

Design of Nanosized TiC Precipitates for Trapping Detrimental Hydrogen in High Strength Steels

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The concept of designing a good hydrogen trap for enhancing resistance to hydrogen embrittlement in high strength steels has been proposed. Coherent nanosized TiC precipitate in a 0.42C-0.30Ti steel has been investigated to prove to be one of the promising candidates for a good trap. High resolution electron microscopic study revealed that nanosized coherent TiC precipitates on (100) ferrite plane and obeys the Baker-Nutting orientation relationship with the ferrite matrix. Thermal desorption spectrometry analysis showed that coherent TiC traps hydrogen effectively. The activation energy for desorption of hydrogen from the coherent TiC precipitate is 58kJ/mol in the samples tempered at 550 to 700°C. Comparison of coherent TiC with incoherent TiC particle as well as dislocation and grain boundary with respect to trapped hydrogen amount and interaction energy with hydrogen was also made.

Key words: hydrogen embrittlement, reversible and irreversible traps, titanium carbide, thermal desorption spectrometry, high resolution transmission electron microscopy

1. INTRODUCTION

It has long been understood that hydrogen is easily trapped by microstructural defects like dislocation [1,2], grain boundary [1,2], and transition metal carbide/matrix interface [3-8] and others [9,10]. Of these hydrogen traps, fine uniform titanium carbide particle [3] and vanadium carbide particle [11] were reported to be beneficial to enhancement of resistance to hydrogen embrittlement in high strength steels. Because hydrogen embrittlement is often characterized by intergranular fracture, grain boundary is obviously not a good trap, instead, accumulation of hydrogen at grain boundary should be avoided. In order to take advantage of hydrogen traps, the question is raised as what is a good trap for enhancement of the resistance to hydrogen embrittlement. To be a good trap, the trap should possess such functions:

- (1) Reduces the diffusible hydrogen level in steel, i.e. scavenges the hydrogen in iron lattice;
- (2) Prevents hydrogen from entering steel interior from environment;
- (3) Prevents hydrogen from migrating to the stress concentration region ahead of the tip of a crack once hydrogen has entered or pre-existed in the steel interior;
- (4) Not to be a crack initiation source.

In order to meet these requirements, the trap should be of the following character and property: (1) high hydrogen trapping capacity, (2) appropriate interaction energy with hydrogen, and (3) fine and uniform distribution. It has been known that hydrogen absorbed from environment changes with temperature and climate, and hydrogen may be present in steel in a large amount in some cases like welding. In this case, it is desirable that the traps absorb hydrogen quickly and release it slowly, acting as a hydrogen capacitor.

Coherent TiC particle is expected to be such a good

hydrogen trap because of its potent strengthening effect and possible hydrogen trapping property. Pressouyre et al. [12,13] found that incoherent TiC particle traps hydrogen irreversibly and becomes more reversible when TiC particle is more coherent. However, no further information has been available about the hydrogen trapping nature of coherent TiC particles. The purpose of the present study is then to examine the capability of hydrogen trapping of coherent TiC and its interaction energy with hydrogen. The coarse incoherent TiC was also investigated for comparison.

2. EXPERIMENTAL PROCEDURE

The composition in mass percentage of the steel for study was: 0.42C, 0.30Ti, <0.01Si, <0.01Mn, <0.003P, <0.0005S, 0.0007N, 0.0021O. Calculation by the Thermo-Calc method showed that this steel contains up to 0.60vol% TiC at low temperature as shown in Fig.1. The steel was supplied in the form of hot-rolled plate. The steel was austenitized at 1350°C for 15min followed by quenching in ice-brine and subsequently tempered at temperatures up to 700°C for 3h followed by water cooling. Both austenitizing and tempering were carried out in flowing argon atmosphere. At 1350°C, 0.38vol%

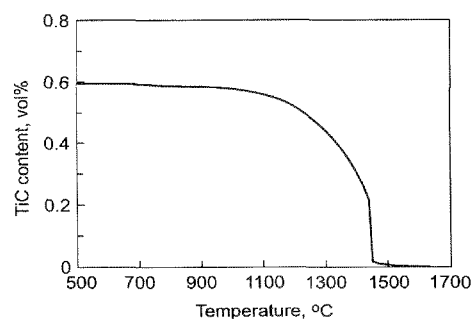


Fig.1 Calculated TiC content as a function of temperature in 0.42C-0.30Ti steel.

TiC remained undissolved in austenite and became incoherent particles in martensite after quenching. The remaining 0.22vol% TiC would precipitate in the martensite during tempering.

Cylindrical samples with a diameter of 5mm and a length of 40mm for thermal desorption spectrometry (TDS) analysis were fabricated from the heat treated specimens and were charged cathodically with hydrogen under charging condition: 0.1mA/cm², 1h, in 3 mass% NaCl aqueous solution with addition of 0.3% mass% NH₄SCN. After charging, the samples were electroplated with cadmium and homogenized at room temperature for 48h. TDS analysis was conducted at a constant heating rate of 100°C/h up to 810°C.

