

Effect of sulphur on the hydrogen trapping phenomena at the grain boundary in iron

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The hydrogen trapping phenomena at grain boundaries in the iron-sulphur system were investigated by the hydrogen thermal analysis technique. The specimens were heat treated to produce the same grain size, and the concentration of sulphur at the grain boundaries was controlled by isochronal treatment at various temperatures. The peak height related to the hydrogen released from the grain boundaries decreased with increasing sulphur content at the grain boundaries. It is suggested that the variations in peak height may be attributed to the lowering of the trap binding energy due to sulphur segregation and the site competition effect between the segregated sulphur and hydrogen which are trapped at the grain boundaries.

1. Introduction

Many similarities have been reported in the literature between the phenomena of hydrogen-induced intergranular fracture and impurity-induced temper embrittlement of steels. In view of the many similarities, several recent studies have attempted to examine the relationship between the two fracture mechanisms.

Studies [1-5] have shown that impurities such as phosphorus, sulphur, antimony, tin, arsenic, etc., which segregate to the grain boundaries and induce intergranular fracture, also promote hydrogen embrittlement.

Yoshino and McMahon [4] suggested the additive effect of segregated impurities and hydrogen on the loss of the cohesive strength of the grain boundaries. It has also been proposed by Latanision and Oppenheimer [5] that some grain-boundary impurities enhance hydrogen permeation and therefore enhance intergranular fracture, i.e. a synergistic effect on hydrogen-induced intergranular fracture. Bernstein [6] found that the fracture mode in hydrogen-charged iron could be changed from transgranular to intergranular by heat-treatment temperature, cooling rate and interstitial content. Solute partitioning between the grain boundaries and the grain was suggested as a controlling factor in the hydrogen-induced cracking.

There is little doubt that grain-boundary impurities enhance hydrogen-induced intergranular fracture; however, there is little quantitative study to explain the mechanism of hydrogen-induced intergranular fracture and the role of impurities. At this point, it is necessary to clarify the variation in the amount of hydrogen trapped at the grain boundaries with the impurity concentration at the grain boundaries.

It has been well established [7-9] that the grain boundaries in iron and steel act as trapping sites for hydrogen. This phenomenon has been verified by many workers using hydrogen diffusion and evolution experiments. In particular the hydrogen thermal desorption experiments give information about the

hydrogen-trapping phenomena and the amount of trapped hydrogen.

Because sulphur is a common impurity which segregates at the grain boundaries and induces intergranular fracture, the present paper describes the variation of the amount of hydrogen trapped at the grain boundaries with the sulphur concentration at the grain boundaries, applying the hydrogen thermal analysis technique in order to elucidate the complex relationship between grain-boundary chemistry and hydrogen-induced intergranular fracture.

2. Theoretical background

2.1. Hydrogen trapping theory

When the energy level of hydrogen around the trapping site is assumed as in Fig. 1, the variation of hydrogen occupancy fraction of the trap sites with time (dn/dt), suggested by McNabb and Foster [10], is expressed as the difference between the rates of trapping and detrapping.

$$\frac{dn}{dt} = kC_L(1 - n) - pn \quad (1)$$

where k is the transition probability for hydrogen transport from a lattice site to a trapping site ($= v_1 \exp(-E_s/RT)$), p is the transition probability for hydrogen transport from a trapping site to a lattice site ($= v_2 \exp[-(E_s + E_B)/RT]$), n the trap occupancy fraction, C_L the number of hydrogen atoms dissolved in interstitial sites of a normal lattice, v_1 the vibrational frequency of hydrogen at a normal lattice site, v_2 the vibrational frequency of hydrogen at a trapping site, t the time, N_L the number of normal lattice interstitial sites. When equilibrium between hydrogen atoms in trapping sites and those in interstitial sites of the normal lattice is achieved, $\partial n/\partial t = 0$ and Equation 1 is written as Equation 2

$$\frac{n}{1 - n} = \left(\frac{k}{p}\right) C_L \quad (2)$$

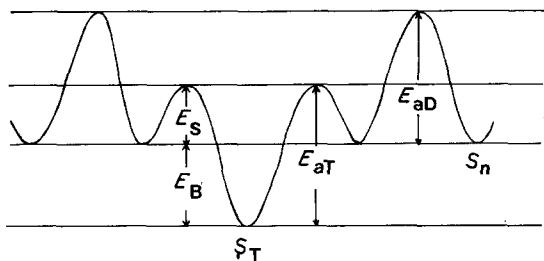


Figure 1 Energy level of hydrogen around trapping sites. E_{ad} diffusion activation energy of hydrogen in normal lattice, E_s saddle point energy, E_{aT} trap activation energy, E_B trap binding energy, S_n normal lattice site, S_T trapping site.

