An Electrochemical Sensor for Measuring Hydrogen Permeation Behavior in Atmospheric Environment

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An electrochemical sensor was used to measure hydrogen permeation behavior in atmospheric environment. The results show that the hydrogen permeation current density increased with the temperature increase. Temperature has strong effects on hydrogen permeation current even to uncorroded alloys due to molecular motion energy increase with temperature increasing. RH changes can also increase hydrogen permeation into alloy due to corrosion process.

Keywords: Electrochemical sensor; Hydrogen permeation; Temperature and Relative Humidity (RH);

1. INTRODUCTION

Atmospheric corrosion is a process of practical importance as it degrades the structures, devices and products exposed to atmosphere. It is mainly depending on exposure time and some climatic factors, like temperature (T), relative humidity (RH), salinity (chloride), sulfur content and the presence of some other pollutants. It has been customary to classify environments as rural, urban, industrial, marine, or combinations of these. Chloride containing environment can be considered as the marine atmosphere.

Al-Mg-Zn-Cu Aluminum alloy as a representative aluminum alloy is widely used for aircraft structural materials because it is a high strength and low density material. And the hydrogen-induced cracking and hydrogen embrittlement have long been recognized as a serious problem for the petroleum and petrochemical industries, particularly in high strength steel [1–3]. But researches on hydrogen permeation of steel are mostly in solutions, while less in atmospheric environment. It is recently that the hydrogen permeation during atmospheric corrosion was studied concerning the environment-sensitive fracture for the high strength steels [4,5]. It is a long time that researchers

consider that the main cathodic process of atmospheric corrosion is oxygen reduction, neglecting H^+ reduction. Yanliang Huang et al. uncovered the hydrogen ion reduction process in the iron rusting process [6].

But a literature search shows less research focus on hydrogen permeation behavior of Al alloy [7-10], because it is very difficult to measure hydrogen permeation current of Al alloy due to the oxidation film on the surface. And it is very difficult to deposit pure Pt or Ni film on the Al surface.

In this paper, hydrogen permeation into an Al-Mg-Zn-Cu alloy during wet-dry atmospheric environment was studied by an electrochemical sensor, the specimen was coated with a thin layer of nickel by magnetron sputtering method.

2. EXPERIMENTAL

Disc plate specimens of 20mm in diameter and 0.4mm in thickness were used as work electrode, the chemical composition of material is given in Table 1.

Table 1. Chemical composition of Al-Mg-Zn-Cu aluminum alloy

| Chemical composition (wt.%)							
Element	Cu	Mg	Zn	Si	Fe	Cr	Others	Al(Min)
wt.%	1.5	2.7	6.8	0.5	0.6	0.15	0.65	Balance
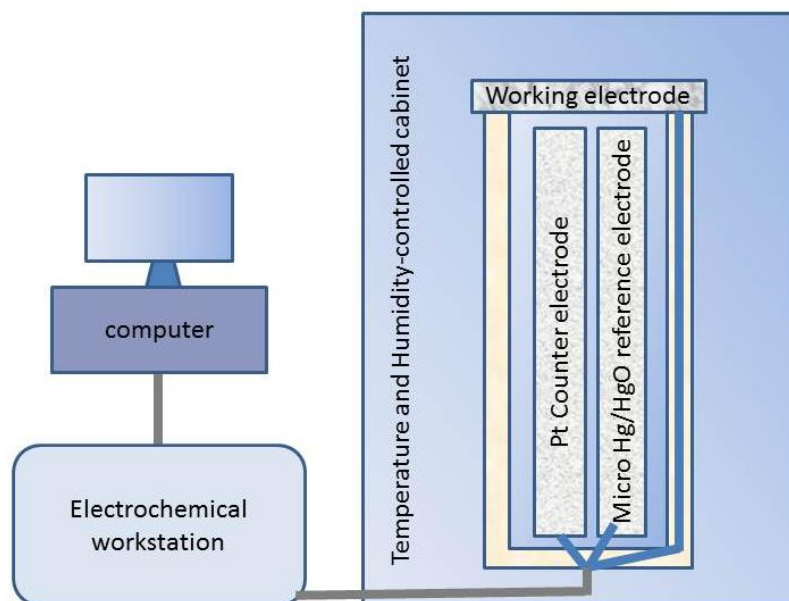
Figure 1. The experimental set-up

Fig.1 shows the experimental set-up. The inner side of the specimen was coated with a thin layer of nickel by magnetron sputtering method. The working pressure is 0.3Pa, the sputtering power is 40W. The inner of the cell was filled with 0.1 mol/L NaOH. Before the test, the specimen was polarized potentiostatically at 0 mV vs HgO/Hg/0.1M NaOH until the passivation current density was less than 0.1 uA/cm^2. A temperature and humidity controlled cabinet was used to change temperature or relative humidity. In order to study the effect of temperature and relative humidity effect on hydrogen permeation behavior of alloy, two sensors were used at the same time. One specimen was covered with a thin stainless steel to prevent the specimen from corrosion while the other specimen was exposed to the atmospheric environment.

