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Hydride formation by high temperature cathodic hydrogen charging method and its effect on the corrosion behavior of Zircaloy-4 tubes in acid solution

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Abstract

Zircaloy-4 cladding tube was hydrided using the high temperature cathodic hydrogen charging method. The optimum conditions for charging more than 1000 ppm of hydrogen was 0.4 A/cm^2 for 24 h at 150°C–0.5°C in an electrolyte containing hydrobisulphate ions. After vacuum annealing at 400°C for 3 h, thin platelet-shaped hydrides were formed within the tubing and were preferentially oriented along circumferential direction, which was related to the texture of the material. The hydride formed was identified as the δ-ZcH$_{1.6}$ and γ-ZrH phases by X-ray diffraction. The corrosion potential of the hydrided alloy was +830 mV$_{SCE}$ in 90% HNO$_3$ at 25°C and the material was rapidly corroded by anodic polarization. The corrosion potential was dramatically decreased in a 20% hydrochloric acid solution containing small amount of a strong oxidizer, such as ferric ion due to the instability of the passive film on zirconium in this environment. The corrosion potentials of the hydrided alloy were lower than those of the as-received alloy in the corrosive environments.

1. Introduction

Zirconium and its alloys have been used for many years in chemical and nuclear engineering applications involving severe combinations of temperature and reactive environments [1]. Zircaloy-4, one of zirconium alloys, has satisfactory corrosion resistance to nitric acid and hydrochloric acid. When the alloy is used in a nuclear reactor, its hydride is necessarily formed from external hydrogen sources such as waterside corrosion, dissolved hydrogen in coolant water and water radiolysis, and internal sources such as hydrogen content in fuel pellets and moisture absorbed by the uranium dioxide fuel pellet [2]. The precipitation of hydride in the Zircaloy-4 cladding tube results in embrittlement of the tubing, especially when it is radially oriented due to the internal pressure of the nuclear fuel rod [3]. Since hydride formation in zirconium and its alloys significantly influences the mechanical properties, the development of both a convenient and reliable hydrogen charging method, and an analysis technique for the amount of charged hydrogen are required in order to study the effect of hydride on related properties.

Various hydrogen charging methods have been developed, including gaseous charging and electrolytic charging [4,5]. In gaseous hydrogen charging, the specimen is brought into contact with pure hydrogen gas at an elevated temperature. Oxygen is usually detrimental to hydrogen pick-up from the gas phases, and an elaborate vacuum system is necessary for the hydrogen charging [6]. In electrolytic charging, hydrogen is charged in an electrolyte solution with a dc power supply at room temperature. This method is characterized by its simplicity. However, it is difficult for hydrogen to diffuse into the material because of the low hydrogen diffusivity at the low temperature of the electrolyte solution [7].

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Table 1
Chemical composition of Zircaloy-4

Element	Sn	Fe	Cr	O	C	Si	H	Zr
Wt%	1.2	0.18	0.07	0.1	0.01	0.008	<20 ppm	Bal.

Recently, John et al. [8] developed an electrolytic charging method using a high temperature salt to enhance the diffusivity of hydrogen into many iron and nickel base alloys and zirconium alloys. They used various salt baths saturated with steam. The absorbed hydrogen content was chemically analyzed by an inert gas fusion technique after charging. Although their method is effective for charging hydrogen, it is still difficult to in situ evaluation of charged hydrogen during the process. Therefore, in this study, a convenient charging method monitoring hydrogen content during the charging process, so called high temperature cathodic hydrogen charging method (HTHCM) was designed and systematically studied. Attention was focused on (i) the types of zirconium hydride formed by HTHCM and (ii) the effects of the hydride on the corrosion behavior in nitric acid and hydrochloric acid solutions with strong oxidizer such as ferric ions.

