Hydrogen damage in metals

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Abstract. In corrosive environment, the hardness along the depth direction and crack propagation direction of specimen is affected by hydrogen concentration and stress. In this paper, micro-hardness tester was employed to quantitatively evaluate the hydrogen distribution in metals. Hydrogen saturated value and hydrogen saturated layer of specimens were obtained. The experimental results demonstrated that hydrogen concentration behavior in a known equibiaxial stress environment can be verified experimentally using micro-hardness technique. There is a simple additive relationship between the hydrogen-induced micro-hardness increment and the stress-induced micro-hardness increment in Vickers micro-hardness measurement. The hydrogen distribution of specimens was analyzed by taking the change of the micro-hardness increment along the depth direction and crack propagation direction of specimens as the indicator.

1. Introduction

Metal corrosion damage can cause catastrophic accidents, resulting in huge economic losses. Hydrogen is one of main corrosive medium in the metal industry. It is expected that hydrogen will be used as an energy carrier in the near future since it is clean, movable and abundant, however, hydrogen always has a deleterious effect on their mechanical properties, e.g. hydrogen-assisted stress corrosion cracking[1] and hydrogen embrittlement[2]. The effect of hydrogen on the metallic material begins when the hydrogen enters the metal. Once the hydrogen enters the metal, it can diffuse through the metal or get entrapped at microstructural features and hydrogen-trapping sites. Changes in the concentration distribution of the diffusible hydrogen are likely to cause changes in the mechanical properties of metals[3,4]. The crux of hydrogen damage study is to accurately evaluate the degree of hydrogen distribution within metals. It is therefore important to analyze the time and applied stress variation of hydrogen distribution in metals to understand the effects of hydrogen on the mechanical properties of materials. However, experimental evaluation of the non-homogeneous hydrogen concentration distribution behavior in a local area such as the vicinity of a crack is very difficult, due to the light weight and high mobility of hydrogen. Thermal desorption analysis can only evaluate the total hydrogen content and separate hydrogen trapping sites. The hydrogen microprint technique can visualize the presence of hydrogen in a local area[5], and Nagao used this technique to observe the effect of the stress fields caused by a bending test on hydrogen transport[6]. However, the hydrogen microprint technique cannot quantitatively evaluate the hydrogen content although it is no doubt a necessary technique for investigating hydrogen trapping and transport in local areas. Thus, an unconventional and quantitative method focusing on a local area, e.g., the vicinity of a crack tip, needs to be established. Until now, the local hydrogen concentration behavior has been evaluated by numerical simulation according to the diffusion equation considering time or stress fields. There are many publications that report numerical simulations of the hydrogen concentration behavior in the

metal[7]. However, this is just an assumption and no experimental research has confirmed this. In order to determine the mechanism for hydrogen damage in metals, the mechanism by which hydrogen distribution in the local area has to be clarified experimentally.
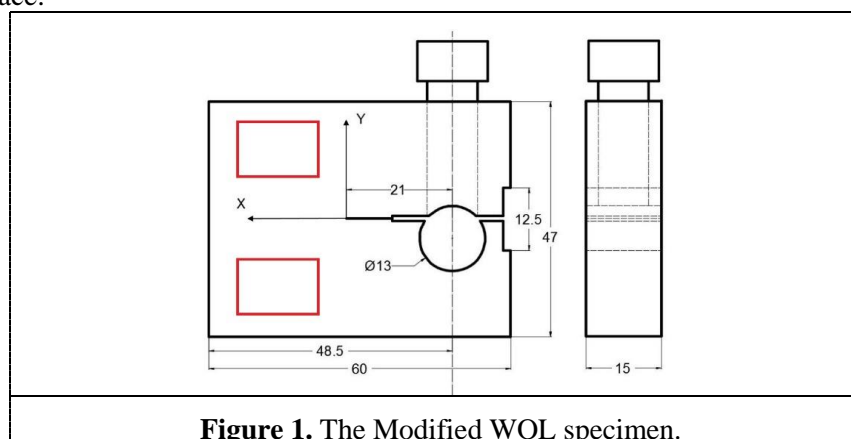
The present study is divided into two parts. First, we use layer stripping micro-hardness method to analyze the hydrogen distribution along the depth direction of the hydrogen-charged specimens without applied stress under different corrosion periods, then to analyze the hydrogen distribution under different applied stress fields with the same corrosion period. In addition, the theoretical time and applied stress variation of the hydrogen distribution in the hydrogen-charged specimen is calculated using models on the basis of Fick's law. The time and applied stress variations of the experimental values and of the theoretical values are compared.

