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Nature of hydrogen trapping sites in steels induced by plastic deformation

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Abstract

Thermal desorption spectroscopy (TDS) has been used to reveal the nature of defects acting as trapping sites of hydrogen. Hydrogen was charged to ferritic and eutectoid steels deformed to various degrees and then given annealing treatment. Desorption with a single peak appeared between room temperature and 600 K from ferritic steels. Under constant hydrogen charging conditions, the amount of desorption increased with strain. However, when the deformed samples were subjected to annealing at temperatures as low as 500 K, the increase of desorbed hydrogen no longer appeared. Vacancy clusters, which themselves annihilate in the course of TDS measurement, are the probable source of hydrogen desorption. When heavy deformation was given to ferritic steels, a two-step decrease of hydrogen desorption took place with increasing annealing temperature, corresponding to annihilation of vacancy clusters and decrease of dislocation density, respectively. The desorption with a single peak has two origins, one due to the annihilation of the trapping sites themselves and the other to desorption from stable sites. For heavily deformed eutectoid steel, an additional desorption peak centered at around 640 K appeared. The peak likely results from deformation-induced defects within the cementite phase or supersaturated carbon in ferrite. Two types of desorption, one due to the annihilation of trapping sites in the course of measurement and the other due to desorption from stable sites, should be discriminated. TDS using hydrogen as a tracer can be applied as a tool to investigate the various defects induced by plastic deformation. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Hydrogen thermal desorption spectroscopy (TDS), initially developed in a study of dangling bond termination by hydrogen on semiconductor surfaces [1], has been applied for the study of hydrogen trapping in steels [2–5]. The very low solid solubility of hydrogen in iron implies that most hydrogen atoms are in trapped states at various defects. The thermal desorption behavior of hydrogen from trapping sites is expected to give information on defects acting as trapping sites from the temperature profile and the activation energy of desorption. A benefit of TDS for hydrogen is that point defects, the size of which are on the atomic scale, can be detected from detrapping of hydrogen by thermal activation.

Plastic deformation is deeply involved in various fracture processes. Hydrogen embrittlement of steels is associated with applied plastic deformation [6–8] which gives rise to the formation of defects acting as new trapping sites. Other fracture phenomena such as nucleation of incipient microcracks [9–11] and ductile crack growth resistance [12,13] are controlled by the plasticity of materials. Our recent results indicated that the constraint of slip extension at ferrite grain boundaries by the presence of second phases such as carbides and pearlite grains decreases the ductile crack growth resistance [14,15]. Defects induced by plastic deformation are expected to be the primary factor which governs the fracture processes. When we introduce hydrogen into defects as a tracer, TDS is a promising tool to reveal the nature of the defects.

However, the distinction of various defects by hydrogen TDS is not straightforward because of the overlapping of temperature regions for the desorption from various kinds of trapping sites. It should be noted that TDS is essentially a thermally destructive test which in turn reflects the recovery of deformation microstructures in the course of measurement. In the analysis of TDS, the essential assumption that the thermal desorption takes place from the trapping sites which themselves remain stable during heating has been postulated implicitly. The assumption is valid for the desorption from stable sites such as grain boundaries, impurity atoms or second phases. However, for point defects which agglomerate or annihilate in the fairly low temperature region, the significance of the

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thermal desorption behavior must be carefully examined because recovery of the deformation structures proceeds in the course of measurement. One method is to examine the effect of the recovery of deformed samples on TDS of hydrogen introduced afterwards as the tracer of defects.

The present paper reports an analysis of the nature of deformation-induced defects through TDS of hydrogen introduced into deformed and annealed samples with particular reference to the role of microstructural inhomogeneity in steels.

