Hydrogen Traps and Hydrogen Induced Cracking in 20CrMo Steel

Wei LI,1,2* Xu ZHU,1) Jianjun YAO,3) Xuejun JIN1,2) and Xifan DING4)*

1) Institute of Advanced Steels and Materials, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240 China. 2) Collaborative Innovation Center for Advanced Ship and Deep-Sea Exploration, Shanghai Jiao Tong University, Shanghai, 200240 China. 3) Asylum Research, an Oxford Instruments company, No.461, Hongcao Road, Shanghai, 200233 China. 4) School of Media and Design, Shanghai Jiao Tong University, Shanghai, 200240 China.

(Received on May 24, 2016; accepted on September 16, 2016)

The hydrogen trapping sites of commercial 20CrMo steel samples with electrochemically charged hydrogen were characterized by thermoelectric power (TEP) and scanning Kelvin probe force microscope (SKPFM). A surface potential drop of about 190 mV was found for the globular MnS inclusion and 150 mV for the elongated one due to the hydrogen absorption of MnS inclusions. Similar to thermal desorption measurement, TEP is a potential method in analyzing hydrogen traps of solid solution, dislocations and irreversible traps. The fracture morphology and hydrogen induced cracking can be explained by combined hydrogen embrittlement mechanisms. Although hydrogen induced cracks are found to initiate at the elongated inclusions, only longitudinal cracks were observed in this study which is not detrimental to the embrittlement.

KEY WORDS: hydrogen trapping; MnS inclusions; hydrogen induced cracking; scanning Kelvin probe force microscope; thermoelectric power.

1. Introduction

It is well known that high strength steels are susceptible to hydrogen embrittlement (HE) with the presence of diffusible hydrogen from various sources. Many theories have been proposed to explain this phenomenon including hydrogen-enhanced localized plasticity mechanism,1–4 hydrogen-enhanced decohesion mechanism,5–7 hydrogen-enhanced vacancies and nanovoids coalescence mechanism.8–11 Among these explanations, there is consensus in hydrogen-enhanced vacancies and nanovoids coalescence mechanism.8–11 In general, trapping sites for hydrogen are separated by reversible traps or irreversible traps with a critical binding energy value, which can be acquired by thermal desorption or permeation analysis.16) Reversible traps include dislocations, microvoids and coherent precipitates/interfaces which can immobilize and release hydrogen at low temperatures normally below 573 K.12 In contrary, irreversible trap absorbs hydrogen and prevent it from escaping until it reaches even higher temperature. For example, H-MnS has a binding energy 72.3 kJ/mol;17) H-Al2O3 has a binding energy 71.4 kJ/mol.18) Many methods have been developed to reveal the hydrogen traps in steels, e.g. by nuclear reaction analysis,19) secondary ion mass spectroscopy,20) tritium autoradiography,21,22) hydrogen microprint technique23,24) and three-dimensional atom probe tomography.25,26) Scanning Kelvin probe force microscope (SKPFM) is normally adapted with an atomic force microscopy (AFM) and it is useful in studying electrochemical process such as corrosion.27) Recent study showed its capacity in revealing the mechanism of stress corrosion cracking in austenitic stainless28) and even hydrogen embrittlement (HE) in aluminium alloys.29) Thermoelectric power (TEP) is highly sensitive to crystal defects such as dislocations, solute atoms and inclusions.30) Few results of TEP study on hydrogen in steel can be found in the literature.

Although large inclusions such as elongated MnS and other oxides clusters and stringers are considered to be detrimental to hydrogen induced cracking (HIC),31) vast results remain unclear in respect of the correlation between inclusion and HIC resistance. The Fe–MnS interface is incoherent owing to the larger thermal expansion coefficient of MnS (18.1×10−6 K−1) than Fe (12.5×10−6 K−1). Dong et al. found that the hydrogen trapping ability can be significantly improved by increasing MnS contents in low-carbon Al-killed steel.32) By using tritium autoradiography technology, Otsuka et al. found hydrogen atoms were accumulated at the MnS precipitates.22) However, they also agreed that there were some gaps at the interface, and hydrogen could be released at this interface gap. Garet et al. demonstrated that hydrogen is not permanently bound to the sulphide compounds at room temperature.33) On the other side, elongated MnS inclusions were identified in the middle of the crack for the DP600 steel by Escobar et al. which suggested that they might play a role in the initiation of hydrogen induced cracks.34) However, no clear correlation could be

* Corresponding author: E-mail: weilee@sjtu.edu.cn, ccding@sjtu.edu.cn
DOI: http://dx.doi.org/10.2355/isijinternational.ISIJINT-2016-281

© 2017 ISIJ

170
found between the sulphur content or the average length of MnS inclusions and the HIC resistance.\(^1\) Although MnS is capable of trapping hydrogen with a relatively large activation energy, microvoids are easily to form in the MnS/\(\alpha\)-Fe interface during the thermomechanical process,\(^3\) which in turn complicates this problem.