2. Experimental Methods

2.1. Experimental design

First, 12 cylindrical specimens with the same diameter of 18 mm and height of 12 mm were soaked in saturated hydrogen sulfide solution for four different corrosion periods (24 h, 48 h, 72 h, 96 h). The experiment was divided into 4 groups, each group with three specimens selected for each test to verify the reproducibility of the material. Ten hardness points were measured to take the average for each test. Starting from the surface, the micro-hardness values were obtained at regular intervals of 50 μm progressing into the thickness of the specimen. Hardness was measured until it reached a constant value. Tested the original hardness of the specimen after grinding the specimen surface before corrosion. The hardness values of each test plane and the depth values of the stripping layer corresponding to the plane were recorded using the layer stripping micro-hardness method after corrosion.

Second, 6 Modified wedge-opening-loading (WOL) specimens were used in this study. Parameters of the WOL specimen size is shown in Figure 1. The constant stress intensity factor at the crack tips was fixed by the bolt. Then we could get the non-uniform applied stress field along the crack propagation direction of the specimens. Starting from the crack tip, the micro-hardness values were obtained at intervals of 80~100 μm progressing along the crack propagation direction of the specimen. Hardness was measured until it reached a constant value. 10 random hardness points of the specimen surface far from the crack tip were measured to determine the hardness value of the unstressed state. Then soaked the specimens in saturated hydrogen sulfide solution for 48 h and repeated the testing process on the specimen surface.

Figure 1. The Modified WOL specimen.

2.2. Test material and experimental apparatus

The test material was #45 steel, its measured tensile strength was 714 MPa, and the yield strength was 408 MPa. The chemical composition of the materials is shown in Table 1.

Table 1. Chemical compositions of #45 steel (mass %)

