Hydrogen Absorption of Hard Steel Wire in Hydrochloric Acid*

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Synopsis

A study has been made of the measurement of the amounts of hydrogen absorbed by a hard steel wire (0.6%C) with scale during immersion in 5, 10 and 15% hydrochloric acid for various times. The amount of absorbed hydrogen increases with the immersion time. The rate of hydrogen absorption increases with the increase in descaling ratio and it reaches maximum at the descaling time at which the scale is completely removed. The amount of absorbed hydrogen after complete descaling is nearly proportional to the square root of the time after the descaling. The proportional constant decreases with the increase in HCl concentration, whereas the increase in HCl concentration results in the increase in the weight loss. The similar relationship between the amount of absorbed hydrogen and weight loss is obtained in the hard steel wire descaled prior to testing.

I. Introduction

A number of investigations concerning hydrogen absorption by steel during immersion in acids have been reported,¹⁻³⁾ where the materials used are usually mild steel with no scale. In this investigation measurements were mainly made of hydrogen absorption and weight loss by hard steel wire with scale during immersion in hydrochloric acid for various times. The relationship between above two factors is significantly different from that¹⁾ by mild steel reported up to present time. In order to clarify the difference between the two steels, measurements were also made of both mild and hard steel wires descaled.

II. Experimental Procedure

Commercial hard steel wire with hot mill-scale used was 7 mm in diameter and its chemical composition was C 0.61, Si 0.26, Mn 0.46, P 0.009 and S 0.002%. Descaled hard steel wire was prepared by removing cathodically the scale of the wire mentioned above in 10% HCl solution at 2 A/dm² for 10 min. In order to remove the hydrogen absorbed during cathodic treatment the wire was subsequently annealed in vacuum of 5×10^{-6} mmHg at 600°C for 2 hr. Mild steel wire used for comparison was as cold drawn core wire of 6.5 mm in diameter. Chemical composition of this wire was C 0.12, Si 0.02, Mn 0.55, P 0.009 and S 0.019%. Prior to use, the wire was annealed in vacuum of 5×10^{-6} mmHg at 600°C for 2 hr, because it has been reported that cold drawn causes the increase of hydrogen absorption during pickling.^{4,5)}

Individual specimens used for this experiment were obtained by cutting from those wires. The length of the specimen was 50 mm. The cutting ends of specimens were polished with emery papers up to 1 000 grade. Specimens were degreased in trichloroethy-

lene, dried and weighed, and then their ends were coated with an acid resistant paint to prevent hydrogen absorption through the ends.

Specimens were immersed in 5, 10 and 15% HCl solutions at 20 and 40°C for various times. Immediately after immersion, the coatings were peeled off and the specimens were rinsed thoroughly in water and acetone, dried and then introduced into hydrogen estimation apparatus as quickly as possible to minimize the loss of hydrogen by diffusion. Normally, these treatments required less than 2 min.

Figure 1 shows an apparatus for the measurement of hydrogen absorbed used in this study. The apparatus is essentially the same as the equipment used by Hudson.^{3,6)} (A) is the hydrogen extraction burette which consists of the bell-shaped end and the capillary tube graduated with 0.01 cc units at intervals of 3 mm. The specimen was inserted in the bell-shaped end of burette. The burette was placed in the mercury-filled vessel (B) and then filled with mercury using an aspirator. The whole assembly was placed in the

Fig. 1. Hydrogen extraction burette

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water bath, and thus the specimens were kept at $45^{\circ}\pm 1^{\circ}\text{C}$ for 48 hr under mercury. The hydrogen evolved from the specimen in the burette was collected in the upper end of the capillary tube by displacement of mercury. The amount of hydrogen absorbed was obtained by converting the readings of the mercury levels in the capillary tube to standard conditions. In this report, the amount of hydrogen absorbed by a specimen is expressed in cubic centimeters of hydrogen per 100 g of steel, according to Hudson.⁶⁾

For hydrogen evolved from deposited metal by welding, a similar extraction method is standardized by JIS (Japanese Industrial Standards) Z-3113, although the deposited are kept at 45°C for 48 hr under glycerin instead of mercury. The extracting conditions used in this experiment are in accordance with those determined by JIS. However, it is doubtful whether the whole amount of hydrogen absorbed by the hard steel specimen evolves completely or not by such an extraction at 45°C for 48 hr, because the deposited metal described in JIS is normally mild steel.