In this study, hydrogen traps and hydrogen induced cracking were investigated via combined methods. SKPFM was used to reveal the surface absorption of hydrogen; TEP evolution with the thermal desorption of pre-charged hydrogen was investigated in the purpose of revealing hydrogen traps; Electron backscattering diffraction pattern (EBSD) and kernel average misorientation (KAM) were used to analyze the HIC microstructures.

2. Materials and Methods

The material employed in this study is a commercial 20CrMo steel with the chemical compositions shown in Table 1. Steels were austenitized at 1323 K for 1 hour, oil quenched and tempered at 423 K for 1 hour to achieve a martensitic structure with a prior grain size about 25 \(\mu\)m.

The tensile test specimens were electrochemically charged with hydrogen using 1 g/L thiourea in 0.5 M H\(_2\)SO\(_4\) as the electrolyte solution at a current density of 9 mA cm\(^{-2}\) for 1 hour and up to 10 hours. Total hydrogen contents were measured by a LECO 600 analyzer on corresponding rod samples (5 mm in diameter and 10 mm in length) after hydrogen charging under same conditions.

Tensile tests were carried out on the cylindrical specimens with a diameter of 5 mm and gauge length of 25 mm at a strain rate of 3.33 \(\times 10^{-4}\) s\(^{-1}\) at 298 K using a SANS universal testing machine. An extensometer with 10 mm in range was used for the strain measurements. Specimen immersed in the electrolyte was covered with water-proof tape except the gage part to ensure a uniform charging condition. 0.5 ppm and 1.0 ppm (in mass) hydrogen contents were chosen for tensile tests based on massive measurements for hydrogen effusion conditions.

Microstructures were observed via optical micrographs (OM) and ZEISS SUPRA55 scanning electron microscopy (SEM). Sample preparation follows normal procedure including mechanical grinding with SiC grit papers and polishing up with 1 \(\mu\)m diamond paste, final polishing with 0.05 \(\mu\)m colloidal silica suspension. SKPFM measurements were carried out in a Cypher AFM (Asylum Research, Santa Barbara) equipped with a Quadrex electronic module. The probes were conductive Pt/Ir-coated silicon tips. The SKPFM potential scans were acquired using ‘nap’ technology which allows the tomography and potential to be collected simultaneously. A height of 30 nm was set for the first pass and the second pass is set smaller. For comparison, both original samples and hydrogen charged samples (10 hours) were polished and measured in air at 298 K and in an ambient relative humidity of 40%. TEP measurements were performed on LSR-3 Seebeck Coefficient measurement (Linseis thermal analysis). TEP samples are circular cylinder in shape (5 mm in diameter and 10 mm in length). The temperature gradient is set to be 50 K at a heating rate of 3 K per minute and the isothermal testing time is 1 minute.

3. Results

3.1. Microstructures and HE Fracture

The microstructure of the studied steel predominantly consists of lath martensite as shown in Figs. 1(a) and 1(b). Globular or rod-like inclusions are observed in Fig. 1(c). Analysis of the inclusions with EDS revealed they were enriched with manganese and sulphur.

Tensile tests for uncharged and hydrogen charged samples are repeated for three times and representative results are shown in Table 2. It is obvious that when the total hydrogen content exceeds about 1 ppmw, the tensile properties are deteriorated abruptly, with an elongation loss of about 55%, and fracture area reduction loss of about 67%. On the contrary, 0.5 ppmw hydrogen has little effect on the HE degradation, which means the hydrogen atoms are possibly immobilized by irreversible traps.

Figure 2 shows the characteristic fractographic results of the steel tensile tested with 1 ppmw hydrogen. The overall fracture surface shows negligible necking with two distinguishing area I and II. A magnified view of area I in Fig. 2(b) reveals fully dimple structure which indicates that this area is typical ductile microvoid coalescence. Detailed observation of area II shows a mixed morphology of dimples mixed with “quasi-cleavage” regions, second cracks (Fig. 2(c)) and flat “featureless” regions (Fig. 2(d)).

3.2. Hydrogen Trapping Sites of MnS Visualized by SKPFM

Figure 3 is the AFM and SKPFM measurement on uncharged sample revealing elongated inclusions. From the topographic images, one can tell that inclusion particles have been grinded off from the surface to form hundreds-nanometers-deep concave on the surface. The SKPFM image demonstrated that the inclusion area has a higher surface potential (in white color) than the martensitic matrix. From line scan analysis, as shown in Fig. 3(c), the potential of inclusions is about 120 mV above the value of martensitic substrate.