2. Experimental procedures

Three steels of compositions shown in Table 1 were employed. The interstitial-free (IF) iron is a very low carbon steel with added titanium to reduce the solubility of carbon and nitrogen in the ferrite matrix. Plate specimens hot-rolled and ground to a thickness of 2 mm were annealed at 1073 K for 1 h in vacuum and then cooled at a rate of 100 K/h. The grain size was about 30 μm. Tensile straining to various degrees was applied at 298 and 223 K. In order to examine the effect of heavy deformation, cold drawn wire specimens were prepared with a pure iron and a eutectoid steel. The pure iron specimens were produced by vacuum melting electrolytic iron and hot-forging to bars. Wire specimens of 5 mm diameter were prepared by cold drawing with 0, 25, 55 and 83% reduction after annealing the hot-forged bars at 823 K for 1 h. The eutectoid steel is a commercial JIS-SWRS 82B steel of 13 mm diameter. After isothermal transformation at 748 K to the eutectoid structure, cold drawings with 0, 25, 55 and 85% reduction were given to the final specimen diameter of 5 mm. Some of the deformed samples were then subjected to annealing at various temperatures preceding hydrogen charging.

Hydrogen charging of specimens was conducted by two methods. That for the interstitial-free steel was by means of electrolytic charging using a 3% NaCl aqueous solution with 3 g/l NH_4SCN added as poison and at a current density of 0.5 mA/cm^2. The other was for the cold drawn pure iron and eutectoid steel. Specimens were soaked in a 20% NH_4SCN aqueous solution kept at 323 K for 6, 24 and 48 h as standardized by Federation Internationale de la Precontrainte (FIP) for the delayed fracture test of a pre-constraint steel bar [16]. TDS of hydrogen-charged steels was conducted using a gas chromatograph for the interstitial-free steel and a quadrupole mass spectrometer for the cold drawn pure iron and eutectoid steel. The maximum heating temperature was 873 and 1100 K, and the heating rate was 100 and 200 K/h for the gas chromatograph and the mass spectrometer, respectively. Argon gas was employed as the carrier gas in both cases. The corrosion products on the specimen surface formed by the FIP solution were removed by polishing and acetone cleaning. Since the charged hydrogen is apt to diffuse out in the course of sample preparation, the time needed for specimen transfer from the finish of hydrogen charging to the start of TDS was kept constant at 15 min.

3. Results

The IF steel specimens showed substantial elongation up to 50% even at 223 K. Hydrogen thermal desorption appeared between room temperature and 450 K with a single desorption peak, as shown in Fig. 1 for specimens deformed at 298 K. While desorption around room temperature distorts the peak profile on the lower temperature side, the peak has a long wing on the higher temperature side. The peak area, i.e. the amount of desorbed hydrogen, increased with strain, although the same hydrogen charging condition was used. Fig. 2 shows the increase of hydrogen desorbed up to 450 K as a function of strain. The increase of desorption was more remarkable at larger strain, and the peak temperatures shifted to higher temperatures. The deformation temperatures of 298 and 223 K had no significant effect on the strain dependence.

Some specimens tensile strained by 25% were then annealed at various temperatures for 30 min prior to hydrogen charging. The TDS profiles and the amount of desorbed hydrogen up to 473 K are shown in Figs. 3 and 4. A remarkable decrease in the desorption, i.e. the amount of occluded hydrogen, appeared as the annealing temperature increased. A substantial decrease by annealing at a temperature as low as 573 K is noted, but some desorption still remained even after annealing the deformed samples at 873 K. The high temperature wing of the peaks disappeared and the peak temperatures decreased as the annealing temperature approached 873 K.

Hydrogen thermal desorption from pure iron specimens given various drawing reductions and hydrogen charged by soaking in FIP solution for 24 h are shown in Fig. 5. Similarly to Fig. 1, a single peak around 500 K appeared

Table 1
Chemical compositions of experimental steels (mass%)

Specimen	C	Si	Mn	P	S	Cu	Ni	Cr	Ti	Al
IF steel	0.002	0.005	0.12	0.012	0.0091	0.01	0.02	0.02	0.039	0.21
Pure iron	0.0015	0.0004	0.0009	0.0010	0.0007	<0.001	–	–	–	<0.001
Eutectoid steel	0.84	0.23	0.77	0.010	0.006	0.01	–	–	–	0.003

