Dependence of trapping states on the hydrogen content of high-carbon ferrite-austenite dual-phase steel

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Abstract States of hydrogen present in high carbon ferrite (α)-austenite (γ) dual phase steel were analyzed under various hydrogen charging conditions using thermal desorption analysis (TDA). Specimens including 0% γ and 10% γ in α were prepared. The 10%γ specimen consisted of bainitic ferrite and thermally stable retained austenite. When the 10%γ specimen were charged with hydrogen under high fugacity condition, the amount of hydrogen rapidly increased, the end temperature of hydrogen desorption in TDA profile increased, the hydrogen degassing time at 30 °C increased, and the trap activation energy increased from about 30 kJ/mol to 47 kJ/mol. This 47 kJ/mol value is in excellent agree with the activation energy of hydrogen diffusion in γ phase. These results probably indicated that hydrogen is not absorbed in γ phase but α phase under lower fugacity conditions, i.e., lower amount of hydrogen. In contrast, hydrogen is absorbed in not only α phase but also γ phase under higher fugacity conditions, i.e., higher amount of hydrogen.

1 Introduction

High carbon ferrite-austenite dual-phase (α/γ) steel is a high strength steel with a tensile strength of about 1540 MPa class and excellent ductility, so it has been used for automobile parts. For weight reduction in automobiles, high strength of α/γ steels have been developed. However, since high-strength steels are susceptible to hydrogen embrittlement, it is necessary to understand hydrogen embrittlement in high carbon α/γ dual-phase steel.

There are many reports on hydrogen embrittlement of materials containing retained γ. For example, it was reported that the diffusion rate of hydrogen inside the retained γ phase is slow¹) and that the phase transformation of retained γ due to heat or hydrogen charging affects hydrogen embrittlement susceptibility²). However, few studies have focused on the trapping states of hydrogen. In this study, we aimed to explicate the role of retained γ in hydrogen embrittlement through evaluating the trapping states of hydrogen present in high carbon α/γ dual-phase steel containing 10% retained γ.

2 Experimental

2.1 Materials

As a high-carbon α/γ dual-phase steel, 10% γ specimens containing 10 vol % thermally stable retained γ in the α phase were prepared. Japanese Industrial Standards (JIS) SCM 435 with no retained austenite (0% γ specimens) was used as a comparative material. The chemical components of the
specimens are shown in Table 1. Tensile strength was about 1540 MPa and about 1300 MPa, respectively. In the hydrogen analysis, flat test pieces of 10 x 10 x 0.2 mm, 10 x 20 x 0.5 mm, and 10 x 20 x 1.0 mm were used. Figure 1 shows a phase map of the 10% γ material obtained by electron back-scattered diffraction (EBSD). Red indicates the α phase and green the retained γ phase. The matrix of 10% γ specimens is composed of bainitic ferrite, ferrite, pearlite which are bcc structure. In this study, the 0% γ specimens using the high carbon model steel rather than the practical steel has a tempered martensite single-phase structure.

2.2 Hydrogen charging

To investigate the trapping states of hydrogen at various hydrogen content, hydrogen charging was carried out under five conditions using a cathodic electrolysis method. The conditions were (i) a current density of 50 A·m⁻² in a 0.1 N NaOH aqueous solution, (ii) a current density of 100 A·m⁻² in a 0.1 N NaOH aqueous solution, (iii) a current density of 100 A·m⁻² in a 2.5 g·L⁻¹ NH₄SCN + 0.1 N NaOH aqueous solution, (iv) a current density of 100 A·m⁻² in a 5 g·L⁻¹ NH₄SCN + 0.1 N NaOH aqueous solution, and (v) a current density of 100 A·m⁻² in a 7.5 g·L⁻¹ NH₄SCN + 0.1 N NaOH aqueous solution. Hydrogen charging time was respectively (i) 48 h, (ii) 48 h, (iii) 96 h, (iv) 120 h, and (v) 96 h. Hydrogen charging was conducted until the hydrogen concentration at the surface and the center of the specimens became constant and reached an equilibrium state.

X-ray diffraction (XRD) was conducted to measure the change in retained γ content in the 10% γ specimens during hydrogen charging and heating. Hydrogen charging was carried out under the condition of (iv). Heating was carried out at 100 °C, 200 °C and 300 °C.

