

# Susceptibility of Steels containing Cr, Ni, and Mo in H<sub>2</sub>S Environments

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## Abstract

The HIC susceptibility of steels containing Cr, Ni, and Mo under stress and hydrogen diffusion was been investigated by electrochemical methods. As the content of alloying elements increased, the apparent hydrogen diffusion coefficient (D) and threshold hydrogen permeation rate ( $J_{th}$ ) for hydrogen embrittlement decreased.

Hydrogen content ( $C_o$ ) in the steel in NACE TM-0177 solutions increased due to decreasing D with increased Cr content, although hydrogen permeability ( $J \times L$ ) decreased, and the susceptibility to sulfide stress cracking (SSC) increased as a result. Moreover, Mo exhibited clear effect of decreasing  $J \times L$ , and consequently the resistance to SSC improved with increasing Cr content.

**Keywords:** hydrogen embrittlement; Cr-Mo-Ni; SCC; HIC; carbon steel; low alloy steel; hydrogen activity, permeation, diffusivity.

## 1. Introduction

Hydrogen induced cracking (HIC) occurs when hydrogen concentration,  $C_o$ , in the steel matrix exceeds the threshold hydrogen concentration,  $C_{th}$ . The  $C_{th}$  might be considered as a parameter unique to a given material [1]. The HIC is mostly caused by the diffusible hydrogen. With increased materials strength, threshold hydrogen content ( $C_{th}$ ) tends to decrease, and threshold stress-intensity factor  $K_{IH}$  becomes dependent on hydrogen concentration ( $C_o$ ) irrespective of material [ $K_{IH}$  tends to decrease with increasing hydrogen concentration ( $C_o$ )].  $C_o$  is known to be dependent on alloy composition, H<sub>2</sub>S partial pressure, and pH, whereas  $C_{th}$  depends on inclusions and segregation in the matrix [2,3]. In general, both HIC and sulfide stress cracking (SSC) of the pipeline steels in H<sub>2</sub>S environments are all closely related to hydrogen entry. Hydrogen diffuses to regions of high triaxial tensile stress or to some microstructural configurations such as the inclusions and segregations



Fig. 1. Two types of HIC: (a) center line cracks, and (b) blister crack.

and becomes trapped. When hydrogen permeation is up to a critical value, it will result in cracking. It is accepted that the cracking in H<sub>2</sub>S environments is associated with banded structure. The interfaces between banded structure and matrix usually act as sinks of hydrogen. Hydrogen is apt to diffuse to these interfaces and reaches the critical value, building up pressure that leads to cracking. Two typical types of HIC cracks are shown in Fig. 1, namely, centre line cracks and blister cracks. Blister cracks are those hydrogen induced cracks that are formed near the surface so that the hydrogen pressure is able to raise the material, developing blisters that are observable on the surface [Fig. 1(b)]. The formation of blister cracks seems to be directly related to the type and distribution of non-metallic inclusions in the steel [4].

Hydrogen sulfide (H<sub>2</sub>S) is known to poison the hydrogen recombination reaction,  $H \rightarrow H_2$ , thereby increasing hydrogen absorption in steel. As a consequence, hydrogen sulphide accelerates HIC and SSC in carbon steel and low-alloy steel in sour environments. In contrast to the research on hydrogen effect in carbon steel and low-alloy steel, research on HIC in chromium steel is sparse. As reported in the literature, chromium steel is highly resistant to CO<sub>2</sub>; however, this steel is known to be susceptible to SSC in sour environments, and the influence of H<sub>2</sub>S on HIC behaviour of chromium steel has not been systematically explored [5,6].

The aim of this work is to understand the chemical composition and alloying elements on both HIC and SSC.

## 2. Experimental Procedure

The chemical compositions of the steels are presented in Table 1.

Table 1 Chemical analysis (wt %).

