Hydrogen Embrittlement of a Manganese–aluminum High-strength Bainitic Steel for Railway Crossings

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The hydrogen embrittlement characteristics of a Mn–Al bainitic steel for railway crossings were studied by means of the slow strain rate test (SSRT), the delayed fracture test and X-ray diffraction (XRD) analysis. The binding energies and hydrogen diffusion barriers of an iron unit cell were tested separately with Al, Si and H, and were evaluated by the first principle calculation. The results showed that the hydrogen embrittlement decreased greatly with increased Al content. Microstructure examinations indicated that the content of retained austenite increased with increased Al content, which was as irreversible hydrogen traps and was not sensitive to hydrogen embrittlement. It is found that the characteristics of hydrogen embrittlement identified by SSRT and the delayed fracture test were different. From the first principle calculation, the binding energy of the iron lattice containing aluminum decreased less as compared to those of the cell containing silicon, but the diffusion barriers increased significantly.

KEY WORDS: bainitic steel; hydrogen embrittlement; aluminum; railway crossing.

1. Introduction

As early as 1980s, a Mo–B bainitic steel named Titan was first used for railway crossings in the United Kingdom,1) and a Mn–Si–Cr bainitic steel named J9 used for railway crossings was studied in the United States in 1995.2) These steels had high strength, high toughness, and excellent fatigue properties. Subsequently, bainitic steel was studied in Japan, Germany and China at the end of 20th century.3,4) However the main problem associated with the use of bainitic steel for railway crossings, has been the lack of plasticity and impact toughness. Failure phenomena such as premature brittle fracture and block dissection often occurred during service in the railway system.5) It is known that resistance of steel to environmental fracture reduces with increasing in its strength. Our previous research6–8) has shown that the same problems occurred with bainitic steel.

In bainitic steels, Silicon is insoluble in cementite and influences the bainitic transformation reaction by preventing carbide precipitation. Aluminum plays a similar role in steels to Si, and partial replacement of Si by Al has been extensively studied in transformation-induced plasticity (TRIP) steels.9–12) The present works are focused on an investigation of TRIP steels, but no previous investigations have been carried out on bainitic steels used for railway crossings with partial replacement of Si by Al. Taking advantage of the beneficial effects of Al in reducing the hydrogen embrittlement, we developed a new type of Mn–Al bainitic steel used for railway crossing. In this work, we investigated the hydrogen embrittlement of the bainitic steel with different Al contents by both the delayed fracture test and SSRT. Microstructural examinations were performed to understand the major mechanisms dominant in the investigated steel. In addition, the first-principle calculation were carried out to compute the binding energy (E_b) and the hydrogen diffusion barrier (ΔG) of the iron lattice containing aluminum or silicon, in an attempt to better understand the hydrogen embrittlement caused by partial replacement of Si by Al.

2. Experimental Procedure

The chemical composition of the bainitic steels (wt.%) was listed in Table 1. The steel to be tested was produced by partial replacement of Si by Al, keeping the total quantity of Al and Si constant. The steel ingots were produced by vacuum melting, and then forged into round bars 20 mm in diameter. The bars were heated to 920°C for 0.5 h before being air-cooled to room temperature, and then tempered at 350°C for 1.5 h. They were then machined to form smooth cylindrical specimens 25 mm × 5 mm diameter. U-notch

Table 1. Chemical composition of the bainitic steels (wt.%).

| Steel No. | C | Si | Mn | Cr | Ni | Mo | Al | P | S |
|-----------|---|----|----|----|----|----|----|---|---|
| 1#        | 0.30 | 1.80 | 1.76 | 1.71 | 0.39 | 0.35 | 0.010 | 0.011 |
| 2#        | 0.30 | 1.55 | 1.78 | 1.73 | 0.41 | 0.35 | 0.19 | 0.010 | 0.011 |
| 3#        | 0.30 | 1.02 | 1.83 | 1.75 | 0.40 | 0.34 | 0.75 | 0.010 | 0.010 |
| 4#        | 0.32 | 0.48 | 1.82 | 1.77 | 0.40 | 0.35 | 1.31 | 0.010 | 0.010 |
specimens 10 × 10 × 55 mm were produced for impact toughness testing. Notched cylindrical specimens for delayed fracture testing were also prepared, of dimensions 25 mm × 5 mm diameter with a 0.5 mm radius notch reducing the specimen diameter to 3 mm. Smooth cylindrical specimens 50 mm × 5 mm diameter were used for testing hydrogen content.