The coarse undissolved TiC particles were observed mainly by optical microscopy and the nanosized coherent TiC precipitates were examined by means of high resolution transmission electron microscopy on a JEOL JEM-2010F microscope operating at 200kV.

3. RESULTS

3.1 Microstructures

Undissolved incoherent TiC particles of an average diameter of 2μm are shown in Fig.2.

No precipitate of TiC was observed when tempered below 500°C. When tempered over 500°C, fine disc-like TiC particle precipitated on the {100} ferrite planes and obeyed the Baker-Nutting orientation relationship [14] with the ferrite matrix. Fig.3 shows the nanosized TiC precipitates in the samples tempered at 600°C and 700°C. The broad face of TiC particle is the coherent interface. TiC precipitated at 600°C (Fig.3 (a)) has a diameter of only 2nm and a thickness of less than 1nm. Tempering at 700°C promoted coarsening and the particle became more granular (Fig.3 (b)).

3.2 Thermal desorption spectrometry

Desorption spectra of hydrogen from the quenched and tempered samples during TDS analysis are shown in Fig.4. All the spectra are interrupted at the Ac1 transformation point at 733°C. Two distinct desorption peaks are observed for each spectrum at 100-200°C and 600-750°C, respectively. The peak at 100-200°C is contributed from dislocation, grain boundary and coherent TiC precipitate depending on tempering temperature. These traps are called reversible traps here because of their relatively lower interaction energy with hydrogen. On the other hand, the peak at 600-750°C is contributed from undissolved incoherent TiC particle

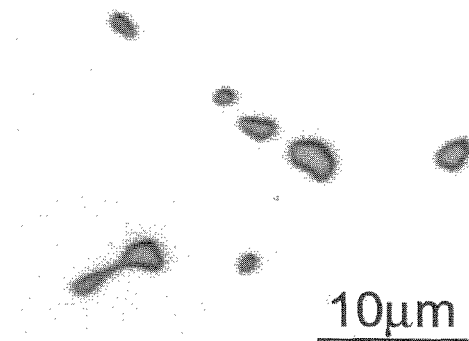


Fig.2 Optical micrograph of undissolved TiC particles in the as-quenched sample.

and the incoherent TiC particle is called irreversible traps because of its strong interaction with hydrogen.

Fig.5 summarizes the amounts of hydrogen trapped by reversible and irreversible traps. Contributions from dislocation and grain boundary are not distinguishable in the present study. In the as-quenched sample and the samples tempered at 300 and 400°C, reversibly trapped hydrogen comes from dislocation and grain boundary (Fig.5 (a)). At 500°C, TiC begins to precipitate and hydrogen is preferentially trapped by coherent TiC particle prior to dislocation and grain boundary. The amount of trapped hydrogen reaches maximum at 550°C. However, tempering above 550°C results in rapid decrease in hydrogen content. On the other hand, it is interesting to note that the amount of hydrogen trapped by undissolved incoherent TiC particle also changes with tempering temperature as shown in Fig.5 (b). No change is found below 400°C but at 500°C the hydrogen content demonstrates a peak value and decreases gradually when tempered at higher temperatures.

3.3 Simulation of the hydrogen desorption spectrum and determination of hydrogen desorption activation energy

The activation energy for hydrogen desorption was usually determined by the desorption peak shift method [1,4] by changing the heating rate of TDS experiment. The method required repeating TDS measurements at several different heating rates. The present authors developed a new method that requires only a single desorption spectrum [15]. The new method applies the

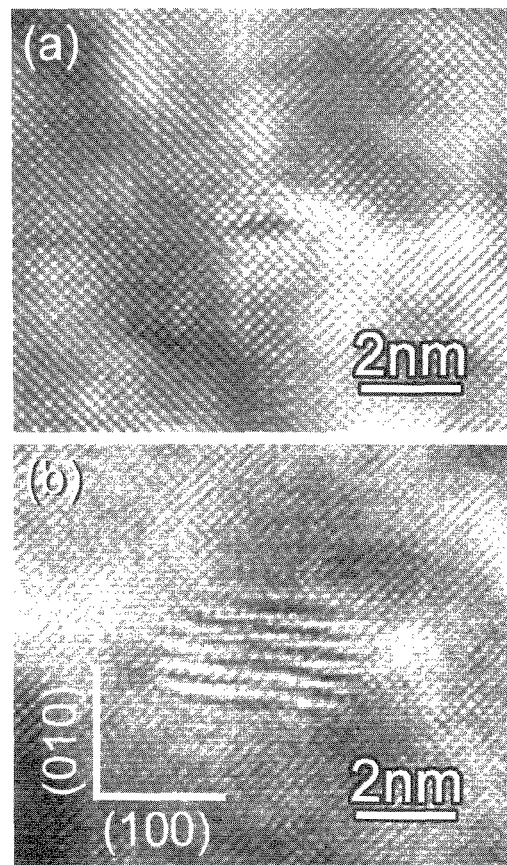


Fig.3 High resolution transmission electron micrograph of nanosized TiC precipitates in the samples tempered at (a) 600°C and (b) 700°C.

