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Report of Hydrogen Analysis (Measurement of Binding Energy)

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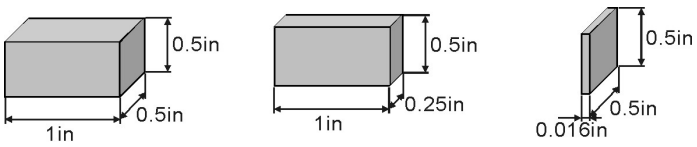
1. Experimental methods

Hydrogen analysis of hydrogen-charged and uncharged samples was carried out by a quadruple mass spectrometer type thermal desorption spectrometer (TDS) and a gas chromatograph type thermal desorption spectrometer (TDA). The samples (AISI 4340) were sent from Lawrence Berkeley National Laboratory. The measurements were carried out up to 600 °C. The heating rates in TDS measurements were 0.028 °C/s (100 °C/h), 0.17 °C/s (10 °C/min), 1 °C/s, and 2 °C/s. The samples are heated by radiating infrared ray to them in the TDS measurements. Due to the heating method, the controlled temperature is not completely equal to the sample temperature. The heating rates in TDA measurements were 0.014 °C/s (50 °C/h), 0.028 °C/s (100 °C/h), and 0.056 °C/s (200 °C/h).

Hydrogen was charged into the samples by the exposure to 97 MPa hydrogen gas at 85 °C for 210 h. After hydrogen-charging, the samples were kept in liquid nitrogen until measurements to avoid hydrogen release from the samples.

Figure 1 shows the dimensions of the samples. Three Type A samples (total weight: ≈ 63 g) and three Type B samples (total weight: ≈ 47 g) were used for the TDA measurement. A Type C sample (weight: 0.3 ~ 0.7 g) was used for the TDS measurement. Hydrogen was charged into the Type A and B samples. After hydrogen-charging, Type C samples were cut from the hydrogen-charged Type A sample under water cooling for the TDS measurements.



(a) Sample A (b) Sample B (c) Sample C

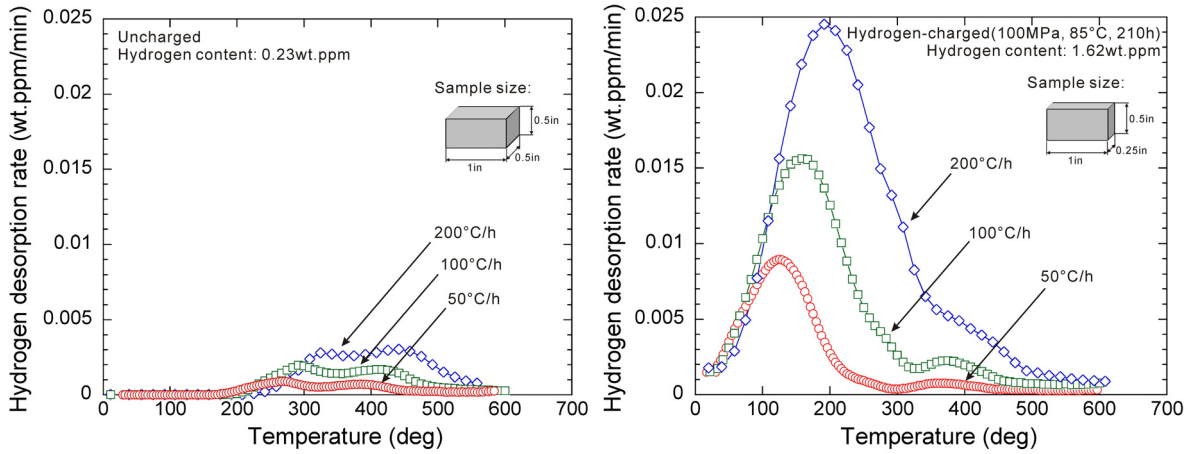
Figure 1 Samples for hydrogen analysis.

