Comparison of hydrogen behavior trapped at precipitated and undissolved vanadium carbide in vanadium-bearing high strength steels

K. HOKAZONO1(a), M. KAWAMORI2, Y. MATSUMOTO3, K. TAKAI4(b)

1Graduate Student, Sophia University, 7-1 Kioi-cho Chiyoda-ku Tokyo 102-8554
2Materials Research Lab., Kobe Steel, Ltd.
3Research and Development Lab., Kobe Steel, Ltd.
4Department of Engineering and Applied Sciences, Faculty of Science and Technology, Sophia University.
Email: a)hokakoda.7.15@gmail.com, b)takai-k@sophia.ac.jp

Abstract. Vanadium carbide (VC) in high strength steels is divided into two types, i.e., finely formed precipitated VC and coarsely formed undissolved VC. The behavior of hydrogen trapped at the two types has been investigated using thermal desorption analysis (TDA). Specimens containing different amounts of V (0, 0.10 and 0.15 %) were prepared. Specimens with 0 % V (QT) and 0.10 % V (QT) were quenched at 900 °C and tempered at 600 °C. Some specimens with 0.15 % V were quenched at 900 °C and are denoted here as 0.15 % V (Q). Hydrogen was charged into specimens by immersion in a NH4SCN aqueous solution and analyzed by TDA. The end temperatures of hydrogen release for 0 % V (QT) and 0.15 % V (Q) specimens were in a range from 76 to 79 °C, and that of the 0.10 % V (QT) specimen was 104 °C. The amounts of hydrogen were 0.10 ppm in the 0 % V (QT) specimen, 0.28 ppm in the 0.15 % V (Q) specimen and 0.54 ppm in the 0.10 % V (QT) specimen. The specimens containing precipitated VC had a higher end temperature of hydrogen release and larger amounts of hydrogen than those containing undissolved VC and matrix. These findings suggest that precipitated VC in high strength steels has a higher hydrogen trapping capacity than undissolved VC.

1 Introduction
Bolts and other structural members made of high strength steels have been widely used in recent years. Hydrogen embrittlement, whereby materials suddenly break down due to the incursion of hydrogen, has thus become a serious problem. In this regard, the hydrogen trapping effects of alloy carbides (V, Ti and Nb) have been noted for developing high strength steels with excellent resistance to hydrogen embrittlement [1]. The behavior of hydrogen trapped at vanadium carbide (VC) has been actively investigated in recent years in connection with the use of the hydrogen trapping effects of VC as a technique for suppressing hydrogen embrittlement. For example, Asahi et al. reported that the activation energy of hydrogen desorption from trapping sites in 0.3 and 0.10 % V-bearing steels under various heat treatment conditions was calculated to be 35.3 and 32.6 kJ·mol⁻¹. These values indicated there was no appreciable change in activation energy in those steels due to the amounts of V and the tempering temperature [2]. Tsuchida et al. reported that V-bearing high strength steels tempered at 600 °C showed TDA profiles having a hydrogen desorption temperature peak at 200 °C due to hydrogen trapping sites at precipitated (V, Mo) C. In addition, V-bearing high strength steels tempered at 700 °C showed a TDA profile having two hydrogen desorption temperature peaks at 100 °C and 260 °C. The temperature peak
at 260 °C was due to hydrogen trapping sites at undissolved (V, Mo) C. These TDA profiles suggest that undissolved (V, Mo) C has a higher hydrogen trapping capacity than precipitated (V, Mo) C [3]. However, these findings have still not provided a fundamental understanding. Accordingly, the behavior of hydrogen trapped at precipitated and undissolved VC was investigated by TDA for high strength steels containing various amounts of V.

2 Experimental

2.1 Materials

The chemical composition of the steels used is listed in Table 1. Three types of high strength steels specimens with various amounts of V were prepared. The amounts of V associated with precipitated and undissolved VC in the γ phase as a function of the various amounts of V in specimens quenched at 900 °C was calculated by Thermo-Calc and the results are shown in Table 2. 0.10 mass % V associated with precipitated VC was present in the 0.10 % V specimen because 0.10 % V completely dissolved when quenched at 900 °C. On the other hand, 0.15 % V did not completely dissolve when quenched at 900 °C. Therefore, 0.122 mass % V associated with precipitated VC and 0.028 mass % V associated with undissolved VC were present in the specimens.

| Steel types | Amounts of V (mass %) | Amounts of V associated with precipitated VC (mass %) | Amounts of V associated with undissolved VC (mass %) |
|-------------|-----------------------|-----------------------------------------------------|-----------------------------------------------------|
| 0 % V       | 0.000                 | 0.000                                               | 0.000                                               |
| 0.10 % V    | 0.100                 | 0.100                                               | 0.000                                               |
| 0.15 % V    | 0.150                 | 0.122                                               | 0.028                                               |

Table 1 Chemical composition of specimens (mass %).

| C | Si | Mn | P | S | Cr | Mo | V |
|---|----|----|---|---|----|----|---|
| 0 % V | 0.39 | 0.15 | 0.70 | 0.011 | 0.010 | 0.97 | 0.21 | 0.001 |
| 0.10 % V | 0.39 | 0.15 | 0.71 | 0.009 | 0.013 | 0.96 | 0.20 | 0.10 |
| 0.15 % V | 0.40 | 0.15 | 0.71 | 0.010 | 0.014 | 0.97 | 0.20 | 0.153 |
2.2 Material characterization
The microstructure of the V-bearing high strength steels was examined by means of transmission electron microscopy (TEM). The chemical composition of precipitates observed by TEM was determined using energy dispersive X-ray analysis (EDX).