3. RESULTS AND DISCUSSION

3.1. Temperature effect

Control the temperature change step by step while studying temperature effect. Fig.2 shows the test temperature change with time while the RH is controlled at 85%. Fig.3 shows the hydrogen permeation current density (i_H) curves change with different temperature. From Fig.3, the i_H increased with the temperature increase. The i_H of exposed to atmospheric environment is bigger than that of covered with stainless steel. Corrosion the specimen exposed to atmospheric environment occurred, and induced that H atom increased by corrosion reactions [11].
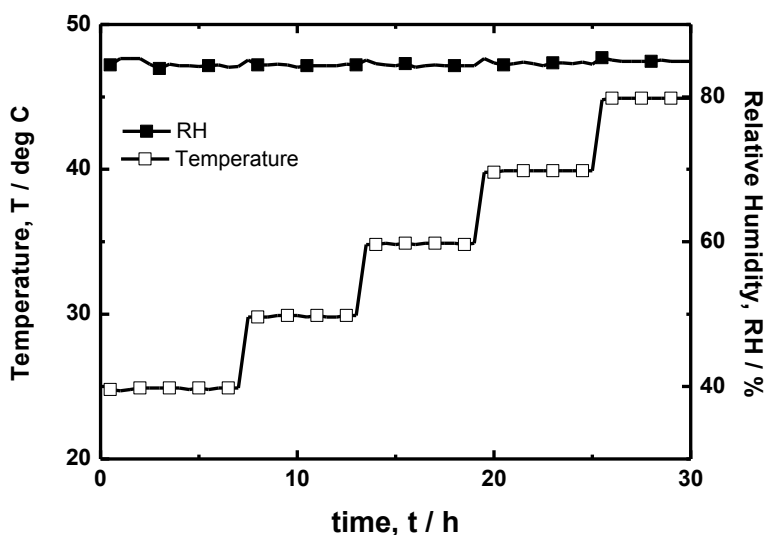
Figure 2. The test temperature and RH changes with time
(Temperature change from 25 ℃,30℃,35℃,40℃,45℃ step by step while controlling RH at 85%)

Hydrogen diffusivity *D* was calculated by Time to brekthough and Time-lag methods, and the calculated values were listed in Table 2.

1)   Time to breakthough, t_b

$$D = \frac{L^2}{15.3\,t_b}$$

Where t_b is found by extrapolating the linear portion of the initial hydrogen permeation current transient to $i_t = 0$. L is the thickness of the specimen.

2)   Time-lag method, t_L

$$D = \frac{L^2}{6t_L}$$

The time of t_L corresponds to the point on the permeation curve at which $i_t = 0.63\,i^\infty$. L is the thickness of the specimen.
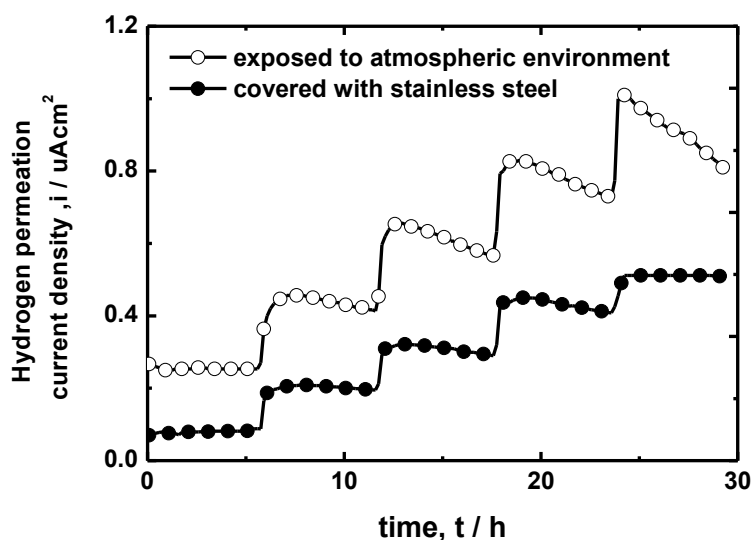

Figure 3. The i_H of specimen at different temperatures shown in Figure 2.

