Effect of Cu on the Hydrogen Induced Cracking of the Pipe Line Steel

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Synopsis
The effect of Cu on the hydrogen induced cracking of the pipe line steel was studied electrochemically and metallographically in detail. It was found out that, if the addition of Cu was more than 0.2%, hydrogen induced cracking could be effectively suppressed. This is because addition of Cu enhances the formation of tight and adherent surface film. This film was found to be quite protective, decreasing the corrosion rate greatly. As a result, the volume of the hydrogen evolved at the steel surface could be appreciably lowered. This surface film was furthermore found to be quite impermeable, so that hydrogen can hardly enter into the steel. Critical concentration of hydrogen that causes cracking cannot therefore be established in the Cu bearing steel.

From these results, it is suggested that surface film control by alloying may be one of the most effective method in preventing hydrogen induced cracking.

I. Introduction
Recently, hydrogen induced cracking(1-27) has become one of the most serious problems to the pipe line industries, because this cracking can, in extreme cases, lead to the failure of the total pipe line systems. It has been recognized that hydrogen induced cracking occurs in a wet H2S atmosphere in the following sequences.
(1) Corrosion of steel by wet H2S atmosphere and evolution of hydrogen at the steel surface.
(2) Chemical adsorption of hydrogen onto the steel surface.
(3) Diffusion of atomic hydrogen into the steel.
(4) Precipitation and recombinatian of atomic hydrogen into molecular hydrogen at pre-existing internal voids such as those existing around sulfide inclusions. This results in the increase in the internal pressure within these voids to such a high level that formation and propagation of cracks become possible.
(5) Interaction between neighboring cracks. This leads to the formation of stepwise cracking. If these grow ultimately through the thickness of the pipe, leakage accident of oil or gas would occur. It has recently been reported that addition of Cu above 0.2% greatly suppresses the hydrogen induced cracking of pipe line steel.(7,11) However, it is not as yet clear, in which of these stages Cu is effective in preventing hydrogen induced cracking.

It is the purpose of the present investigation to study this effect of Cu more extensively. Both commercial and laboratory melted steels containing various amount of Cu were subjected to the hydrogen induced cracking test(6,7) and the effects of Cu on the corrosion rate, the amount of diffusible hydrogen*** and cracking susceptibilities were studied. Furthermore, the mechanism by which Cu suppresses the hydrogen induced cracking was investigated both metallographically and electrochemically.

II. Experimental
To study the effect of Cu on the hydrogen induced cracking, 52 steels having the common composition of 0.1%C-0.25%Si-1.4%Mn-0.03%Nb-0.03%Al and containing various amount of Cu up to 0.40% were melted in a 50 kg high frequency induction furnace. After hot rolling to the thickness of 90 mm, they were finally control-rolled to the thickness of 16 mm. Specimens taken from these steels were then subjected to the hydrogen induced cracking test. Corrosion rate, amount of diffusible hydrogen and average crack length were determined after prescribed method.(6,7)

To confirm this effect of Cu also on commercial products, slabs of a commercial X-65 grade steel A and a Cu bearing steel B, both manufactured from 25 t ingots, were also control-rolled into 16 mm thick plates using production mill. Specimens were taken both from the center (designated hereafter by the suffix, M) and from the quarter from the edge (designated hereafter by the suffix, Q) of the 2 400 mm wide plates. Chemical compositions of these specimens are given in Table 1. These specimens were similarly subjected to the hydrogen induced cracking test.