The tensile test specimens were used for cathodic hydrogen charging using a stabilized power supply (YJ83/2 type DC). The electrolyte was a mixed solution of 0.5 mol/L H2SO4 + 200 mg/L Na3AsO3. The current density for hydrogen charging was 10 mA cm–2. The charging times were selected to be 5, 20, 100 and 180 min, respectively. Uniform distribution of hydrogen was achieved by homogenization heat treatment at 190°C for 11 h. In order to prevent the hydrogen escaping from the samples, protective bright cadmium plating was applied using a 1 000 ml mixed solution of distilled water, 98% oil of vitriol (50 g), dried CdSO4 powder (50 g), anhydrous Na2SO4 (45 g), glutin (6 g) and phenol (3 g), and 25 mA cm–2 current density. The specimen and the cadmium were used as anode and cathode, respectively. Cadmium plating for 5 min was sufficient to prevent hydrogen diffusing and dissipating.13)

The hydrogen content in the steel samples was analyzed using a hydrogen content analyzer (CQY-2). The hydrogen embrittlement sensitivity of the steels was investigated by SSRT using an electronic universal testing machine (DDL-100). A slow strain rate of 5.6 × 10−5 s−1 was used to fully reflect the hydrogen embrittlement sensitivity of the steels. The delayed fracture test was carried out using a stress corrosion testing machine (NHK-1). The stress range was from 80% to 100% of the yield strength (σ0.2). The microstructures of the steels were observed with an Axiovert 200 Mat digital metallographic microscope. The retained austenite content and the carbon content in the austenite were analyzed by a D/max-2500/PC X-ray diffractometer with Cu Kα radiation. Moreover, to further understand the effects of Si or Al on the hydrogen embrittlement of the investigated alloy, the binding energy (Eb) and the hydrogen diffusion barriers (ΔG) of the iron supercells were calculated by means of the first principles using the CASTEP 4.1 software. The supercell is a 3 × 2 × 2 cell model for 24 atoms with Al, Si or H added separately. Iron atoms at the vertices of body-centered cubic (bcc) or face-centered cubic (fcc) structure were partially replaced by either Al or Si. One of the tetrahedral interstitial sites (T) of the bcc or the octahedral interstitial sites (O) of the fcc was occupied by the atom of hydrogen. While the hydrogen atom transits to another interstitial site, e.g. T2, or O2 site from T1 or O1 via the adjacent O3 or T3, causes a change in the energy of the system: this is the hydrogen diffusion barrier (ΔG): see Fig. 1.

### 3. Results and Discussion

#### 3.1. Effects of Al Content on the Hydrogen Embrittlement Characteristics of the Mn–Al Bainitic Steel

The mechanical properties of the bainitic steels are shown in Table 2. It can be seen that the strength and the hardness of the steels decreased, but the plasticity, impact toughness and the yield: tensile strength ratio increased with increasing Al content.

The relationship between total hydrogen content and hydrogen charging time are shown in Fig. 2. The total hydrogen content in steels 1# and 4# increased with longer charging time, and the increasing trends were similar. The hydrogen absorption properties of 1# and 4# were not significantly different, since the microstructures of the two steels were similar. The performance of the delayed fracture of the steels is represented in Fig. 3, which shows that the ratio of fracture stress (σf):yield stress (σy) of the steels containing Al is greater than for those without Al, increasing from 96.0% to 97.5%. The delayed fracture property of the steels was improved with the addition of Al, but differed slightly with changes in Al content.

