Evaluation of Hydrogen Content Trapped by Vanadium Precipitates in a Steel

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Hydrogen content trapped by vanadium precipitates was evaluated using vanadium bearing martensitic steels which show single TDA desorption peak. The peak consists of desorption from various sorts of trap site with different detrapping activation energy, even if it appears to be a single peak. Experimentally obtained single desorption profile taken from vanadium bearing martensitic steels was decomposed to multiple profiles with different peak temperature. Form of each desorption profile was approximated to Gaussian function. Area surrounded by each Gaussian function was calculated by integrating the functions to obtain decomposed hydrogen contents related to each peak temperature. It was revealed that decomposed profile with 140°C peak was caused by vanadium precipitates trapping, by comparing an amount of vanadium precipitates with decomposed hydrogen contents. Most of hydrogen in vanadium bearing tempered martensitic steel was revealed to be trapped by vanadium precipitates.

KEY WORDS: hydrogen; thermal desorption analysis; trap site; vanadium precipitate; martensitic steel.

Table 1. Chemical composition of the steel examined. (mass%)

| C  | Si  | Mn  | P   | S   | sol.Al | N   | V   | B   |
|----|-----|-----|-----|-----|--------|-----|-----|-----|
| 0.25 | 0.30 | 1.50 | 0.008 | 0.0008 | 0.053 | 0.0029 | 0.30 | 0.0006 |

1. Introduction

It is suggested that only a part of total hydrogen is involved with delayed fracture (hydrogen embrittlement cracking) of high strength steels.\(^1\) It is very important to evaluate hydrogen content which affects delayed fracture characteristics substantially in order to clarify delayed fracture mechanism as well as to develop high delayed fracture resistant steels. There are many kinds of trap site such as grain boundary, dislocation and precipitates in steel. It has been reported that weakly trapped hydrogen has significant effect on delayed fracture property of steels.\(^2\) Thermal desorption analysis (TDA) is often utilized to know trapped state of hydrogen. This method is expected to have a possibility to separate and extract substantial hydrogen that affects delayed fracture.

Takai et al.\(^3\) have clarified that hydrogen desorption profiles taken from heavily drawn pearlitic steels showed apparently separated two peaks and high temperature peak did not have a significant effect on hydrogen embrittlement. They also have clarified that high temperature peak corresponded to desorption from cementite/ferrite interface or within ferrite between lamellar cementites. On the other hand, generally single desorption peak is observed in low or middle carbon tempered martensitic steels\(^4,5\) in which delayed fractures are often focused on practically. It has been often discussed the relationship between hydrogen content desorbed below around 300°C and delayed fracture property in tempered martensitic steels.\(^6,7\) However, it should be noticed that the peak consists of desorption from various sorts of trap site with different detrapping activation energy, even if it appears to be single peak. Especially in vanadium precipitated martensitic steels, a part of peak remains after leaving it at room temperature.\(^8\) This means hydrgens detrapped from multiple trap sites with different trap ability are included in single desorption peak. In this case, it is not always reasonable that whole single peak is regarded as hydrogen related to delayed fracture.

It has not been clearly understood yet whether hydrogen trapped by vanadium precipitates has significant effect on delayed fracture or not. One of the reasons why the problem remains unsolved is that hydrogen trapped by vanadium precipitates can not be estimated quantitatively so far. Therefore we have tried to evaluate hydrogen content trapped by vanadium precipitates using vanadium bearing martensitic steel which shows single desorption peak.

2. Experimental and Results

Chemical composition of an examined steel is shown in Table 1. To obtain steels with various precipitation states, several heat treatments were conducted as listed in Table 2. Steel A and B were quenched from 930°C, 1,050°C respectively and were not tempered, then microstructure of these
two steels was fresh martensite. Steel C and D were quenched and tempered to obtain tensile strength levels of 1500 MPa and 800 MPa respectively, and then microstructure of these two steels was tempered martentite. To evaluate an amount of vanadium precipitates in each steel, extracted residue analysis was performed. Residue was extracted by means of electrolytic method using 10% acetylacetone–1% tetramethylammonium chloride-methanol to obtain carbide, carbo-nitride and nitride all together. The amount of precipitated vanadium was then analyzed by ICP (Inductively Coupled Plasma). Residue was also extracted using 10% Bromo-methanol and analyzed in the same manner to obtain vanadium content precipitated as nitride.