Steel	C	Cr	Ni	Mo	(Cr + Ni + Mo)	Yield Strength	
						MPa	ksi
<b>CRB</b>	0.171	–	–	–	–	633	96
<b>Low Alloy</b>	0.260	0.521	0.021	0.212	0.754	690	100
<b>9Cr-1Mo</b>	0.110	8.488	0.111	0.921	9.520	568	82
<b>13Cr</b>	0.212	12.50	0.010	–	12.510	644	93
<b>13Cr-5Ni</b>	–	13.10	4.501	4.501	17.601	721	104
<b>13Cr-5Ni-Mo</b>	–	13.51	5.00	2.00	20.510	709	103

### 2.1 Electrochemical Hydrogen Permeability Evaluation

The hydrogen permeability J was evaluated from the ionization current of hydrogen atoms diffusing out of the steel substrate on a Ni-plated anode surface maintained at the controlled potential of 50 mV/SCE by a potentiostat in a 0.1N NaOH solution. The principle is based on the Devanathan-Stachurski technique [7]. Hydrogen concentration, C, can be given in terms of J, L (specimen thickness), and D (hydrogen diffusion coefficient) as follows:

$$C(\text{ppm}) = \frac{J(\text{A/cm}^2) \times L(\text{cm})}{1.318 \times D(\text{cm/s}^2)} \quad \text{Eq. (1)}$$

$$C(\text{ppm}) = \frac{J \times L}{1.318 \times D}$$

In order to evaluate C using this equation, hydrogen permeability (J x L) was obtained from a cathodic polarization test, and this J x L was considered to be the threshold hydrogen permeability  $J_{th} \times L$  of a given specimen. D was then considered from time t yielding  $J_{th}/J = 0.5$ , where J refers to the steady-state level of hydrogen permeation.

The test solution in the cathodic cell was saturated with pure H<sub>2</sub>S gas. Measurements were undertaken without applying stress. On the basis of these measurements, C<sub>th</sub> (threshold hydrogen concentration for cracking) and C<sub>o</sub> (hydrogen solubility under H<sub>2</sub>S environments) were estimated using Eq. (1). C<sub>th</sub> was estimated by substituting  $J_{th} \times L$  into Eq. (1), whereas C<sub>o</sub> was estimated by substituting J x L. In electrochemical hydrogen charging, hydrogen is permeated through the specimen from one side of the specimen sheet.

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## 2.2 Sulphide Stress Cracking (SSC) Tests

A tensile test has been used for ranking materials and for qualifying alloys for sour service. An apparent threshold stress for initiation of SSC is frequently obtained using this method. Test duration is the time required for test specimen failure or after 1 month (720 h), whichever occurs first.

The SSC susceptibility of Cr content steel specimens was evaluated by a constant-load cathodic hydrogen charging test with the tensile test specified in NACE TM0177-96 Method A [8].

In the constant-load cathodic hydrogen charging test, a smooth tensile specimen of diameter 6.35 mm and of length 25.4 mm was cathodically polarized in NACE solution to measure the current density yielding fracture (threshold fracturing current density). Hydrogen susceptibility was evaluated by the threshold of fracturing current density. For this test, NACE TM-0177 solution saturated with H<sub>2</sub>S, and there is an additive of 5 mg As<sub>2</sub>O<sub>3</sub>/L to enhance hydrogen absorption. At the threshold fracturing current density level determined from this test, threshold fracturing hydrogen permeability ( $J_{th} \times L$ ) was measured electrochemically according to the procedure summarized in Section 2.1.

Sulphide stress cracking(SSC) susceptibility evaluation was made in terms of the ratio of threshold fracturing stress ( $\sigma_{th}$ ) to true yield stress ( $\sigma_{ys}$ ).

### 3. Results and Discussion

#### 3.1 Effect of Cr, Mo, and Ni on the HIC and SSC

With the aim of elucidating the influence of Cr content on the susceptibility of steel to hydrogen damage by HIC or SSC, steel specimens with different levels of Cr content and with different Mo levels were studied (Table 1). Table 1 summarizes the chemical compositions and tensile properties of the representative steel specimens examined.