C	Si	Mn	S	P	Cr	Ni
0.46	0.27	0.65	0.015	0.018	0.20	0.214

Experimental apparatus was a universal hardness tester produced in Germany Zwick Company, its model was Zwick Roell ZHU2.5. The test method was according to the GB/T4340.1.
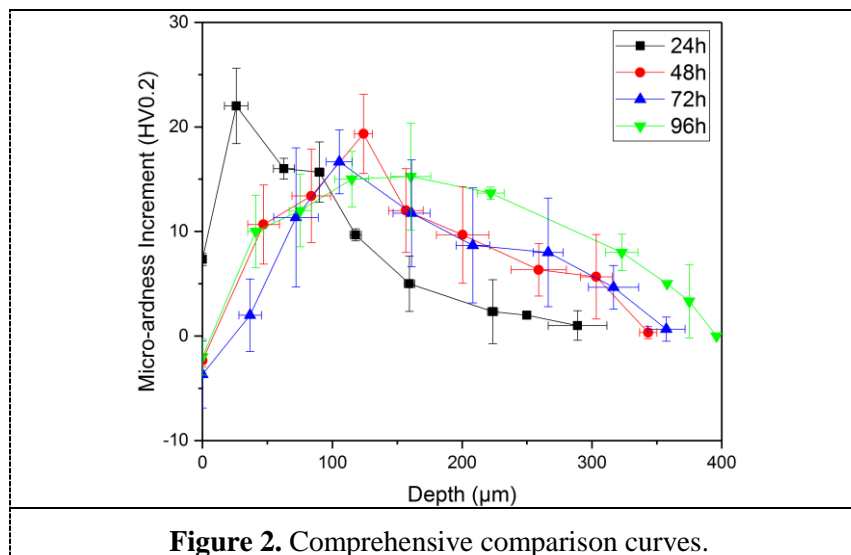In this study, Vickers hardness HV0.2 was chosen as the hardness index of the material, which could meet the highly sensitive experimental requirements.
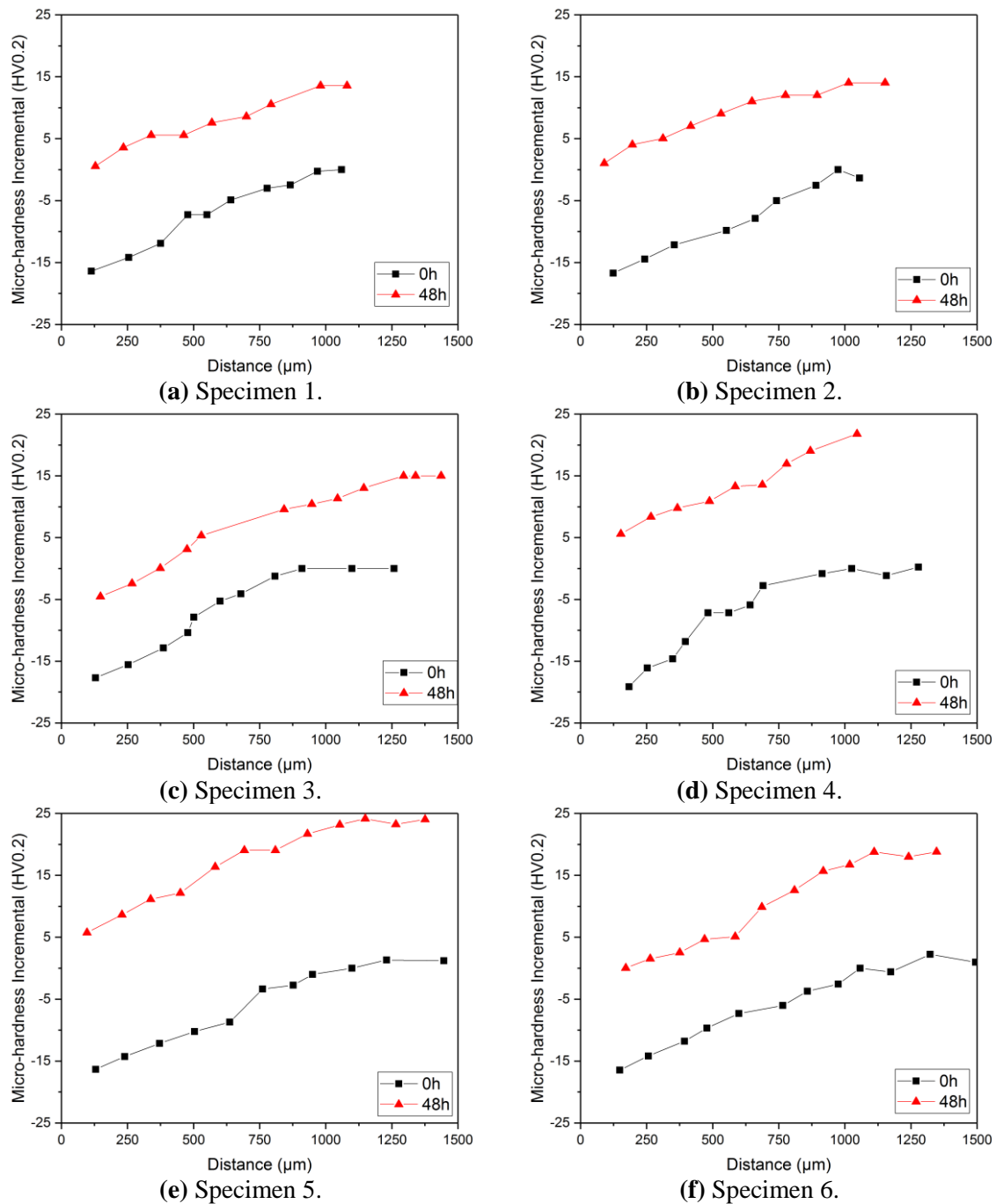
2.3. Test environment
H_2S gas was produced by the reaction of 30% Na_2S solution with 30% H_2SO_4 solution. Hydrogen sulfide was dissolved in the American Society of Corrosion Engineers NACE standard A standard solution (containing 5% sodium chloride and 0.5% glacial acetic acid). Specimens were soaked into the hydrogen sulfide corrosion environment after the solution concentration was stable. Used acetone to remove grease and rust from the surface of the specimens before soaking.