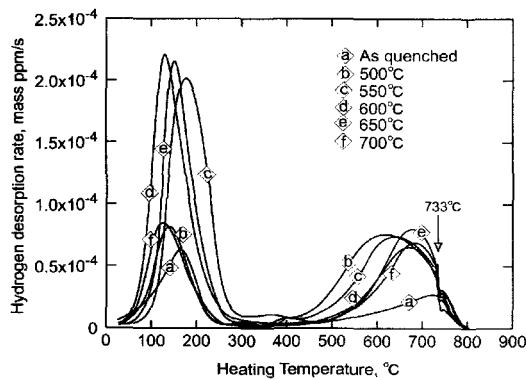


Fig.4 TDS spectra for samples tempered at various temperatures. Heating rate is 100°C/h.

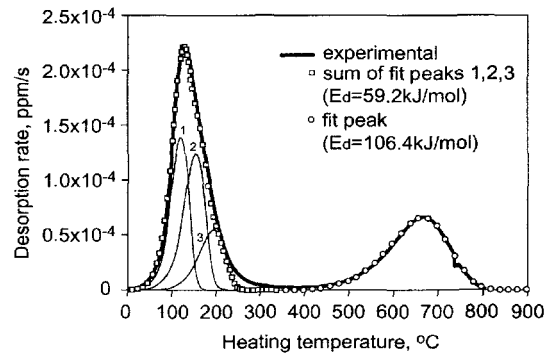


Fig.6 Fit of the experimental spectrum for the sample tempered at 600°C.

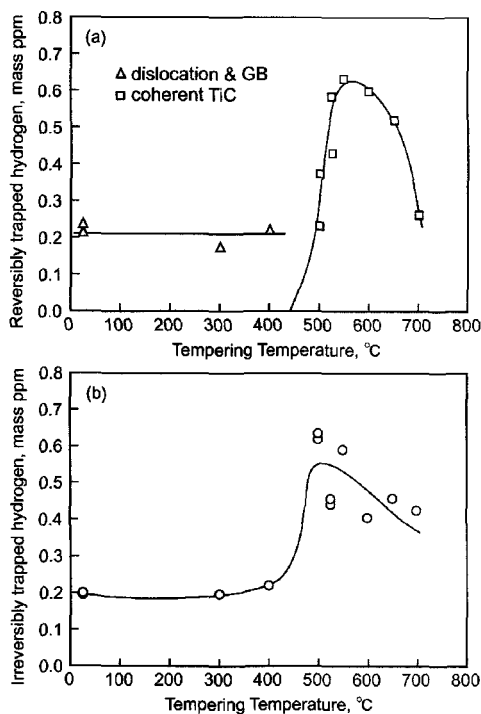


Fig.5 Dependence of the amount of hydrogen trapped by (a) reversible trap and (b) irreversible trap on tempering temperature.

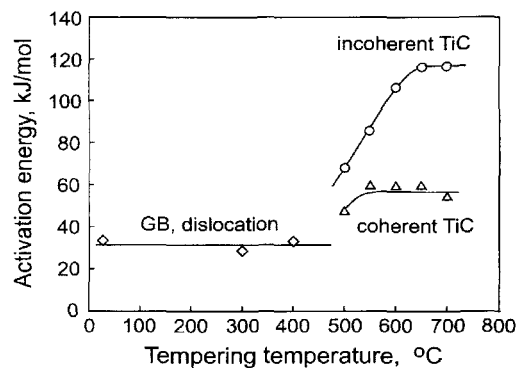


Fig.7 Activation energy for desorption of hydrogen from coherent, incoherent TiC particles, dislocation and grain boundary.

desorption peak. This process gives an activation energy of 59.2kJ/mol for the coherent TiC particle. Similar to incoherent TiC particle, a single curve is sufficient to fit the hydrogen desorption from dislocation and grain boundary in the samples tempered below 500°C.