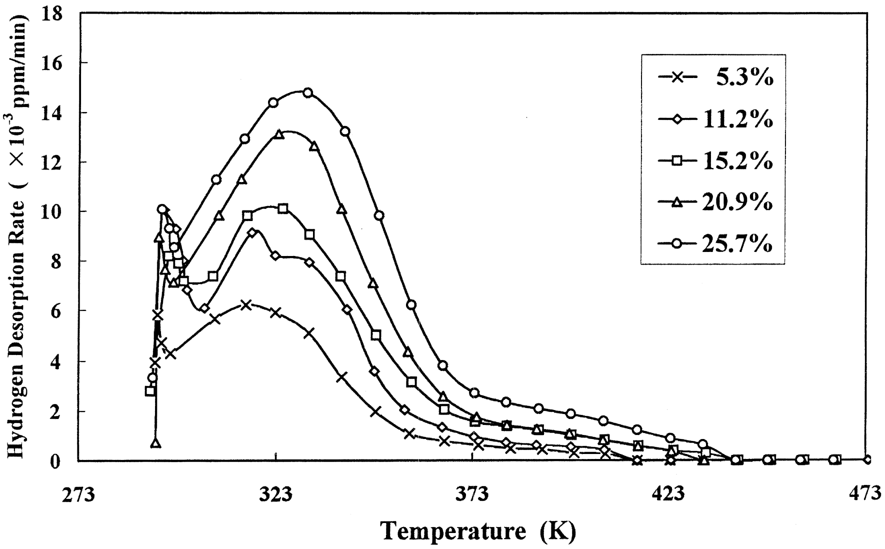

Fig. 1. Hydrogen thermal desorption spectra of IF steel specimens tensile strained to various degrees at 298 K.

with the amount of desorption increasing with drawing reduction, as shown in Fig. 6b. In this case, however, the lower temperature side of the peak was enhanced with reduction. The increase of the desorption with drawing reduction was parallel to the increase of hardness shown in Fig. 6a. Annealing the cold drawn wires remarkably reduced the peak height and the lower temperature side desorption, as shown in Fig. 7. The reduction took place in two steps, as shown in Fig. 8b for samples cold drawn to 83%. A first rapid decrease appeared by annealing to 473 K followed by a more remarkable second decrease by annealing at higher temperatures from 673 to 873 K. The decrease associated with increased annealing temperature was parallel to the reduction of hardness shown in Fig. 8a.

When compared with the behavior for ferrite monophase steels, hydrogen thermal desorption from the cold drawn eutectoid steel was quite distinct. Fig. 9 shows the TDS profiles of specimens given various drawing reductions and hydrogen charged by soaking in FIP solution for 24 h. Besides a peak centering around 460 K (Peak 1), an additional peak (Peak 2) appeared around 640 K increasing in height and shifting to higher temperature with drawing reduction. When drawing was not given, the second peak did not appear. Fig. 10b shows the amount of desorption as a function of drawing reduction. The first peak increases prominently at small reductions and tends to saturate at higher reductions. The second peak progressively increases at larger reductions, covering the increase of the total amount of desorption.

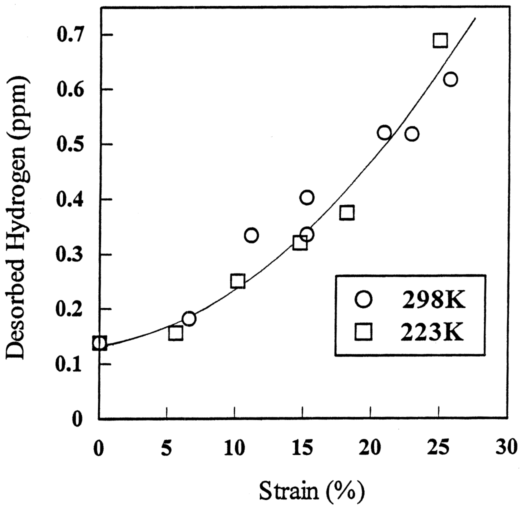

Fig. 2. Amount of desorbed hydrogen up to 450 K from IF steel specimens deformed at 298 and 223 K as a function of tensile strain.