2. Results and discussion

Figure 2 shows hydrogen desorption spectrums of hydrogen-charged and uncharged samples, which were obtained by TDA. Figure 3 shows hydrogen desorption spectrums of hydrogen-charged and

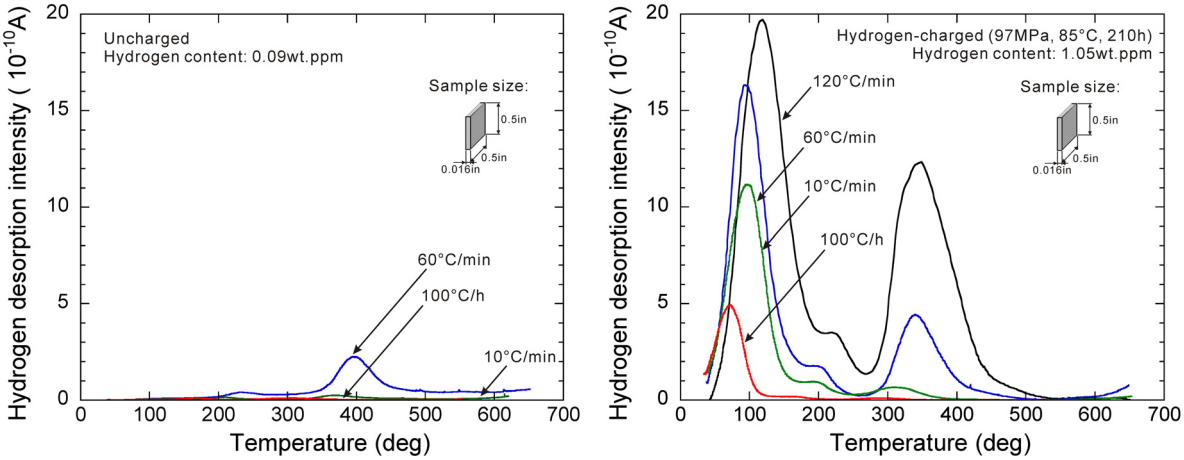
uncharged samples, which were obtained by TDS. The hydrogen content of the uncharged sample was 0.23 wt.ppm in TDA measurement. The hydrogen content of the hydrogen-charged sample was 1.62 wt.ppm in TDA measurement. On the other hand, the hydrogen content was 0.09 wt.ppm for the uncharged sample and 1.05 wt.ppm for hydrogen-charged sample in TDS measurement. The smaller hydrogen content in TDS measurement is presumed to be caused by cutting a thin sample from an original sample.

Three hydrogen desorption peaks were detected from the hydrogen desorption spectrums. We call the peaks with number orders, from the lowest temperature. The first peak was not detected in the spectrum of the uncharged sample. The amount of hydrogen desorption in the 1st peak was increased by hydrogen-charging. On the other hand, the increase in the amount of hydrogen desorption in the 2nd and 3rd peaks by hydrogen-charging was small.



(a) Uncharged sample (b) Hydrogen-charged sample

Figure 2 Hydrogen desorption spectrums by TDA.



(a) Uncharged sample (b) Hydrogen-charged sample

Figure 3 Hydrogen desorption spectrums by TDS.

The relationship among the peak temperature T_c in hydrogen desorption spectrums, the heating rate α and the binding energy E of a trap site was described as follow [1].

$$\frac{E\alpha}{RT_c^2} = Ae^{-E/RT_c} \quad (1)$$

where R denotes the gas constant (8.314 J/(mol·K)) and A is constant. Taking logarithm of Eq. (1) and differentiating with respect to $(1/T_c)$ yields

$$\frac{\partial \ln(\alpha / T_c^2)}{\partial(1/T_c)} = -\frac{E}{R} \quad (2)$$

The binding energy E of a trap site can be easily calculated from the slope of a $\ln(\alpha/T_c^2)$ vs $(1/T_c)$ plot. Table 1 and 2 show the data for binding energy calculation (the peak temperature T_c in hydrogen desorption spectrums, heating rate α, etc.).

