

## Effect of Cu on Hydrogen Permeation for the Low Carbon Steel under Mildly Sour Environments

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Hydrogen Induced Cracking (HIC) and Sulfide Stress Cracking (SSC) are the major issue for low carbon alloyed steels applied to sour line pipes at oil and natural gas fields. It is caused by the presence of hydrogen sulfide, which enhances hydrogen entry into steels and causes the environmental cracking. It is well known that Cu is effective element for preventing HIC in mildly sour environments in which the solution pH is more than 5.0[1]. However, the mechanism of Cu rolls on HIC prevention has not been fully clarified. It was found that Cu addition remarkably decreased hydrogen entry into steel[2] and Cu was enriched in the corrosion product based on EPMA micron order analysis [3]. In present paper, corrosion test under H<sub>2</sub>S environments are carried out with measuring the amount of hydrogen permeation. Microstructural morphologies of corrosion products, especially Cu distribution and morphologies are investigated through FIB/SEM and STEM analysis for understanding its rolls on preventing the corrosions.

Two samples, concentration of 0.06C-1.7Mn-0.1Si with and without 0.3wt%Cu, were prepared through a vacuum melting. Corrosion tests were performed under 100%H<sub>2</sub>S gas environment in 5%NaCl+1N(CH<sub>3</sub>COOH+CH<sub>3</sub>COONa) solution for 96hrs. The hydrogen permeation was measuring during corrosion test. For evaluating effects of solution environment on corrosion product, two pH conditions of 5.0 and 5.3 were performed. After corrosion test, samples were picked up from the solution and SEM and TEM observations were carried out. Cross section samples of SEM and TEM were prepared by FIB techniques. Distribution of alloy elements in the corrosion product and steel were measured through EDS analysis equipped with SEM and TEM

Fig.1 shows plane view SEM images of corrosion product of Cu added steel immersed in the pH 5.3 and 5.0 solutions. It is observed that the surface morphology of corrosion products formed in high pH solution were smooth compared with that of in low pH solution. Micrographs of SEM cross sectioning are show in Fig. 2, together with the hydrogen permeation value at 90 hours of corrosion test. Several micro-meter thickness of corrosion product is formed during immersion test and there are roughly two layers in that product. Different microstructure is recognized dependent on the Cu concentration and pH value. The upper layer formed on the Cu added steel in high pH solution is uniform even though it structure is porous. On the other hand, that of formed on non-Cu added steel in low pH solution is very rough and has many large cracks. The bottom layer formed on the Cu added steel in high pH solution has dense structure and no cracks. The hydrogen permeated value is increasing when the corrosion layer has large cracks. It is supposed that adding Cu is very useful for forming uniform tight corrosion layer without large cracks for preventing hydrogen permeation. For evaluating the Cu distribution in the corrosion film, cross sectional TEM analysis is carried out and the STEM images shown in Fig.3. It is found that the small crystal size of FeS (~less than 10nm) is formed at the bottom layer of corrosion products from electron diffraction analysis. The upper layer of corrosion products has bigger crystal

size and has many pores. EDS mapping results of Cu in the corrosion layer is shown in Fig.4. Thickness of Cu enriched layer is about 100nm. This tiny Cu layer would prevent the hydrogen permeation and form a tight corrosion layer in pH 5.3 solution. Based on SEM cross section result (Fig.2), this Cu layer effectiveness for preventing hydrogen permeation is decreasing under pH 5.0 solution because of less of uniformity of bottom corrosion layer in this case. It is suggested that the formation of this tight layer is very important for preventing HIC for preventing hydrogen immersion and Cu adding is enhancing to form this layer.