Table 1. Chemical compositions of commercial X-65 grade steel A and Cu bearing steel B. Suffixes M and Q denote specimens taken from the center and quarter from the edge of 2 400 mm wide plates, respectively.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Ni</th>
<th>Nb</th>
<th>sol. Al</th>
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<tr>
<td>Conventional steel (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>AQ</td>
<td>0.11</td>
<td>0.31</td>
<td>1.28</td>
<td>0.022</td>
<td>0.004</td>
<td>0.017</td>
<td>0.02</td>
<td>0.04</td>
<td>0.040</td>
</tr>
<tr>
<td>AM</td>
<td>0.11</td>
<td>0.31</td>
<td>1.27</td>
<td>0.022</td>
<td>0.004</td>
<td>0.017</td>
<td>0.02</td>
<td>0.04</td>
<td>0.041</td>
</tr>
<tr>
<td>Cu bearing steel (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BQ</td>
<td>0.11</td>
<td>0.32</td>
<td>1.29</td>
<td>0.018</td>
<td>0.004</td>
<td>0.297</td>
<td>0.13</td>
<td>0.04</td>
<td>0.051</td>
</tr>
<tr>
<td>BM</td>
<td>0.11</td>
<td>0.32</td>
<td>1.30</td>
<td>0.018</td>
<td>0.004</td>
<td>0.302</td>
<td>0.13</td>
<td>0.04</td>
<td>0.051</td>
</tr>
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* Presented at the 91st ISIJ Meeting, April, 1976, at The University of Tokyo, in Tokyo. Manuscript received January 27, 1977.
*** Hydrogen that could be absorbed into steel at 25°C and that could be liberated from steel at 45°C.
Corrosion rate was measured on specimens taken from the plates of steels A and B. Specimens, 50×50×1 mm were polished with emery paper up to #800 and degreased with acetone. After immersing these specimens for various period in H₂S saturated synthetic sea water, weight loss was measured. Also, dynamic polarization measurements were made on specimens taken from steels A and B. After immersing specimens for various period in H₂S saturated synthetic sea water, potential was applied and changed at a rate of 25 mV/min and resulting polarization current was recorded.

The effect of Cu on the diffusion of hydrogen in these steels was next investigated. After placing one side of the 0.8 mm thick specimen in contact with the H₂S saturated synthetic sea water, the volume of the hydrogen penetrating to the other side of the specimen was measured with the manometer method. Diffusion constant determined in this way was found to be sensitively influenced by the surface film formed on the reaction side. Diffusion constant independent of such surface film could be determined with the electrochemical method. Specimen, whose anodic side was plated with Pd, was mounted in an H cell. The anodic cell was filled with 0.1 N NaOH and polarized to +100 mV (SCE), whereas cathodic cell was filled with 0.1 N Na₂SO₄. After charging the specimen with hydrogen to a steady state in the cathodic cell, cathodic current was switched off and decay curve of the anodic current was recorded. From this, diffusion constant was calculated.

As it was suggested that black surface film which was formed on the surface of Cu bearing steel played an important role in preventing hydrogen induced cracking, detailed studies were made on the nature of this film. Its chemical composition and structure were analysed with an ion microanalyzer (Hitachi IMA II) and with an X-ray diffractometer. The cross section of the surface film layer was observed with a scanning electron microscope (JEOL JSM III).

III. Results

1. Hydrogen Induced Cracking Test

The results of the hydrogen induced cracking test are shown in Figs. 1 to 3. It is interesting to note that, if the addition of Cu was more than 0.18%, average corrosion rate* decreased greatly (Fig. 1). Both the amount of diffusible hydrogen and average crack length decreased similarly with increasing Cu content (Figs. 2 and 3), but they decreased at lower Cu content than the average corrosion rate. If the addition of Cu was more than 0.2%, hydrogen induced cracking could be completely suppressed. All the specimens that were free from cracking were, without exception, covered with thin, tight and adherent black surface film. The excellent corrosion and cracking resistance Cu bearing steel may therefore be related with the formation of this surface film. In Figs. 1 to 3, results obtained on steels A and B are also shown by solid symbols. It is evident that the effect of Cu is not deteriorated by the segregations and inhomogenities contained in large production ingots. Since Cu thus seemed to affect corrosion of steel and diffusion of hydrogen in steel, detailed studies were made on these processes next.

* Weight loss divided by the time of immersion (4 days)
2. Corrosion Rate Measurements

Figure 4 represents the weight loss of steels A and B measured after immersing specimens for various period in H₂S saturated synthetic sea water. Corrosion occurred more slowly in Cu bearing steel B than in conventional steel A. The volume of hydrogen generated at the surface of the former might therefore be smaller. These results are plotted in log-log form in Fig. 5. In both cases, weight loss, \( w \), can be expressed in the form

\[
w = kt^n
\]

where, \( t \): the time of immersion
\( n \): the time exponent
\( k \): constant.

It should be noted that the effect of Cu is sensitively reflected in the value of \( n \). For steel A, \( n \) is 1.0, while for steel B, \( n \) is 1/2. It is generally thought that corrosion in the former case is controlled by the interface reaction, whereas corrosion in the latter case is controlled by the diffusion process in the surface film. These results again suggest that film layer formed on the surface of Cu bearing steel is important in reducing corrosion rate.