2. Experimental procedure

The Zircaloy-4 used in this study was supplied by the Korea Nuclear Fuel Company in a seamless tube form with a thickness of 0.96 mm. Its chemical composition is given in Table 1. The tubing was high temperature cathodically hydrogen charged by using the unit described by Choi [9]. Fig. 1 is a schematic of experimental apparatus. The chemistry of the electrolyte solution is shown in Table 2. A direct current was supplied galvanostatically to the working electrode, a Zircaloy-4 specimen, and a counter electrode at 0.2 ~ 0.5 A/cm^2. The counter electrode was a platinum tube. Since the decomposition of water in the NaOH and sulphate/bisulphate salt system is the preferred reaction for the temperature above the 80°C, the electrolysis of the water in a container can liberate hydrogen [10,13]. During the charging process, the voltage change between the reference electrode and working electrode was recorded.

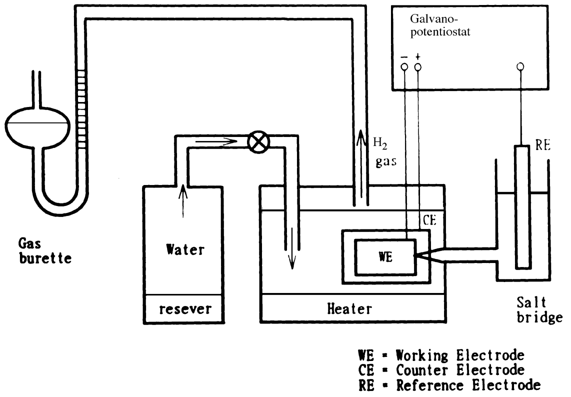

Fig. 1. Schematic diagram of experimental apparatus.

When the electrochemically evolved hydrogen ions are applied to the Zircaloy-4 working electrode, apart of the absorbed ions diffuses into the alloy and the other part is liberated from the surface as a hydrogen gas. The volume of the gaseous hydrogen is measured by an attached burette, which is converted to the number of hydrogen ions by the ideal gas equation. Since the amount of hydrogen evolution (C_{H^+}) in the solution is proportional to the total applied current (i), the charged hydrogen content at a certain time in the Zircaloy-4 specimen ($C_{H(Zr)}$) is determined by subtracting from the hydrogen ion evolution content (C_{H^+}) by the applied current to form the gaseous hydrogen content ($1/2C_{H_2}$) measured with an attached burette: $C_{H(Zr)} = i - \frac{1}{2}C_{H_2}$.

In order to stabilize hydrogen in the specimens as hydride form, vacuum annealing was carried out at 400°C for 3 h after chemically cleaning of the specimen surface with acetic acid. Hydride morphology was observed with an optical microscope (Nickon HFX-DX 114) after etching with a solution ($H_2O_2 : HNO_3 : HF = 70$ ml : 35 ml : 1 ml) after polishing from 220 grit to 1200 grit emery papers followed by 3.0, 1.0 and 0.03 μm alumina powder.

Phase identification after hydrogenation was carried out with X-ray diffractometer (Rigaku). The thin wall tube specimen was sectioned into several pieces with about 30 mm lengths and 3 mm widths to make a plate by stacking the pieces. The surface of the specimen was chemically polished for 20 s in a 45% H_2O : 45% HNO_3 : 10% HF solution to avoid the machining effect. Cu–Kα radiation was utilized with which permitted the 2θ range of 20–80°.

In order to study the effect of hydride formation and oxidizer in solution on the corrosion behavior of the alloy, potentiodynamic polarization curves were determined with a potentiostat (Hokuno Dinko 121) in deaerated 90% HNO_3 and in 40% HCl + 500 ppm $FeCl_3$

Table 2
Composition of the electrolytic solution

$NaHSO_4$ (mg)	Na_2SO_4 (mg)	K_2SO_4 (mg)	H_2O (ml)
500	50	10	100

at 25°C. Tube specimens for the electrochemical measurements were cut 50 mm in length, ground with from 320 grit to 600 grit emery papers, rinsed in deionized water, and introduced into a standard corrosion cell after measuring the exposure area. They were allowed to equilibrate prior to the measurement of their corrosion potential (E_{corr}) and before the initiation of the cathodic and anodic scans at 10 mV/s. The potential-vs.-current curves were recorded. Deaeration was achieved by bubbling inert argon gas through the electrolyte before and during measurements.