3. Experimental results
The distribution curves of the micro-hardness increment along the depth direction of specimens in each group after soaking in saturated hydrogen sulfide solution for various corrosion periods (24 h, 48 h, 72 h, 96 h) are shown in Figure 2. The curves under the same corrosion condition have a strong consistency, indicating the stability of the corrosion soaking in the hydrogen sulfide solution. Figure 3 also shows that the micro-hardness increment increases first and then decreases until micro-hardness increment returns to zero along the depth direction, indicating that there is a clear stratification phenomenon along the depth direction of specimens after soaking in hydrogen sulfide solution.

Figure 2. Comprehensive comparison curves.

The distribution curves of the micro-hardness increment along the crack propagation direction of specimens before and after soaking in saturated hydrogen sulfide solution are shown in Figure 3.

Figure 3. Distribution curves of the micro-hardness increment.

4. Discussion

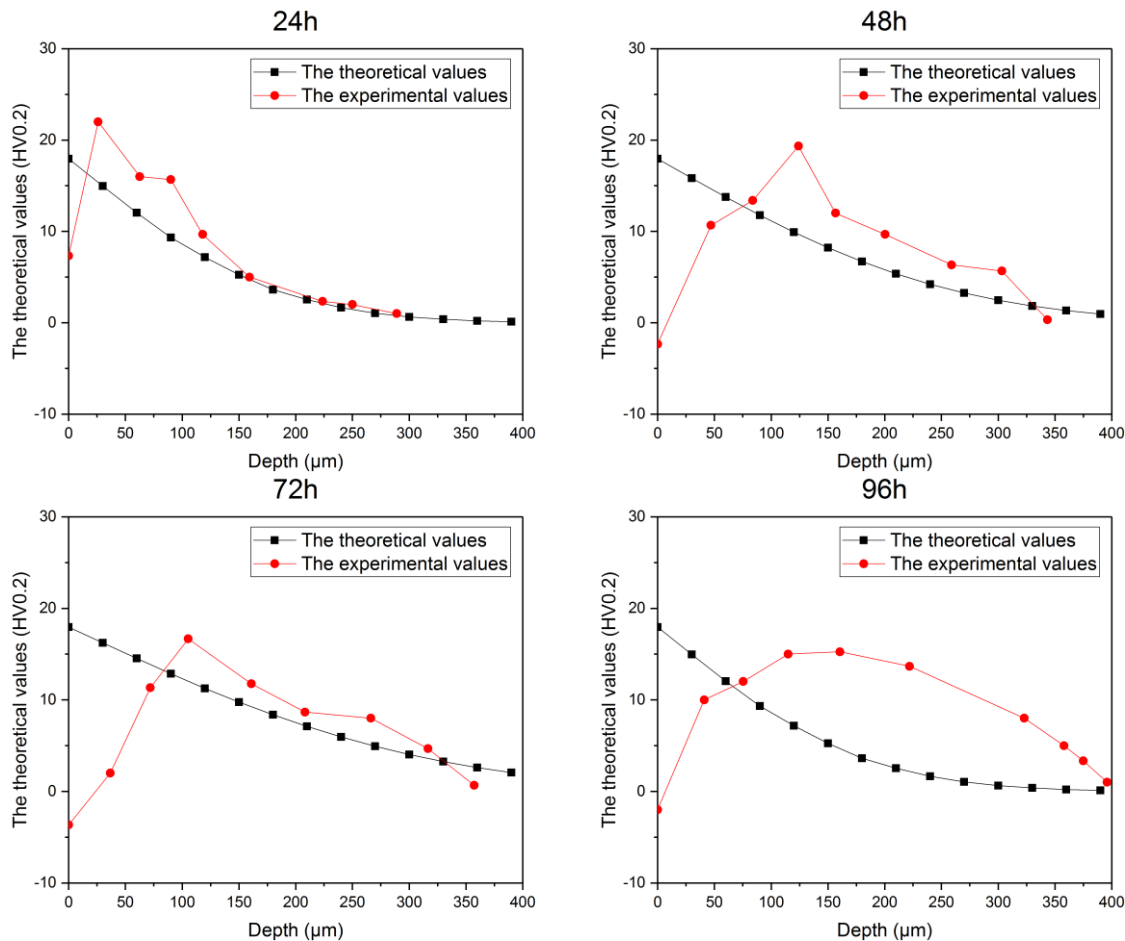### 4.1. Hydrogen saturated value and hydrogen saturated layer