For the low trap occupancy fraction, $n \ll 1$, which can be assumed for weak trap sites with low trap binding energy, such as grain boundary and dislocation, Equation 2 is expressed as follows

$$n = \left(\frac{k}{p}\right) C_L \quad (3)$$

Assuming that the vibrational frequencies (ν_1, ν_2) are the same, the following equation is obtained from Equation 3

$$n = \frac{C_L}{N_L} \exp\left(\frac{E_B}{RT}\right) \quad (4)$$

Considering the definition of

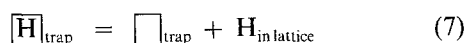
$$n = \frac{C_T}{N_T} \quad (5)$$

where C_T is the amount of trapped hydrogen, and N_T the amount of trapping sites, Equation 6 is obtained

$$C_T = \frac{N_T}{N_L} \exp\left(\frac{E_B}{RT}\right) C_L \quad (6)$$

2.2. Hydrogen thermal analysis

The hydrogen evolution reaction from trapping sites can be described as in Equation 7



The hydrogen evolution rate, as a thermally activated process, from trap sites is written as in Equation 8

$$\frac{dx}{dt} = A(1 - x) \exp\left(-\frac{E_{aT}}{RT}\right) \quad (8)$$

where $x = (N_0 - N)/N_0$, N_0 is the amount of hydrogen in trapping sites at $t = 0$, N the amount of hydrogen in trapping sites at $t > 0$, A a reaction constant, R the gas constant, and T the absolute temperature.

In Equation 8, the term $(1 - x)$ expresses the fractional amount of hydrogen remaining at trapping sites and $\exp(-E_{aT}/RT)$ is the probability of hydrogen overcoming the energy barrier from the trap sites to normal lattice interstitial sites. When the hydrogen-charged specimen is heated at a constant heating rate, the hydrogen evolution rate peak is formed at a certain temperature related to the trap activation energy of the trap site. Therefore, if there were several kinds of the trap sites in a specimen, several peaks should appear related to the trap sites in the (dx/dt) and $(1/T)$ plot. The details of the thermal analysis theory were previously described [11].

3. Experimental details

3.1. Specimen preparation

The alloys were prepared by arc melting of electrolytic iron in an argon atmosphere. To render the alloy free of sulphur a small amount of manganese was added. The chemical compositions of the alloys are given in Table I. The manganese concentration is the major compositional difference in these two alloys. Alloy A contains the same quantity of sulphur as alloy B but it has been fixed by manganese addition.

The alloys were remelted six times and annealed at 1273 K for 20 h to improve the homogeneity and then cold rolled.

The alloys were then heated at 1173 K for 16 h and water quenched to control the grain size. These alloys were then reheated to various temperatures (1023, 1073 and 1123 K) and held for 7 h to allow various amounts of grain-boundary sulphur segregation. They were then quenched into water. Heat treatments were performed in a vacuum. The average grain size of both types of alloy after the 1173 K annealing was 130 μm and maintained constant regardless of the subsequent heat treatment. Before hydrogen charging, the specimens were ground with emery paper No. 1200 to give the same surface condition.

3.2. Thermal analysis method

Before thermal analysis experiments, the specimens were thermally charged with hydrogen under 0.1 MPa hydrogen pressure at 773 K for 1.5 h and quenched to liquid nitrogen temperature to prevent the evolution of hydrogen from the specimen under the hydrogen atmosphere. The hydrogen-charged specimen was transferred to the reaction chamber, subjected to flowing argon gas for 30 min at 273 K in order to remove the mobile hydrogen, and then heated at a constant heating rate of 3 K min^{-1} . Experimental details of the hydrogen charging and thermal analysis have been described previously [11, 12].