Figure 2 shows the relationships between the extracting time and the hydrogen evolved from the hard steel and mild steel specimens used for comparison, where these specimens were immersed in 5% HCl solution at 40°C for 30 min. The hard steel specimen with scale continues to evolve the hydrogen after holding of 700 hr; thus, it is apparent that the whole amount of absorbed hydrogen does not evolve for 48 hr extraction at 45°C . On the other hand, the hydrogen from the mild steel specimen saturates after 200 hr holding time. It has been reported that hydrogen absorbed by steel is located at various traps, *i.e.* ferrite-carbide interfaces, ferrite-inclusion interfaces,⁷⁾ as well as interstitial sites. The extraction of hydrogen located at the traps requires long time, especially at lower temperature below 350°C .⁸⁾

Boniszewski⁹⁾ measured hydrogen evolution at room temperature from the sulphur-bearing free-cutting steel containing 5.5 cc/100 g hydrogen, indicating that the saturation of hydrogen evolution required the holding time of 100 days, whereupon residual hydrogen in steel was negligible. If hydrogen does not exist in steel after saturation of hydrogen evolution, then it is

Fig. 2. Hydrogen evolution curves at 45°C for mild and hard steel specimens immersed in 5% HCl at 40°C for 30 min

concluded from Fig. 2 that the amount more than 90% of hydrogen absorbed by the mild steel specimen evolves by the extraction for 48 hr. The whole amount of hydrogen absorbed by the hard steel specimen is unknown, since hydrogen continues to evolve after 700 hr holding time. However, if the saturation time of hydrogen evolution from the hard steel specimen is taken to be 100 days as same as the case of the free-cutting steel, it can be estimated that about 70% of hydrogen absorbed by the hard steel specimen is evolved for 48 hr when the whole amount of absorbed hydrogen is estimated by extrapolating the hydrogen evolution curve in Fig. 2 to 100 days. Actually, the amount more than 70% of absorbed hydrogen may be extracted for 48 hr, because the extracting temperature in this experiment is 45°C whereas hydrogen extraction from the free-cutting steel is carried out at room temperature. Even though the amount of hydrogen extracted for 48 hr is not more than 70% or absorbed hydrogen, it is possible to discuss the amount of hydrogen absorbed by the hard steel specimens using this value.

Although the extracting method used in this experiment has some inaccuracies, the extracting operation is very simple and the measurements of many specimens can be made at the same time using many hydrogen extracting burettes. For this reason, the extracting method of hydrogen by displacement with mercury at 45°C for 48 hr was chosen, nevertheless more suitable other methods^{10,11)} for hydrogen extraction have been well known.

III. Experimental Results

1. Hard Steel Specimens with Scale

1. Weight Loss and Average Weight of Scale

Figure 3 shows the relation between weight loss and immersion time for hard steel specimens with scale immersed in 5, 10 or 15% HCl solutions at 40°C . As immersion time increases, weight loss increases rapidly at first and then slowly, and reaches the steady-state at which weight loss increases at a constant rate. Since the slough-off of scale was observed at the immersion

Fig. 3. Weight loss of hard steel specimens with scale in 5, 10 and 15% HCl at 40°C

times denoted with $\blacktriangle$, $\blacksquare$ and $\bullet$ symbols in Fig. 3, it appears that the rapid increase of weight loss at the initial immersion stage is mainly due to scale removal and weight loss at a constant rate due to the dissolution of steel matrix. The immersion times denoted with the above symbols mean the descaling time, and the weight losses corresponding to the symbols can be regarded as the average weight of scale when the dissolution of steel matrix is negligible small. The descaling times in 5, 10 and 15% HCl solutions at 40°C were 7~9, 4~5 and 3~4 min respectively; at a constant temperature, the descaling time decreased with the increase in the concentration of HCl. The similar relationships were obtained at 20°C immersion. The dispersion of the descaling time at a constant temperature and HCl concentration is due to the difference in the scale weight of individual specimens. Weight loss data were obtained from 68 specimens immersed in 5% HCl solution at 40°C for 9 min which is the upper range of the descaling time. The weight loss showed a normal distribution. Since the weight of scale is approximately equivalent to the weight loss as mentioned above, the weight of scale per unit area can be obtained from the weight loss data. The average weight of scale is 3.55 mg/cm² and its standard deviation is 0.35 mg/cm².

2. The Amount of Absorbed Hydrogen

Figure 4 shows the relation between the hydrogen concentration (amount of absorbed hydrogen) and immersion time for hard steel specimens with scale which were immersed at 40°C in 5, 10 or 15% HCl solutions. Hydrogen concentration increases with the increase in immersion time and the rate of hydrogen absorption depends markedly on the concentration of HCl. As shown in Fig. 4, the effect of HCl concentration on the hydrogen concentration is significantly different between before and after the immersion time of 4~9 min. After this immersion time, hydrogen concentration decreases with the increase in HCl concentration, and this trend reverses before that time. This reversion time of immersing seems to be closely related to the descaling time mentioned previously. The similar time dependence of hydrogen concentration was also obtained by immersion in HCl solution at 20°C.