Table 1 Peak temperature in hydrogen desorption spectrums by TDA.

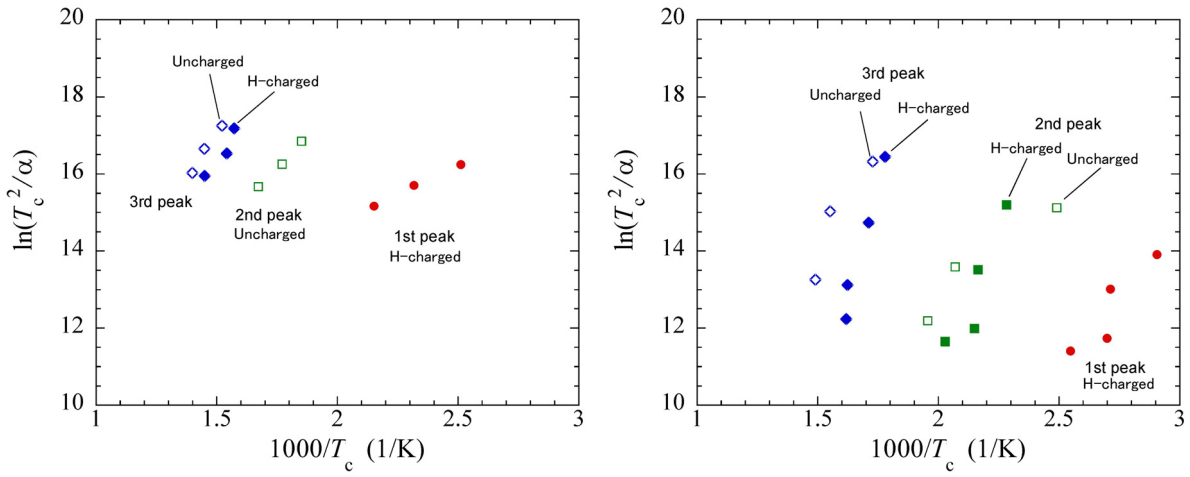
	Peak	Heating rate α (K/s)	Peak temperature Tc (K)	1000/Tc	$\ln(Tc^2/\alpha)$
Hydrogen-charged	1st	0.056	464.85	2.151	15.17
		0.028	431.65	2.317	15.71
		0.014	398.15	2.512	16.24
	2nd	—	—	—	—
		—	—	—	—
		—	—	—	—
	3rd	0.056	689.15	1.451	15.95
		0.028	648.55	1.542	16.53
		0.014	635.85	1.573	17.18
Uncharged	1st	—	—	—	—
		—	—	—	—
		—	—	—	—
	2nd	0.056	598.15	1.672	15.67
		0.028	564.75	1.771	16.25
		0.014	540.15	1.851	16.85
	3rd	0.056	715.15	1.398	16.03
		0.028	689.95	1.449	16.65
		0.014	657.15	1.522	17.24

Table 2 Peak temperature in hydrogen desorption spectrums by TDS.

	Peak	Heating rate α (K/s)	Peak temperature Tc (K)	1000/Tc	$\ln(Tc^2/\alpha)$
Hydrogen-charged	1st	1.71	392.65	2.547	11.41
		1.1	370.65	2.698	11.74
		0.305	368.65	2.713	13.01
		0.108	344.15	2.906	13.91
	2nd	2.12	493.15	2.028	11.65
		1.35	465.65	2.148	11.99
		0.287	462.15	2.164	13.52
		0.048	438.15	2.282	15.20
	3rd	1.86	617.65	1.619	12.23
		0.76	615.65	1.624	13.12
		0.137	584.15	1.712	14.73
		0.0228	562.15	1.779	16.44
Uncharged	1st	—	—	—	—
		—	—	—	—
		—	—	—	—
	2nd	1.33	511.15	1.956	12.19
		0.293	483.15	2.070	13.59
		0.0438	401.65	2.490	15.12
	3rd	0.787	671.15	1.490	13.26
		0.123	644.15	1.552	15.03
		0.0273	578.65	1.728	16.32