AFM/SKPFM morphology of hydrogen charged sample is illustrated in Fig. 4. It is interesting to find a drop in surface potential (in dark colour) within those inclusions. From line scan in Fig. 4(c), the decrement is about 70 mV for the globular inclusion and about 30 mV for the elongated one. Therefore, the overall surface potential drop caused by introducing hydrogen is 190 mV for the globular MnS inclusion and 150 mV for the elongated one. The decreasing potential value can be attributed to the absorption of hydrogen because first principle calculation proved that surface energy was reduced by adding hydrogen into ferrite or austenite in steels,\(^2\) which also implied that hydrogen lowers the cohesive bonding force due to the accumulation of immobile hydrogen. In our SKPFM observation, the globular inclusion reveals larger and uniform decrement in surface potential than the elongated one. Therefore, the

| Table 1. Chemical compositions (wt.%) of the 20CrMo steel. |
|-----------------|-----|----|----|----|----|----|----|----|----|    |
| C    | Si   | Mn  | P  | S   | Cu  | Ni  | Cr  | Mo  | Al  | Fe  |
| 0.20 | 0.26 | 0.80 | 0.023 | 0.015 | 0.13 | 0.07 | 1.11 | 0.17 | 0.033 | 0.0139 | Bal. |

© 2017 ISIJ
Table 2. Tensile properties of samples with different hydrogen contents.

<table>
<thead>
<tr>
<th>Hydrogen content</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>TEI (%)</th>
<th>RA (%)</th>
<th>$E_l$ loss</th>
<th>$RA$ loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ppm</td>
<td>776±4</td>
<td>1054±4</td>
<td>16.9±0.6</td>
<td>59.9±0.5</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>0.5 ppm</td>
<td>715±6</td>
<td>1065±3</td>
<td>16.4±0.4</td>
<td>57.3±0.4</td>
<td>3±6</td>
<td>4±2</td>
</tr>
<tr>
<td>1 ppm</td>
<td>775±9</td>
<td>1090±5</td>
<td>7.6±0.3</td>
<td>19.9±0.4</td>
<td>55±3</td>
<td>67±1</td>
</tr>
</tbody>
</table>

* $E_l$ loss = 100 × ($E_{l\text{uncharged}}$-$E_{l\text{charged}}$) / $E_{l\text{uncharged}}$

** $RA$ loss = 100 × ($RA_{l\text{uncharged}}$-$RA_{l\text{charged}}$) / $RA_{l\text{uncharged}}$

hydrogen trapping capacity of globular MnS is larger than elongated MnS considering the surface potential drops caused by hydrogen absorption.

3.3. Thermal Desorption of Hydrogen Revealed by TEP

It is worth noting that TEP evolution with temperature (as shown in Fig. 5) revealed information about hydrogen trapping and desorption. By comparing two TEP curves of hydrogen charged and untreated samples, three stages can

Fig. 1. Microstructure of the 20CrMo steel. (a) OM micrograph. (b) SEM micrograph. (c) SEM micrograph of inclusions. (d) EDS analysis of selected area in (c). (Online version in color.)

Fig. 2. (a) Overview of the fracture surface of the steel tensile tested with 1 ppmw hydrogen. (b) Detail of the fracture surface of I in (a). (c) and (d) Detail of the fracture surface of II in (a). (Online version in color.)
be identified with two inflection points of temperatures, at about 550 K and 780 K. The result is in accordance with previous research work by thermal desorption spectroscopy (TDS) which showed release peak temperature of hydrogen trapping in dislocations (reversible) and MnS inclusion (irreversible) is around 488 and 768 K, respectively. Therefore, it is reasonably assumed that TEP can trace desorption of hydrogen upon heating. Relative TEP(S) of the hydrogen charged steel sample with respect to the TEP of uncharged steel sample can be attributed to the effect of hydrogen. According to previous researchers’ TEP study on interstitials, we describe the relative TEP evolution caused by hydrogen with following: $S = \Delta S_{ss} + \Delta S_d + \Delta S_{irt}$, where $\Delta S_{ss}$, $\Delta S_d$ and $\Delta S_{irt}$ are due to the hydrogen in solid solution (ss), in dislocations (d) and in irreversible traps (irt), respectively. The first stage (300–550 K) is corresponding to the effusion of hydrogen in solid solute or trapped at dislocations. As temperature rises over 550 (second stage), hydrogen in solid solute or trapped at dislocation effuses out totally and thus no discrepancy of TEP is found due to the vanishing of dislocations. In the third stage (> 780 K), desorption of hydrogen trapped in irreversible traps (MnS inclusions) leading to the increment of TEP. It is known that the Seebeck effect or TEP defines the elec-

Fig. 3. (a) AFM, (b) SKPFM combined with morphology images of MnS inclusion in untreated samples and the potential is shown by color, (c) Line scan curves from AFM/SKPFM results. (Online version in color.)