Test specimens for TDA were machined from steel A, B, C and D with configuration of 5×5×50 mm. These specimens were immersed in 50°C, 20% NH₄SCN solution for hydrogen introducing before TDA. Employed immersing period was determined so as to make it possible to identify multiple desorption peaks in a profile, in spite that it would not be apparent like the profile taken from heavily drawn pearlitic steels. Figure 1 shows an effect of immersing period on TDA profile in steel D. Small desorption peaks of hydrogen are emerged at around 140°C and 200°C by 0.3 h immersing, while no hydrogen is detected in the temperature range below 300°C by 0.1 h immersing. Multiple desorption peaks or shoulders can be seen in case of immersing period from 0.3 h to 1 h. However, desorption peak of 140°C increases rapidly with immersing period and other peak and shoulders are merged into that peak by 20 h immersing. Therefore, 0.5 h was chosen as optimum immersing period as experimental condition. Then TDA was conducted from ambient temperature up to 630°C with heating rate of 200°C/h. Gas chromatography was used for hydrogen detection.

Figure 2 shows TDA profiles taken from the specimens immersed in 50°C, 20% NH₄SCN solution for 0.5 h. Basically, they show single desorption peak. Desorption peak is located around 100°C for steel A and B of quenched steels, while desorption peaks of 140°C are observed for steel C and D of quenched and tempered steels. Desorption peak of 200°C is also observed in steel C. In the case of steel D, shoulder can be seen at 200°C. Desorption peak of 140°C in steel D is much larger than that in steel C. Table 3 shows the results of extracted residue analysis. Vanadium precipitates including vanadium nitride are almost soluted in austenite at 1050°C, while they remains at 930°C as undissolved state. Tempering at 675°C brings

| Steel | Heat treatment | Microstructure |
|-------|----------------|----------------|
| A     | 930°Cx30min WQ | Martensite     |
| B     | 1050°Cx30min WQ| Martensite     |
| C     | 930°Cx30min WQ | Tempered martensite |
| D     | 930°Cx30min WQ | Tempered martensite |

![Fig. 1. The effect of immersing period on TDA profile in steel D.](image)

![Fig. 2. TDA profiles taken from the specimens.](image)
about enormous amount of vanadium precipitates, and almost all the precipitates are considered to be vanadium carbide, since nitrogen is not enough to form vanadium carbo-nitride. In the case of steel C and D, extracted vanadium precipitates include two kinds of vanadium precipitates, namely undissolved precipitates on reheating process (930°C for 30 min) and precipitated carbide on tempering process.

### 3. Decomposition of Experimentally Obtained Desorption Profiles Using Gaussian Function

Trapping effect by vanadium precipitates was reported to be very strong and could be irreversible trapping. Therefore, it will be possible to assume hydrogen detrapping process dominates hydrogen desorption kinetics. In this case, a theoretical formula proposed by W. Y. Choo et al. is often utilized to calculate detrapping activation energy. As described above, however, it is important to evaluate hydrogen content trapped by vanadium precipitates. We have tried to analyze it under the following assumptions.

#### Assumptions

1. Hydrogen detrapping process dominates hydrogen desorption kinetics. In other words, peak location is dominated by detrapping activation energy, although it would be shifted by trap density and specimen size as well actually.
2. Experimentally obtained hydrogen desorption profile could be decomposed to multiple desorption profiles with different peak temperature thus different detrapping activation energy.
3. Decomposed desorption profile related to each trapping site is approximated to Gaussian function to simplify the analysis and obtain decomposed hydrogen content easily. However it must be so far from the value obtained from theoretical function such as W. Y. Choo’s formula.

At first, experimentally obtained hydrogen desorption profile was fitted to the function (1) of which form is summation of Gaussian functions.

\[
F(x) = \sum_{i} a_i \cdot \exp(- (x - i)^2 / b_i^2) \quad \text{(1)}
\]

- \( F(x) \): Hydrogen desorption rate (wt ppm/min)
- \( x \): Variable (temperature; °C)
- \( i \): Peak locations; 100°, 140°, 200°C
- \( a_i \): Fitting parameter (peak height)
- \( b_i \): Fitting parameter (peak width)

Peak locations were determined as 100, 140 and 200°C from experimentally obtained desorption profiles in Fig. 2 at which desorption peaks or shoulders can be seen in common. Fitting parameters \( a_i \) and \( b_i \) correspond to peak height and width respectively, and \( b_i \) could be related to an extent of dispersion in detrapping activation energy. Figure 3 shows the results of Gaussian functions fitting analysis. Experimental profiles are well fitted to summation of multiple Gaussian functions and linear correlation coefficients are around 0.97 in all cases. Figure 4 shows an example that experimentally obtained hydrogen desorption profile is decomposed into two Gaussian functions.