Table 2. D values calculated by two methods (m^{-2}/s)

Temperature(℃)	25	30	35	40	45
D (t_L method)	2.48×10^{-11}	3.74×10^{-11}	4.45×10^{-11}	5.65×10^{-11}	6.77×10^{-11}
D (t_b method)	1.23×10^{-11}	1.51×10^{-11}	1.67×10^{-11}	1.93×10^{-11}	2.31×10^{-11}

From Table 2, the *D* values calculated by two methods also show an increasing trend with temperature increasing. Molecular motion increases with temperature increasing. At higher temperature, diffusion of hydrogen was accelerated, so hydrogen diffusivity increased with temperature increasing.

The temperature dependence of diffusivity was fitted using the Arrhenius relationship:
$D = D_0 \exp(-Q/RT)$

Where D_0 is a temperature-independent constant, Q (J/mol) is the activation energy for diffusion, R (J/mol K) is the gas constant and T (K) is the temperature.

Fig. 4 showed the $\lg(D)$ vs. 1/T and linear regression fits for the sample, and the activation energy was calculated

Time to breakthough method: Q=40.4kJ/mol

Time lag method: Q=34.8kJ/mol.

The calculated activation energy shows accordant with H. Addach [12]. The energy is bigger than that of steel, so the temperature effect on hydrogen diffusivity is little than steel.

Ferro [13] assumed that the energy of activation for diffusion was the energy required to distort and octahedral to accommodate a diffusing hydrogen atom arriving from a neighbouring interstitial site. And he considered the rate-determining step in the diffusion of hydrogen consists in the creation of sites (distorted octahedral holes) into which hydrogen can jump. W. Beck [14] considered that diffusion is the rate-determining step of the permeation of hydrogen through zone-refined iron by determining the linearity of the plot of the permeation rate against reciprocal thickness and the linearity of the plot of time to reach half the steady state permeation rate against thickness. The difference between steel and Al alloy is the atomic structure. Al alloy is body-centred cubic structure, the gaps between atom are little than steel (face-centred cubic structure) [15].
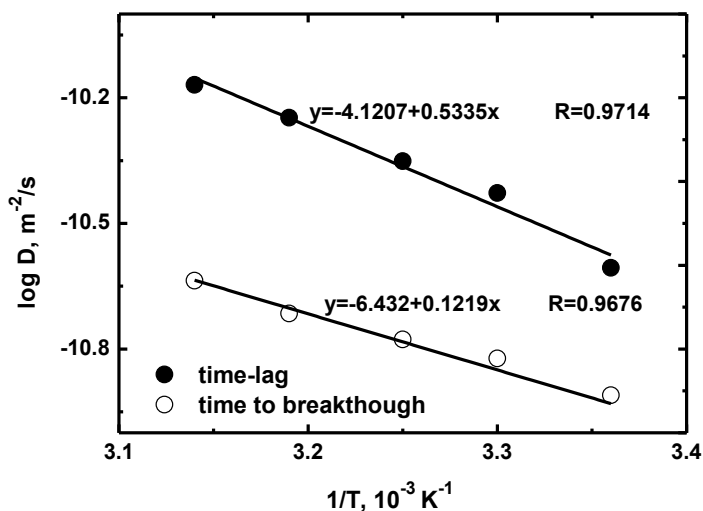

Figure 4. The $\lg(D)$ vs. 1/T

3.2. RH effect

Fig.5 shows the test RH change with time, the temperature was controlled at 25℃. Fig.6 shows the hydrogen permeation current density (i_H) curves change with different RH. From Fig.6, the i_H

increased with the RH increase. The i_H of exposed to atmospheric environment is bigger than that of covered with stainless steel. The i_H of covered with stainless steel almost kept steady. This shows the reason of i_H increasing is corrosion reactions, which can increase H atom by hydrolysis reaction. And i_H showed an increasing trend with increasing wet-dry cycles.

Fig.7 shows the maximum hydrogen permeation current values in each wet-dry cycle. The maximum hydrogen permeation current density increased with wet-dry cycles at beginning, and then decreased to steady value. This indicates that corrosion increase hydrogen permeation current at beginning due to hydrolysis reaction, and decrease with corrosion rust forming [11].
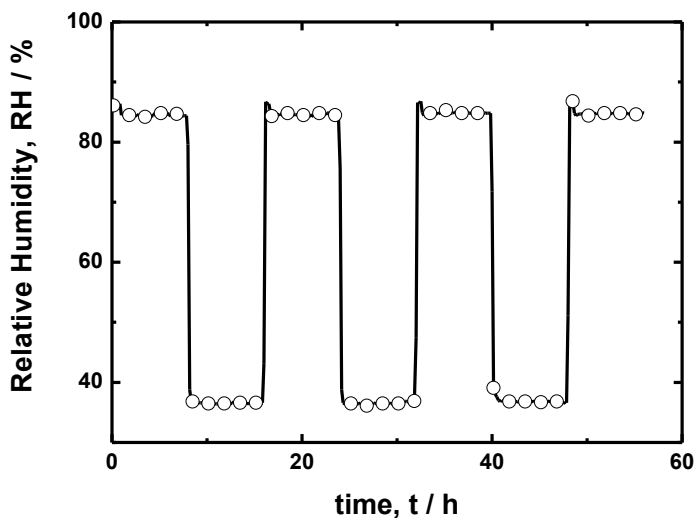