2.3 Hydrogen analysis and evaluation of activation energy

The thermal desorption method is a method of measuring the desorption rate of atoms and molecules desorbed by heating a sample that adsorbed or occluded atoms or molecules, and analyzing the adsorption and occlusion states. In this study, thermal desorption analysis (TDA) was conducted at a heating rate of 100 °C·h⁻¹.

The activation energy was calculated to evaluate the dominant factor of hydrogen traps. Hydrogen charging was conducted for the 10% γ specimens under conditions (i) to (iv). TDA was conducted at a heating rate of 50-200 °C·h⁻¹. Based on the peak temperature of the profile obtained, activation energy values were calculated under the various conditions using the equation proposed by Choo and Lee.³

| Table 1 Chemical composition of 0% γ and 10% γ steel (mass %). |
|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | S | Al | Cr | Mo |
| γ 0% | 0.35 | 0.24 | 0.79 | | | | 1.09 | 0.15 |
| γ 10% | 0.79 | 2.42 | 0.51 | 0.008 | 0.002 | 0.036 | | |

Fig. 1 Phase map of specimen obtained by EBSD: red represents α and green represents retained γ. (Online version in color.)
2.4 Effect of retention time after hydrogen charging

The effect of the retention time after hydrogen charging on the TDA profile was investigated to evaluate the trapping states of hydrogen present in retained γ utilizing low hydrogen diffusivity of retained γ. Hydrogen charging was conducted using 0% and 10% γ specimens under the conditions of (ii) and (iv). After degassing the specimens for 0 to 48 h in an environment of 30 °C, TDA was conducted at 100 °C/h.

3 Results and Discussion

3.1 Role of retained austenite in trapping states of hydrogen present in α/γ dual-phase steel

Figure 2 shows the change in retained γ content in the 10% γ specimens during hydrogen charging and heating. The results showed that there was no change in the retained γ content in the 10% γ specimens after hydrogen charging and heating.

Figure 3 shows the change in the hydrogen content of the 0% γ and 10% γ specimens charged with hydrogen under the conditions of (iv) described in section 2.2. It took more time for the hydrogen content to reach the equilibrium state for the 10% γ specimens than for the 0% γ specimens, and the hydrogen content of the former was larger than that of the latter.

Figure 4 shows the TDA profile of the 10% γ specimens with the different thicknesses and hydrogen-charged under the conditions of (iv) described in section 2.2. The result shows that the peak temperature and the release end temperature shifted to a lower temperature as the specimen thickness became thinner. Therefore, the influence of retained γ on the trapping states of hydrogen was found to be an increase in the hydrogen content and a decrease in the hydrogen diffusion rate. The result in Fig 4 also indicates that the hydrogen present in retained γ was not non-diffusible because the peak of non-diffusible hydrogen was not retained at high temperature side as the specimen thickness became thinner.

\[ \text{Contents of retained austenite } V_\gamma (\%) \]

![Fig. 2 Contents of retained austenite in 10%γ specimens (a)heated and (b)hydrogen charged at 100 A·m⁻² in 0.1N NaOH solution adding 5 g·L⁻¹ NH₄SCN analyzed by XRD.}

\[ \text{Hydrogen content, } C \text{ (mass ppm)} \]

![Fig. 3 Hydrogen absorption behavior of (a)[0%γ] and (b)[10%γ] specimens hydrogen charged at 100 A·m⁻² in 0.1N NaOH solution adding 5 g·L⁻¹ NH₄SCN.}
3.2 Hydrogen penetration into retained γ in high carbon α/γ dual-phase steel

Figure 5 shows the TDA profiles of the 0% γ and 10% γ specimens charged with hydrogen under the conditions of ( i), ( ii), ( iv) and ( v) described in section 2.2. In the 0% γ specimens, there was no change in either the peak temperature or the release end temperature for the different hydrogen charging conditions. On the other hand, both the peak temperature and the release end temperature of the 10% γ specimens shifted to a higher temperature, and the hydrogen occlusion amount sharply increased. These results suggest that the trapping states of hydrogen changed in the high carbon α/γ dual-phase steel as the hydrogen content increased.