4. Results and discussion

Fig. 2 shows a typical result of the hydrogen thermal analysis experiments on specimens with a controlled amount of sulphur at the grain boundaries. In this case, only one hydrogen evolution rate peak appears. When the hydrogen-charged iron single crystal was heated at a heating rate of 3 K min^{-1} , there was no hydrogen evolved from the iron single crystal. This means that the hydrogen dissolved in the interstitial sites of a normal lattice was evolved completely during holding for 30 min at 273 K under flowing argon before thermal analysis. Therefore, the hydrogen evolution rate peaks in Fig. 2 are not due to the evolution of hydrogen dissolved in the normal lattice sites.

Substituting the trap binding energy and trap density of the grain boundary (2.1 kcal mol^{-1} and 10^{19} sites/g Fe calculated by Choo and Lee [9] and Oriani

TABLE I Composition of the alloys

Alloy	C	P	S	Mn	Fe
A	0.006	0.005	0.006	0.26	bal.
B	0.005	0.005	0.005	0.003	bal.

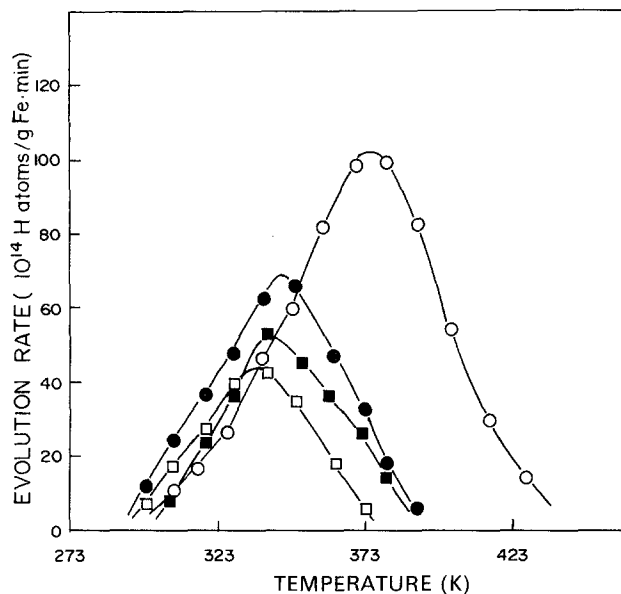


Figure 2 Variation of peak height with specimen. (O) Alloy A, annealed at 1173 K for 16 h. (●) Alloy B, annealed at 1173 K for 16 h and aged at 1123 K for 7 h. (■) Alloy B, annealed at 1173 K for 16 h and aged at 1073 K for 7 h. (□) Alloy B, annealed at 1173 K for 16 h and aged at 1023 K for 7 h.

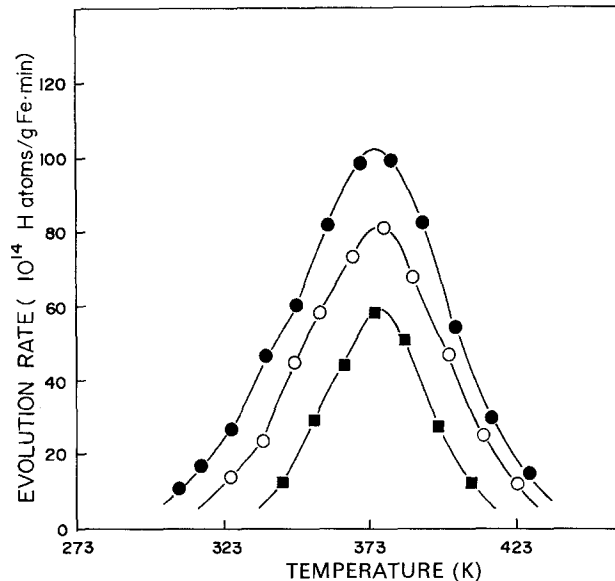


Figure 3 Variation of peak height with holding time at 273 K in vacuum, of alloy A. (●) 30 min, (O) 185 min, (■) 415 min.