Under the condition of varies corrosion periods, the average values of maximum micro-hardness increment of the test specimens is almost the same, the mean is 17.94 HV0.2, and the standard deviation is 0.98. This shows that there are no significant difference in the maximum micro-hardness increment under varies corrosion periods.

Since the maximum micro-hardness increment of the metal under the condition of varies corrosion periods are almost constant, and due to that increase in hydrogen concentration is proportional to the

increase in hardness[8], the hydrogen concentration corresponding with the micro-hardness increment can be defined to saturated state. That is, the hydrogen concentration reaches the saturated concentration (solubility) c_{max} in metal. For the same material, c_{max} is a constant. Because the present study focus on the analysis of hydrogen distribution in metals, the behavioral analysis of hydrogen in metal can be analyzed by the distribution of the micro-hardness increment instead of the hydrogen concentration.

Put the diffusion coefficient D, the average maximum hardness increment and the corrosion periods (24 h, 48 h, 72 h, 96 h) into the Eq. (1). The corresponding theoretical micro-hardness increment distribution curves of hydrogen diffusion in the metal are obtained. Compare the theoretical micro-hardness increment distribution curves with the experimental increment distribution curves according to the corrosion periods 24 h, 48 h, 72 h, 96 h, respectively, as shown in Figure 4.

$$\Delta HV(x,t) = \Delta HV_s \left[1 - erf\left(\frac{x}{2(Dt)^{1/2}} \right) \right] = \Delta HV_{max} \left[1 - erf\left(\frac{x}{2(Dt)^{1/2}} \right) \right] \tag{1}$$

