

High temperature electrochemical charging of hydrogen and its application in hydrogen embrittlement research

Ming Au*

Savannah River National Laboratory, Aiken, SC 29808, United States

Received 10 August 2006; received in revised form 13 November 2006; accepted 14 November 2006

Abstract

A high temperature electrochemical charging technique was developed for effective introduction of hydrogen or tritium into the metallic materials to a high level in a short period of time. The samples of the steels and alloys, as the cathode, were charged in an electrochemical cell consists of Pt anode and molten salt electrolyte. After 3, 6 and 12 h charging, the 304 stainless steel absorbed 25, 45 and 60 ppm of hydrogen, respectively. Correspondingly, the mechanical strength lost 10, 16 and 23%. The plasticity was also reduced to 20, 23 and 38%. The fractography showed the hydrogen embrittlement effect on the fractures. The electrochemical hydrogen charging technique was successfully used for introducing tritium, an isotope of hydrogen, into the super alloys for visualization of hydrogen trapped in the microstructure of the materials. It is found that the hydrogen is trapped at the grain boundaries, in inclusions and carbides. The deformed and twisted grain boundaries trap most hydrogen under stress.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Hydrogen; Embrittlement; Materials; Electrochemical charging; Fractography

1. Introduction

Hydrogen embrittlement is a critical issue with respect to materials used in nuclear, chemical, petrochemical and marine industries. Specimens charged with hydrogen are investigated typically for material behavior in hydrogen environments such as mechanical properties, fracture feature and hydrogen locations and distribution in the microstructure of the materials. 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 973 K) to drive hydrogen diffusing 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 exposed to hydrogen for a long period of time (days or weeks) at high pressure (20–35 MPa) and high temperature (above 623 K). At the same pressure and temperature, the hydrogen concentrations of 304 stainless steel calculated by dif-

ferent researchers using the equation $C_H = kP^{1/2} \exp(-\Delta H/RT)$ vary largely from 16 to 118 ppm [3]. The actual hydrogen concentrations measured by the experiments are much less than the calculated values. The main explanation is that hydrogen desorption occurred during autoclave cooling down [4]. Some researchers were able to introduce up to 50 ppm of measurable hydrogen into 304 steel using this technique in their best effort [5]. The gaseous hydrogen charging has to be conducted in the special high pressure and explosive proof facility that is not easily available for most materials research laboratories.

Higher levels of hydrogen (60–100 ppm) are often required to evaluate critical components in nuclear structures. To introduce high-level hydrogen into steels and alloys, an electrochemical method was developed. Instead of using a gaseous hydrogen charge, the hydrogen enters the materials as atoms in the electrochemical cells. In this case, the driving force is the electrochemical potential instead of a hydrogen pressure gradient. The motion of the fresh-formed atoms in materials is faster than diffusion of hydrogen molecules in gaseous hydrogen charging. It builds up higher levels of hydrogen in the materials at a short period of time. At 423 K and the -1 V Ag/Ag⁺ charging potential, the equivalent hydrogen pressure applied to 316 stainless steel specimen submerged in the molten salt is 3000 MPa that is ultra higher than any steel autoclave can bear [4]. The electrochemical hydrogen charging is also used for introducing of

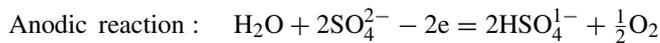
* Tel.: +1 803 507 8547; fax: +1 803 652 8137.
E-mail address: ming.au@srl.doe.gov.

tritium, an isotope of hydrogen, into materials for visualization of hydrogen locations and distribution through autoradiography process [6–8]. In this work, a high temperature electrochemical cell was set up to charge the tensile specimens of 304 stainless steel and autoradiography specimens of 600 and 750 super alloys as literature [6,8] described. The changes in mechanical properties and fracture feature of 304 steel with different hydrogen concentrations and the hydrogen distribution in 600 and 750 super alloys were investigated.

2. Experiment

Hydrogen charging was conducted in an electrochemical cell shown in Fig. 1.