2.3 Hydrogen trapping state analysis
Figure 1 shows the procedure for the hydrogen trapping state analysis. Specimens containing 0% V, 0.10% V and 0.15% V were quenched at 900 °C and tempered at 600 °C and are denoted here as 0% V (QT), 0.10% V (QT) and 0.15% V (QT). Some specimens containing 0.15% V were quenched at 900 °C and are denoted here as 0.15% V (Q). Specimens were machined to 10 mm in diameter and 0.3, 0.5 and 1.0 mm in thickness. Specimens were polished with emery paper (#2000) and hydrogen was charged into the specimens by immersion in 1 or 5 mass% NH₄SCN aqueous solution at 30 °C for 24 h until hydrogen reached equilibrium at the center of the specimens. After that, the specimens were analyzed by TDA at a heating rate of 100 °C · h⁻¹.

3 Results and discussions

3.1 Material characterization
TEM and EDX images of the 0.15% V (Q) specimen quenched at 900 °C are shown in Fig 2. Coarse spherical precipitates of approximately 50 nm in diameter were observed by TEM. Element analysis by EDX was performed on coarse spherical precipitates indicated by an arrow in Fig 2(a). Coarse spherical precipitates were VC because they were found to consist of much larger quantities of V and C than other elements. As a result, the coarse spherical precipitates were regarded as undissolved VC in the 0.15% V (Q) specimen. A TEM observation was attempted for precipitated VC obtained by quenching and tempering. Precipitated VC consisted of very fine precipitates that could not be observed.

3.2 Thickness dependence of TDA profiles
Figure 3 shows the TDA profiles of 0.15% V (QT) specimens having various thicknesses in case of charging hydrogen into those specimens by immersion in 1 mass% NH₄SCN aqueous solution. The TDA profiles indicate that the end temperatures of hydrogen release decreased with decreasing specimen thickness. It is assumed that the TDA profiles indicate a transition from hydrogen diffusion-controlled to hydrogen desorption-controlled due to decreasing specimen thickness. According to a previous study, the specimen thickness that determined the hydrogen desorption peak temperature due to hydrogen-desorption control at hydrogen trapping sites was 0.3 mm [4]. Thus, we decided to compare the hydrogen trapping behavior in V-bearing high strength steels for specimens of 0.3 mm in thickness.
3.3 Comparison of behavior of hydrogen trapped at precipitated and undissolved VC in TDA profiles

Figure 4 shows the TDA profile of 0 % V (QT) specimen containing no VC, fig 5 shows the TDA profile of the 0.15 % V (Q) specimen containing undissolved VC and fig 6 shows the TDA profile of the 0.10 % V (QT) specimen containing precipitated VC. The TDA profiles in figs 3-5 are the results for specimens of 0.3 mm thickness charged with hydrogen by immersion in a 5 mass % NH₄SCN aqueous solution. The results in these figs showed that the end temperatures of hydrogen release of the 0 % V (QT) and 0.15 % V(Q) specimens were in a range from 76 to 79 °C, and that the end temperature of hydrogen release of the 0.10 % V (QT) specimen was 104 °C. The amounts of hydrogen were 0.10 ppm in the 0 % V (QT) specimen, 0.28 ppm in the 0.15 % V (Q) specimen and 0.54 ppm in the 0.10 % V (QT) specimen. The specimens containing precipitated VC had higher end temperatures of hydrogen release and larger amounts of hydrogen than the specimens containing undissolved VC and matrix. These findings suggest that precipitated VC in high strength steels has a higher hydrogen trapping capacity than undissolved VC.
Conclusions
The behavior of hydrogen trapped at precipitated and undissolved VC was compared for V-bearing high strength steels in the present study. The results obtained are summarized as follows.

(1) In the TDA profiles, the end temperatures of hydrogen release decreased with decreasing specimen thickness. Thus, this result suggested a transition from hydrogen diffusion-controlled to hydrogen desorption-controlled due to decreasing specimen thickness.

(2) When hydrogen was charged into specimens by immersion in a 5 mass % NH$_4$SCN aqueous solution, TDA profiles showed the end temperatures of hydrogen release of 0 % V (QT) and 0.15 % V (Q) specimens were in a range from 76 to 79 °C, and that the end temperature of hydrogen release for 0.10 % V (QT) specimen was 104 °C. The amounts of hydrogen were 0.10 ppm in the 0 % V (QT) specimen, 0.28 ppm in the 0.15 % V(Q) specimen and 0.54 ppm in the 0.10 % V (QT) specimen. In comparison of the behavior of hydrogen trapped at finely formed precipitated VC and coarsely formed undissolved VC in V-bearing high strength steels, the results suggested that precipitated VC in high strength steels had the higher trapping capacity than undissolved VC.

References
[1] T. Omura, T. Kushida, K. Miyata, and Y. Komizo, “Hydrogen absorption of high Nb bearing Steel”, Tetsu-to-Hagane, 90, No. 2 (2004), 106-112.
[2] H. Asahi, D. Hirakami and S. Yamasaki “Hydrogen trapping behavior in vanadium-added Steel”, ISIJ International 43, No. 4 (2003), 527-533.
[3] T. Tsuchida, T. Hara and K. Tsuzaki, “Relationship between microstructure and hydrogen absorption behavior in a V-bearing high strength steel”, Tetsu-to-Hagane, 88, No. 11 (2002), 771-778.
[4] K. Saito, H. Suzuki and K. Takai: CAMP-ISIJ, 27 (2014), 955, CD-ROM.