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Mechanical Behavior and Fractography of 304 Stainless Steel with High Hydrogen Concentration

Ming Au*

Westinghouse Savannah River Company

Aiken, SC 29808

KEY WORDS

Hydrogen embrittlement, stainless steel, electrochemical charge, fractography

ABSTRACT

Hydrogen embrittlement of 304 stainless steel with different hydrogen concentrations has been investigated. An electrochemical technique was used to effectively charge the high level of hydrogen into 304 stainless steel in a short period of time. At 25 ppm of hydrogen, 304 stainless steel loses 10% of its original mechanical strength and 20% plasticity. Although the ductile feature dominates the fractography, the brittle crown area near the outer surface shows the intergranular rupture effected by hydrogen. At 60 ppm of hydrogen, 304 stainless steel loses 23% of its strength and 38% plasticity, where the brittle mode dominates the fracture of the materials. Experimental results show that hydrogen damage to the performance of 304 stainless steel is significant even at very low levels. The fractograph analysis indicates the high penetration ability of hydrogen in 304 stainless steel. This work also demonstrates the advantages of the electrochemical charging technique in the study of hydrogen embrittlement.

1. INTRODUCTION

Hydrogen embrittlement is a critical issue with respect to materials used by nuclear, chemical, petrochemical, and marine industries. Specimens charged with hydrogen are typically investigated for material behavior in hydrogen environments such as mechanical properties, microstructure, fracture feature, and hydrogen distribution. Gaseous hydrogen charge is a traditional approach to introduce hydrogen into the materials. Usually, the specimens are placed in an oxygen-free, high-conductivity copper chamber with tantalum hydride. The tantalum hydride decomposes and creates a high partial pressure of hydrogen gas at high temperatures (above 700°C), that forces hydrogen to diffuse into the specimens. Up to 40 ppm of hydrogen can be introduced into steels and alloys by this technique [1, 2]. High-pressure hydrogen autoclave is another technique using gaseous hydrogen to charge materials. Specimens are charged for a long period of time (weeks or months) at high pressure (about 35 MPa) and high temperature (above 350°C). The maximum hydrogen concentration obtained is 50 ppm by this method [3].

Higher levels of hydrogen (60-100ppm) are often required to evaluate critical components in nuclear structures. To introduce high-level hydrogen into steels and alloys, an electrochemical method was utilized. Instead of using a gaseous hydrogen charge, the hydrogen enters the materials as ions (protons) in the electrochemical cells. In this case, the driving force is the electrochemical potential instead of a hydrogen pressure gradient. The migration of protons in materials is faster than diffusion of hydrogen molecules in a gaseous hydrogen charge. It builds up higher levels of hydrogen in a very short period. In this work, a high-temperature electrochemical cell was set up to charge the tensile specimens of 304 stainless steel. Changes in mechanical behavior and fracture feature were investigated on the 304 stainless steel with various hydrogen concentrations.

2. EXPERIMENT

Hydrogen charge was conducted in an electrochemical cell shown in Fig.1 and Fig.2. Hydrogen was introduced into the specimens by cathodic charging in a melted salt bath. The molten salt consisted of 57% $NaHSO_4$ (Sodium Bisulfate T_m=315°C) and 43% $KHSO_4$ (Potassium Bisulfate T_m= 210°C). In this work, 1500 g mixed salt (2.03 g/ml bulk density) was used. The eutectic mixture of the salts starts to melt at 135°C. Cathodic charging was conducted under a 0.850 V Ag/Ag^+ fixed potential and at 150°C with the specimens acting as the cathode. The electrochemical reactions in the hydrogen-charging cell are given as follows:

Anodic reaction: $$H_2O + 2SO_4^{-2} - 2e = 2HSO_4^{-1} + \frac{1}{2}O_2$$

Cathodic reaction: $$HSO_4^{-1} + e = H + SO_4^{-2}$$

The salt mixture of sodium bisulfate monohydrate and potassium bisulfate was melted and maintained at 200°C in a glass kettle. A constant potential was applied between the cathode (specimens) and anode (Pt counter electrode) by the EG&G 273 Galvno/Potentialstat for a pre-determined period. The Ag/Ag+ reference electrode was connected to the Galvno/Potentialstat to monitor any change in cathode potential. The platinum anode was set at a fixed distance to the specimen (cathode). An ohmmeter was connected to the cathode and anode to monitor changes in electrical resistance of the salt.

The ohmmeter reading represents the concentration of hydrogen ions in molten salt. A condenser recovered the water evaporated from molten salt bath. To compensate for the decrease of hydrogen ion concentration caused by hydrogen generation on the cathode surface (specimens), deionized water was injected into the salt bath to maintain a constant ohmmeter reading. The temperature, potential, current, and ohmmeter readings were acquired, displayed, and recorded by the computer. Special specimen holders were designed to effectively introduce current and minimize the charge times. All specimens and holders except the surfaces to be charged were coated by thermal resistant silicone sealant to avoid galvanic reaction. After charging, the specimens were removed from the cell and rinsed with distilled water. The specimens remained at -40^{o}C in the dry ice box to prevent hydrogen from off gassing.

To investigate hydrogen effects on mechanical strength of stainless steels, compact tensile specimens of 3 mm diameter and 55 mm length were prepared from the annealed 304 stainless steel. The specimens were charged at different times at a fixed potential of 0.850V Ag/Ag$^+$. Three groups of compact tension specimens of 304 stainless steel were charged in the electrochemical cell for 3, 6, and 12 hours respectively. Each group consists of three identical specimens. For reference, one extra group of tension specimens was prepared for tension tests without hydrogen charging. The tension specimens were removed from the dry ice box and submerged into 25^{o}C water for 5 minutes to raise the temperature. Tension tests on the specimens were conducted immediately using an Instron Model 1125 tension machine with 5000 kg full scale load, 1 mm/min crosshead speed, and 20mm/min chart speed. For accuracy, the test data of the three individual specimens in same group were averaged.

After tension testing, segments of specimens were immediately analyzed for their hydrogen concentration by using a LECO RH-402 Hydrogen Determinator. To understand the mechanism and the fracture feature, the morphology observation of fractures was performed using a CamScan 600 scanning electron microscope.