Results obtained for  $C_{th}$  are reported in Fig. 2. Threshold hydrogen concentration,  $C_{th}$ , is considered as a measure of the susceptibility to HIC of a given material. Constant cathodic hydrogen charging test results indicated that threshold fracturing current density tended to decrease as follow:

carbon steel > low-alloy steel > 9Cr steel > 13Cr steel

Among 13Cr steels, threshold fracturing current density was lower for 13Cr steel containing Ni and Mo than for 13Cr steel containing no Ni and no Mo. Figure 2 shows threshold hydrogen permeability for cracking ( $J_{th} \times L$ ) estimated from threshold fracturing current density measurement as a function of (Cr + Ni + Mo)%. Clearly ( $J_{th} \times L$ ) tended to decrease with increasing (Cr + Ni + Mo). The HIC would occur when ( $J \times L$ ) exceed ( $J_{th} \times L$ ); that is the lower the ( $J_{th} \times L$ ), the higher the susceptibility

of the material. The trend observed in Fig. 2 indicates that HIC susceptibility tends to increase with the increasing content of alloying elements Cr, Ni and Mo.

Figure 3 shows the diffusion coefficient,  $D$ , as a function of (Cr + Ni + Mo), indicating that  $D$  decreases with increasing (Cr + Ni + Mo). Smaller  $D$  signifies a lower hydrogen diffusion rate. Under these conditions, hydrogen that penetrate the steel matrix tends to reside there longer; that is, substitutional alloying elements Cr, Ni, and Mo in the steel matrix tend to retard hydrogen diffusion. The trend shown in Fig. 3 indicates that the extent of decline in  $D$

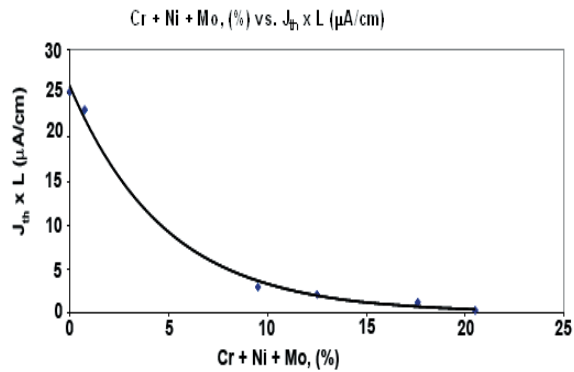


Fig. 2. Effect of sum (Cr+Ni+Mo) content on threshold hydrogen permeability.

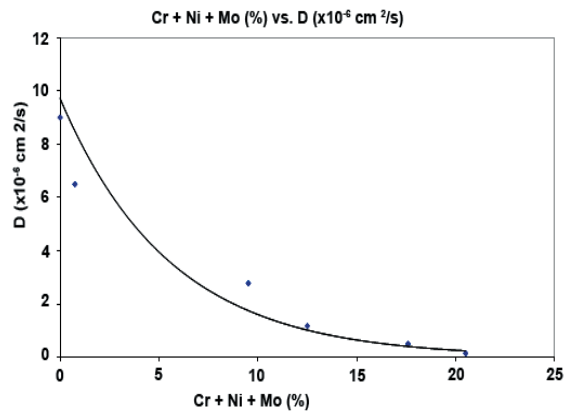


Fig. 3. Effect of sum (Cr+Ni+Mo) content on diffusion coefficient of hydrogen in tested steel.

depends on the sum (Cr + Ni + Mo). Values of ( $J_{th} \times L$ ) and D (in Figs. 2 and 3) of steel specimens with high (Cr + Ni + Mo) level were drastically lower than those of carbon steel and low-alloy steel.

### 3.2 Hydrogen Concentration in the steel Matrix, $C_0$ .

Hydrogen concentration,  $C_0$ , is considered to be a factor that determines HIC behavior. As represented by Eq. (1),  $C_0$  depends on hydrogen diffusion coefficient, D, in the steel matrix and hydrogen permeability ( $J \times L$ ). D is a material constant, but the ( $J \times L$ ) may vary depending on the extent of corrosion. In general ( $J \times L$ ) becomes higher when corrosion rate is greater, and at this time the rate of hydrogen evolution per unit of time is also higher.

