MECHANISM OF SCC AND HYDROGEN-INDUCED DELAYED CRACKING

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ABSTRACT

The nucleation and propagation of stress corrosion cracking (SCC) and hydrogen-induced delayed cracking (HIDC) in various environments were followed metallographically, using polished WOL type constant deflection specimen. The results show that if $K_I > K_{ISCC}$ and the strength of steel is larger than a critical value, the size of the plastic zone and the degree of plastic deformation ahead of the crack is enlarged continuously with time, i.e.,a hydrogen-induced delayed plasticity (HIDP) is observed and SCC and HIDC will nucleate and propagate, when it develops to a critical condition.

The effect of hydrogen on the yield strength of a smooth tensile specimen is insignificant. However, for the bending or pre-crack specimen with a stress gradient, hydrogen decreases the yield strength considerably if the strength of steel and the hydrogen amount exceed critical values. This is the cause of HIDP and HIDC. The variation of the K_{ISCC} and da/dt with the strength of steel and the environments has been explained and a new mechanism of SCC or HIDC in steels has been suggested.

KEYWORDS

Hydrogen-induced delayed plasticity; Hydrogen-induced delayed cracking; Hydrogen-induced reduction of apparent yield strength;

INTRODUCTION

The mechanism of the stress corrosion cracking (SCC) of high strength steel in water is widely accepted as due to "hydrogen embrittlement". Beachem (1972) suggested that the term "hydrogen-assisted crack" is more descriptive than hydrogen embrittlement, and proposed, from the concept of microplasticity, that hydrogen aids plasticity, which, in turn, facilitate the entry of hydrogen into the critical region. Using a polished WOL type constant deflection specimen, the nucleation and propagation of SCC of ultra-high strength steel in water have been followed metallographically (Chu, 1979 a). It has been shown that cathodic hydrogen during stress

corrosion significantly enlarges the plastic zone ahead of the crack. The enlargement of the plastic zone by hydrogen is a manifestation of hydrogen-induced delayed plasticity (HIDP) which preceeds the hydrogen-induced delayed cracking (HIDC).

In the present work, the nucleation and propagation of SCC and HIDC have been studied in four low-alloy steels with a wide range of the strength in various environments, such as H_2 or H_2S gas, charging, water and aqueous solution of H_2S. The effect of hydrogen on the yield strength of the steel was investigated with smooth tensile, bending and pre-crack WOL specimens in order to find out the cause of HIDP.

EXPERIMENTAL METHODS

The composition and strength of steels are given in Table 1 and 2.

TABLE 1   The Composition of Steels, 10^{-2} Wt%

Steel	C	Si	Mn	Cr	Ni	Mo	Steel	C	Si	Mn	Cr	Mo	V	Nb
30CrMnSiNi2	29	111	115	107	157	--	40CrMnSiMo	39	127	91	125	50	--	--
30CrMnSi	30	118	95	91	--	--	32SiMnMoV	33	158	181	--	42	29	--
40CrNiMo	38	22	64	69	159	19	40MnNb	46	26	155	--	--	--	3
ZG-18	24	65	87	127	--	54	30Cr2MoV	33	48	66	136	66	28	--
20	18	31	51	--	--	--	45	46	17	63	--	--	--	--
16Mn	18	40	142	--	--	--	40Cr	40	21	52	90	--	--	--

TABLE 2   The Strength of Steels, MPa

Steel	30CrMnSiNi2							30CrMnSi		40CrNiMo			ZG-18
NO.	1	4	6	8	12	13	15	16	17	18	19	20	22
T.S.	1760	1300	1620	1580	1230	1090	900	1420	1270	1810	1400	1320	1580
Y.S.	1440	1180	1280	1200	1120	980	-	1280	1180	1560	1290	1210	1310

The thickness of all the modified WOL specimens was 20mm. The K_{ISCC} and da/dt can be measured with one specimen (Chu, 1979 b). The polished pre-crack specimens were loaded and then put into water or H_2S solution with polished surface remaining in air. The nucleation and propagation of SCC can be followed with time. The polished specimens were completely dried before loading, then put into the flowing gas of H_2 or H_2S and taken out periodically for examination. The polished and dried pre-charged specimen was examined directly in air.