Hydrogen was introduced into the specimens by cathodic charging in a melted salt bath that consisted of sodium bisulfate monohydrate and potassium bisulfate. The mixed salt was melted and maintained at 473 K in a glass kettle. In this work, 1500 g mixed salt (2.03 g/ml bulk density) was used. Most evaporated water was collected and dripped back to the salt bath through a condenser. The water was maintained at a constant level through the dynamic evaporation–condensation process and periodical water injection. Cathodic charging was conducted under a 0.850 V Ag/Ag⁺ fixed potential and at 423 K with the specimens acting as the cathode. The electrochemical reactions in the hydrogen-charging cell are given as follows:



The cathodic reaction produces the fresh-formed atomic hydrogen on the surface of the cathode (specimens). Under the force of the electric potential, an extreme high concentration of fresh-formed hydrogen atoms was built up and drove hydrogen atoms diffusing into the bulk of metals. A constant potential

was applied between the cathode (specimens) and anode (Pt counter electrode) by the EG&G 273 Galvano/Potentiostat for a pre-determined period. The Ag/Ag⁺ reference electrode was connected to the Galvano/Potentiostat 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 for monitoring electrical resistance change of the salt. The ohmmeter reading represents the concentration of hydrogen ions in the molten salt. 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 for maintaining a constant ohmmeter reading. At above condition, the charging current density of 20 mA/cm² was maintained. 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 233 K in the dry ice box to prevent hydrogen from off gassing. To investigate hydrogen effects on mechanical strength, the compact tensile specimens of 3 mm diameter and 55 mm length were prepared from the annealed 304 stainless steel bar. The specimens were charged at different times at a fixed potential of 0.850 V Ag/Ag⁺. Three groups of the compact tension specimens of the 304 stainless steel were charged in the electrochemical cell for 3, 6 and 12 h, respectively. Each group consists of three identical specimens for objective and accuracy of the measurement. 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 the water at 298 K for 5 min to raise the temperature. The tension tests of the specimens were conducted immediately using an Instron Model 1125 tension machine with 5000 kg full scale of the load, 1 mm/min crosshead speed and 20 mm/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 observation of fractures morphology was performed using a CamScan 600 scanning electron microscope.

The tritium charging was conducted in a radiation shielding glove box equipped with the tritium monitors shown in Fig. 2. The system set-up, the charging procedure and the parameter control were similar to the non-tritium hydrogen charging, but added 50 ml tritiated water. The pre-prepared metallographic specimens of 600 and 750 super alloys and were electrochemically charged in the tritium added salt bath for 3 h at the fixed potential of 0.850 V Ag/Ag⁺. The specimen of 750 super alloy was under a tensile stress at 1000 MPa. The tritium concentration of the melted salt at 423 K was maintained at 12.7 mCi/ml. After charging, the specimens were remained in the glove box de-gassing for 24 h. Then, the specimens were processed through

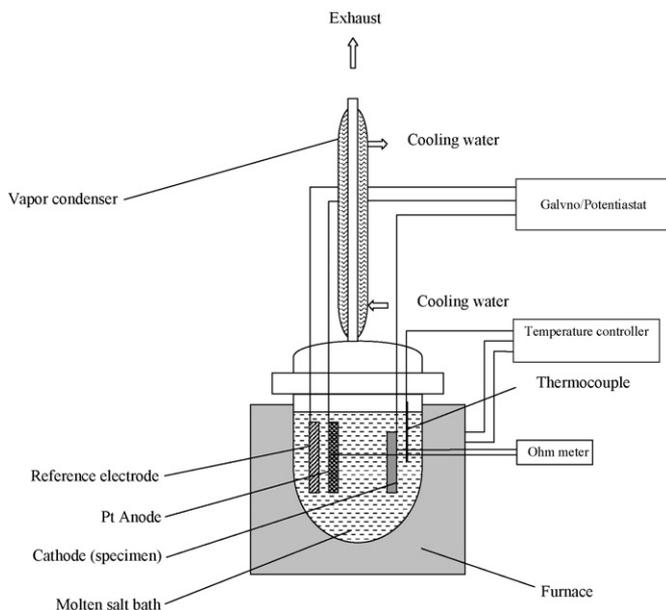


Fig. 1. Schematic diagram of the electrochemical cell for hydrogen charging.



Fig. 2. The radioactive-proof electrochemical apparatus for tritium charging.

Table 1

The results of tension testing of the 304 stainless steel with different hydrogen concentrations

Charging time (h)	0	3	6	12
Hydrogen concentration (ppm)	0	25	45	60
Strength limit (MPa)	6200	5600	5200	4800
Elongation (%)	26	21	20	16

the autoradiography procedure and observed under SEM. The experimental details are reported in elsewhere [8].