3. RESULTS

3.1 Tension strength, elongation and hydrogen concentration

After hydrogen was introduced, the average strength limit and elongation rate of the 304 stainless steel decreased. For example, after 12 hours of hydrogen charging, the strength limit and elongation of 304 stainless steel was reduced 22.57% and 38.46% respectively. That means the material became brittle and lost its original mechanical strength and toughness. In addition, the analysis of hydrogen content shows a significant increase in hydrogen concentration in the materials (Table1 and Fig.3). The reduction of necking and elongation of the tension specimens (Fig.4) can also evidence the effects of hydrogen embrittlement.

3.2 Fractograph analysis

3.2.1 Uncharged specimens

The freshly broken specimens were analyzed for fracture features using a Scanning Electron Microscope. The fractures of the uncharged specimens show a typical ductile feature mode with matte and rough surfaces. Large neck shrink and shear lips were also observed (Fig.5). At high magnification, the fracture is characterized by the presence of a great number of small microvoids (dimples). Some fine precipitates (general inclusions) are observed (Fig.6). Ductile failure is commonly associated with nucleation and growth of the microvoids around particles of a second phase (such as precipitations and inclusions) in metal when a critical value of stress is exceeded. Due to the ductile nature of the austenitic stainless steels, transgranular rupture and deep tear ridges were observed in their fracture (Fig.7).

3.2.2 The specimens after 3-hours hydrogen charging

After 3 hours of electrochemical hydrogen charging, 25 ppm hydrogen was introduced into the materials. The surface fracture appears essentially composed of two parts: a brittle crown area near the sample surface followed by ductile part in the center. It reflects the hydrogen migration from the outer surface to the central area (Fig.8). Most fractures still show the gray and matte nature of the ductile fracture mode, but the shiny and inter-granular brittle fracture is observed along the surface area of the specimen. The influence of hydrogen on ductile fractures is attributed to an accumulation of hydrogen at matrix-particles interfaces, which lowers the interfacial strength[3]. The detail features of the brittle crown and transition area are shown in Fig.9-10.

3.2.3 The specimens after 6-hours hydrogen charging

After 6 hours of charging, more hydrogen enters the materials. The brittle crown grew forward to the central area as shown in Fig.11 and Fig.12. Due to the loss of ductility and plasticity, the necking area increases in comparison to Fig.4. Although the overall hydrogen level in the specimens is about 45 ppm, it is believed that the hydrogen concentration is much higher near surface area, which demonstrates typical brittle fracture mode shown in Fig.12. In the central area, the fracture shows the mixed fracture mode owing to the lower hydrogen concentration(Fig.13).

3.2.4 The specimens after 12 hours hydrogen charging

When the hydrogen level is increased to 60 ppm after 12 hours of extended charging, the materials become most brittle. Tension tests show that the strength limit and elongation rate decrease 23% and 38% from original uncharged state respectively. The fracture of the necking section shows the flat and smooth brittle feature (Fig.14). Under high magnification, the inter-granular brittle rupture dominates the whole fracture of materials (Fig.15). Although the ductile feature can be spotted in central areas of the fracture, the average size of the dimples is increased and the density of micro-voids is decreased. Comparing Fig. 16 with Fig.6 and Fig.10 shows this.

4. DISCUSSION

Electrochemical hydrogen charge is a special technique to introduce high concentrations of hydrogen into materials in a relatively short period. The method is particularly useful for the metals with an austenitic phase, such as stainless steel and Ni super alloys, which have low hydrogen diffusivity. In our previous work, it took about 72 hours to get 25 ppm hydrogen in 304 stainless steel with gaseous hydrogen charge at 400^{o}C and 6.0 MPa. It takes only 3 hours to obtain the same level of hydrogen using an electrochemical charge at 200^{o}C and ambient pressure. As a result, the driving force of hydrogen migration is the electric potential between cathode and anode instead of the pressure gradient in gaseous hydrogen charge. This driving force may be more powerful. The directional movement of protons forced by the electric potential is faster in liquid electrolyte than the random motion of hydrogen molecules in hydrogen gas. Furthermore, the surface of the specimens was bombarded by the moving hydrogen ions along the direction of electric current, which makes the specimen surface active to accept the hydrogen. This is more significant for the stainless steels and super alloy that is covered by the passive protective layer. In our unpublished work, a 120-ppm hydrogen concentration has been obtained in 347 stainless steel in 72 hours of electrochemical hydrogen charging that the gaseous charge never achieved [5].

The equipment cost is very low compared to a high-pressure autoclave. The electrochemical hydrogen charge is performed in a glass cell with ambient pressure and moderate temperature.

For each individual material, a limit of hydrogen concentration is introduced by electrochemical charging. After reaching certain levels of hydrogen, extending charge time does not increase hydrogen level further as expected. For example, with 304 stainless steel, 25 ppm hydrogen was obtained in the first three hours of charging. For the next three hours, the hydrogen level increases by only 20 ppm. After that, the hydrogen level was raised 15 ppm in six hours of charging as shown in Fig.16. This reflects the nature of hydrogen diffusion in the solid metals. The dimensions of the specimens are subject to this limitation. Samples with a diameter smaller than 6 mm are preferred.

The specimens are usually charged in the melted salt. Minor corrosion will occur in carbon steels with prolonged charge times. No corrosion was discovered for stainless steels and superalloys charged less than 72 hours.

5. CONCLUSION

Hydrogen deteriorates material mechanical properties significantly even at small concentrations. At 25 ppm of hydrogen, 304 stainless steel shows notable hydrogen embrittlement that lost 10% mechanical strength 20% plasticity. The hydrogen-affected zone (the brittle crown) forms around the outer surface of specimens. By extending the charge time, the hydrogen embrittlement zone expands from the outer surface to the central area of specimens. At 60 ppm hydrogen, this material became more brittle, lost 23% strength 38% plasticity. At this point, the brittle mode dominates the fracture of the material. The density of dimples in the residual ductile area decreases remarkably. The hydrogen penetration in 304 stainless steel is faster than expected. At 45 ppm hydrogen concentration, the brittle inter-granular ruptures were already observed in the center of the specimen although the ductile rupture still dominates the most central area. The electrochemical hydrogen charge is a unique method to introduce high levels of hydrogen into the metals in a very short period. The cost of experimentation is relatively low in comparison to gaseous hydrogen charge.