The specimens used for investigating the influence of hydrogen on the yield strength of the steel were the smooth tensile specimen of 10 mm diameter, the three-point bending specimen with a cross section of 12x12mm and WOL specimen with thickness of 20mm. The resistance strain gage was stuck on the tensile surface of the bending specimen. The load-strain ($P-\varepsilon$) and the usual load-displacement ($P-\delta$) curves could be recorded during test. According to the load at whcih the $P-\varepsilon$ and $P-\delta$ curves began to deviate from the straight line, the yield strength could be calculated. For WOL specimens, the resistance strain gages were stuck on the front of the crack tip and a clip gage was mounted on the specimen as used. The load-strain ($P-\varepsilon$) and load-displacement ($P-V$) curves could be recorded. The load at which the $P-\varepsilon$ curve began to deviate from the straight line was taken as the critical load, and then the corresponding apparent stear stress could be calculated. The charging conditions were as follows : the specimens were immersed for 13 hours in H_2SO_4 solutions with pH

values of 4,3, 2 or 0.1 or were electrolytically charged for 13 hours in 1 N H_2SO_4 solution with current density i=0.2, 1, 5, 20, 50 or 80 mA/cm^2. All charged specimens were loaded slowly. The rate of the displacetment of the cross head was 0.006 mm/min

EXPERIMENTAL RESULTS

The Nucleation and Propagation of SCC and HIDC

The progress of the nucleation and propagation of SCC is shown in Fig.1 for ultra-high strength steel (No. 8, in H_2S solution). As soon as the specimen was loaded, pre-crack was blunted (Fig. 1.1). When K_I was higher, there was a visible plastic zone in front of the crack tip (Fig. 1.2). This plastic zone did not change when the specimen remained in air after loading. But when it was put into water or H_2S solution with the polished surface in air, the size of the plastic zone enlarged continuously with time (Fig. 1.3), i.e., HIDP was observed. After the closure of the delayed plastic zone, a discontinuous SCC was nucleated at its tip B (Fig. 1.4), this is called HIDC. These processes were repeated and these discontinuous cracks grew and linked together during the progress of the delayed plasticity (Fig. 1.5 to 1.7). When the K_I was greater than the K_{ISCC}, the same sequences of the HIDP-HIDC were also observed for other ultra-high strength steels, such as No.1, No.6, No.18 and No.22.

For lower strength steels, the progress of HIDP and HIDC were somewhat different, as shown in Fig.2 (No.19, in water). The size of the plastic
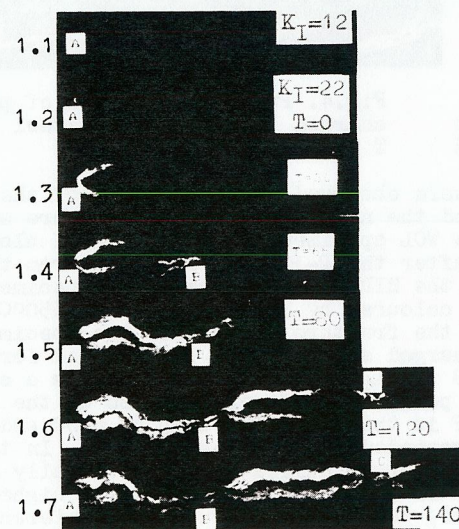

Fig.1. Nucleation and propagation of SCC of ultra-high strength steel in a H_2S solution, T in minutes. x30   No.8,   dark field
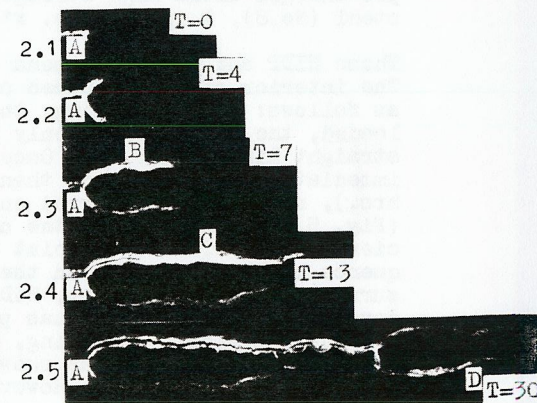
Fig.2. Nucleation and propagation of lower strength steel(No.19) in water, T in hrs.