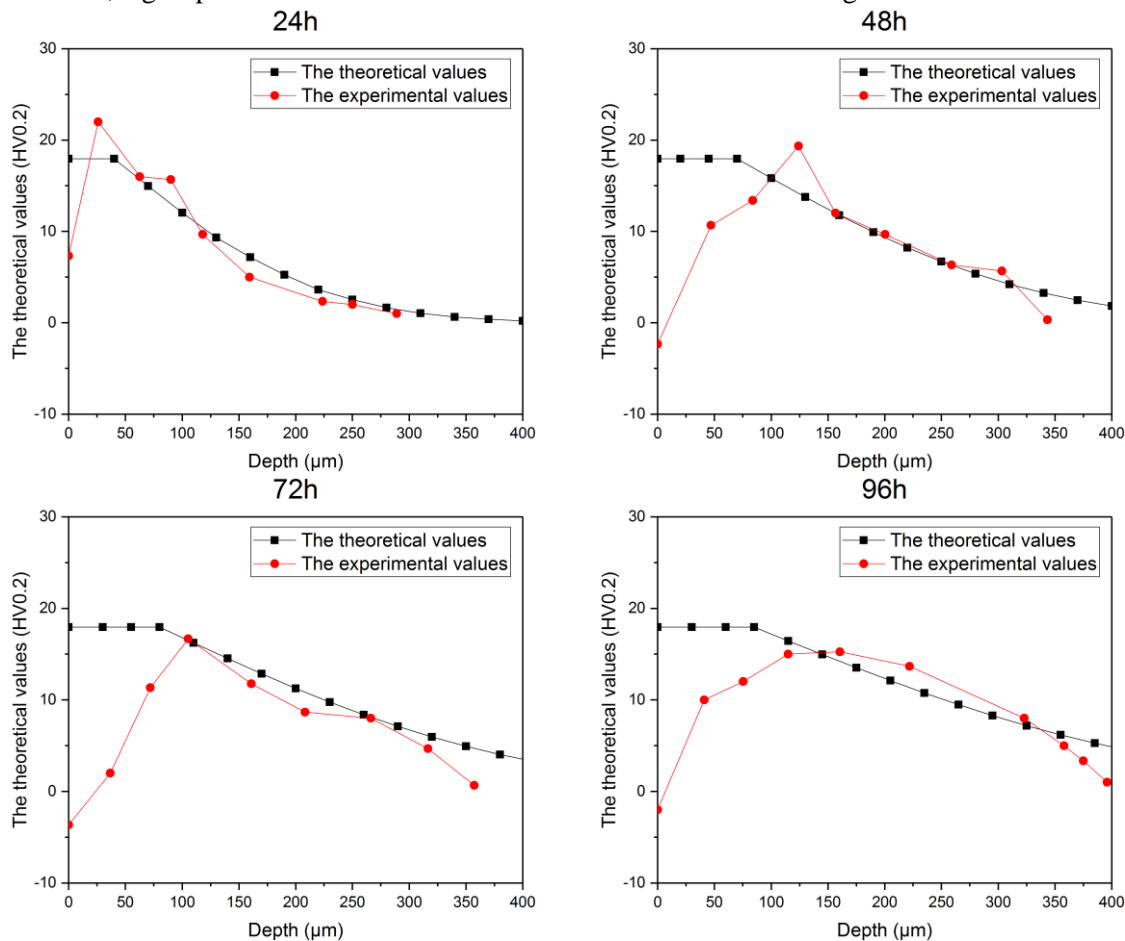**Figure 4.** Theoretical and experimental contrast curves.

The present study used the hydrogen diffusion coefficient determined by J. P. Hirth [9] to calculate the macroscopic hydrogen distribution for materials.

Since the theoretical curves of hydrogen diffusion are analyzed using a numerical simulation according to Fick's second law. The curves are always from big to small along the depth direction using the hydrogen diffusion theory. This is inconsistent with the actual situation as shown in Figure 4.

It can be seen that the big-to-small section of experimental curves has a certain distance from the theoretical curves along the depth direction.

Keep the maximum value and move the theoretical curves along the depth direction until the theoretical curves coinciding with the experimental curves and keep the value of the front distance as the maximum micro-hardness increment. The moving distance for each corrosion period as follows: 40 μm to the right for 24 h, 70 μm to right for 48 h, 80 μm to right for 72 h, 85 μm to right for 96 h. Therefore, a group of new theoretical curves are obtained as shown in Figure 5.

Figure 5. Theoretical and experimental contrast curves.