[13], respectively) and lattice hydrogen solubility given by Quick and Johnson [14] into Equation 6, the amount of hydrogen trapped at the grain boundaries under 0.1 MPa hydrogen pressure at 773 K is calculated as 2.82×10^{14} H atoms/g Fe. This value is very small compared to the thermal analysis results. Fig. 3 shows the thermal analysis result of alloy A with holding time in vacuum at 273 K before the thermal analysis experiment. The height of the hydrogen evolution rate peak decreases with increasing holding periods at 273 K. Pressouyre and Bernstein [15, 16] have suggested that the hydrogen trapped in the trap with low binding energy maintains dynamic local equilibrium with the hydrogen at the normal lattice sites. Therefore, in the case of polycrystalline iron, some of the hydrogen at the normal lattice sites would remain in a specimen to maintain a dynamic local equilibrium with the hydrogen trapped at the grain boundaries after holding in vacuum at 273 K before thermal analysis. Recently, Lee and Lee [17] have shown that the hydrogen in normal lattice sites and grain boundaries in iron maintained dynamic local equilibrium with each other. Hence, from the fact that the thermal analysis result is very large compared to the amount of hydrogen trapped at the grain boundaries, which is calculated from Equation 3, it can be thought that the hydrogen evolution rate peaks in Fig. 2 are related to the hydrogen released from the grain boundaries, maintaining a dynamic local equilibrium with the hydrogen dissolved in normal interstitial lattice sites.

The sulphur segregation at the grain boundaries for the Fe-S system has been well interpreted in terms of the Langmuir-type adsorption theories by many workers [18, 19], who showed that at temperatures above the solubility limit, the equilibrium grain-boundary sulphur segregation in iron decreased rapidly with increasing temperature. The solubility of

sulphur in iron is given by [20].

$$\log(\text{wt \% } S) = -3800/T + 1.44 \quad (9)$$

Because the sulphur concentration in alloy B is 50 wt p.p.m., the temperature where the sulphur bulk concentration equals the solubility is about 1016 K. Therefore, it is believed that the equilibrium grain-boundary sulphur segregation in alloy B increases very rapidly with decreasing temperature down to 1016 K. For the heat-treatment temperatures and times given above, calculated according to the treatment of McLean [21], it is shown that the equilibrium segregation level was attained. Consequently under the above heat-treatment conditions, the grain-boundary sulphur concentrations in alloy B are highest in the specimen aged at 1023 K and lowest in that aged at 1123 K. For the case of alloy A, all the sulphur should be present in manganese sulphide because of the presence of a sufficient amount of manganese. Therefore, it is believed that sulphur segregation in alloy A did not occur. The suppression of sulphur segregation by addition of manganese was reported by Seah and Hondros [18].

Considering the above argument, Fig. 2 shows that the height of the peak related to grain boundaries decreases and the position of the hydrogen evolution rate peak shifts to the lower temperature side as the sulphur content at the grain boundaries increases.

In the thermal analysis experiment, the specimen is charged with hydrogen at a high temperature, followed by rapid cooling of the specimen to low temperature. The drop in temperature causes a new equilibrium state between the supersaturated hydrogen and the trapping sites during quenching and/or holding at low temperature before thermal analysis. From Equation 6, when a new equilibrium state is formed, the amount of hydrogen constituting the new equilibrium state is determined by the trap binding energy and/or trap density. As the trap binding energy and/or trap density increase, the amount of hydrogen constituting a new equilibrium state increases. Thus, it is considered

that the decrease in peak height with increasing sulphur segregation at the grain boundaries in Fig. 2 can be attributed to the following possibilities. The first is the decrease in the trap binding energy between the grain boundary and hydrogen due to the grain-boundary segregation of sulphur. This can be recognized from Fig. 2. The position of the hydrogen evolution rate peak is shifted to the lower temperature side with increasing sulphur content at the grain boundaries. The evolution of hydrogen maintaining the dynamic local equilibrium between normal lattice sites and grain boundaries is controlled by the detrapping of hydrogen trapped at the grain boundaries. At maximum hydrogen evolution rate, the derivative of Equation 8 is zero, so Equation 10 can be obtained.

$$A \exp\left(\frac{E_{aT}}{RT_c}\right) = \frac{E_{aT}}{RT_c^2} \phi \quad (10)$$

where ϕ is the heating rate, and T_c the temperature of maximum hydrogen evolution rate. The trap activation energy (E_{aT}) is the sum of the trap binding energy (E_B) and saddle point energy (E_S) from Fig. 1. Assuming that the saddle point energy is constant, i.e. saddle point energy is equal to the diffusion activation energy (E_D) [22] and does not change by sulphur segregation at the grain boundaries, the peak temperature (T_c) decreases with decreasing trap binding energy. Therefore, the lowering of the peak temperature in Fig. 2 indicates that the trap binding energy decreases with increasing sulphur content at the grain boundaries.