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List of Figures

Table 1. The results of tension testing of the 304 stainless steel with different hydrogen concentration

Charging time (hour)	0	3	6	12
Hydrogen concentration (ppm)	0	25	45	60
Strength limit (MPa)	6,200	5,600	5,200	4,800
Elongation (%)	26	21	20	16

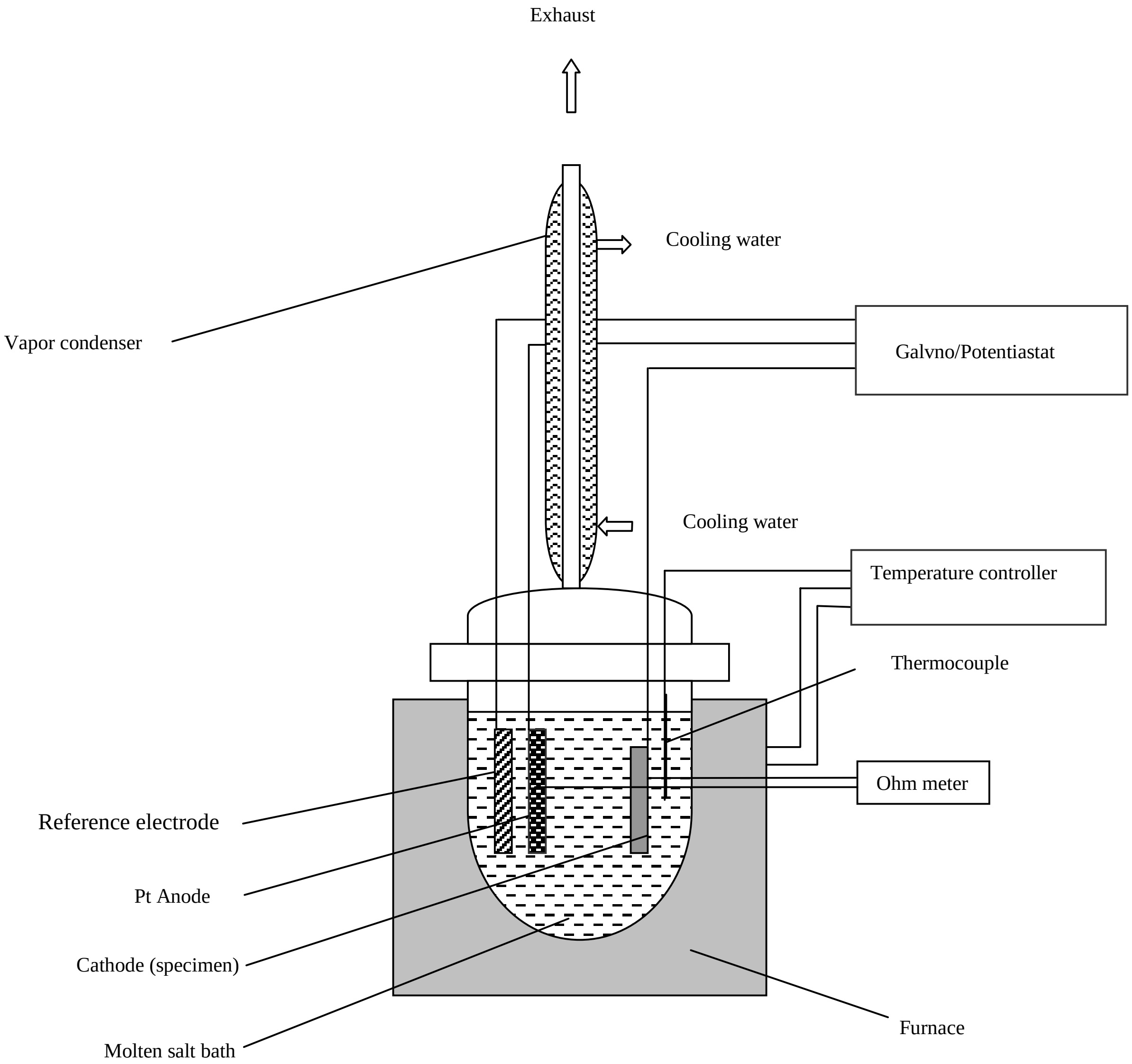


Fig.1 Schematic diagram of the electrochemical hydrogen charge apparatus