Figure 4 shows the relationship between ( $J \times L$ ) and Cr content in the NACE TM-0177 environment. The hydrogen permeability ( $J \times L$ ) values plotted are a steady-state values. As shown, ( $J \times L$ ) decreased with increasing Cr content.

The data in NACE TM0177 solution Method A, as shown in Fig. 5, for threshold cracking stress,  $\sigma_{th}$ , were as follows:

$$\text{low-alloy steel} > 13\text{Cr steel} > 13\text{Cr-5Ni-2Mo}$$

lowest for 13Cr-5Ni-2Mo steel, and as that of low-alloy steel was the highest. In NACE TM0177 solutions,  $C_0$  tended to increase with increasing (Cr + Ni + Mo) and in the following order:

$$\text{low alloy steel} > 13\text{Cr steel} > 13\text{Cr-5Ni-2Mo steel}$$

This trend agree with the observation that  $\sigma_{th}$  decreased in the same order as in Fig. 4.

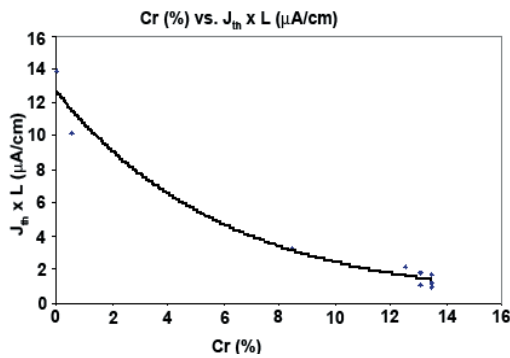


Fig. 4. Effect of chromium, Cr, content on hydrogen permeability in NACE TM-0177 solution.

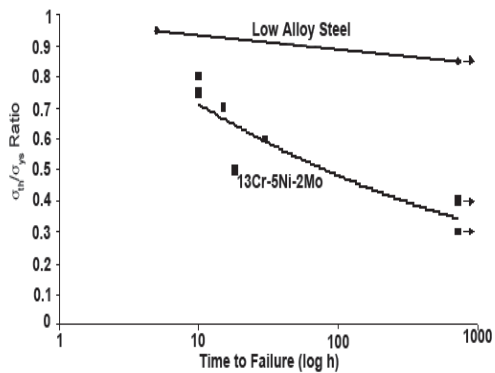


Fig. 5. Threshold stress for sulphide stress cracking (SSC) tested in NACE TM-0177-96 Method A.

As represented by Eq. (1),  $C_o$  is proportional to permeability of hydrogen penetrating from the environment ( $J \times L$ ) and inversely proportional to the hydrogen diffusion coefficient,  $D$ . Thus,  $C_o$  becomes smaller as  $J \times L$  become smaller and as the diffusion coefficient,  $D$ , becomes greater. In general, increased proportions of substitutional alloying elements, Cr, Ni, and Mo, lead to decreased  $D$ . Thus, by alloying, if the extent of decrease in ( $J \times L$ ) is higher than the extent of decrease in  $D$ , susceptibility to HIC might be reduced through a reduction in  $C_o$ .

The greater the  $C_o$  value, the smaller the stress intensity factor,  $K_{IH}$ . Thus, what determined was  $C_{th}$  at the given stress level (i.e.,  $C_o$  yielding failure at the initial stress intensity factor,  $K$ , level). The test results indicate that  $K_{IH}$  depends on  $C_o$ , alone, irrespective of alloy composition ranging from carbon steel and 13Cr steel to stainless steel such as 13Cr-5Ni-Mo.

According to the reduced atomic cohesion/model for hydrogen embrittlement proposed by Oriani [9], hydrogen embrittlement might be interpreted as being due to reduced atomic cohesion at the location of stress concentration by the accumulation of hydrogen atoms. Present results indicate that the higher the  $C_o$  value, the greater the extent of reduction in atomic cohesion at the stress concentration location. As such, hydrogen embrittlement behavior was found to depend largely on  $C_o$ .