Figure 5. The test RH changes with time during hydrogen permeation experiment; the temperature was controlled at 25℃
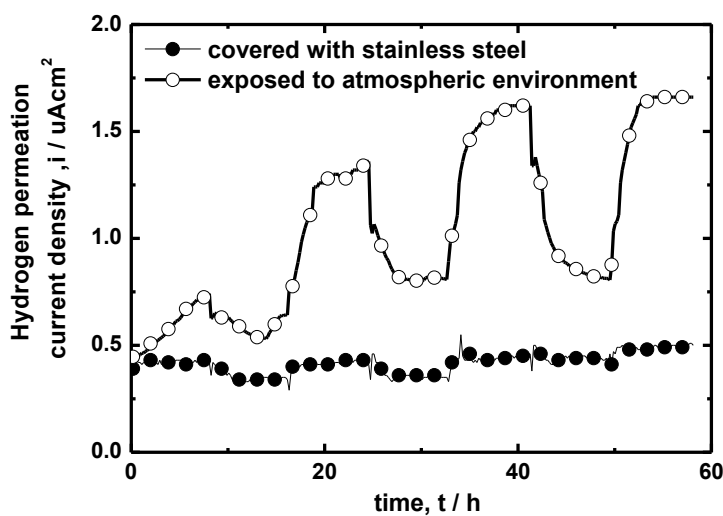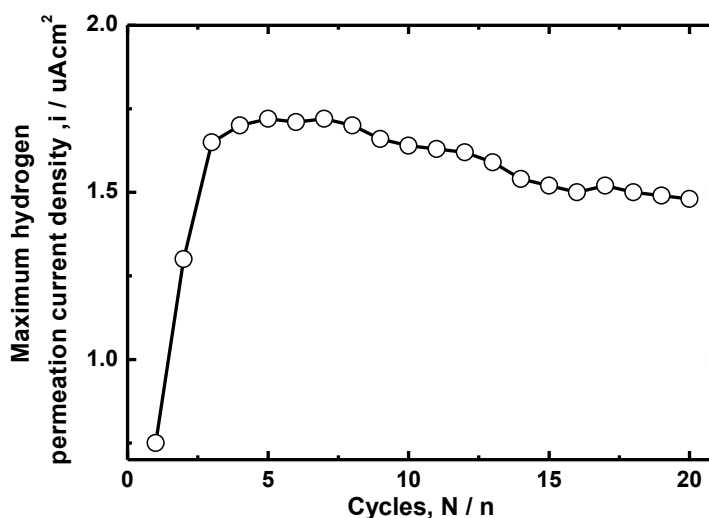

Figure 6. The i_H curves changes with RH at different RH shown in Figure 5

Figure 7. The maximum i_H values in each wet-dry cycle by controlling the RH change from 35% to 85% circularly

Fig.8 shows the possible mechanism of i_H changes with RH. At first, in high RH environment, water vapor was adsorbed at the alloy surface and corrosion occurred. Some hydrolysis reactions occurred and H^+ atom was adsorbed and absorbed by alloy surface. i_H increased with corrosion process. In low RH environment, corrosion rust deposited at the alloy surface. In following wet-dry cycle, some H^+ atoms were adsorbed by rust, the H^+ on alloy surface decreased result in i_H decreasing.
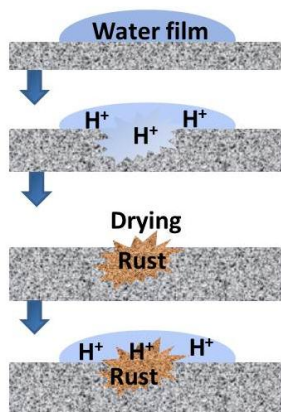
Figure 8. The possible mechanism of i_H changes with RH

4. CONCLUSION

An electrochemical sensor was used to measure hydrogen permeation behavior in atmospheric environment. The hydrogen permeation current density increased with the temperature increase.

Temperature has strong effects on hydrogen permeation current even to uncorroded alloys due to molecular motion energy increase with temperature increasing. RH changes can also increase hydrogen permeation into alloy due to corrosion process.

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