Fig. 4. Hydrogen absorption by hard steel specimens with scale in 5, 10 and 15% HCl at 40°C

3. Relationship between Weight Loss and Hydrogen Concentration

Weight loss data obtained under the same condition do scatter, because of difference in the average weight of scale of individual specimens. Therefore, the relationship between weight loss and hydrogen concentration must be decided synthetically on the basis of the results obtained from many specimens. Thus, the relation between weight loss and hydrogen concentration was examined for many hard steel specimens with scale immersed in HCl solution at 40°C. The result obtained is shown in Fig. 5 in which the Δ , $\bullet$ and $\circ$ symbols present the data in 5, 10 and 15% HCl solutions, respectively. As the weight loss increases, the Δ , $\bullet$ and $\circ$ symbols tend to locate separately at the upper, medium and lower region, respectively. But this trend reverses for the fewer weight loss less than 3.55 mg/cm². Since the existence of scale affects remarkably on the hydrogen absorbed by hard steel specimens as mentioned above, measurements were also made of descaled hard steel specimens.

2. Hard Steel Specimens with No Scale

Figure 6 shows the relationship between weight loss and immersion time for descaled hard steel specimens immersed in 5, 10 and 15% HCl solutions at 40°C. After a short immersion time, weight loss reaches the steady-state at which the rate of dissolution is constant. Figure 7 shows the relationship between hydrogen concentration and immersion time for descaled hard steel specimens and mild steel specimens used for comparison, where the specimens were immersed in 5, 10 and 15% HCl solutions at 40°C. The hydrogen concentrations in both kinds of steels increase approximately linearly with the increase in the square root of immersion time. This trend is in agreement with the results^{1-6, 12-14)} by mild steel reported up to the present time.

Since weight loss at the steady-state increases

Fig. 5. Relationship between hydrogen concentration and weight loss for hard steel specimens with scale in 5, 10 and 15% HCl at 40°C

Fig. 6. Weight loss of descaled hard steel specimens in 5, 10 and 15% HCl at 40°C

Fig. 7. Hydrogen absorption rate curves for mild steel and descaled hard steel specimens immersed in 5, 10 and 15% HCl at 40°C

linearly with immersion time and hydrogen concentration increases also linearly with the increase in the square root of immersion time, hydrogen concentration is naturally proportional to the square root of weight loss at the steady-state. The relation between them are shown in Fig. 8 for hard steel specimens immersed in HCl solutions at 20° and 40°C. Between hydrogen concentration H and weight loss ΔW , a linear relationship ($H=k\sqrt{\Delta W}$) is held under the same condition of immersing. Table 1 shows the values of constant k , which are obtained directly from Fig. 8. The value of k at a constant temperature decreases with the increase in the concentration of HCl; for hard steel specimens hydrogen concentration decreases with the increase in HCl concentration, whereas the increase in HCl concentration results in the increase in the weight loss.

Photograph 1 shows the scanning electron micro-

Fig. 8. Relationship between hydrogen concentration and weight loss for descaled hard steel specimens in 5, 10 and 15% HCl at 20° and 40°C

Table 1 Values of k

Temperature °C	HCl %	k (cc/100 g)/(mg ^{1/2} /cm)
20	5	0.127
	10	0.085
	15	0.069
40	5	0.520
	10	0.265
	15	0.133

graphs for the surface of the hard steel specimens after immersion in HCl solutions at 40°C. A series of micrographs for the specimens immersed in 10% HCl solution is shown in Photos. 1 (a)~(c), where immersion time increases in alphabetical order. It is well known that cementite acts as cathodic site in corroding in acids and ferrite acts as anodic site and consequently the later dissolves preferentially.^{15,16)} Similar corrosion behaviour was observed for the hard steel specimens. As shown in Photos. 1 (a), (b) and (c), the preferential attack of proeutectoid and eutectoid ferrite phases occurs more vigorously with immersion time. Photos. 1 (d), (e) and (f) show the micrographs for the specimens immersed in 5, 10 and 15% HCl solutions for 30 min. In this case, the preferential attack occurs so vigorously that no ferrite can be observed. As the concentration of HCl increases, cementite is also attacked and its original platelet form becomes obscure.

IV. Discussion

Hudson¹⁾ examines the relation between weight loss and hydrogen concentration for low carbon steel immersed at 38°C in HCl solution with the various concentrations, and consequently obtains the following equation between hydrogen concentration H (cc/100 g) and weight loss ΔW (mg/cm²);

(a) 10% HCl, 30 sec $\times 1\,000$ (b) 10% HCl, 5 min $\times 1\,000$ (c) 10% HCl, 10 min $\times 3\,000$ (d) 5% HCl, 30 min $\times 3\,000$ (e) 10% HCl, 30 min $\times 3\,000$ (f) 15% HCl, 30 min $\times 3\,000$

Photo. 1. Scanning electron micrographs for the surface of hard steel specimens immersed in HCl solutions at 40°C

$$H = 8.54W^{0.37}$$

Further he has noted that the hydrogen concentration corresponding to a given weight loss varies slightly with immersion temperature, but does not vary with HCl concentration. This result differs remarkably from that for hard steel in this study in which the hydrogen concentration for a given weight loss does vary with HCl concentration as shown in Fig. 8.