A reduction of desorption by annealing drawn wires was also observed in eutectoid steel. Fig. 11 shows TDS profiles of specimens cold drawn to 85% and subjected to annealing. The decrease in the amount of desorption is associated with the decrease of the peak temperature. The behavior is in reverse order of the increasing drawing reduction shown in Fig. 9. The quantitative relations shown in Fig. 12 reveal that the monotonic decrease of the total desorption is primarily due to Peak 2, which almost totally disappears on annealing above 700 K.

4. Discussion

Hydrogen desorbed between room temperature and 500 K by TDS is generally referred to as ‘‘diffusive’’ hydrogen because it diffuses out when the hydrogen-charged specimen is left at room temperature for a few days [17]. It implies that the binding between hydrogen and defects acting as trapping sites is weak. The desorption temperature can be an intuitive indication of the binding energy, while the activation energy of desorption is obtained from

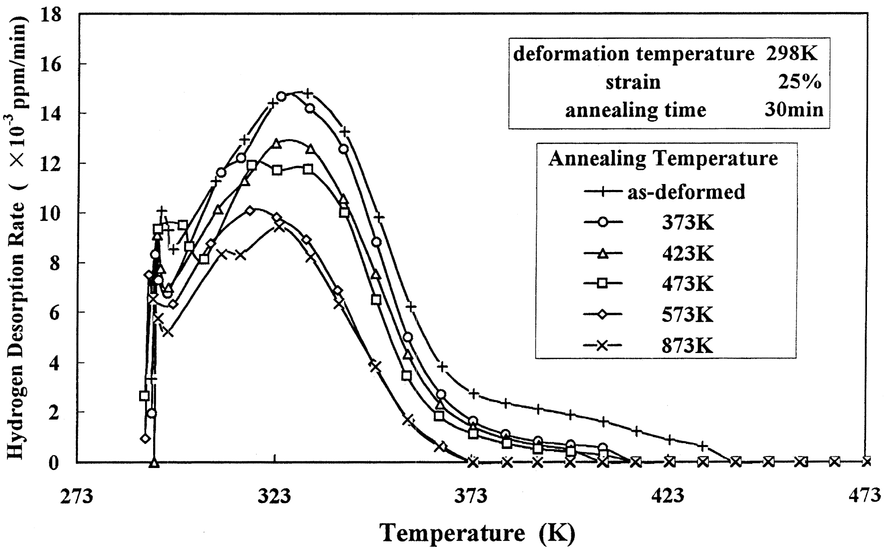

Fig. 3. Hydrogen thermal desorption spectra of IF steel specimens tensile strained to 25% at 298 K and annealed at various temperatures for 30 min.

the desorption peak shift associated with the heating rate [3].

It has been reported that desorption from various defects such as grain boundaries, dislocations and microvoids take place in the same temperature region reported here, making the identification of defects from TDS difficult [3]. As stated in the Introduction, it should be noted that TDS is essentially a thermally destructive test. Since the recovery of deformation microstructures takes place in the course of measurement, the assumption of thermal desorption from trapping sites which themselves remain stable during heating is not valid. The present study, which employs annealing of deformed samples prior to hydrogen charging, was expected to reveal the nature of trapping sites, particularly of point defects which recover in a rather low temperature region.

A common feature of the three steels is the increase of desorbed hydrogen with strain and its disappearance by annealing under several hundred Kelvin. The defects which act as the trapping sites of hydrogen must be introduced by plastic deformation, but they are not likely to be dislocations because their densities are not expected to be reduced in that temperature region. The most probable type of defect which corresponds to the annealing behavior is point-like defects. Point defects introduced by plastic deformation have been investigated by several authors [18–20]. The production of point defects during plastic deformation can take place in several ways, and a model that emphasizes the role of localized deformation during slip band formation was proposed by Essmann and Mughrabi [21]. The atomic vacancy concentration in deformed metals estimated theoretically or experimentally amounts to 10^{-2}–10^{-4} [18–20]. The numerical figures,