The reduction of area is sensitive to hydrogen, and is often used to evaluate the sensitivity of hydrogen embrittlement, as is calculated from:

\[
\eta = \left[ \left( \frac{\sigma_y}{\sigma_u} \right) \right] \times 100\% \quad \text{......... (1)}
\]
where $\eta$ is the embrittlement index of the steel, $\phi_0$ is the reduction of area without hydrogen charging, and $\phi_H$ is the reduction of area with hydrogen charging. The sensitivity to hydrogen is greater as $\eta$ increases, and the chance of hydrogen-induced fracture is also greater.

Figure 4 shows the effects of charging time on reduction of area and hydrogen embrittlement sensitivity of the steels. It can be seen that with increased hydrogen content, the reduction of area decreases and the embrittlement index increases. With increased Al content, the reduction of area increases but the embrittlement index falls sharply. Therefore, it can be concluded that hydrogen embrittlement of the steels was significantly delayed by the introduction of Al to the steel. With increased Al content and reduced Si content, the tendency for hydrogen embrittlement in the steel decreased substantially, which is quite different from the results from the delayed fracture tests.

### 3.2. Effects of Microstructure on the Hydrogen Embrittlement of the Mn–Al Bainitic Steels

Chemical composition, microstructural features and strength of the material, as well as environmental conditions, have effects on hydrogen embrittlement characteristics, but the effect of microstructure is the most important. Therefore, the microstructures of the investigated steels shown in Fig. 5 were carefully examined.

As aluminum content increased, the microstructure became finer and the number of phase interfaces between bainite, residual austenite and martensite increased substantially. The mechanical properties of the steels improved as a result. Phase interfaces, where the number of binding positions for hydrogen increases, act as hydrogen ‘traps,’ thus, a more uniform distribution of phase interfaces creates a more uniform distribution of hydrogen. Pressouyre has calculated that the binding energy for hydrogen, $E_b$, is 70 kJ mol$^{-1}$ at grain boundaries, and 26–59 kJ mol$^{-1}$ at phase boundaries. Phase interface and grain boundaries are thus irreversible hydrogen traps ($E_b > 40$ kJ mol$^{-1}$) which inhibit the exchange of hydrogen atoms, reducing the diffusion coefficient of the hydrogen so that it cannot readily migrate to any single location; in this way, the hydrogen
embrittlement characteristics of the steel is improved. X-ray diffractograms of the bainitic steels are shown in Fig. 6. The calculations were based on the integrated intensity of the (200)$_{\alpha}$, (211)$_{\alpha}$, (200)$_{\gamma}$, (220)$_{\gamma}$, and (311)$_{\gamma}$ peaks. The calculated results for retained austenite in the steels are shown in Table 2.

The carbon content of retained austenite ($x_C$) is calculated from:

$$a_\gamma = 3.556 + 0.0453x_C + 0.00095x_{\text{Mn}} + 0.0056x_{\text{Al}}...$$

where $a_\gamma$ is the lattice parameter of austenite, $x_{\text{Mn}}$ and $x_{\text{Al}}$ are the content of the individual alloying elements (wt%) in the retained austenite.

In this study, for convenience we have used the added content instead of these concentrations. The calculated results for the carbon content of retained austenite in the investigated steels are also shown in Table 2.

With Al content increasing, the retained austenite content increase. The retained austenite is a supersaturated solid solution of carbon, which largely stabilizes the retained austenite. The austenite possesses excellent toughness, and hinders crack propagation. It can act as a trap for hydrogen, which has a higher solubility and a lower diffusion coefficient in austenite. This means that the hydrogen is hindered from gathering in one local area, thus reducing the hydrogen embrittlement. The microstructure of martensite is recognized as being the most sensitive to the presence of hydrogen, followed by bainite, with austenite the least sensitive. Thus, as retained austenite content increases, the hydrogen embrittlement characteristics of the bainitic steel decrease.