Fig. 4. (a) AFM, (b) SKPFM combined with morphology images of MnS inclusion in hydrogen charged samples and the potential is shown by color, (c) Line scan curves from AFM/SKPFM results. (Online version in color.)
The electron-state density at the Fermi level and the interaction between dislocations and interstitial hydrogen can be evaluated by ab initio calculations. Similar to thermal desorption measurement, TEP can also give the desorption peak temperatures of different hydrogen traps. Moreover, TEP may give further information on the interaction among hydrogen atoms, substitution atoms and dislocations. Currently, it is only phenomenal recognized that free hydrogen in solid solution increase the TEP while hydrogen trapped in dislocations decrease the TEP.

3.4. Observation of Hydrogen Induced Cracks
As shown in Fig. 6(b), HIC was found in hydrogen charged sample (1 ppmw) along the tensile direction comparing to the uncharged sample in Fig. 6(a). As shown in Fig. 7(a), detailed EBSD observation of the HIC demonstrated that the crack passed along the interface of martensite laths because the orientations of these two adjacent martensite are different. EDS analysis in Figs. 7(c)–7(e) revealed that HIC are connected with elongated MnS inclusions. Furthermore, martensite laths close to the elongated MnS inclusions had larger deformation indicated by KAM values. It is worth noting that the observed HIC only has longitudinal direction which is assumed to have little detrimental effect on the embrittlement. Meanwhile, no HIC was found near the inclusions with small size and globular shape.

Fig. 5. TEP evolution during heating process ranging from 300 to 973 K. Inserted sketch of TEP measurement: two thermocouples are held at two different temperatures T1 and T2. The TEP value is the ratio of the generated potential drop $\Delta V$ over the temperature gradient $\Delta T$. (Online version in color.)

Fig. 6. Longitudinal sectional SEM images of fractured samples (a) without hydrogen charging and (b) charged with 1 ppmw hydrogen showing hydrogen induced cracks formed along the tensile direction.

Fig. 7. (a) EBSD, (b) kernel average misorientation (KAM) (the color represents misorientation values from low (blue) to high (red) and (c) Fe, (d) Mn & (e) S mapping of a HIC crack. (Online version in color.)
4. Discussions

The presented results confirm that 20CrMo steel suffers from HE in degradation of tensile properties when the hydrogen content is over 1 ppmw. The fractography shows the existence of ductile deformation trace in the flat “featureless” regions rather than a sharp cleavage fracture and it can be explained by hydrogen-enhanced localized plasticity (HELP) mechanism in which dissolved hydrogen enhances decohesion mechanism (HEDE) mechanism. The propagation of cracks passes along the interface of martensite laths (in Fig. 7(a)) and also along the prior austenite grain boundaries (in Fig. 6(b)). Therefore, it is rational to explain the HE fracture and HIC phenomena in 20CrMo steel by the HELP & HEDE mechanism. It is known that voids are nucleated at relatively low plastic strains due to the incoherency of Fe–MnS interface. And with the overall effect of hydrogen stabilized vacancy damage, vacancy aggregation and NVC mechanism, diffusive hydrogen would quickly segregate near the MnS/α-Fe interfaces upon straining. And the surrounding martensites formed lattice defects assisted by the diffusible hydrogen released from the MnS inclusions and cracks propagated until fracture. The surface potential change measurements. Several conclusions can be summarized as follows:

1) Hydrogen embrittled in 20CrMo steel is apparent for 1 ppmw hydrogen and it can be explained by combined HE mechanisms.

2) SKPFM results show surface potential drops of about 190 mV for the globular MnS inclusion and 150 mV for the elongated one due to the hydrogen absorption. Hydrogen trapping capacity can be compared for elongated and globular inclusions by SKPFM.

3) TEP measurement proved to be a potential method in analyzing hydrogen traps of solid solution, dislocations and irreversible traps.

Acknowledgments

This work was supported by HIMITMTC joint research project, National Key Research and Development Program of China (No. 2016YFB0308601), National Natural Science Foundation of China (U1564203, Nos. 51571141) and the Ministry of Industry and Information Technology of China under the project of LNG shipbuilding.

REFERENCES