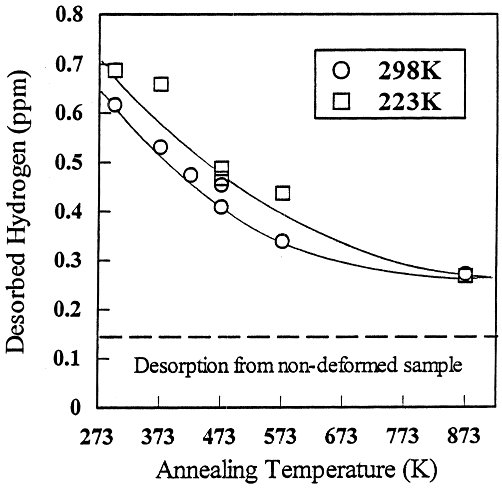

Fig. 4. Decrease of desorbed hydrogen as a function of annealing temperature of IF steel specimens tensile strained to 25% at 298 and 227 K.

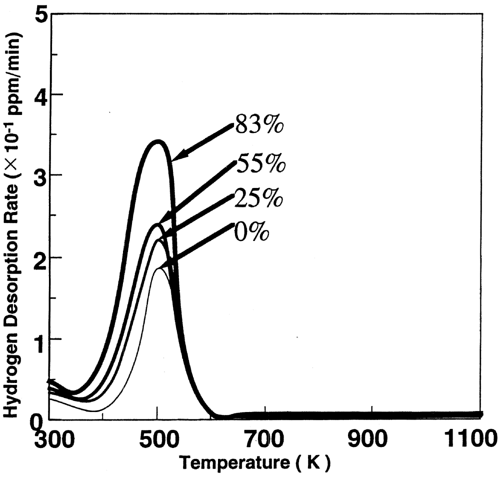

Fig. 5. Hydrogen thermal desorption spectra of pure iron specimens cold drawn to various reductions.

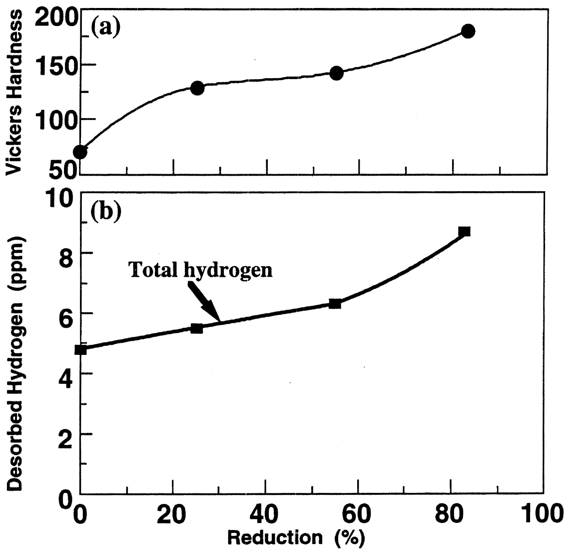

Fig. 6. Effect of drawing reduction on (a) Vickers hardness, and (b) the amount of desorbed hydrogen up to 1100 K of pure iron specimens after soaking for 24 h in FIP solution.

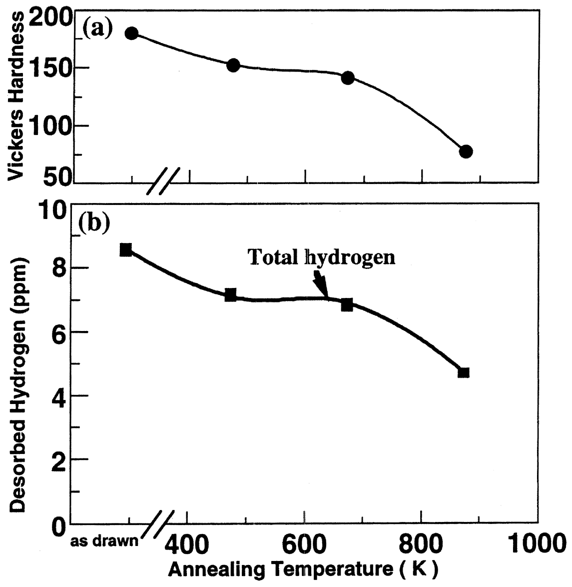

Fig. 8. Effect of annealing temperature on (a) Vickers hardness, and (b) the amount of desorbed hydrogen up to 1100 K of pure iron drawn to 83%. Hydrogen charging was by soaking in FIP solution for 24 h.