3. Results and discussion

Fig. 2 shows the optical micrographs of hydride in Zircaloy-4 cladding tubing after hydriding by a high temperature cathodic hydrogen charging method, followed by annealing at 400°C for 3 h in a vacuum atmosphere. After homogenization at 400°C under the environment, both intergranular and intragranular hydride precipitates have grown circumferentially. It can be seen that hydrogen has penetrated deep into the tubing. To identify the phases in the specimen after vacuum annealing, X-ray diffraction studies were carried out. Fig. 3 shows the X-ray spectra obtained in the Zircaloy-4 specimens before and after hydriding. By comparing the spectra 3-(a) and 3-(b), the peaks corresponding to zirconium and its hydride can be identified. *a*-Zr, δ-hydride ($ZrH_{1.6}$) and γ-hydride (ZrH) were predominantly observed in this study. It was difficult to determine whether any other hydrides had formed because of their closely spaced peaks.

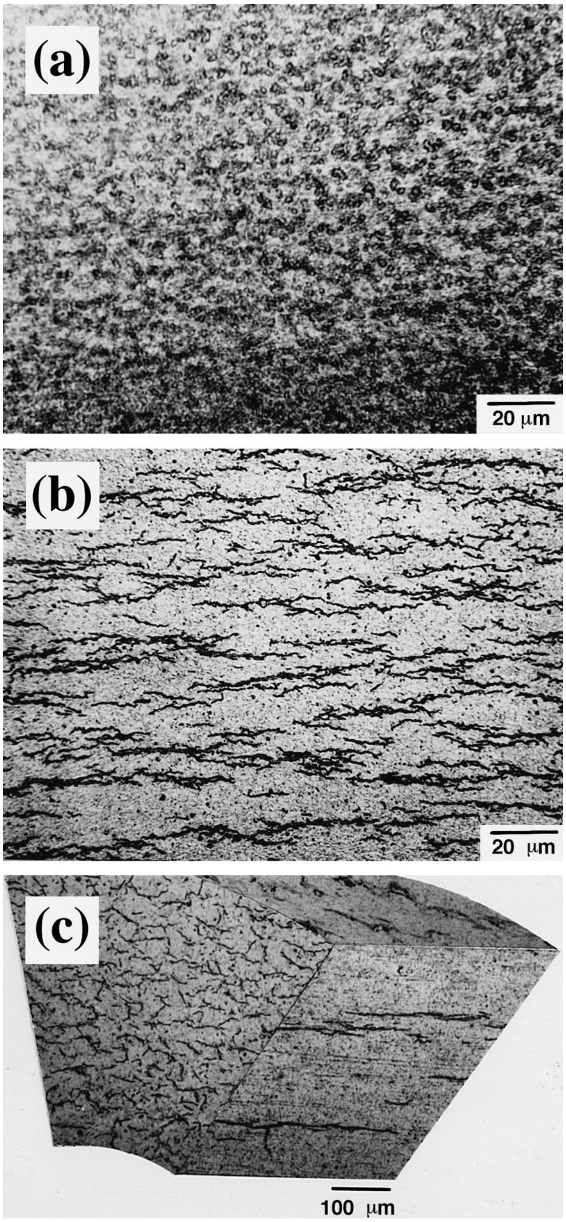

Fig. 2. Optical micrographs of hydride in the normal to the longitudinal direction of Zircaloy-4 cladding tube: (a) as-received (b) high temperature cathodic hydrogen charged at 150 ± 0.5°C for 24 h followed by annealing at 400°C for 3 h in an inert argon atmosphere. (c) three-dimensional view.