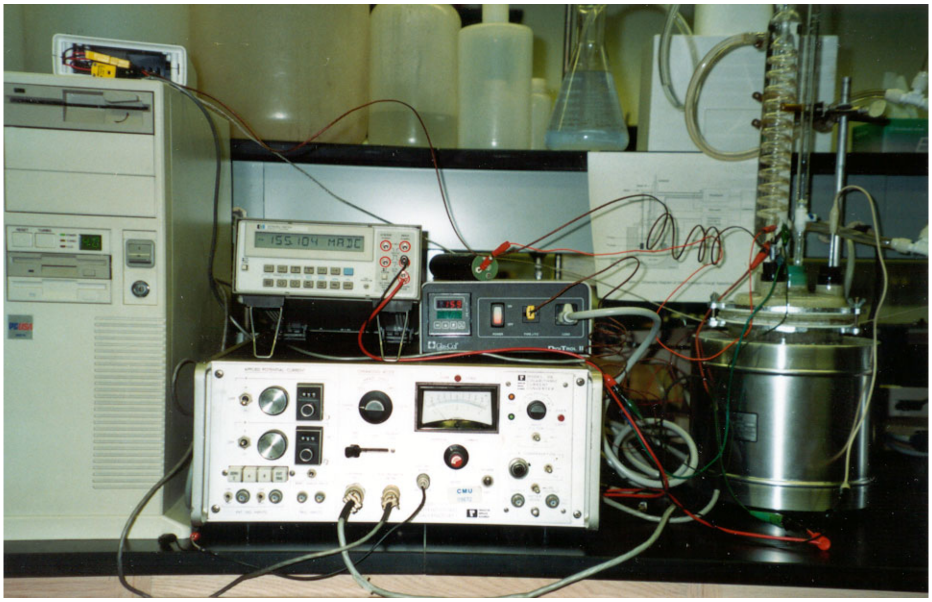


Fig.2 A photo of the electrochemical hydrogen charge system

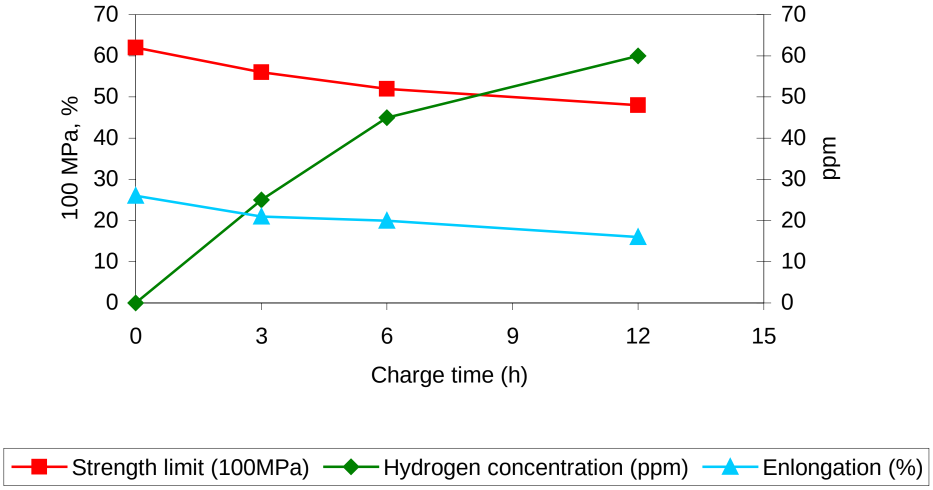


Fig. 3 The mechanical properties of 304 stainless steel with different hydrogen concentration

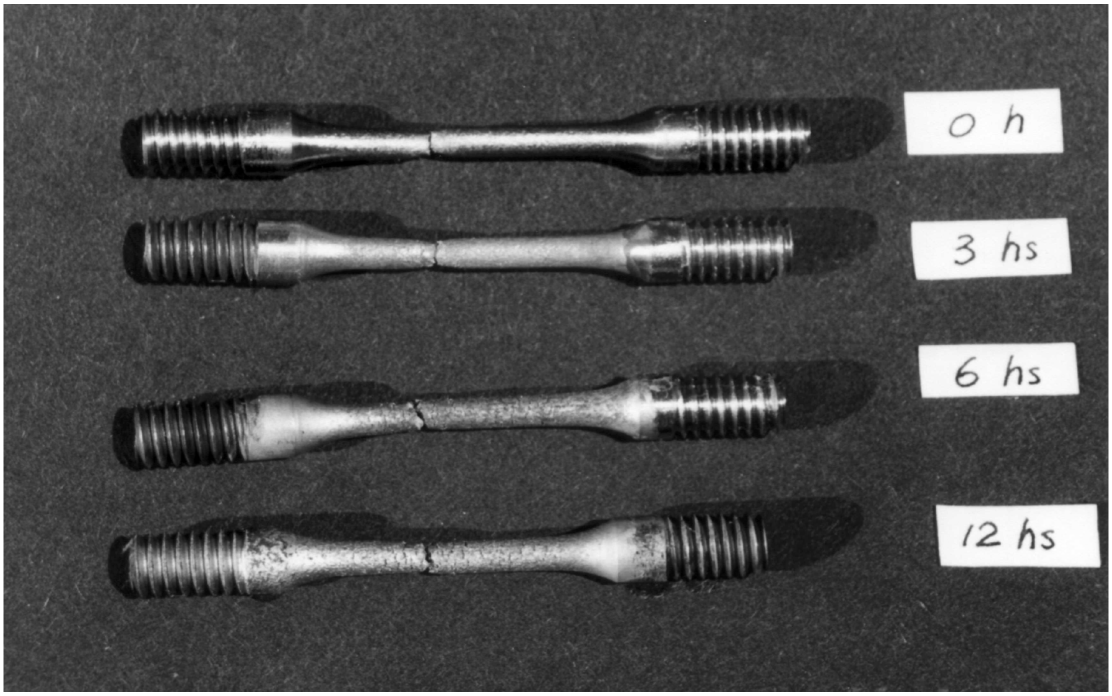


Fig.4 The ruptured tensile specimens of 304 stainless steel charged by hydrogen electrochemically at the different time