Figure 4(a) shows $\ln(\alpha/T_c^2)$ vs $(1/T_c)$ plot of the TDA data. Table 3 shows the binding energies calculated from the TDA data in Table 1. The binding energy of 3rd peak of hydrogen-charged sample is approximately equal to that of uncharged sample. This result indicates that the binding energy of the trap site is not influenced by the hydrogen-charging by the exposure to 97 MPa hydrogen gas at 85 °C.

Figure 4(b) shows $\ln(\alpha/T_c^2)$ vs $(1/T_c)$ plot of the TDS data. Table 4 shows the binding energies calculated from the TDS data in Table 2. The values of the binding energies calculated from the TDS data are much higher than those calculated from the TDA data. Besides, the binding energy of hydrogen-charged sample is not as same as that of the uncharged sample. Table 5 shows the binding energies calculated from the TDS data with no distinction between the hydrogen-charged samples and the uncharged samples, because the binding energy of the trap site is not influenced by the hydrogen-charging. The values of the binding energies calculated from the TDS data is almost equal to those calculated from the TDA data.



(a) TDA (b)TDS

Figure 4 $\ln(\alpha/T_c^2)$ vs $(1/T_c)$ plot

Table 3 Binding energies calculated from the TDA data.

	Peak	Binding energy (kJ/mol)
Hydrogen-charged	1st	24.8
	2nd	—
	3rd	76.6
Uncharged	1st	—
	2nd	54.5
	3rd	81.1

Table 4 Binding energy calculated from the TDS data.

	Peak	Binding energy (kJ/mol)
Hydrogen-charged	1st	59.3
	2nd	119
	3rd	199
Uncharged	1st	—
	2nd	41.5
	3rd	96.9

Table 5 Binding energies calculated from the TDS data with no distinction between the hydrogen-charged samples and the uncharged samples.

Peak	Binding energy (kJ/mol)
1st	—
2nd	55.2
3rd	86.7

Hydrogen desorption spectrums are influenced by following factors.

1. Diffusion rate
2. Shape and dimension of sample
3. Surface condition of sample
4. Trap sites included in material
5. Heating rate
6. The amount of hydrogen content of sample

In TDS measurements, sample thickness d is about 0.016 in. The hydrogen diffusion coefficient at room temperature of the material is guesstimated at ~ 10^{-10} m^2/s [2] because the crystal structure of the material is bcc. Considering the dimension of the sample and the diffusion coefficient of the material under TDS measurement, the factor 1 and 2 cannot significantly affect hydrogen desorption spectrums. On the other hand, the effect of deformation in the surface layer and the surface condition of the samples on hydrogen desorption spectrums is considered not to be neglect because the sample thickness for the TDS is small. As the result, the peak temperature varies widely in hydrogen desorption spectrums obtained by TDS. Therefore, in case of the calculation based on TDS data with no distinction between the hydrogen-charged samples and the uncharged samples, the value of the binding energy is close to those by TDA.

3. Conclusions

The binding energies of the material (AISI 4340) were calculated from the data obtained by thermal desorption spectrometry. The values of the binding energy are 25 kJ/mol, 55 kJ/mol and 79 kJ/mol.

Reference

[1] W Y Choo and J Y Lee, Thermal Analysis of Trapped Hydrogen in Pure Iron, *Metal. Trans. A*, vol. 13 (1982), pp. 135-140.

[2] K Yamakawa *et al*., Hydrogen Absorbability of SCM Steels and Its Effect on Cracking Behavior, *J. Soc. Mater. Sci., Japan*, vol. 29 (1980), pp. 1101-1107.