3. Polarization Studies

Figure 6 represents the polarization behaviours of steels A and B measured in H₂S saturated synthetic sea water after 24 hr immersion. Although natural potential of these steels were about \(-760\) mV (SCE) irrespective of Cu content, both the anodic and cathodic polarization curves were largely affected by the addition of Cu. The fact that Cu bearing steel exhibited lower current density at the same applied potential, also indicates that the rate of hydrogen generation is lower in this steel. Such difference could be observed even after 30 min immersion, during which formation of black film was already completed on the surface of steel B. But polarization curves obtained after short time of immersion were quite irreproducible.

4. Permeation of Hydrogen

The volume of hydrogen that has permeated from the flat specimen whose one side was placed at time \( t = 0 \) in contact with the H₂S saturated synthetic sea water was measured with manometer as a function of time, \( t \) (Fig. 7). The volume of hydrogen that permeated through the conventional steel A increased linearly showing only small incubation time, while hydrogen permeated through Cu bearing steel B indicated large incubation time and increased only slightly showing saturation at a later stage. Since the absolute amount of hydrogen generated at the surface of Cu bearing steel was smaller, volume of the hydrogen permeated through this steel should naturally be smaller. However, if diffusion can take place without any significant barrier, both steels should show the same time transient curve. The fact that this was not the case and especially the fact that incubation time for steel B was larger, indicate that diffusion of hydrogen either through the surface film or through the matrix of steel B is quite difficult.
The diffusion constant of hydrogen in the matrix of these steels were determined electrochemically. Decay curves of the anodic current is shown in Fig. 8. It is evident that Cu does not affect the diffusion of hydrogen through iron matrix.

Impermeable behaviour of hydrogen through steel B shown in Fig. 7, should therefore be ascribed to the presence of the surface film. Saturation observed on the transient curve of steel B in Fig. 7, might correspond to the fact that surface film becomes quite impermeable at a later stage of its growth.

5. Surface Film

Since all the results described above suggested that excellent corrosion and cracking resistances of Cu bearing steel were related to the presence of the surface film, the nature of this film was investigated next.

Photograph 1 shows cross section of the corrosion product layer which was formed during hydrogen induced cracking test. It is clearly seen that corrosion product layer of steel A is much thicker than that of steel B. This is in accordance with the observation that corrosion rate of steel A was much faster than that of steel B.

After removal of the loosely adherent corrodent, steel A exhibited blisters (Photo. 2). On the other hand, the surface of steel B revealed peculiar black film, as is already pointed out. This film was very tightly adherent to the iron matrix. Using an ion microanalyser analysis was made of this film and the blistered surface of steel A. The diameter of the Na+ primary ion was about 20 μ. The results are shown in Photo. 3. From the surface film of the Cu bearing steel, Cu, S, Fe, O, OH and other elements contained in synthetic sea water could be detected. Although these elements were found also from the surface of the conventional steel, the amount of Cu was extremely small. The depth etched by the ion beam during these analyses was estimated to be about 50 Å, so that the iron matrix would not have been analysed simultaneously. In fact, Nb which was detected in the matrices of steels A and B was not present in the sur-

![Fig. 7. Permeation of hydrogen from the specimen whose one side is placed in contact with an H2S saturated synthetic sea water](image1)

![Fig. 8. Decay curves of anodic current normalized with respect to its initial value](image2)

![Photo 1. Cross sections of steels A and B after hydrogen induced cracking test. Approximate thickness of the corrosion product layer is shown by arrows](image3)
Photo. 2. Appearance of the specimen surface after hydrogen induced cracking test. Loose corrodent was removed.

Photo. 3. Results of IMA analysis

Photo. 4. Appearance of the specimen surfaces after cathodic charging in 4%H₂SO₄ solution poisoned with 100 mg/1 NaAsO₂. (Current density was 10 mA/cm².) Even after 96 hr, protective surface film was not formed. In this case, numerous blisters were produced not only on the surface of steel A but also on the surface of Cu bearing steel B (Photo. 4). After sectioning these specimens, stepwise cracking was found out on the transverse sections of both steels. Thus, if sufficient amount of hydrogen is introduced into the interior, even the Cu bearing steel is not free from cracking.