Since the as-fabricated Zircaloy-4 tubing contained less than 20 ppm of hydrogen as shown in Table 1, the excess hydrogen resulted from the hydrogen picked-up. In order to verify the in situ monitoring method for the determination of hydrogen content, hydrogen was charged with various charging times and current densities. The hydrogen content in the charged specimen was analyzed by a conventional wet analysis method and in situ monitoring method suggested in this study. Fig. 4 is the amount of hydrogen pick-up by Zircaloy-4 cladding tube determined by a conventional wet analysis method and in situ monitoring method suggested in this study. The amount of hydrogen picked-up by Zircaloy-4 cladding tube increases with increasing charging time and applied current density. Although the values determined by in situ monitoring method shows slightly higher than those determined by a conventional wet analysis method, the amounts of hydrogen determined by both methods were well agreement within the empirical error ranges. Table 3 is the average amount of hydrogen in Zircaloy-4 cladding tubing. The amount of hydrogen picked-up in the Zircaloy-4 tubing increased with charging time and applied current density. The amount of the hydrogen picked-up is able to be evaluated by the charge balance. Since hydrogen ions are evolved from a high temperature aqueous solution in this study, the charge transfer takes place and hydrogen should be absorbed before forming the hydride in the Zircaloy-4 specimen. Potential of any process in which the charge transfer can be explained with the Nernst

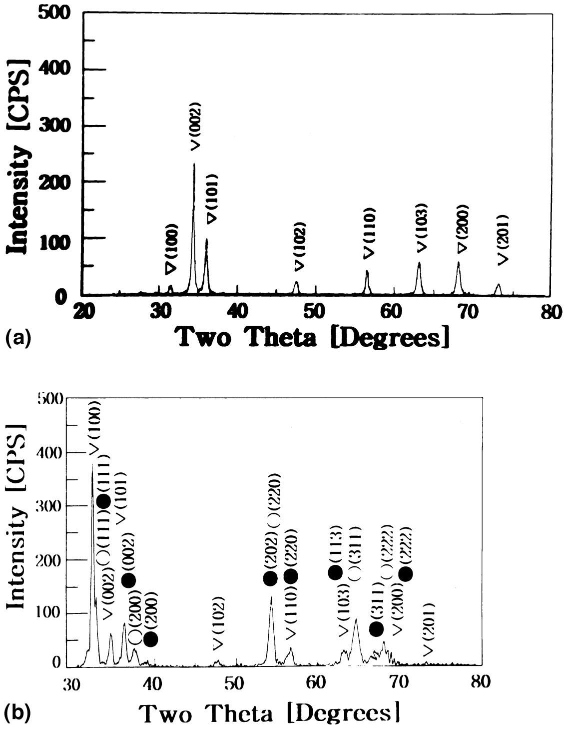

Fig. 3. X-ray spectra of Zircaloy-4 cladding tube (a) as received (b) hydriding by a high temperature cathodic charging method for 24 h followed by annealing at 400°C for 3 h (▽: Zr, ○: δ - $ZrH_{1.6}$, ●: γ-ZrH).

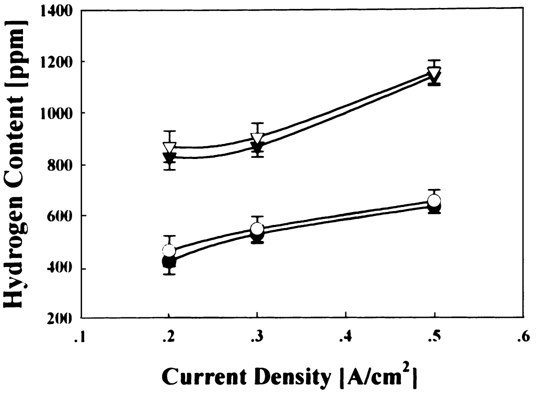

Fig. 4. Hydrogen content in Zircaloy-4 tubings with charging time and current density determined by a conventional wet method (●: 12 h charging, ▼: 24 h charging) and in situ monitoring method (○: 12 h charging, ▽: 24 h charging).