dark field   x30

zone enlarged with time continuously after loading (Fig. 2.2). When this delayed plasticity developed to a critical extent, SCC occurred and propagated along a path near the border of the delayed plastic region (Fig. 2.3). These processes were repeated. The same sequence of the delayed plasticity and SCC were also observed for other lower strength steels, such as No.4, No.12, and No.13, No.15 in H_2S solution, No.16, No.17 and No.20.

Same features of HIDP and SCC were observed in the various aqueous solution, such as H_2O, H_2S, 0.1N $K_2Cr_2O_7$, etc. Neither the anodic nor the cathodic polarization in water or H_2S solution changed these features. Furthermore, the same phenomena were observed on the specimens tested in flowing H_2 or H_2S gas and on charged specimens tested in air (Fig.3 and Fig.4).
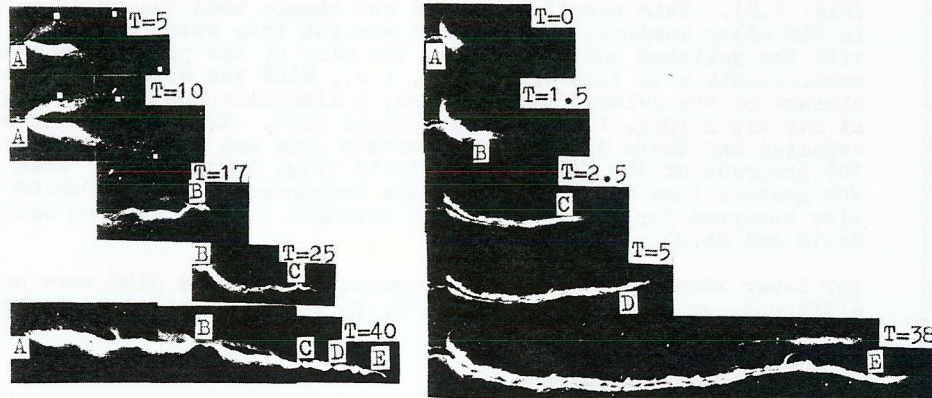

Fig.3. Process of HIDP-C of pre-charged ultra-high strength steel (No.8), T in minutes. x15

Fig.4. Process of HIDP-C of pre-charged lower strength steel (No.19), T in hrs. x30

These HIDP and HIDC phenomena were observed on the surface of the specimen. The interior of the specimen and the nature of the "delay" were examined as follows: After charging, the WOL specimen was polished and slowly loaded, the HIDP occured only after the P-ε curve deviated from the straight line (Fig.5.1). Once the HIDP was observed, the specimen was immediately unloaded, and then coloured by heating tinting (350°C, 1.5 hrs.), no HIDC was observed on the fracture surface of the specimen (Fig. 5.2). However, if the charged specimen had been loaded for sufficient period of time at point B in Fig. 5.1, HIDC appeared as a consequence of HIDP not only on the polished surface, but also on the fracture surface (Fig. 5.3). Thus, HIDP is the preceding step of HIDC and HIDC develops only after HIDP has proceeded to a certain extent. In the case of electrolytically charging, the crack nucleated preferentially on the surface of a specimen, as shown in Fig. 5.3, because of its higher concentration of hydrogen. However, the crack may nucleate preferentially either in the interior or on the surface of a specimen during SCC. The change of SCC with the depth from the surface has been investigated. Figure 6 indicated that HIDC has not yet occurred inside the delayed plastic zone between discontinuous cracks B and C and in front of the last crack D. Removed the surface by polishing layer by layer, no cracks were observed in there regions until 0.1mm has been removed, as shown in