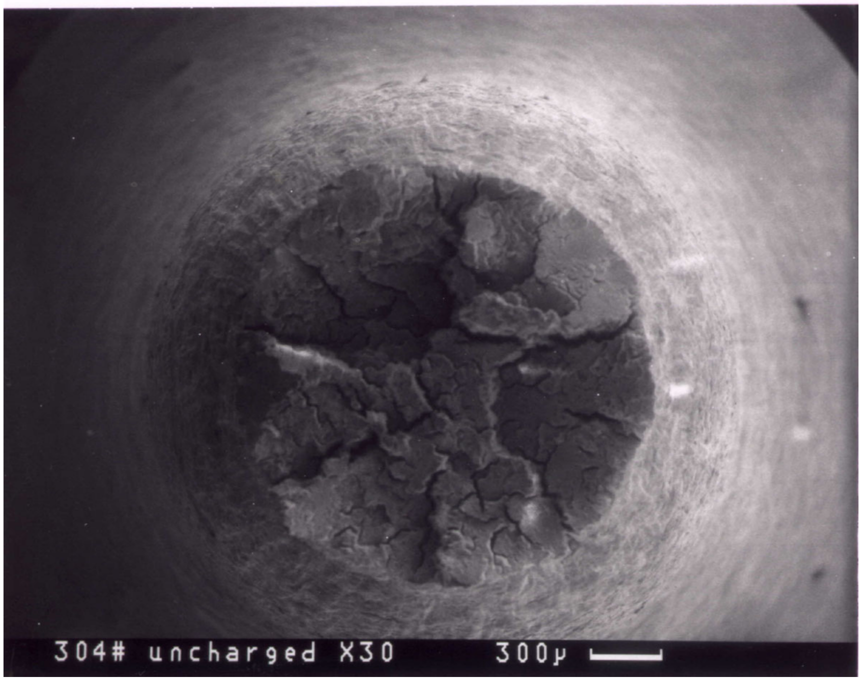
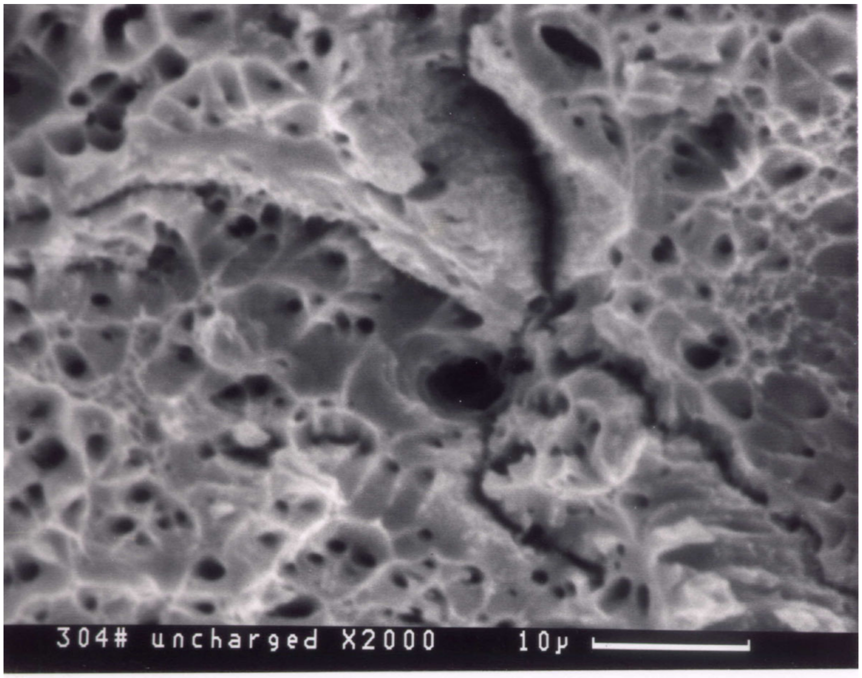


Fig.5 The rough and gray fracture of the uncharged tension specimens of 304 stainless steel with the deep tear ridges.(X30)



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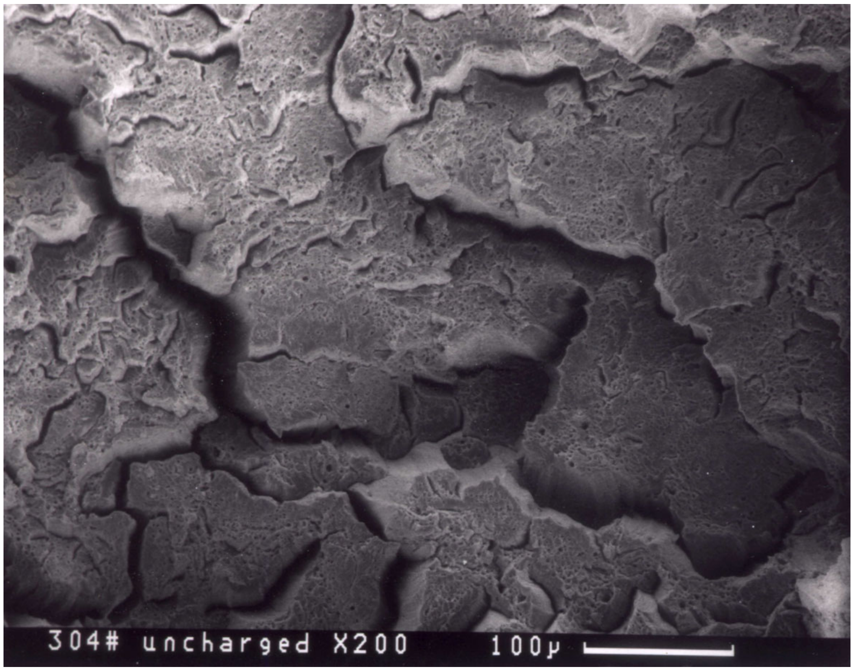


Fig.7 The transgranular cracking, rupture and tear ridges in the uncharged 304 stainless steel specimens (X200)

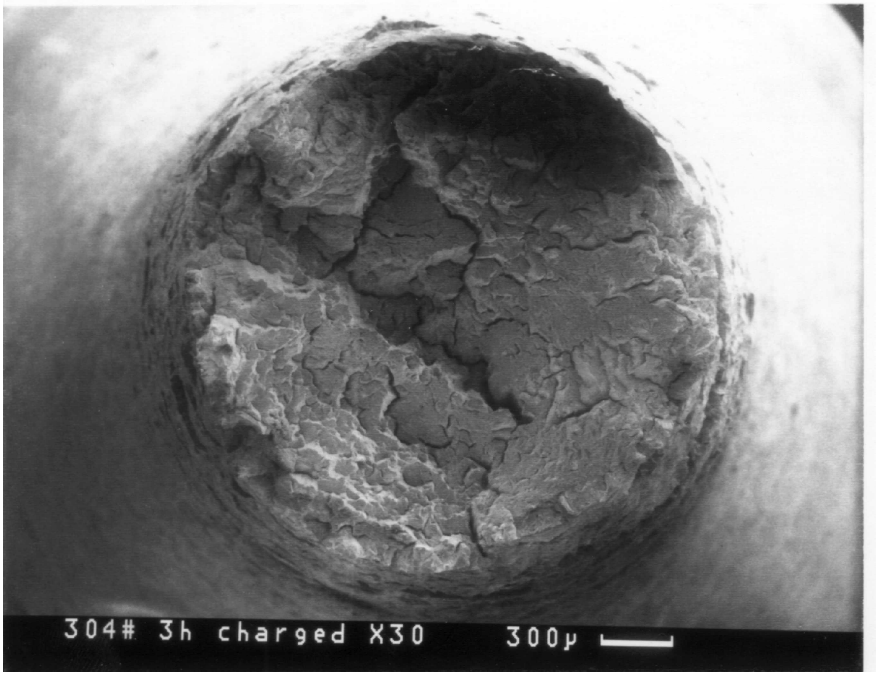


Fig.8. The hydrogen enters the surface of the specimens resulting the brittle feature around the outer surface after 25 ppm hydrogen introduced - charged for 3 hours (x30)