3. Results

3.1. Hydrogen concentrations and its influence on mechanical properties of 304 stainless steel

After 3, 6 and 12 h electrochemical charging, the hydrogen concentration of 304 stainless steel was increased from 0 to 25, 45 and 60 ppm, respectively, see Table 1. The strength limit of the 304 stainless steel was reduced from 6200 to 5600 MPa (−10%), 5200 MPa (−16%) and 4800 MPa (−23%), respectively. The elongation, an indicator of the plasticity, was also reduced from 26 to 21%, 20 and 16% correspondingly, see Fig. 3. Obviously, the material became brittle and lost its original mechanical strength, toughness and plasticity. The tension specimens evidence necking and less elongation caused by hydrogen,

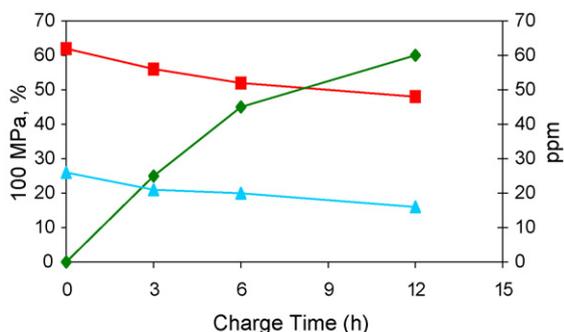


Fig. 3. The mechanical properties of 304 stainless steel at different hydrogen concentrations.



Fig. 4. The ruptured tensile specimens of 304 stainless steel with different hydrogen charging time.

see Fig. 4. The 120 ppm of hydrogen concentration was obtained in the 347 stainless steel in 72 h of electrochemical hydrogen charging in the experiments.

3.2. Fractography analysis

The freshly broken specimens were analyzed for fracture features using a scanning electron microscope. The fractures of the uncharged specimens showed the typical ductile feature mode with matte and rough surfaces. Large necking shrinking and shear lips were also observed, see Fig. 5(a). At high magnification, the fracture was characterized by the presence of a great number of small microvoids (dimples), see 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 the metals 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 fractures, see Fig. 6.

After 3 h of electrochemical hydrogen charging, 25 ppm hydrogen was introduced into the materials. The surface fracture appeared essentially composed of two areas, that is a brittle crown area near the sample surface followed by ductile area at the center (Fig. 7). It evidences the hydrogen migration from the outer surface to the central area. Most area of the fractures still showed the gray and matte nature of the ductile fracture mode, but the shiny and inter-granular brittle fracture was observed along the surface area of the specimen. The influence of hydrogen on fractures is attributed to an accumulation of hydrogen at matrix-particles interfaces, which lowers the interfacial strength [9]. The detailed features of the transition area between the ductile and the brittle area are shown in Fig. 8.

After 6 and 12 h of charging, more hydrogen entered the materials. The brittle crown grew toward the central area, the fractures were flattened and the necking was decreased due to the loss of ductility and plasticity as shown in the Fig. 5(c and d). Although the overall hydrogen levels in the specimens were 45 and 60 ppm, it is believed that the hydrogen concentration is much higher in near surface area, where the typical brittle fracture mode demonstrates. In the central area, the fracture showed the mixed fracture mode owing to a lower hydrogen concentration (Fig. 9). Under