Fig. 6.5. After a layer of o.3mm had been removed, the crack propagated to H instead of D, but no crack appeared between the discontinuous crack E and F, G and H (Fig.6.6). This result implys that there existed delayed plastic zones between the discontinuous cracks and HIDC nucleated
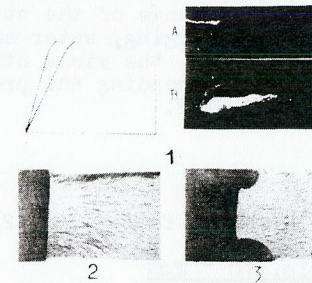

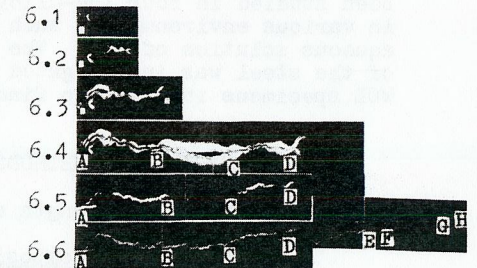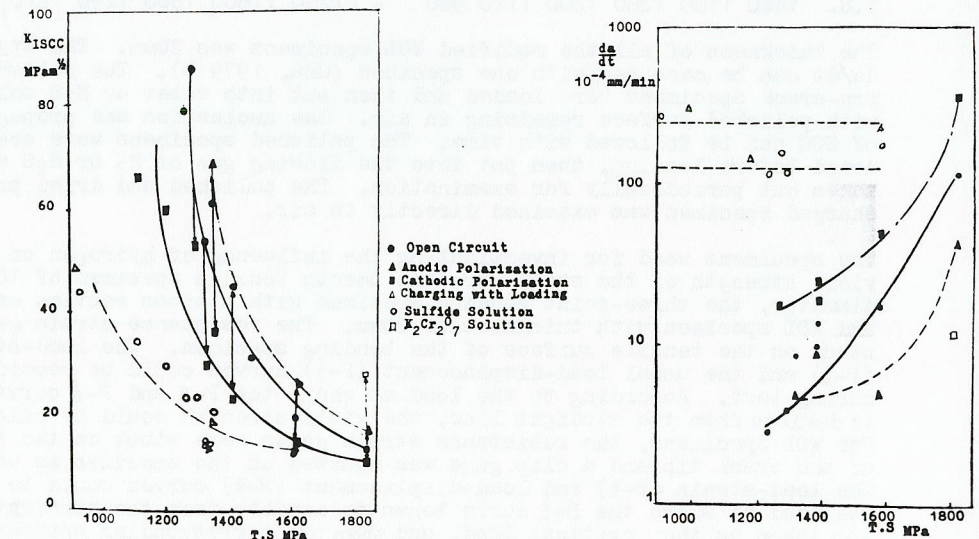Fig.5. Relation between HIDP and HIDC (No.8, pre-charged)

Fig.6. Change of SCC with the depth from the surface (No.8, in water) x15 dark field

also discontinuously by HIDP in the interior of the specimen.

The K_{ISCC} and da/dt in Various Environments

The variation of the K_{ISCC} (or K_{IH}) and da/dt with the tensile strength of steel and the environments used are shown in Fig. 7. As expected, the K_{ISCC} is decreased and da/dt increased with the increase of the

- ● Open Circuit
- ▲ Anodic Polarisation
- ■ Cathodic Polarisation
- △ Charging with Loading
- ○ Sulfide Solution
- □ $K_2Cr_2O_7$ Solution

(a) K_{ISCC}

(b) da/dt

Fig.7. Variation of K_{ISCC} or da/dt with the tensile strength of steels in various envionments.

tensile strength of the steels. For same tensile strength of the steels, cathodic polarization would decrease K_{ISCC} and increase da/dt, anodic polarization or inhibiting with 0.1 N $K_2Cr_2O_7$ solution would increase K_{ISCC} and decrease da/dt, and charging during loading or SCC in H_2S solution are the worst conditions with the lowest K_{ISCC} and the highest da/dt.

The Influence of Hydrogen on the Yield Strength

The ratio of the yield strengths of the charged and uncharged smooth tensile specimens is given in Fig. 8 for five steels with different strengths. There were not effect due to hydrogen, only the yield strength of 20 steel decreased and those of 30CrMnSiNi$_2$ and 45 steel increased very slightly.