It is evident from Fig. 7 that hydrogen concentration in mild steel is larger than that in hard steel by more than one order. From the above equation presented by Hudson, the hydrogen concentration per 1 mg/cm² of weight loss is calculated at 8.5 cc/100 g which is about 30 times of that for the hard steel specimen immersed in 5% HCl solution shown in Fig. 8. Although direct comparison of these values is not justifiable because of considerable difference in the immersion temperature and the size of the specimens between the study by the present authors and that by Hudson, it appears from this comparison that carbon content in steel affects strongly hydrogen absorption by steel.

Abdul Azim¹⁷⁾ measured weight loss of carbon steel in HCl solutions with various concentrations, and showed that weight loss increased with the increase in carbon content. Since the hydrogen overpotential on cementite is lower than on ferrite,¹⁵⁾ weight loss should increase with the increase in the amount of cementite so far as the corrosion is controlled by the activation process of hydrogen evolution. Thus, it is quite reasonable to suppose that a large amount of hydrogen is evolved on cementite for high carbon steel and on ferrite for low carbon steel. Such a difference in sites at which hydrogen evolution occurs will naturally affect the amount of hydrogen absorbed by steel. As a result, small amounts of hydrogen are absorbed in hard steel and large amounts in mild steel.

The relation between weight loss and hydrogen concentration for hard steel specimens should be characterized in the result that the increase in HCl concentration causes the decrease in the hydrogen concentration, whereas weight loss increases with the increase in the HCl concentration. This is not fully understood, but a following explanation may be possible. As shown in Photos. 1 (d), (e) and (f), the dissolution of

cementite is accelerated with the increase in HCl concentration. Staicopolus¹⁵⁾ and Cron *et al.*¹⁸⁾ have shown that cementite is decomposed into iron and hydrocarbons (predominantly methane) by the attack of deposited hydrogen. If the dissolution of cementite is due to deposited hydrogen, the increase in the HCl concentration results in the more vigorous attack of cementite and subsequently in the increase in the amount of hydrocarbons, since the amount of deposited hydrogen increases with the increase in the HCl concentration. As the HCl concentration increases, the ratio of the amount of produced hydrocarbons to the amount of deposited hydrogen will increase, and consequently the amount of hydrogen absorbed by steel will decrease.

Since the removal rate of scale oxide by pickling is affected by the composition and structure of scale,¹⁹⁻²¹⁾ it is expected that the hydrogen absorption in descaling process depends also on them. The scale structure is decided by the time and temperature of scale formation as well as the cooling rate of the scale below 570°C. Although the fabrication history of the hard steel wire is unknown, the wire is mainly covered with the scale of the typical three layers structure; a very thin outer layer of hematite, a thick magnetite layer and an inner wüstite layer in contact with steel matrix. Exclusive of the dissolution problem of the inner wüstite layer into HCl solution,²⁰⁾ the scale is cathodic to the steel matrix when the acid comes into contact with the steel matrix through the fissures and pores in the scale. As the scale is removed and the steel matrix is exposed, the cathodic site is gradually altered from scale to cementite. For the shorter time of immersing at which the scale still plays as cathodic site, the amount of absorbed hydrogen increases with the increase in HCl concentration, because of the increase in the amount of deposited hydrogen. After the steel matrix is exposed and cementite is predominant cathodic site, weight loss increases with increasing concentration of HCl, but absorbed hydrogen decreases as mentioned previously. The relation between the amount of absorbed hydrogen and the HCl concentration, in short, is determined by the result whether cathodic site is scale or cementite. The intersection of hydrogen concentration curves in Fig. 4 may be interpreted in the way mentioned above.

V. Summary

Measurements have been made of the amount of hydrogen absorbed by hard steel specimens with scale during immersion in 5, 10 and 15% HCl solutions for various times. As HCl concentration increases, the

descaling time, namely, the pickling time decreases and consequently the amount of hydrogen absorbed also decreases.

Further the relation between the amount of absorbed hydrogen and weight loss has been investigated, using the descaled hard steel specimens. At a given concentration of HCl, the amount of absorbed hydrogen increases with the increase in weight loss. As HCl concentration increases, the amount of absorbed hydrogen decreases and weight loss increases. The latter result differs apparently from that by mild steel reported up to present time in which the increase in HCl concentration results in the increase in the amount of absorbed hydrogen. Such a difference in the HCl concentration dependence of the amount of absorbed hydrogen is probably due to the difference in the site where hydrogen evolution occurs, *i.e.* either ferrite or cementite.

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