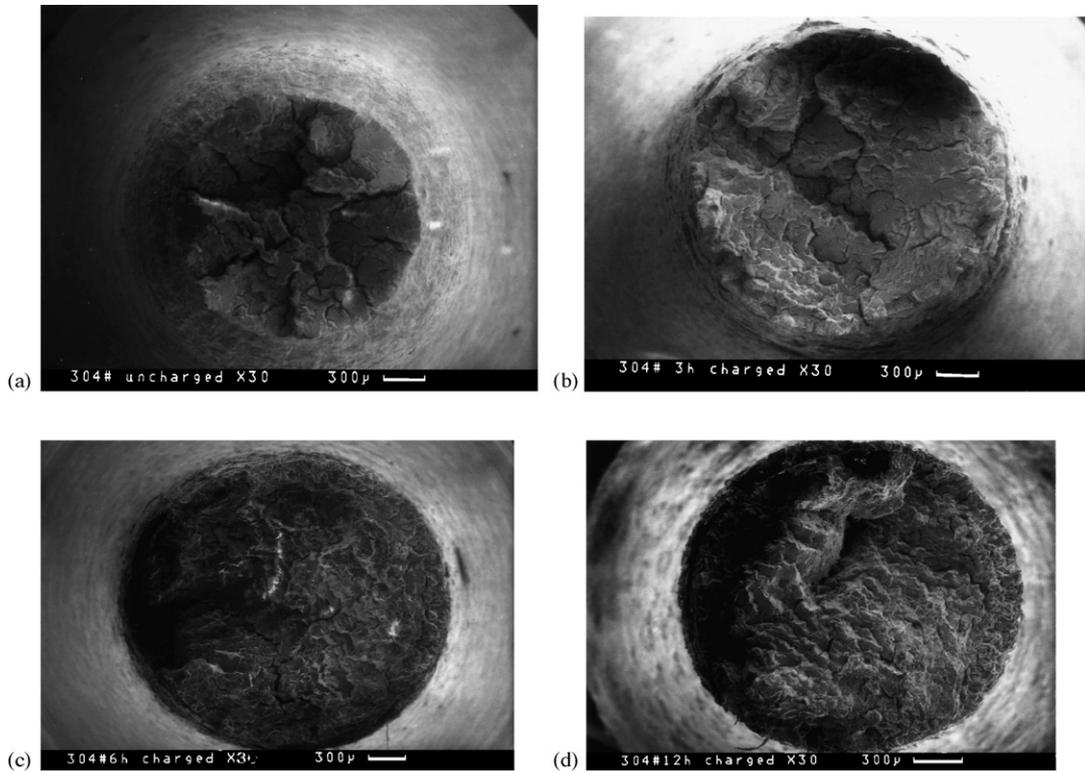


Fig. 5. The necking fractures of the tension specimens of 304 stainless steel with different hydrogen concentrations. (a) The rough and gray fracture with the deep tear ridges in uncharged 304 stainless steel specimen ($\times 30$). (b) The brittle crown surround the outer surface in 3 h-charged specimen with 25 ppm hydrogen introduced ($\times 30$). (c) The necking fracture of the 6 h-charged specimen with 45 ppm hydrogen introduced ($\times 30$). (d) The flat and shiny fracture of the 12 h-charged specimen with 60 ppm hydrogen introduced ($\times 30$).

high magnification, it could be seen that the inter-granular brittle rupture dominated the whole fracture of materials (Fig. 10).

3.3. Hydrogen visualization in the tritium charged specimens

Fig. 11 shows that the hydrogen was trapped in the interface of the inclusion and matrix (A); the interface of the

primary carbides and matrix (B); the grain boundaries (C); and the dislocation pile-ups (D). Fig. 12 shows that the hydrogen was mainly concentrated at deformed and twisted grain boundaries when the materials were under the mechanical stress. It is consistent with the theory that the hydrogen migrates with the movement of the dislocations that end in the grain boundaries and generates hydrogen enrich environment [4].

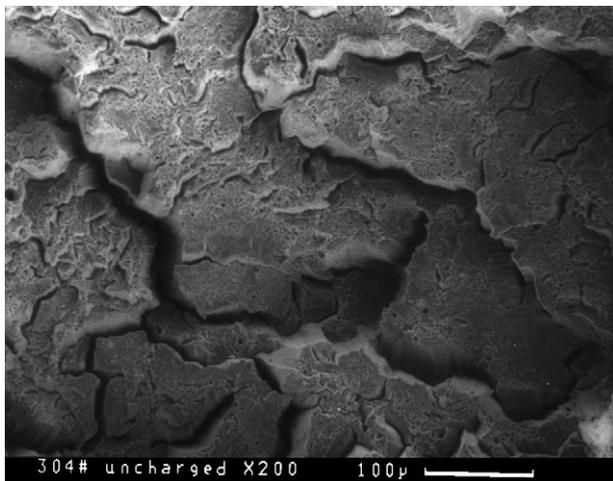


Fig. 6. The transgranular cracking, rupture and tear ridges on the fracture of the uncharged 304 stainless steel specimen ($\times 200$).