As above, the values of the hydrogen embrittlement sensitivity of the four bainitic steels differed markedly by SSRT, but the fracture stress test results differed by only a small percentage from the delayed fracture test results. The reasons for this are as follows: when there is no applied stress (or low stress), the hydrogen in the irreversible traps cannot diffuse or aggregate at room temperature, so that the hydrogen embrittlement susceptibility is not obvious. As the stress gradually increases to a high value in the SSRT, the induced stress modifies the irreversible hydrogen traps into reversible hydrogen traps. This hydrogen diffuses and aggregates in localized areas, creating very high local hydrogen concentrations; the tendency to hydrogen embrittlement increases, and the hydrogen embrittlement characteristics become more significant. It has been reported that enriched hydrogen reduces the critical concentration of hydrogen embrittlement under stress. Elsewhere it has been reported that strain induces martensitic transformation in TRIP steels. Similarly, plastic deformation of bainitic steels occurs during SSRT. The deformation induces the transformation of some of the retained austenite into martensite: the retained austenite content decreases with increasing deformation and the content of martensite, which is sensitive to hydrogen, increases correspondingly. In addition, supersaturated hydrogen may be released from the austenite, increasing local hydrogen concentration. These results in the hydrogen embrittlement characteristics measured by SSRT being very different from those obtained in the delayed fracture test.

3.3. Effects of Electronic Structure on Hydrogen Embrittlement of Mn–Al Bainitic Steels

The Decohesion Theory indicates that, when the electron of hydrogen enters the unfillable 3d electronic shell in the pure iron cell, the repulsive force increases and the binding energy decreases. Based on the bcc structure of iron ($\alpha$-Fe), we constructed six supercells. The calculation results are listed in Table 3, which shows that the binding energy of the supercells with hydrogen is lower than those without hydrogen. This suggests that the binding energy between two atoms is reduced by adding a hydrogen atom. The binding energy of a supercell containing an aluminum or silicon atom is also reduced, the reduction being greater with added silicon than with added aluminum. This indicates that, in microcosm, the hydrogen embrittlement characteristics of
the iron supercell with added silicon is more sensitive than that with added aluminum.

The calculated diffusion energy barrier in the supercells is listed in Table 3. It shows that the diffusion of hydrogen in the pure iron supercell is the most rapid, and that the diffusion energy barrier is increased by adding the alloy elements which inhibit the diffusion of hydrogen. The hydrogen diffuses less in the supercell with silicon than in the one with aluminum. Consequently, the hydrogen embrittlement of the bainitic steels with added aluminum is lower than that with silicon.

4. Conclusions

The hydrogen embrittlement characteristics of a new type of air-cooled Mn–Al system bainitic steel used for railway crossings are investigated, and conclusions are drawn as following:

(1) Addition of aluminum refines the microstructure of the bainitic steel, and increases the phase interfaces and the content of the retained austenite. These interfaces and retained austenite act as the irreversible hydrogen traps, so that the hydrogen cannot readily aggregate in a local area. Moreover, the amount of bainite increases while the amount of martensite, which is the component of steel that is most sensitive to hydrogen, decreases with the addition of aluminum, further reducing the hydrogen embrittlement of bainitic steel.

(2) Stress induced hydrogen diffusion and strain induced phase transformation are the major reasons for the different hydrogen embrittlement properties evaluated by the SSRT and the delayed fracture test.

(3) The first principle calculations show that the decay rate of the binding energy of the supercell is less with Al than with Si. The diffusion energy barrier for hydrogen increases in the supercell with partial replacement of Si by Al, therefore, hydrogen is more difficult to diffuse and aggregate, and the hydrogen embrittlement of the bainitic steels is decreased by the addition of aluminum.

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|          | Fe24H | Fe23Al | Fe23AlH | Fe23Si | Fe23SiH |
|----------|-------|--------|---------|--------|--------|
| $\alpha$Fe $E_d$(eV) | 8.9954 | 8.7536 | 8.8054 | 8.8992 | 8.6468 |
| $\Delta G$(eV) | 0.75  | 1.19   | 0.93    |        |        |
| $\gamma$Fe $E_d$(eV) | 8.9779 | 8.7688 | 8.8058 | 8.8992 | 8.6688 |
| $\Delta G$(eV) | 1.06  | 1.36   | 1.28    |        |        |

$E_d$: The binding energy, $\Delta G$: the diffusion energy barrier.