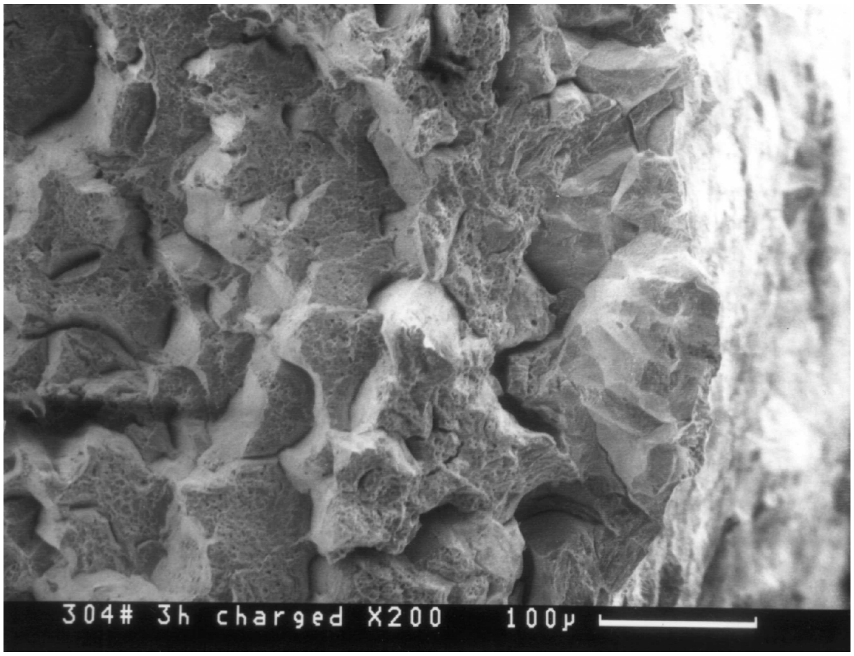


Fig.9 The brittle crown and the ductile (right)-brittle (left) transition area of in 304 stainless steel tension specimen with 25 ppm hydrogen – charged for 3 hours (X200)

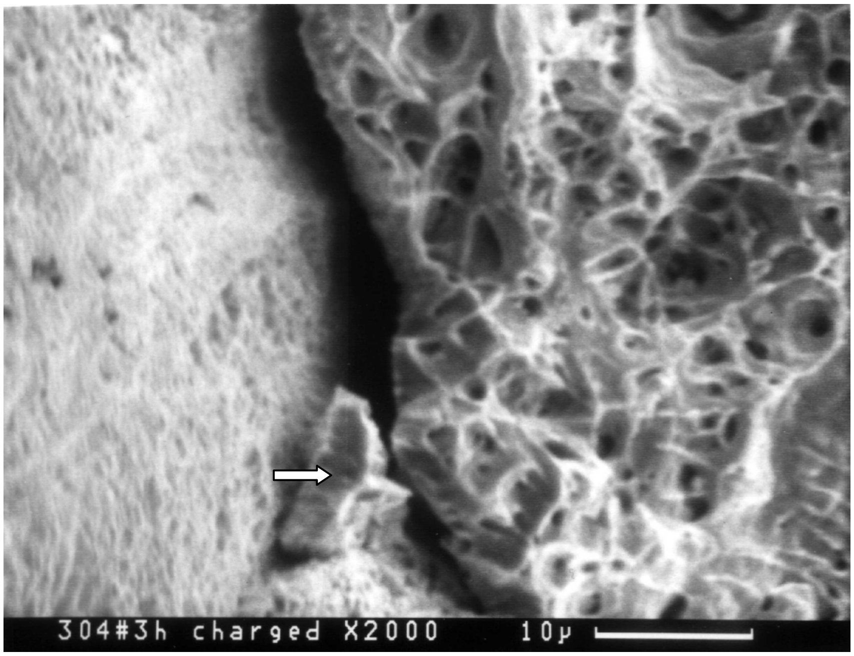


Fig.10 The transition area of ductile (right) to brittle fracture (left). The brittle rupture may start from the interface of the matrix-particle marked by the arrow (X2000)

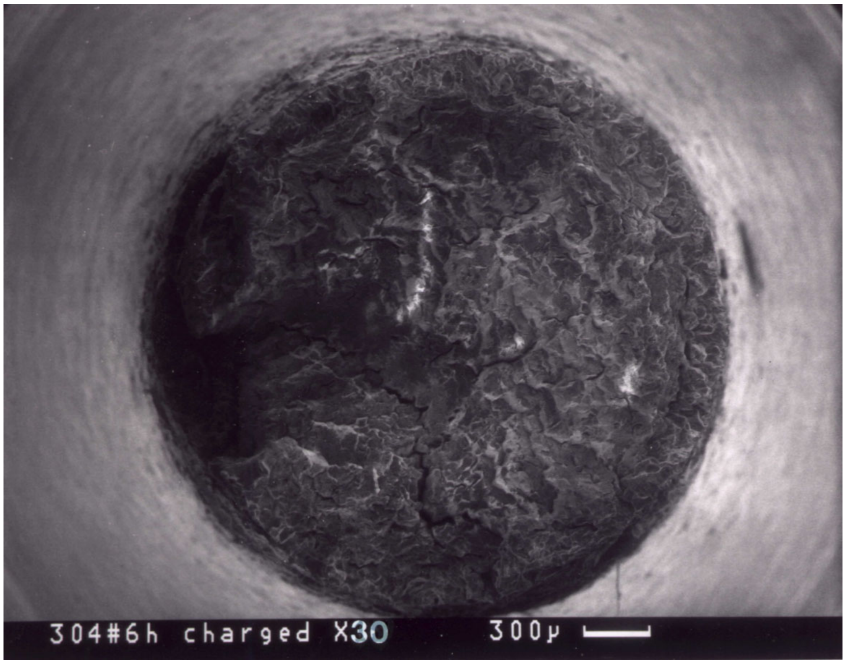


Fig.11 The necking fracture of the tension specimen with 45 ppm hydrogen – charged for 6 hours (x30)