Fig.7 shows the change in activation energy with tempering temperature for coherent and incoherent TiC particles as well as dislocation and grain boundary. Desorption activation energy for dislocation and grain boundary is 32kJ/mol. For coherent TiC, it is 47kJ/mol at 500°C and keeps constant above 500°C at about 58kJ/mol. Incoherent TiC shows a high activation energy of 116kJ/mol when tempered at and above 650°C but decreases to 68kJ/mol at 500°C.

reaction kinetic formula [16] directly to simulation of the desorption spectrum. The formula is represented by

$$dX/dt=A(1-X)\exp(-E_d/RT)$$

where X is the fraction of hydrogen released, t the time, A a constant, E_d the activation energy, R the gas constant and T the absolute temperature. Best fit to the experimental desorption spectrum gives the activation energy (E_d) and the constant A, as well as the total amount of hydrogen trapped by a corresponding trap. Fig.6 gives an example of the simulation for desorption spectrum of the sample tempered at 600°C. The desorption peak associated with incoherent TiC particle is well fitted by a fit curve which results in an activation energy of 106.4kJ/mol. A single curve failed to fit the peak around 150°C that is associated with coherent TiC. It was found that a set of curves with the same activation energy and different values of constant A can fit well the

4. DISCUSSION

4.1 Factors that influence the hydrogen capacity and the hydrogen-trap interaction energy of coherent and incoherent TiC particles

Tempering treatment resulted in change in hydrogen in two aspects: hydrogen content and interaction energy. Dislocation and grain boundary trap a small amount of hydrogen. 0.22vol% coherent and 0.38vol% incoherent TiC particles absorb large amount of hydrogen. The hydrogen trapped by coherent TiC precipitates decreases rapidly with increasing tempering temperature above 500°C. This is easily explained by decrease in the total coherent interface when TiC particles coarsened at higher temperatures. As shown in Fig.3, at 700°C, preferential growth in thickness direction is significant, resulting in rapid decrease in the total coherent

interfacial area. Despite great change in the amount of hydrogen trapped by coherent TiC particle, desorption activation energy does not change with tempering temperature. This result indicates that the nature of coherent interface does not change with tempering temperature. However, activation energy shows a small decrease in the sample tempered at 500°C, approaching towards that of dislocation and grain boundary (Fig. 7). At 500°C, prior to its precipitation TiC might nucleate as a TiC cluster staying on dislocation line or grain boundary. As a result, transition of interaction energy from dislocation and grain boundary to coherent TiC could be observed around 500°C.

The interaction energy between hydrogen and second phase in steel has long been considered as a constant parameter. The present result clearly showed that activation energy for hydrogen desorption from incoherent TiC changes depending on the heat treatment. The reason for changes in hydrogen capacity and interaction intensity is not clear now but it is probably related with the change in TiC chemistry. TiC chemistry may be affected by carbon depletion [17] and possibly also by oxygen contamination during heat treatment. Huang et al. [19] found that oxygen segregates at the Pd/oxide coherent interface and traps hydrogen when heat treated in air. No hydrogen trapped was observed when treated in vacuum. Oxygen can form a stable TiO with the same crystal structure as TiC [18]. However, further investigation is necessary for the present case of TiC in steel before any conclusion is made.

4.2 Coherent TiC particle acting as a beneficial hydrogen trap in high strength steels

Coherent TiC has been shown by the present study to be an effective hydrogen trap. According to the proposed conditions for a good trap mentioned in the Introduction, coherent TiC seems to meet the requirements. Even at 700°C, it still keeps a small size, showing a high resistance to coarsening. Although the release kinetics of hydrogen from coherent TiC at ambient temperature needs further investigation, TiC is expected to absorb hydrogen immediately in case of hydrogen flood and releases it slowly, keeping the hydrogen in iron lattice at a low level. Additionally, coherent TiC may be easily utilized in combination of incoherent TiC particles. According to Oriani's local equilibrium assumption [20], hydrogen concentration in the iron lattice (diffusible hydrogen) will be reduced when hydrogen-trap interaction energy is increased. Because the interaction energy of incoherent TiC with hydrogen is changeable, hydrogen trapping property of steel can be easily controlled to adapt to environmental change such as temperature variation.

5. CONCLUSIONS

The possibility of coherent TiC particle as a beneficial trap to enhance resistance to hydrogen embrittlement has been investigated by determining its hydrogen trapping property. The major results are summarized as follows:

(1) Coherent TiC begins to precipitate when tempered at 500°C and traps the maximum hydrogen at 550°C. Tempering above 550°C results in rapid decrease in the total trapped hydrogen amount. Decrease in total TiC/ferrite coherent interfacial area is presumed to

account for the decrease in hydrogen trapped.

- (2) The interaction energy between hydrogen and coherent TiC/ferrite was found to be 58kJ/mol when tempered at 550 to 700°C.
- (3) The amount of hydrogen trapped by incoherent TiC particles retained after austenitizing changes with tempering temperature. Tempering at 500°C shows the maximum hydrogen content and tempering above 500°C decreases the hydrogen content. The activation energy for hydrogen desorption from incoherent TiC particle changes from 116kJ/mol at 650-700°C to 68kJ/mol at 500°C.

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