Figure 6 shows the relationship between the hydrogen content and the activation energy of the 10% γ specimens charged with hydrogen under the conditions of ( i) to ( iv) described in section 2.2. The activation energy values of the 10% γ specimens were about 30 kJ / mol when the hydrogen content was 2.5 ppm or less and about 47 kJ / mol when it was 7.7 ppm. The value of the activation energy at high hydrogen content corresponds to the activation energy of diffusion in the γ phase. Accordingly, it is suggested that the low hydrogen diffusion of retained γ under the conditions of ( iv) was the rate-controlling for hydrogen desorption of the 10% γ specimens. That is, it indicates that hydrogen entered retained γ under the condition of a high hydrogen content of 7.7 ppm.

Fig. 4 TDA profiles of 10% γ specimens hydrogen charged at 100 A·m⁻² in 0.1N NaOH solution with 5.0 g·L⁻¹ NH₄SCN and having a thickness of (●) 1.0 mm, (■) 0.5 mm, and (▲) 0.2 mm.

Fig. 5 TDA profiles of (a) 0% γ and (b) 10% γ specimens hydrogen charged at 100 A·m⁻² in 0.1N NaOH solution with (●) 7.5 g·L⁻¹ NH₄SCN, (■) 5.0 g·L⁻¹ NH₄SCN, (▲) 0 g·L⁻¹ NH₄SCN and (○) 50 A·m⁻² in 0.1N NaOH solution with 0 g·L⁻¹ NH₄SCN having a thickness of 1.0 mm.
Subsequently, the test results of hydrogen desorption behavior from the 0%γ and 10%γ specimens in an atmospheric environment at 30°C are shown in Fig 7 (a) and (b). Hydrogen charging was conducted under the conditions of ( ii) described in section 2.2. Hydrogen desorption time was consistent for both specimens. These results indicate that most of the hydrogen in the high carbon α/γ dual phase steel was trapped in the α phase under the condition of a low hydrogen content.

Figure 7 (b) and (c) shows the results of hydrogen desorption behavior from the 10%γ specimens in an atmospheric environment at 30°C charged hydrogen under the conditions of ( ii) and ( iv) described in section 2.2. In the 10% γ specimens, hydrogen penetration into retained γ occurred as the hydrogen content increased and it was found that a long desorption time was required.

**Fig. 6** Activation energy of hydrogen desorption as a function of the hydrogen content of 10%γ specimens.

**Fig. 7** TDA profiles of (a) 0%γ and (b) 10%γ specimens hydrogen charged at 100 A·m⁻² in 0.1N NaOH solution and 10%γ specimens hydrogen charged at 100 A·m⁻² in 0.1N NaOH solution adding (c) 5.0 g·L⁻¹ NH₄SCN and degassed at 30°C for 0 h(●), 24 h(■), 48 h(▲) having a thickness of 1.0 mm.
4 Conclusion

The hydrogen content in high carbon α/γ dual-phase steel was investigated by thermal desorption analysis (TDA), and the following findings were obtained.

(1) Hydrogen content in the 10% γ specimens having retained γ was larger than that in the 0% γ specimens, and a long desorption time was required. This indicates that retained γ had the effect of increasing the hydrogen content and delaying hydrogen diffusion.

(2) Under both low and high hydrogen content conditions, no change occurred in either the peak temperature or the release end temperature of the TDA profile of the 0% γ specimens. In contrast, both the peak temperature and the release end temperature of the 10% γ specimens shifted to a higher temperature. In addition, the activation energy was about 30 kJ/mol when the hydrogen content was 2.5 ppm or less and about 47 kJ/mol when it was 7.7 ppm. This implies that in high carbon α/γ dual-phase steel, hydrogen penetration into retained γ occurs only under a high hydrogen content.

(3) As the thickness of the specimens became thinner, the TDA profile of the 10% γ specimens moved to a lower temperature. This result suggests that hydrogen desorption of the 10% γ specimens was rate-limited by low hydrogen diffusion under a high hydrogen content.

(4) Hydrogen charging was carried out on 0% and 10% γ specimens under the conditions of (ii) (a current density of 100 A m$^{-2}$ in a 0.1 N NaOH aqueous solution) and degassed at 30 °C. As a result, both specimens completely released hydrogen at 24 h. Therefore, the bcc phase was the rate controlling for hydrogen desorption of the 10% γ specimens at low hydrogen content.

References

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