which far exceed the thermal equilibrium concentration of vacancies, are reasonable to account for the observed hydrogen concentration of the order of mass ppm as desorbed from trapped states.

The annealing behavior of vacancies in electron-irradiated or deformed α-iron was studied by positron lifetime measurements by Vehanen et al. [22]. Monovacancies are mobile at around 220 K, and the temperature range from room temperature to 550 K is just the stage where vacancy clustering and carbon–vacancy pairs are formed, dissociate and then annealed out. The increase of desorption with straining and its disappearance by annealing up to 573 K is in accordance with a model that vacancy clusters produced by plastic deformation are primary trapping sites of hydrogen. For IF steel, the role of carbon–vacancy pairs may be excluded. In Fig. 2 for IF steel, the increase of desorption in the main peak by straining accompanies the enhancement of the higher temperature wing of the main peak as well as the shift of the desorption peak to higher temperatures. This implies that vacancy clusters acting as trapping sites of hydrogen have higher binding energy with hydrogen than traps existing in non-deformed samples. The background desorption from non-deformed samples may originate in stable trapping sites such as impurity atoms, precipitates, grain boundaries, etc.

This should be noted for the interpretation of TDS

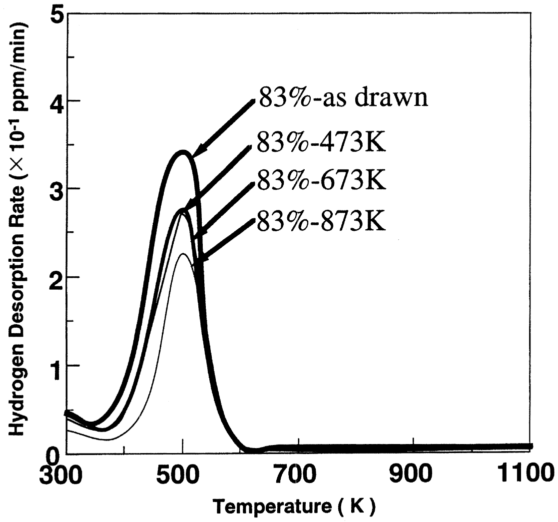

Fig. 7. Hydrogen thermal desorption spectra of pure iron cold drawn to 83% reduction and annealed at various temperatures.

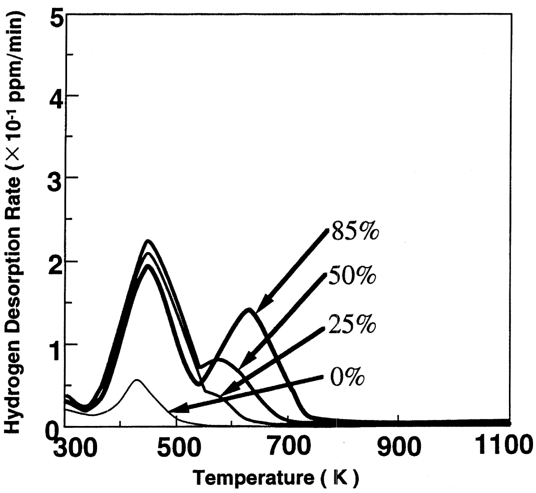

Fig. 9. Hydrogen thermal desorption spectra of eutectoid steel given various drawing reductions and hydrogen charged by soaking in FIP solution for 24 h.