IV. Discussion

Hydrogen induced cracking has been known for many years in oil and pipe line industries.¹⁻⁴ Its mechanism of formation is generally thought to be similar to that of blisters. The addition of Cu which suppresses formation of blisters and corrosion of steel in a wet H₂S atmosphere,⁵ has recently been found to be also effective in preventing hydrogen induced cracking.⁶⁻⁸,¹¹ The result of the present investigation indicates that the most important role that Cu plays in preventing hydrogen induced cracking lies in the formation of both protective and impermeable...
iron sulfide film.

Iron sulfide film formed in a wet H₂S atmosphere is known to be largely influenced by pH\(^{35-37}\) and H₂S concentration\(^{34,35,38,39}\) of the solution. The iron sulfide formed under experimental conditions adopted in the hydrogen induced cracking test \((i.e., \text{pH}=4.8-5.6, \text{concentration of} \ H₂S=2300-3500 \text{ppm})\) is reported to be Mackinawite, FeS₁₋ₓ, where \(x=0.11,34,36,41\). This was confirmed also in the present investigation for both commercial and Cu bearing steels.

The protective behaviour of the surface film is often discussed in terms of Pilling and Bedworth's law.\(^{41}\) If the ratio of the specific volume of the surface film to that of the steel is smaller than 1, tensile stress is produced in the surface film, so that crevices would be formed. This ratio was estimated to be larger than 1 for Mackinawite.\(^{36}\) As is expected from this, Mackinawite is reported to be protective at least at an early stage of its formation.\(^{35}\) However, with the growth of the individual Mackinawite crystallites, many deep crevices and pores are formed, so that easy path for diffusion could be formed.\(^{35}\) Mackinawite film is therefore considered to be nonprotective at later stages of its growth.\(^{34-37,39}\) Since solution can readily penetrate through these crevices and pores up to film-metal interface, interface reaction, \(i.e.,\) discharge of the hydrogen at the interface would become the rate controlling process. Linear rate law which should be expected in this case could really be observed in Fig. 5.

Low corrosion rate\(^{32}\) or excellent stress corrosion cracking resistance\(^{35}\) of Cu plated steel in an H₂S bearing aqueous solution have been explained in terms of the formation of the cuprous sulfide film. Since the solubility of cuprous sulfide is quite low in this solution, and since its formation occurs quite rapidly, it might be effective in reducing corrosion rate. However, any crystalline compound of Cu could not be detected in the present investigation. It might be concluded that Cu is contained in an atomic form in Mackinawite.

The fact that the surface film of Cu bearing steel is quite tight and adherent, seems to suggest that the formation of pores and crevices within the surface film is suppressed by the addition of Cu. Since solution cannot penetrate up to film-metal interface, discharge of hydrogen cannot occur before diffusion of ions and/or electrons takes place within the film. If this diffusion process is more difficult to occur than the interface reaction, corrosion would obey parabolic law.\(^{30,31,35}\) This is really observed in Fig. 5. Cu atom seems thus to improve tightness and adherence of the surface film.

It has been reported that protectiveness of the surface film is strongly dependent on its electronic an/or ionic conductivity.\(^{34,35,42}\) Furthermore, impurity ions, such as Na⁺ and Cl⁻, have been found to have large influences on the conductivity of the film formed in an H₂S bearing aqueous solution.\(^{35}\) Judging from these results, it might be possible that Cu⁺ ions similarly affect the conductivity of the surface film.

Since Mackinawite is a semiconductor which has defective structure, its conductivity arises from migration of these defects. Its conductivity may therefore be dependent on the concentrations and mobilities of these defects. If these defects are somehow to be attracted and trapped by Cu⁺ ions, mobilities of these defects would be reduced and the conductivity of the film would be lowered by the addition of Cu. Difference in valence between Fe and Cu which would affect defect concentrations, might also reduce the conductivity of the film.\(^{43}\)

Its has already been shown in Fig. 1, that above critical concentration of Cu, \(i.e., 0.18\%\), corrosion rate decreases rapidly. This critical concentration of Cu might probably correspond to the concentration of defects that can exist in thermal equilibrium. If all these defects are either immobilized or annihilated above this critical concentration, conductivity of the film would be lowered and lower corrosion rate would be expected.