It can be clearly seen from Figure 5 that the theoretical curves after translation is in good agreement with the experimental curves, indicating that the hydrogen saturated layer is appeared along the depth direction of hydrogen-charged specimens. The presence of hydrogen saturated layer can be speculated that hydrogen can get entrapped and generate at the microstructural trap sites in the specimens[10]. The thickness of hydrogen saturated layer increases as the corrosion period increases.
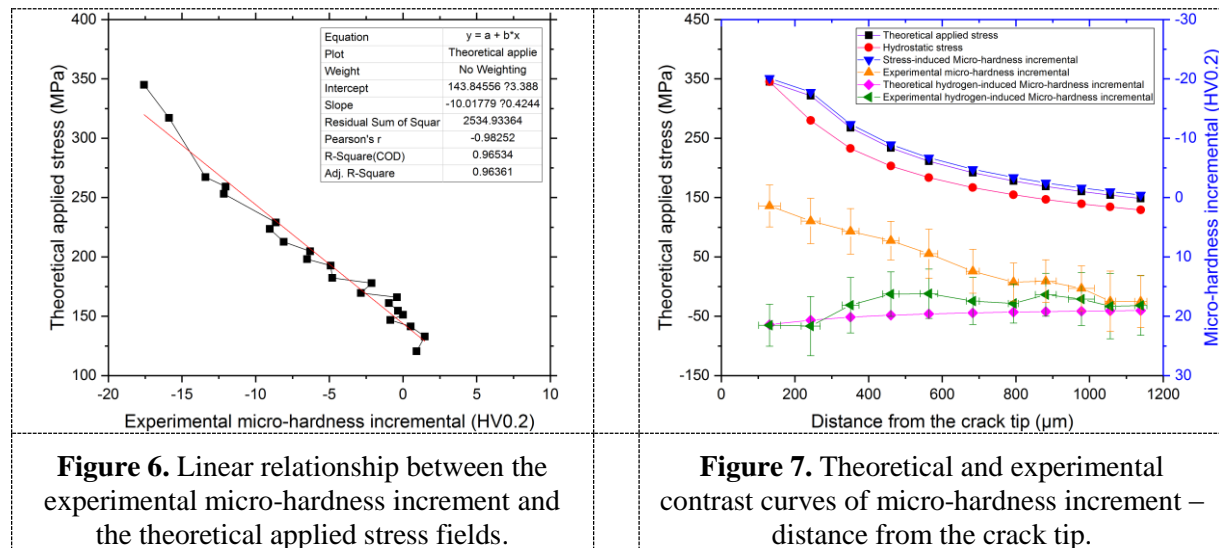
It can be seen from figure 6 that the hydrogen concentration in the metal gradually decreases along the depth direction until zero after the hydrogen saturated layer. The trend of changes is consistent with the theoretical one for the same corrosion period.

4.2. Hydrogen distribution with applied stress

The distribution curves of the micro-hardness increment along the crack propagation direction of specimens before soaking in saturated hydrogen sulfide solution is shown in Figure 6.

In the non-corrosive environment, the micro-hardness increment versus the applied stress fields have strong linear correlation with a correlation coefficient, R, of 0.98 and significance level of 0.04×10^{-14}.

Based on the relationship between hardness and stress, we extract the experimental hydrogen distribution from the applied stress fields of hydrogen-charged specimens. Then the applied stress variations of the experimental hydrogen-induced micro-hardness increment and of the theoretical value are compared. The trend of changes is consistent along the crack propagation direction of specimens, as is shown in Figure 7.

Figure 6. Linear relationship between the experimental micro-hardness increment and the theoretical applied stress fields.	**Figure 7.** Theoretical and experimental contrast curves of micro-hardness increment – distance from the crack tip.

5. Conclusions

The micro-hardness tests for various corrosion periods or various applied stress fields were performed at room temperature. Took the change of the micro-hardness increment along the depth direction or the crack propagation direction of specimens as an index, then analyzed and evaluated the hydrogen distribution in the metal after soaking in hydrogen sulfide solution. Our conclusions are summarized as follows.

- There was a stable saturated hydrogen concentration (solubility) in the metal in hydrogen sulfide solution of various corrosion periods. And there is a hydrogen saturated layer hydrogen saturated layer along the depth direction of specimens pre-charged with hydrogen. The thickness of hydrogen saturated layer increases as the corrosion period increases in specimens.
- There is a simple additive relationship between stress-induced micro-hardness increment and hydrogen-induced micro-hardness increment in Vickers micro-hardness measurement.
- The hydrogen concentration behavior in a known equibiaxial stress environment can be verified experimentally by micro-hardness tester. References

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