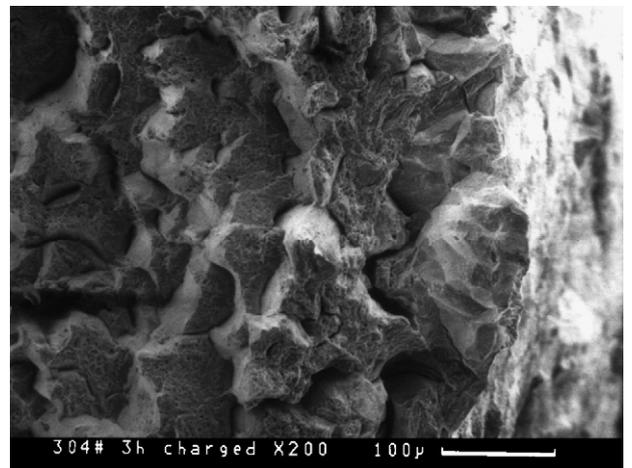


Fig. 7. The brittle crown was formed around the outer surface of 304 stainless steel specimen with 25 ppm of hydrogen (charging for 3 h) ($\times 200$).

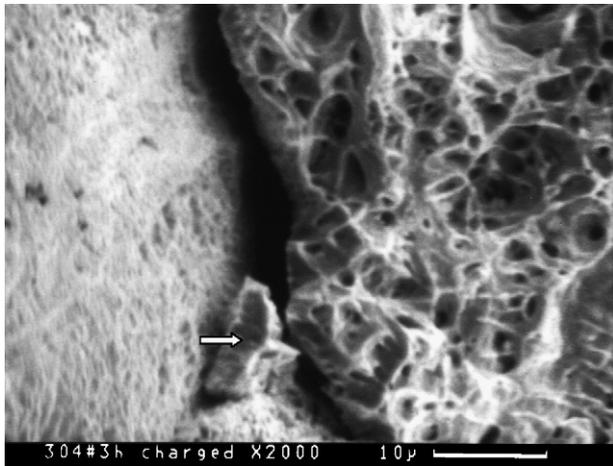


Fig. 8. The transition area of ductile (right) to brittle fracture (left). The brittle rupture may start from the interface of the matrix-particle pointed by the arrow ($\times 2000$).

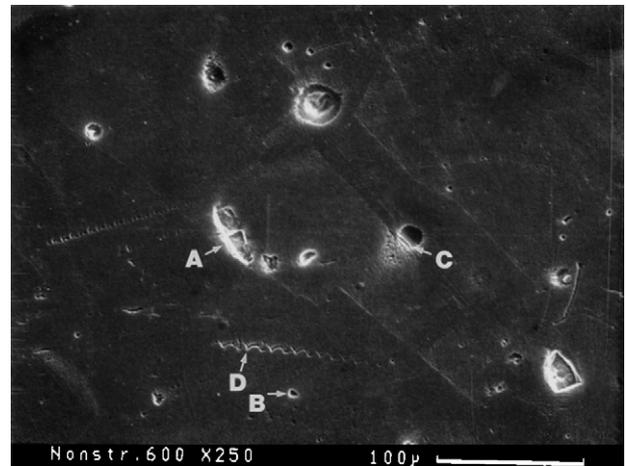


Fig. 11. Hydrogen is trapped around the inclusion (A), carbides (B), grain boundaries (C) and dislocation pile-ups (D) in the annealed 600 super alloy ($\times 250$).