The variation of ratios of yield strengths of the charged and uncharged bending specimens with charging conditions are shown in Fig. 9. No effect was observed when the tensile strength of steel was less than 900 Mpa, even after severe charging. But for ultra-high strength steel 30CrMnSiNi$_2$ and 40CrMnSiMo, the yield strength of the charged specimen was steeply lowered with the increasing current density of charging. The yield strength did not decrease even for ultra-high strength steel in the severely charging condition when the specimen was pulled at fast speed (Comparing curve 2 in Fig. 10 with curve 1). When the charged specimen
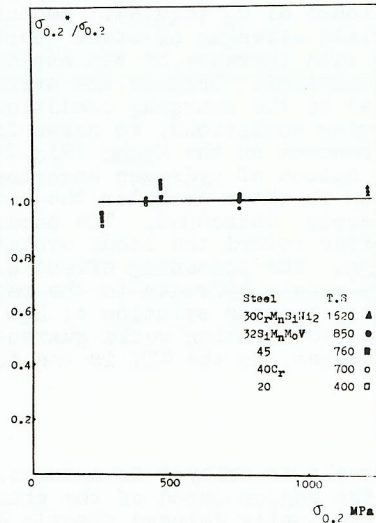
which had been fastly loaded over the yield point was unloaded and slowly loaded again, the yield strength was again lowered (curve 3, Fig.10) and was similar to that of the specimen not previously overloaded but slowly loaded after charging. After hydrogen in the charged specimen had been removed (280°C, 44 hrs.), the yield strength returned to the value of the uncharged specimen (the curve 4 in Fig.10). Figure.11 shows that the hydrogen-induced yield strength reduction is not related to pre-overload before charging.

The hydrogen induced delayed plastic deformation extented approximately along $\theta = \pm\pi/4$ for ultra-high strength steels, as shown in Fig.1. Rotating the co-ordinated axex $\theta = \frac{\pi}{4}$, the shear stress τ along the direction of deformation is:

$$\tau = \frac{1}{2}(\sigma_y - \sigma_x)\sin 2\theta + \tau_{xy}\cos 2\theta \qquad (1)$$

Substituting the stress components of a crack tip and $\theta = \frac{\pi}{4}$, then

$$\tau = 0.328\ K_I\ /\ (2\pi r)^{1/2} \qquad (2)$$

when τ in a large enough distance from the front of the crack tip is equal to the apparent shear strength of the steel τ_c^*, HIDP will occur, the P-$\mathcal{E}$ curve will also begin to deviate from the straight line at the critical load P_c^* (see Fig. 5.1),

$$\tau_c^* = 0.328\ K_{ISCC}/(2\pi r c)^{\frac{1}{2}} = 0.328\ P_c^*\ F(a/w)/B(2\pi r_c\ w)^{1/2} \qquad (3)$$

Therefore, the ratio of the apparent shear strength between the charge and uncharged specimen is

$$\tau_c^*/\tau_c = P_c^*\ /P_c \qquad (4)$$

The variation of τ_c^*/τ_c with charging conditions for WOL specimens with various strength is shown in Fig. 12. If the tensile strength of steel was lower than 800 MPa, the apparent shear stress of the charged specimen did not decrease with the charging conditions used and HIDP did not occur. But τ_c^*/τ_c decreased significantly with increasing strength and with the amount of hydrogen introduced when the tensile strength was higher than 1300 MPa. For ultra-high strength, τ_c^*/τ_c was about 1/10 in the severly charging condition.

Fig. 10. Load-strain curve of the bending specimen in different test conditions (30CrMnSiNi$_2$, No.6)