The lowering of trap binding energy due to sulphur segregation can be explained as follows. If interfacial free energy can be lowered by hydrogen trapping at the interface, it provides a large driving force for such hydrogen trapping. Combining Equation 6 and the Gibbs adsorption isotherm [23] of Equation 11, Equation 12 is derived.

$$\frac{d\gamma}{d \ln a} = -RT\Gamma \quad (11)$$

where γ is the grain-boundary energy, Γ the concentration of the hydrogen at the grain boundary, and a the activity of hydrogen [= $n/(1-n)$]

$$\frac{d\gamma}{d \ln a} = -RT\Gamma = -RTN_T n \quad (12)$$

On integrating between the composition limits zero and n , Equation 12 becomes

$$\gamma^0 - \gamma = -RTN_T \ln(1-n) \quad (13)$$

On substitution of Equation 4 into Equation 13, Equation 14 is derived.

$$\gamma^0 - \gamma = -RTN_T \ln \left[1 - \frac{1}{N_L} \exp\left(\frac{E_B}{RT}\right) C_L \right] \quad (14)$$

where γ^0 is the interfacial free energy of the hydrogen-free grain boundary.

One can recognize the basic feature of the hydrogen trapping behaviour from this form: the larger decrease of the grain-boundary energy by hydrogen trapping at the grain boundary, the larger trap binding energy of

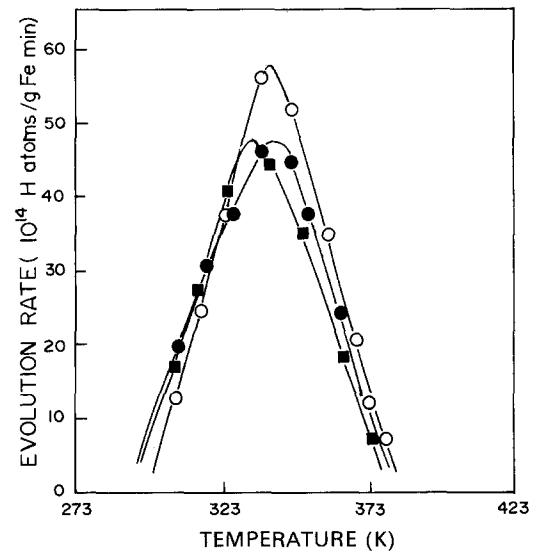


Figure 4 Variation of peak height with ageing time of alloy B. Annealed at 1173 K for 16 h and then aged at 1023 K for (○) 3 h, (●) 7 h and (■) 22 h.

hydrogen at the grain boundaries. It is well known that the grain-boundary energy is lowered by impurity segregation at the grain boundary [16, 24, 25]. When sulphur segregates to the grain boundaries, $\Delta\gamma$ ($=\gamma^0 - \gamma$), the change in the grain-boundary energy due to the hydrogen trapping, may be decreased because of the decrease in γ^0 . Consequently, the binding energy between grain boundary and hydrogen decreases with sulphur segregation to the grain boundaries.

The second possibility is the decrease of the number of trap sites for hydrogen due to the preoccupied sulphur atoms. Fig. 4 show the variations of hydrogen evolution rate peak with ageing time for alloy B. Only one hydrogen evolution rate peak around 338 K is observed. As the ageing time increased, the peak height decreased and was saturated for about 7 h. But the peak temperatures were nearly the same. From McLean's equation for segregation kinetics [21], the grain-boundary sulphur content gradually increases with ageing time and finally reaches the saturated value. Therefore, Fig. 4 implies that the equilibrium grain-boundary sulphur segregation was attained within the period of 7 h at temperatures above 1023 K. Also, the decrease of peak height with a constant peak temperature means the available number of trap sites for hydrogen decreases with sulphur segregation.

5. Conclusions

Based on the results of the hydrogen thermal analysis study, the following conclusions can be made.

As the concentration of sulphur at the grain boundaries increases, the height of hydrogen evolution rate peak, related to the hydrogen released from the grain boundary, decreases. It is considered that this effect is attributed to the decrease of the trap binding energy and the decrease of the numbers of the trap sites for hydrogen with the increase of grain-boundary sulphur segregation.

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