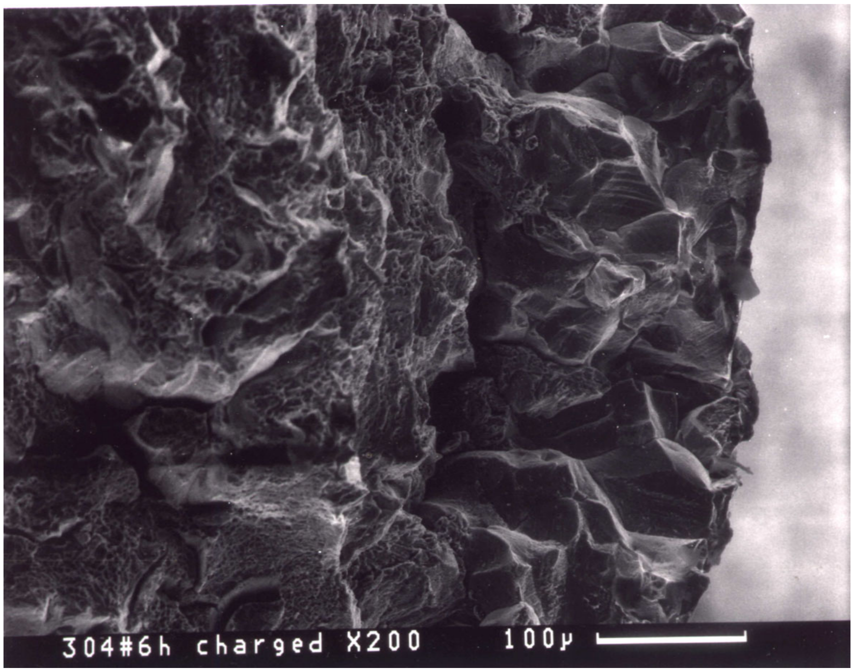
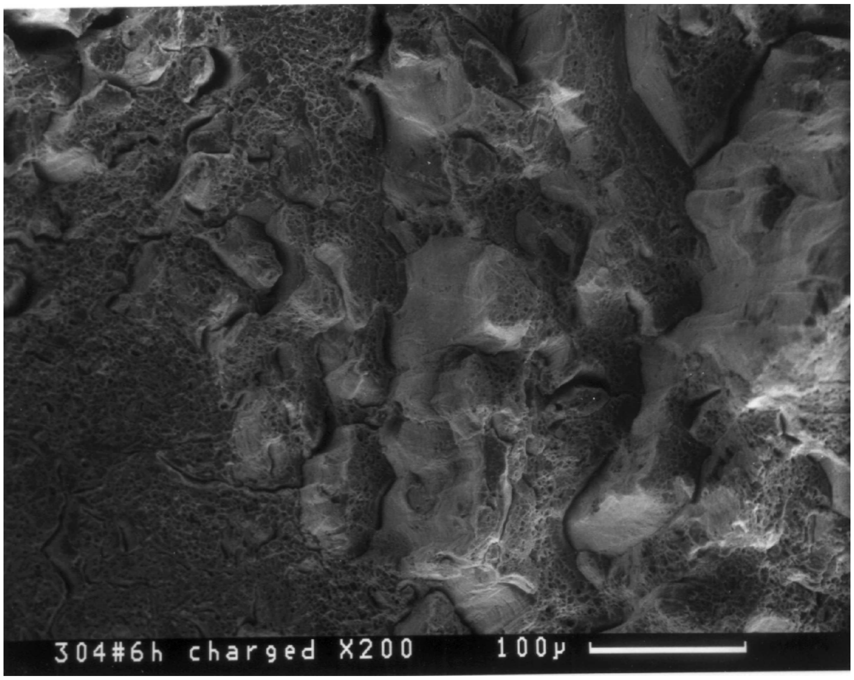


Fig. 12 The brittle crown expands toward to central area in 304 stainless steel specimens with 45 ppm hydrogen – charged for 6 hours (X200)



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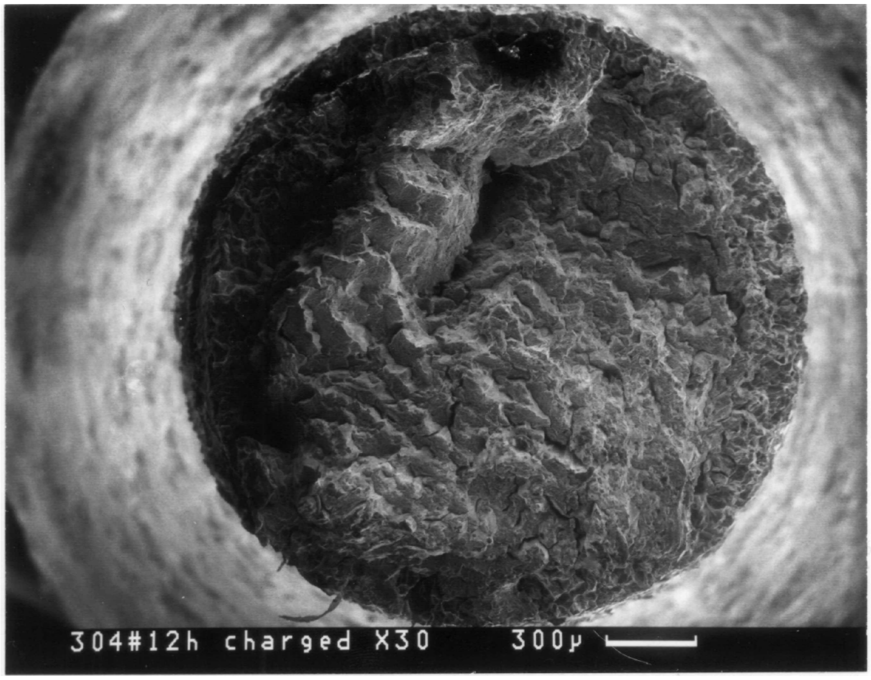