The position at which hydrogen discharge occurs within the film would also be affected by the conductivity of the film,\(^{37,42}\) if it is assumed that surface film does not contain pores and crevices. If discharge of hydrogen occurs within the film at a place sufficiently distant from the film-metal interface, the discharged hydrogen atom must diffuse long distance within the film before it is absorbed into metal. If this is the case in Cu bearing steel, diffusion of hydrogen atom through the surface film would play very important role in suppressing hydrogen induced cracking. This is in fact shown in Fig. 7. But more direct evidence in support of this possibility would be obtained, if results shown in Figs. 1 and 2 are rearranged in the form of Fig. 9, in which the amount of diffusible hydrogen is plotted against corrosion rate. It is seen that in the range in which corrosion rate was below 60 mdd, the amount of diffusible hydrogen became extremely lower than that expected from corrosion rate. Since surfaces of these specimens were covered invariably with black film, this film might have inhibited the penetration of hydrogen into steel, although evolution of hydrogen due to corrosion occurred appreciably at the steel surface. Thus, diffusion of hydrogen through the surface film might be the more difficult process than corrosion. Diffusible hy-

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**Fig. 9.** Relationship between corrosion rate and amount of diffusible hydrogen
Hydrogen content decreased therefore at lower Cu content than corrosion rate (Figs. 1 and 2).

Thus, it might be concluded that, since both the evolution of hydrogen at the steel surface and its permeation through the surface film are largely suppressed by the addition of Cu, probably by the improvement of the adherence and tightness of the surface film, the amount of hydrogen available to the crack formation becomes extremely low in Cu-bearing steel, so that hydrogen induced cracking could be suppressed.

So far, we have discussed the effect of Cu on the evolution and permeation of hydrogen, since these seem, according to the result of the present investigation, to be the most important steps in which Cu suppresses hydrogen induced cracking. Cu might also affect the adsorption of hydrogen onto steel surface, for example by weakening the poisoning effect of S-ions or by decreasing the coverage of the adsorbed hydrogen on steel surface. The amount of hydrogen that enters into steel would then be reduced. However, since little is known about the mechanisms involved in these processes, it is not at present possible to evaluate how far Cu is effective in controlling the adsorption of hydrogen onto steel surface.

As an another possible mechanism in which Cu suppresses hydrogen induced cracking, Murata has recently pointed out that, Cu enriched zone which would be formed near the surface after hot rolling, prevents corrosion and permeation of hydrogen. However, results in Figs. 4, 6 and 7 were obtained from 1 mm thick specimens taken from the midsection of the 16 mm thick plates. The fact that, although Cu enriched zones were clearly absent, these specimens showed excellent protective and impermeable behaviour, does not support his explanations.

Hitherto, elimination of microstructural inhomogeneities, such as elongated sulphide inclusions and band low temperature transformation products, has been considered most essential in reducing hydrogen induced cracking. With this method, however, complete suppression of this cracking has not been possible.

The result of the present investigation, on the other hand, seems to suggest strongly that development of the protective and impermeable surface film by proper addition of alloying element, might be more effective in preventing hydrogen induced cracking. The result shown in Fig. 10 was constructed from the results shown in Figs. 2 and 3. It may be seen that, to suppress the hydrogen induced cracking the amount of diffusible hydrogen must be kept below critical concentration which lies at about 1 cc/100 g Fe. This seems to be possible only by proper surface film control.

V. Conclusion

Using both metallographical and electrochemical methods, detailed studies were made on the effect of Cu on the hydrogen induced cracking of the pipe line steel. It turned out that addition of Cu more than 0.2% completely suppresses the hydrogen induced cracking. This was ascribed to the formation of thin, tight and adherent surface film containing Cu. This surface film suppresses hydrogen induced cracking due to following reasons:

1. The surface film is quite protective, so that corrosion is controlled by the diffusion process occurring within surface film, rather than by the interface reaction at the film-metal interface. Since corrosion rate is therefore markedly decreased, the amount of the hydrogen generated at the steel surface is very small.

2. Since this surface film is quite impermeable, hydrogen can hardly enter into the steel. Hydrogen pressure inside internal voids in the steel is therefore too low to cause cracking.

From these results, it may be suggested that surface film control by proper addition of alloying elements is one of the most effective methods in preventing hydrogen induced cracking.

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REFERENCES

4) F. K. Naumann and F. Spies: Praktische Metallographie, 10 (1973), 475.
6) M. Kowaka, F. Terasaki, S. Nagata and A. Ikeda: Sumi­tomo Metals, 27 (1975), 12. (In this paper, standard method of hydrogen induced cracking was first established. Effects of testing conditions are discussed in great detail.)
11) A. Ikeda, S. Nagata, A. Okamoto, F. Terasaki and M.