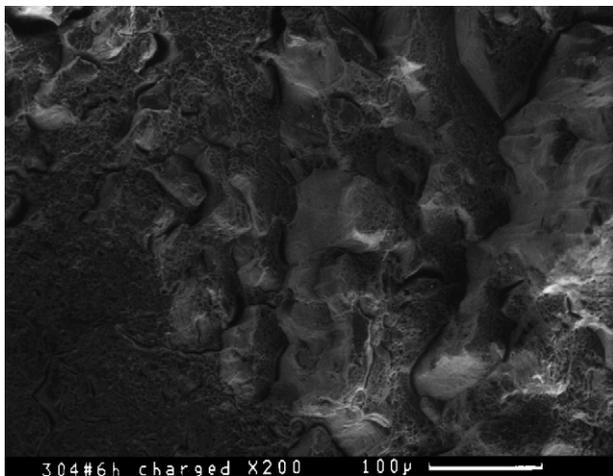
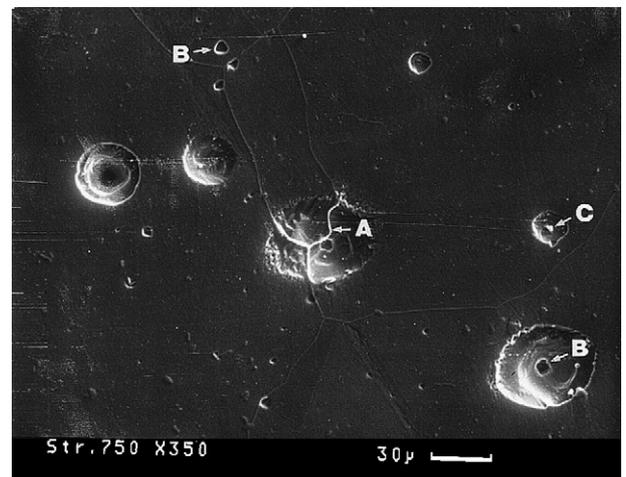


Fig. 9. The mixed mode of the brittle and ductile fractures in the central area of the specimens with 45 ppm of hydrogen (charging for 6 h) ($\times 200$).



(1)

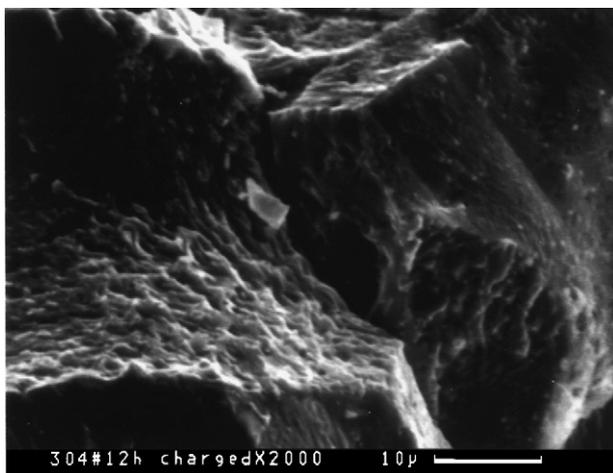
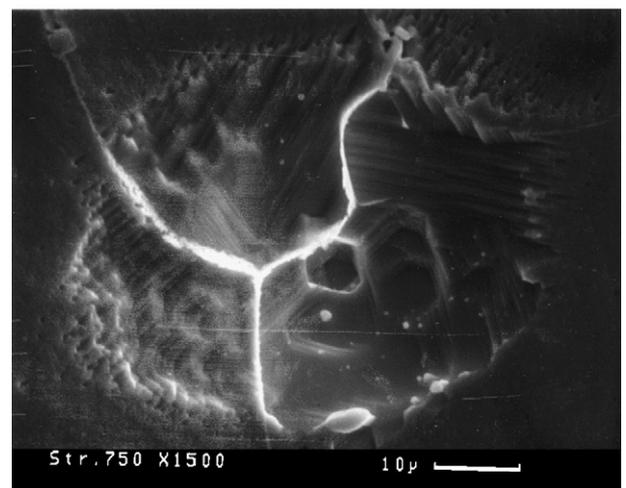


Fig. 10. The inter-granular ruptures dominates the fracture of the specimens with 60 ppm of hydrogen (charging for 12 h) ($\times 2000$).



(2)

Fig. 12. (1) Most hydrogen is concentrated along the deformed and twisted grain boundaries (A) and some gather around inclusions (B) and carbides (C) in stressed 750 super alloy ($\times 350$). (2) The enlargement of the area (A) ($\times 1500$).

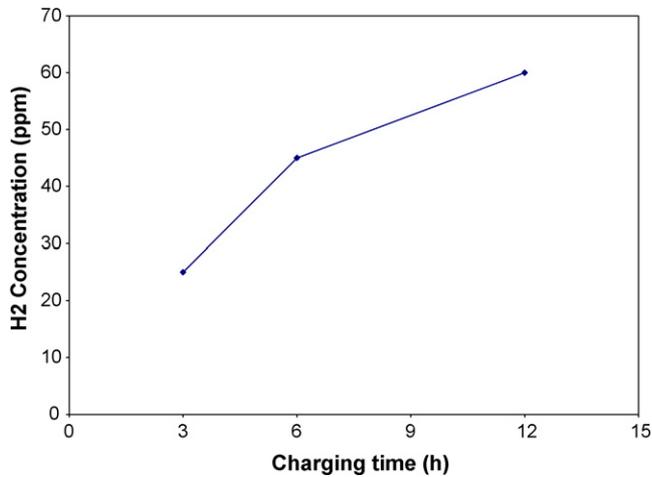


Fig. 13. Hydrogen concentrations in 304 stainless steel with different electrochemical charging times.