Fig.8. Ratio of the yield strengths between charged and uncharged smooth tensile specimens (i=40-80 mA/cm^2, 6-8 hrs., slowly load)
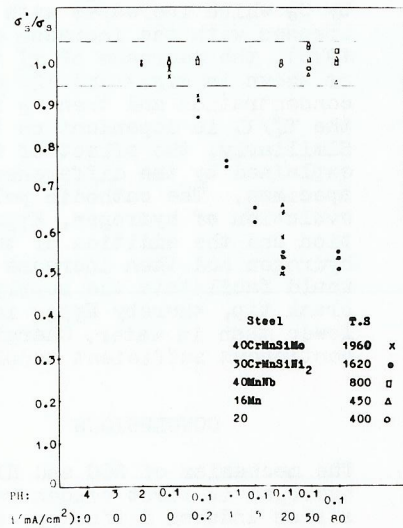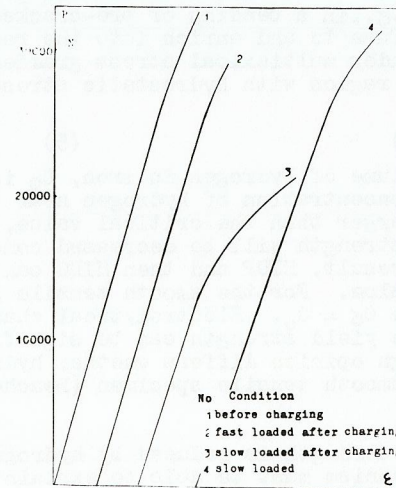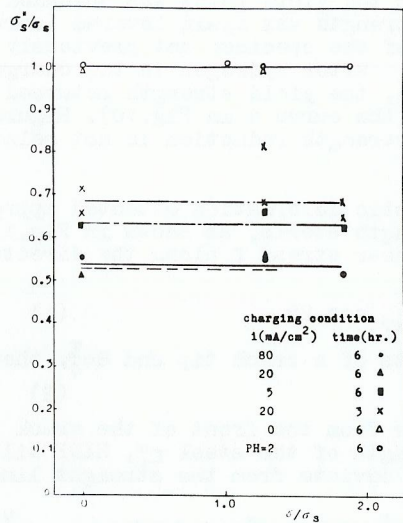
Fig.9. Variation of ratio of yield strength of the charged and uncharged bending specimens with charging conditions

Fig.11. Effect of pre-overloading on the yield strength of the charged bending specimen (30CrMnSiNi$_2$, No.6)

Fig.12. Variation of τ_c^*/τ_c of the charged and uncharged WOL specimens with charging conditions.

DISCUSSIONS

The experiments showed that when the strength of steel and K$_I$ were larger than certain values, which were dependent on the environment used, HIDP occurred in a loaded pre-cracked specimen in all the environments which supply atomic hydrogen. Only when this delayed plastic deformation had developed to certain extent, SCC or HIDC could nucleate and propagate. When a stress gradient exists, e.g., in a bending or pre-cracked specimen, the atomic hydrogen tends to diffuse to and enrich into the region with the maximum hydrostatic stress under multiaxial stress gradient. The concentration of hydrogen in the region with hydrostatic stress σ_p is shown to be (Gerberich, 1976)

$$C_\sigma = C_o \exp(\sigma_p V_H / RT) \qquad (5)$$

where V_H is the partial molar volume of hydrogen in iron, C_o is the average concentration. If the concentration of hydrogen near the region of the maximum multi-stress is larger than the critical value, the yield strength or the apparent shear strength will be decreased considerably, as shown in Fig.9 and 12. As a result, HIDP and then HIDC can occur under the action of a lower K$_I$ value. For the smooth tensile specimen, no stress gradient exists and the $C_\sigma = C_o$. Electrolytic charging alone can not make C_o so large that the yield strength can be significantly reduced, as shown in Fig.8, though opinion differs whether hydrogen reduces the yield strength of a smooth tensile specimen (Beachem, 1972; Oriani, 1978)