#### References:

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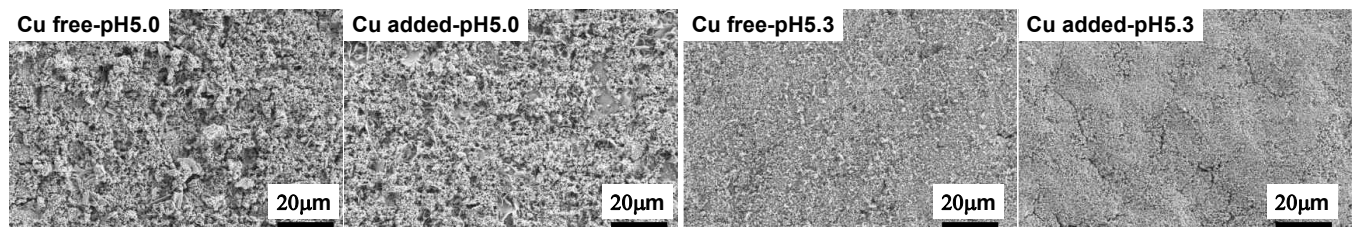


Figure 1. SEM plan view of corrosion product

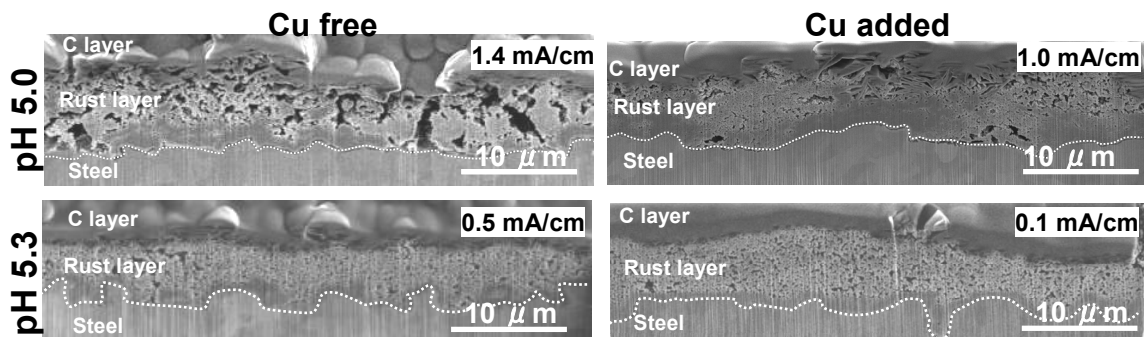


Figure 2. SEM cross sectional view of corrosion product

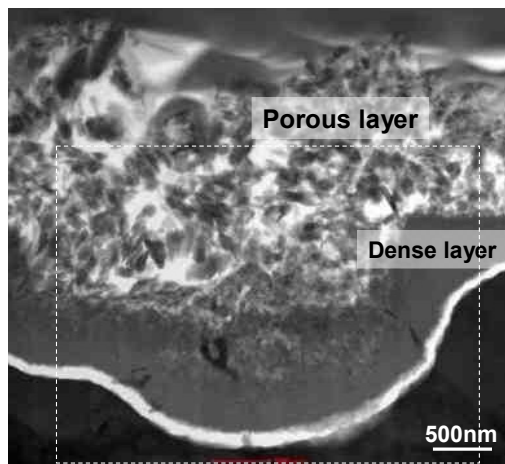


Figure 3. STEM image of corrosion product of Cu added steel in pH5.3 sample

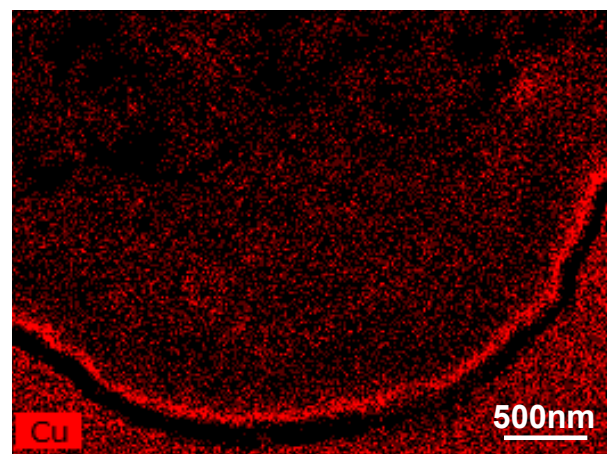


Figure 4. STEM-EDS mapping of Cu in the indicated area of figure 3