4. Discussion

The high temperature electrochemical hydrogen charge is an effective 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 h to get 25 ppm hydrogen in 304 stainless steel using gaseous hydrogen charge at 673 K and 6.0 MPa. It takes only 3 h to obtain the same level of hydrogen using an electrochemical charge at 473 K and ambient pressure. As a result, the driving force of hydrogen migration is the electric potential that is equivalent to a few thousands MPa pressure of hydrogen. It is extremely powerful because 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 ions. This is more significant for the stainless steels and super alloy that is covered by the passive protective layer. The electrochemical hydrogen charge is performed in a glass cell at ambient pressure and moderate temperature. The equipment cost is very low compared to the high-pressure gaseous hydrogen charging that has to be carried out in the special high-pressure and explosive proof facility. Depend on material, hydrogen concentrations have its limit in electrochemical charging. Extending charge time does not increase hydrogen level further after reaching certain levels. For example, 25 ppm hydrogen was obtained in the first 3 h of charging of 304 stainless steel. For the next 3 h, the hydrogen level was increased by only 20 ppm. After that, the hydrogen level was raised 15 ppm in 6 h of charging as shown in Fig. 13. This corresponds to the nature of hydrogen ion diffusion in the solid that

depends on the gradient of hydrogen concentration. 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 super alloys charged less than 72 h.

5. Conclusion

The high temperature electrochemical hydrogen charge is the most effective technique to introduce high levels of hydrogen into the materials in a short period of time. The cost of experimentation is relatively low. It is normally performed at ambient pressure and less than 473 K. There is no safety concerning associated with high-pressure gaseous hydrogen charging. This method is also can be used for research of the hydrogen storage materials that cannot be charged easily by hydrogen gas. Hydrogen deteriorates material mechanical properties significantly even at small concentrations. For example, 25 ppm of hydrogen introduced by electrochemical charging reduced the mechanical strength and the plasticity of the 304 steel 10 and 20%, respectively. At 60 ppm of hydrogen, this material became more brittle and lost 23% strength. The hydrogen trapped in the microstructure of the super alloys was successfully visualized by the autoradiography of the tritium charged samples. The hydrogen was trapped around the grain boundaries, inclusions and the interface of the carbides and matrix. Most hydrogen gathered around the deformed and twisted grain boundaries when the materials were under mechanical stress.

Acknowledgements

This work has been done in author's previous employment. Author thanks Drs. T. Motyka and P. Cloessner for their comments and encouragement. Savannah River National Laboratory is operated by Washington Savannah River Company for US Department of Energy under contract DE-AC09-96SR18500.

References

- [1] R. Garber, I.M. Bernstein, A.W. Thompson, *Scripta Met.* V10 (1976) 241–244.
- [2] R. Garber, I.M. Bernstein, A.W. Thompson, *Met. Trans.* V12A (1981) 225.
- [3] D. Hardie, Y. Wei, et al., *Corros. Sci.* 46 (2004) 3089–3100.
- [4] A.M. Brass, J. Chene, *Corros. Sci.* V48 (10) (2006) 3222–3242.
- [5] R. Garber, M. Bernsten, *Conference on Environmental Degradation of Engineering Materials*, Blacksburg, Virginia, 1997.
- [6] C.L. Baker, J. Chene, I.M. Bernstein, J.C. Williams, *Met. Trans. A* 19A (1) (1988) 73–82.
- [7] A.M. Brass, J. Chene, *Mater. Sci. Eng. A* 242 (1998) 210–221.
- [8] M. Au, *J. Alloys Compd.* 293–295 (1999) 317–323.
- [9] E. Herms, J.M. Olive, M. Puiggali, *Mater. Sci. Eng. A* 272 (1999) 279–283.