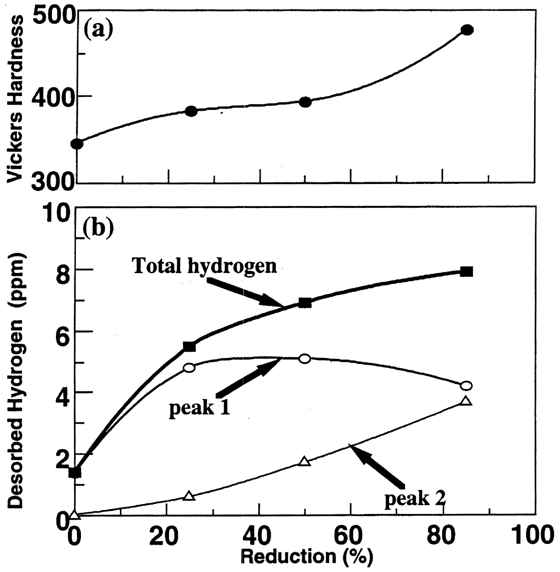

Fig. 10. Effect of drawing reduction on (a) Vickers hardness, and (b) the amount of desorbed hydrogen up to 1100 K of eutectoid steel after soaking for 24 h in FIP solution.

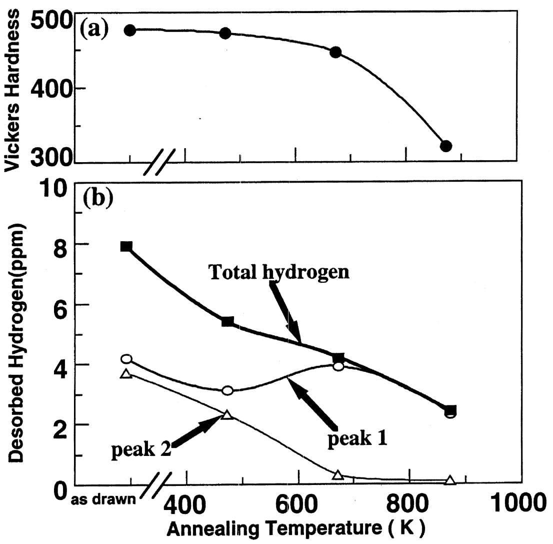

Fig. 12. Effect of annealing temperature on (a) Vickers hardness, and (b) the amount of desorbed hydrogen up to 1100 K of eutectoid steel drawn to 85%. Hydrogen charging was by soaking in FIP solution for 24 h.

results, since annealing of specimens inevitably proceeds in the course of TDS measurement. The fact that the increased desorption from deformed specimens vanishes when the deformed specimens have been annealed under 573 K implies that hydrogen desorption is not always the result of hydrogen removal from stable trapping sites, but annihilation of trapping sites themselves is a possible mechanism of hydrogen desorption. The amount of desorbed hydrogen can then be a measure of defect density rather than the amount of hydrogen occluded in specimens.

When heavy deformation was applied to pure iron, the decrease of desorption with annealing took place in two steps, as shown in Fig. 8. The first decrease, which appeared by annealing under 473 K, is similar to the IF steel specimens. The second decrease, which appeared by annealing at high temperatures above 673 K, is likely due to the recovery of dislocations. Both reductions are associated with the decrease of hardness. Actually, transmission electron microscopy conducted separately confirmed a decrease of dislocation density by annealing at 673 K [23]. Thus, the desorption of hydrogen from hydrogen-charged heavily deformed iron on heating under 600 K has two origins, one due to the annealing out of vacancy clusters and the other to the removal from dislocations. When one compares the TDS shown in Figs. 1 and 5, a difference appears on the wing of the peaks. For the IF steel or heavily cold drawn pure iron, the higher or lower temperature side of the peak, respectively, is enhanced with the amount of deformation. The lower temperature side desorption is likely due to the removal of hydrogen from stable dislocations. It should be noted, however, that the role of dislocation configurations, either as cell structures or as isolated single lines, in the trapping of hydrogen cannot be discriminated in the present experiment.