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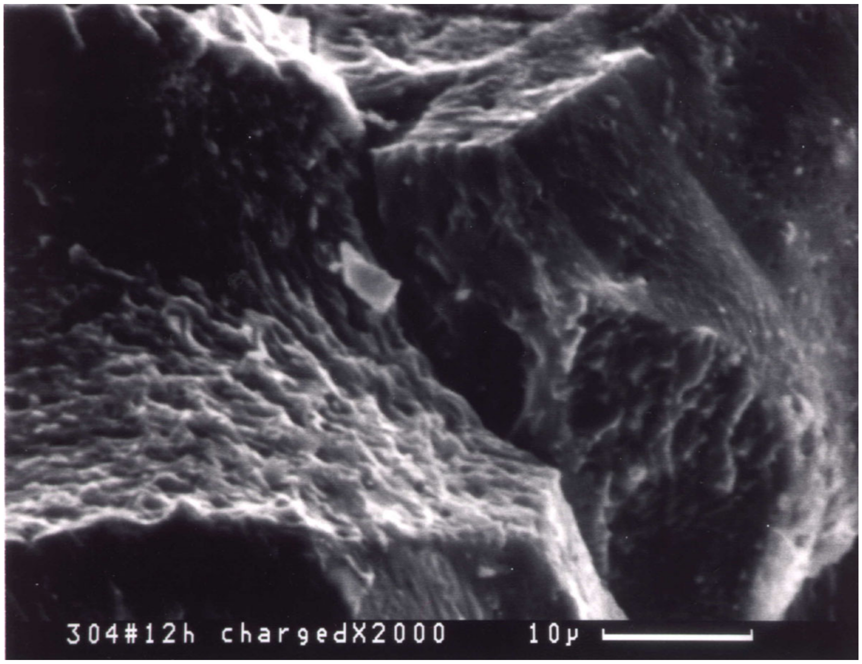

Fig.15 The inter-granular ruptures dominates the fracture of the specimens with 60 ppm hydrogen- charged for 12 hours (X2000)

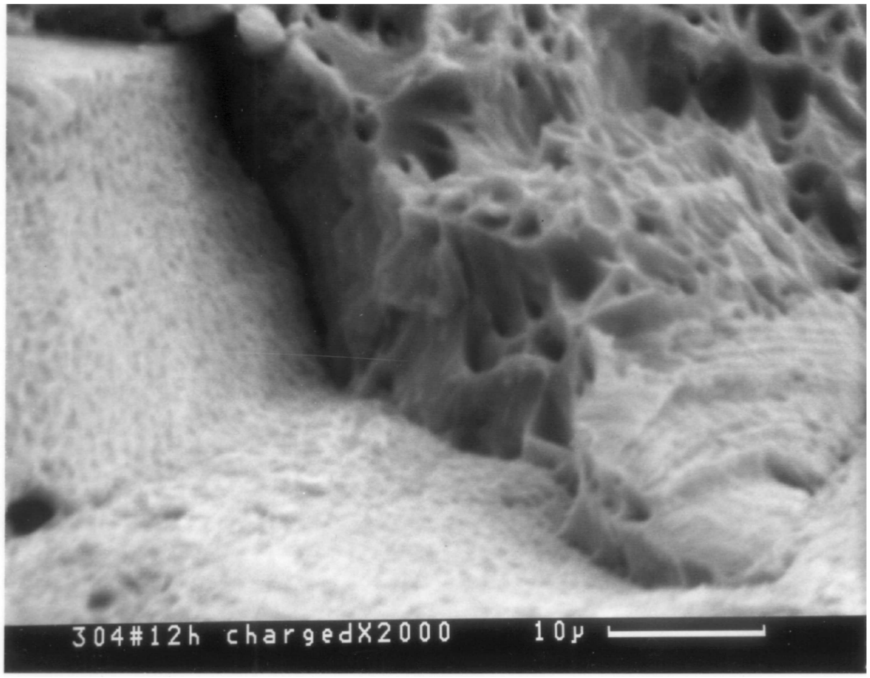

Fig. 16 The increased size of the dimples and the deceased density of the microvoids in some residual ductile areas in the specimens with 60 ppm hydrogen – charged for 12 hours (X2000)

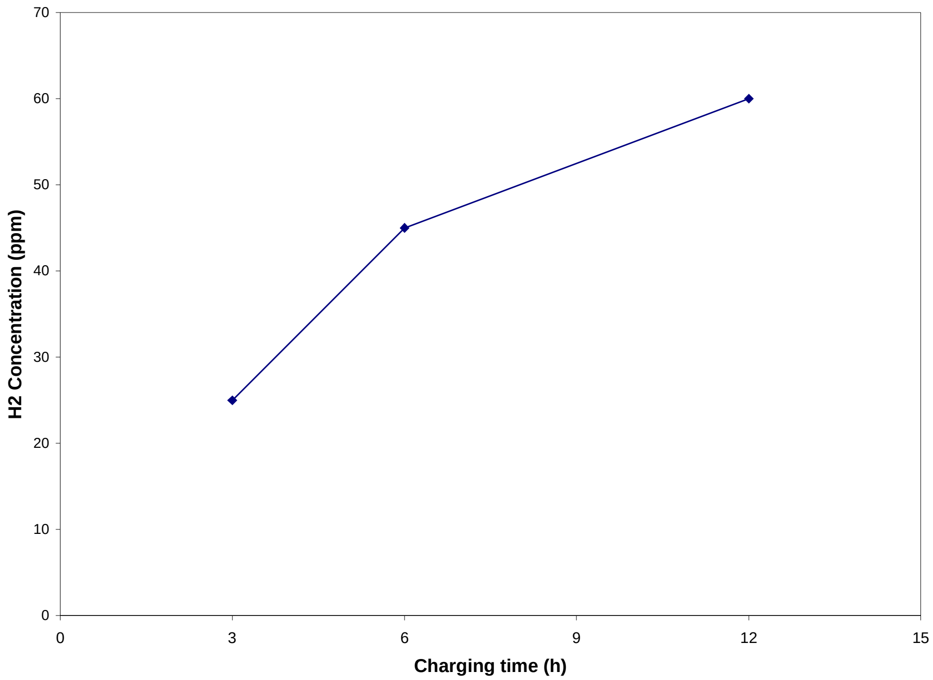

Fig.17 Hydrogen concentrations in 304 stainless steel after different electrochemical charging periods