen exists in $\varepsilon$-martensite. However, as is clear from the difference in peak height between the first and second peaks, the amount of the extra hydrogen in $\varepsilon$-martensite is much lower than the total amount of diffusible hydrogen.

4. Conclusion

Through cryogenic thermal desorption analysis, the following facts associated with $\varepsilon$-martensite and Mn content were clarified in the binary Fe–Mn austenitic alloys.

1. Weakly trapped hydrogen desorption was initiated at temperatures lower than room temperature.

2. Hydrogen uptake was promoted by increasing Mn content in electro-chemical hydrogen-charging. $\varepsilon$-martensite formation is not the major factor promoting the hydrogen uptake in the present case.

3. Reverse transformation from $\varepsilon$ to $\gamma$ induced hydrogen desorption.

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