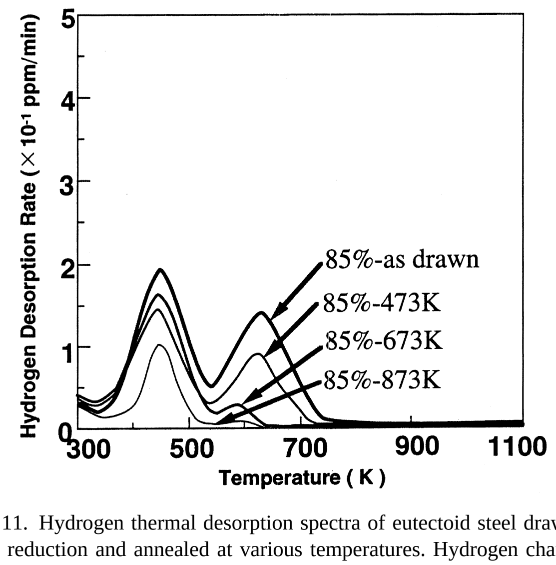

Fig. 11. Hydrogen thermal desorption spectra of eutectoid steel drawn to 85% reduction and annealed at various temperatures. Hydrogen charging was by soaking in FIP solution for 24 h.

Contrary to monophase iron, TDS of cold drawn eutectoid steel specimens gave rise to two distinct peaks, as shown in Fig. 9. Since Peak 2 at higher temperature is absent for non-deformed specimens and increases at larger drawing reductions, it is certain to originate from deformation substructures which develop in the course of deformation. The decrease of desorption associated with annealing of the deformed sample is primarily due to the monotonic decrease of Peak 2 up to 700 K. The decrease which takes place by annealing under 473 K implies that dislocations are not the primary trapping sites. The presence of cementite and a large amount of strain are essential factors for the appearance of Peak 2.

Transmission electron microscopy has revealed that the microstructure of the eutectoid steel given the reduction of 85% is composed of a fine lamella of cementite and ferrite with a spacing of about 60 nm [23]. The dislocation density in ferrite is high and forms cell structures. The monotonic decrease of desorption by annealing at 473 K suggests that point-like defects, which annihilate at low annealing temperatures, are the source of desorption. It was shown that cementite in heavily deformed eutectoid steel has a large internal strain and high dislocation density [24,25]. Recently, it was also revealed by atom probe field ion microscopy that ferrite is highly supersaturated with carbon [26]. The heavily distorted interface of cementite and ferrite might be the cause of cementite dissolution. The increase of Peak 1 by annealing at 673 K shown in Fig. 12 suggests that the defects which give rise to Peak 2 change their character so as to participate in Peak 1. If hydrogen interacting with such defects composes Peak 2, the desorption in Peak 2 is mostly due to the annihilation of trapping sites in the course of TDS measurement.

5. Conclusions

Hydrogen trapping sites in ferritic and eutectoid steels have been analyzed by TDS of hydrogen introduced into specimens subjected to deformation and annealing. Desorption with a single peak appeared from ferritic steels between room temperature and 600 K. Under constant hydrogen charging conditions, the amount of desorption, i.e. that of occlusion, increased with strain and reversed when samples were annealed at temperatures as low as 500 K. Vacancy clusters, which themselves annihilate in the course of TDS measurement, are the probable source of hydrogen desorption. When heavy deformation was applied, a two-step decrease of desorption with increasing annealing temperature occurred. One step took place under 473 K and the other above 673 K, corresponding to annihilation of vacancy clusters and a decrease of dislocation density, respectively. Thus, the desorption with a single peak has two origins, one due to the annihilation of trapping sites and the other from stable sites. From eutectoid steel given heavy deformation, an additional desorption peak centering around 640 K appeared. The peak decreased monotonically with increasing annealing temperature and totally disappeared on annealing above 700 K. This peak likely results from deformation-induced defects within the cementite phase or from supersaturated carbon in ferrite. The desorption in the peak is mostly due to the annihilation of trapping sites in the course of TDS measurement. Hydrogen TDS can be applied as a tool to investigate various defects induced by plastic deformation.

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