Secondly, area surrounded by each Gaussian function

| Steel | Extracted by electrolytic method | Extracted by 10% Bromo-methanol |
|-------|---------------------------------|---------------------------------|
| A     | 0.054                           | 0.037                           |
| B     | 0.001                           | < 0.001                         |
| C     | 0.047                           | 0.017                           |
| D     | 0.292                           | 0.022                           |

Table 3. Results of extracted residue analysis.
was calculated by integrating the functions to obtain decomposed hydrogen contents. Figure 5 shows decomposed hydrogen contents of the specimens. Decomposed hydrogen contents with 100°C peak are around 0.3 wt ppm in steel A and 0.4 wt ppm in steel B. Decomposed hydrogen content with 140°C peak is around 0.16 wt ppm in steel A, while it decreases down to 0.05 wt ppm in steel B. Figure 5 shows a drastic increase up to 0.57 wt ppm in steel D tempered at 675°C, while it shows slightly increase up to 0.2 wt ppm in steel C tempered at 350°C. Decomposed hydrogen content with 200°C peak is found in steel C and D and it increases with tempering temperature.

4. Discussion

Both vanadium precipitates and cementite are regarded as candidates to cause 140°C and 200°C peaks, because the peaks are remarkably increased by tempering treatment. On the other hand, hydrogen content related to 100°C peak observed in steel A and B would be caused by detrapping from weak trap sites such as dislocation, grain boundary or other defects, which are not the category we aimed at in this study. 140°C peak should not be caused by cementite, since it is observed in steel A and B, as quenched steels. And also, it has been reported that 140°C and 200°C peak were not observed in vanadium free tempered martensitic steel (Fig. 6). Therefore 140°C and 200°C peak should be caused by vanadium precipitates. Figure 7 shows the relationship between decomposed hydrogen content with 140°C peak and the amount of extracted vanadium precipitates. Decomposed hydrogen content with 140°C peak was in good proportion to an amount of vanadium precipitates existing in martensite, even though it includes both undisolved precipitates on reheating process and precipitated carbide on tempering process. This suggests that decomposed hydrogen content with 140°C peak is caused by vanadium precipitates with a size of 100 nm order. However, it should be noticed that ultra fine precipitates can not be extracted by the method adopted in this study. Recently, Hara et al. have reported that ultra fine vanadium precipitates with a thickness of 1 nm formed through tempering at 650°C caused characteristic hydrogen desorption behavior in vanadium bearing martensitic steels. It is probable that decomposed hydrogen content with 200°C peak would be caused by these ultra fine vanadium precipitates. Since ultra fine vanadium precipitates has coherency with matrix, it is natural that detrapping activation energy is different from that of vanadium precipitates with much larger size. Finally, we obtained Fig. 8 from above analysis, which shows desorped hydrogen content and decomposed hydrogen content trapped by vanadium precipitates. It was revealed that, most of hydrogen (more than 90%) in vanadium bearing tempered martensitic steels such as steel C and D are trapped by vanadium precipitates.
5. Conclusions

Hydrogen content trapped by vanadium precipitates was evaluated using vanadium bearing martensitic steel which shows single desorption peak. Obtained results are summarized as follows.

1) Hydrogen desorption peak was located around 100°C for as quenched steels, while desorption peaks of 140°C were observed for quenched and tempered steels.

2) Experimentally obtained single desorption profile taken from vanadium bearing martensitic steels was decomposed to multiple profiles with different peak temperature.

3) It was revealed that decomposed hydrogen content with 140°C peak was in good proportion to an amount of vanadium precipitates, thus the 140°C peak is caused by vanadium precipitates trapping.

4) Most of hydrogen in vanadium bearing tempered martensitic steel are trapped by vanadium precipitates.

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