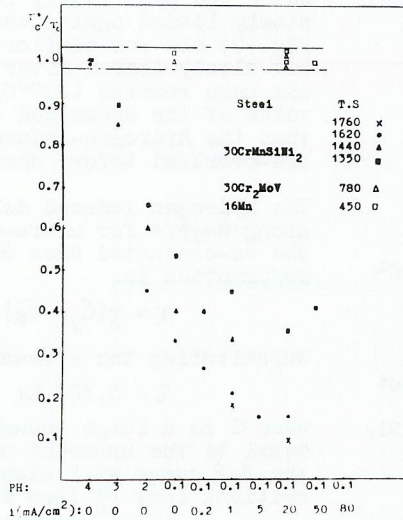The mechanism by which the yield strength is reduced by hydrogen is not clear. However, any possibe mechanism must be able to explain following experimental facts: the hydrogen-induced apparent yield strength reduction is controled by hydrogen diffusion and is reversible (see Fig.10); this reduction is not related to the pre-plastic deformation (see Fig.12) and thus independent of the original dislocation structure. According to these facts, a possible mechanism of apparent yield strength reduction by hydrogen can be proposed. When the hydrogen concentration C_σ exceeds a critical value, the "hydrogen cluster or atmosphere" similar to what proposed by Fujita (1978) could form and exert a high interior pressure. This pressure does not decohere the crystallography plane and produce small cracks, but aids the external load to start the local plastic deformation. Therefore, though the true yield strength of the material may not decrease significantly, the apparent yield strength can be considerably decreased owing to the contribution of a stear stress component of the pressure from the hydrogen cluster. Because the formation of the "hydrogen atmosphere" is controled by diffusion of hydrogen, the hydrogen-induced plastic deformation is "time-dependent", the plasticity so induced is called HIDP.

From equ.(3), can get
$$K_{ISCC} = D \tau_c^*$$

where D is a constant. Therefore, the variation of the K$_{ISCC}$ with strength of steel and with the amount of hydrogen entering into the specimen, which is related to be the environments, is the same as that of τ_c^* (comparing Fig.7 with Fig.12). Assume that τ_c^*/τ_c is mainly decided by C_σ which increases with the increase of σ_p (equ.5). Because σ_p increases with the increase of the yield strength of steel (Gerberich, 1976), the decrease of τ_c^* or K$_{ISCC}$ with increase of the strength of steel, as shown in Fig.7 and 12, can be explained. Because the average hydrogen concentration and then C_σ is related to the charging conditions, evidently the τ_c^*/τ_c is dependent on the charging conditions, as shown in Fig.12. Similarly, the effect of the environment on the K$_{ISCC}$ (Fig.7) can be explained by the difference of the amount of hydrogen entering into the specimen. The cathodic polarization in water promotes the cathodic evolution of hydrogen, K$_{ISCC}$ is thereby decreased. The anodic polarization and the addition of the inhibitor retard the local evolution of hydrogen and then increase the K$_{ISCC}$. The poisoning effect of S ion would facilitate the supply of more atomic hydrogen to the region of the crack tip, thereby K$_{ISCC}$ in saturated aqueous solution of H$_2$S would be lower than in water. Charging during the loading would guarantees a continuous sufficient supply of hydrogen, so the K$_{IH}$ is the lowest (Fig.7).

CONCLUSIONS

The mechanism of SCC and HIDC in steels is delayed in nature: atomic hydrogen is first concentrated in the region ahead of the crack tip by stress induced diffusion, causing eventually delayed plastic deformation; when this HIDP has developed to a critical condition, HIDC or SCC nucleates and propagates. Therefore, HIDP is the necessary condition of HIDC or SCC of low-alloy steels.

The effect of hydrogen on the yield strength of the smooth tensile specimen is not evident. But if there is a stress gradient in the specimen, e.g., bending or pre-cracked specimen, hydrogen can decrease the apparent yield strength considerably. The effect of hydrogen induced reduction of yield strength increases with increasing strength of the steel and the average hydrogen concentration in the specimen.

The hydrogen induced reduction of yield strength is due to process which is controlled by hydrogen diffusion and is reversible. It is not related to the overloading and work hardening. This hydrogen induced reduction of apparent yield strength is the primary cause of HIDP and then HIDC.

The K_{ISCC} increases and the da/dt decrease with the strength of steel in all the environmemts used. The anodic polarization in water or the addition of $K_2Cr_2O_7$ will increase the K_{ISCC} and decrease the da/dt. the effect of the cathodic polarization in water is just reversed. The K_{ISCC} is the lowest and the da/dt is the highest for stress corrosion in saturated aqueous solution of H_2S or charging during loading. Both of the strength and environment effect can be explained by hydrogen induced reduction of apparent yield strength and HIDP.

ACKNOWLEDGEMENTS

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