As indicated above,  $C_o$  depends on both ( $J \times L$ ) and  $D$  Eq. (1). As such,  $D$  might be considered as a representative materials index for hydrogen susceptibility. One of the factors determining  $D$  is strength; with increasing strength,  $D$  decreases. It has been proposed in earlier studies [10-11] that heavily banded microstructures provide high hardness and a low fracture resistance. The higher their hardness, the lower  $D$  would become, and, as the consequence, ( $J_{th} \times L$ ) would tend to decrease.

#### 4. Conclusions

Steels with different Cr, Ni, and Mo contents were studied electrochemically in terms of ( $J_{th} \times L$ ), ( $J \times L$ ), and  $D$ , and the following conclusions were reached:

- With increasing (Cr + Ni + Mo) (%), decreases in ( $J_{th} \times L$ ) and  $D$  were observed. Decreasing ( $J_{th} \times L$ ) signifies increased susceptibility to HIC.
- $C_o$  depended on ( $J \times L$ ) (parameter depending on corrosion rate) as well as on  $D$  (materials parameter). The extent of the influence of  $D$  on  $C_o$  in NACE test solutions was higher for 13 Cr steel than for low-alloy steel, and therefore,  $C_o$  of 13Cr steel was higher than that for low-alloy steel.

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## References

1. A. Ikeda, Y. Morita, F. Terasaki and M. Takeyama, Proc. 2<sup>nd</sup> International Congress on Hydrogen in Metals, Paris, 1977, 4A-7
2. L. Tau, S.L.I Chan, and C.S. Shin, Effects of anisotropy on the hydrogen diffusivity and fatigue crack propagation of a banded ferrite/pearlite steel, Proc. of the 5<sup>th</sup> International Conference on Hydrogen Effect in Materials, A.W. Thompson and N.R. Moody (Eds.), The Minerals, Metals and Materials Society, 1996, p. 475
3. A. Ikeda, T. Kaneke, I. Hashimoto, M. Takeyama, Y. Sumitomo, and T. Yamura, Proc. Symposium on Effect of Hydrogen Sulphide on Steels, 22<sup>nd</sup> Annual Conference of Metallurgists, , Canadian Institute of Mining and Metallurgy (CIM), Montreal, August 22-24, 1983 (Edmonton, Canada) p. 1-7
4. M. Elboudjaini, R.W. Revie, M.T. Shehata, V.S. Sastri, R.R., and Ramsingh, Hydrogen-induced cracking and effect of non-metallic inclusions in linepipe steels, NACE International, Houston, Texas, Paper No. 748, (1998)
5. A. Turnbull, M. Saenz de Santa Maria and N.D. Thomas, Corrosion Science, (29), 1989, p. 89
6. K. Tamaki, T. Shimuzu, and Y. Yamane, Corrosion/91, Paper 14, (1991).
7. M.A.V. Devanathan and Z. Stachurski, The adsorption and diffusion of electrolytic hydrogen in palladium, Proceedings of Royal Society, (A270), 1962, pp. 90-102
8. Standard Test Method TM-0177, Laboratory testing of metals for resistance to specific forms of environmental cracking in H<sub>2</sub>S environments, NACE International, Houston, Texas, (2000)
9. R.A. Oriani and P.H. Josephic, Metallurgical Transaction, 11A, (1980), p. 1809
10. J. Bowker, O. Dremailova, and M. Elboudjaini, H<sub>2</sub>S testing of 4130 specification steel fitting, Internal Report MTL2000-39(CF)
11. M. Elboudjaini, J. Gianetto, and R.W. Winston, Full ring ovalization tests of X-65 linepipe, Internal Report MTL96-56(CF)
12. M. Elboudjaini, E. Essadiqi and C. DeRushie, Hydrogen permeation in experimental casing steels, Internal Report MTL98-03(CF)