equation [10]. For the galvanostatically supplied-current, the relationship between current and the concentration of the evolved hydrogen ion is

$$i_- = C_{H^+}. \tag{1}$$

Table 3
The average amount of hydrogen pick up by Zircaloy-4 cladding tube

Charging time (h)	Hydrogen content (ppm)		
	0.2 (A/cm^2)	0.3 (A/cm^2)	0.5 (A/cm^2)
12	419	525	633
24	830	970	1138

For the hydrogen charging reaction, equilibrium can be attained in principle on the metal side of the interface. If we write the equilibrium constant (K) between the adsorbed hydrogen pressure (P_{H_2}), initial hydrogen pressure (P^0) and adsorbed hydrogen activity (a_H) as

$$K = a_H/(P_{H_2}/P^o)^{1/2}. \tag{2}$$

The Nernst equation becomes

$$E = (RT/F)\ln(Kh_{H^+}/a_H), \tag{3}$$

where R, T and F are the gas constant, temperature and Faraday constant, respectively. At 150°C, the equation is

$$E = -0.0837(\mathrm{pH} + \log a_H - \log K). \tag{4}$$

It is difficult to determine the equilibrium constant in this study, however, we expect that the equilibrium activity of adsorbed hydrogen can attain high values. For example, at pH = 3 and $E = -0.83\ V_{SHE}$, we get $a_H/K = 6.9$, and at more acidic pH values or more negative potentials, this figure may reach several hundred. Hence, we expect that a sufficient amount of hydrogens to form hydride was adsorbed by the metal. The hydrogen solubility in a-Zr is reported to be [11]

$$C_{(\mathrm{ppm})} = 1.61 \times 10^5 \exp\left(-\frac{8950}{RT}\right). \tag{5}$$

Since the hydrogen solubility at the annealing temperature of 400°C is about 200 ppm, the excess hydrogen ions above the solubility limit are precipitated as zirconium hydride during annealing. Table 3 shows the amounts of hydrogen picked-up by the zirconium alloy, which are above the solubility limits. Hence, both intergranular and intragranular hydride precipitates were observed after vacuum annealing at 400°C, as shown in Fig. 2. The X-ray spectra in Fig. 3, which shows δ-hydride ($ZrH_{1.6}$) and γ-hydride (ZrH) peaks, support the microstructural observation.

As shown in Fig. 2, the hydride orientation was observed. The form and morphology of the hydride depend on metallurgical factors such as texture and crystal orientation because the hydride nucleates at the grain boundaries and has the primary habit plane of {1 0 1 7} [12]. One of the most common methods for representing crystal orientation is through the construction of a stereographic basal pole figure. In this study, the texture parameter, f_i, is the fraction of all the basal poles in a specimen that are effectively oriented in a reference direction (i). It is defined by the following equation

$$f_i = \frac{\int_0^{\pi/2} I(\phi)\ \cos^2\phi\ \sin\ \phi\ \mathrm{d}\phi}{\int_0^{\pi/2} I(\phi)\ \sin\ \phi\ \mathrm{d}\phi},$$

where ϕ is the angle between the basal pole and the reference direction. Fig. 5 and Table 4 show the basal pole figures and their Kerns parameters (f_i), respectively. As shown in the figure and table, most of basal poles are parallel to radial direction, which means the basal planes are normal to the radial axis. From the observation of hydride orientation in Fig. 2 and the crystal orientation shown in Fig. 5, the hydride prepared by HTHCM was mainly formed on the basal plane with strain ellipse originated from a pilgering process.

Table 4
Texture coefficients

Orientation	Avg. f_i
Radial	0.52
Axial	0.06

Fig. 6 shows the typical polarization curves of the Zircaloy-4 containing hydride in two types of deaerated electrolyte solutions, (a) 90% HNO_3 and (b) 40%

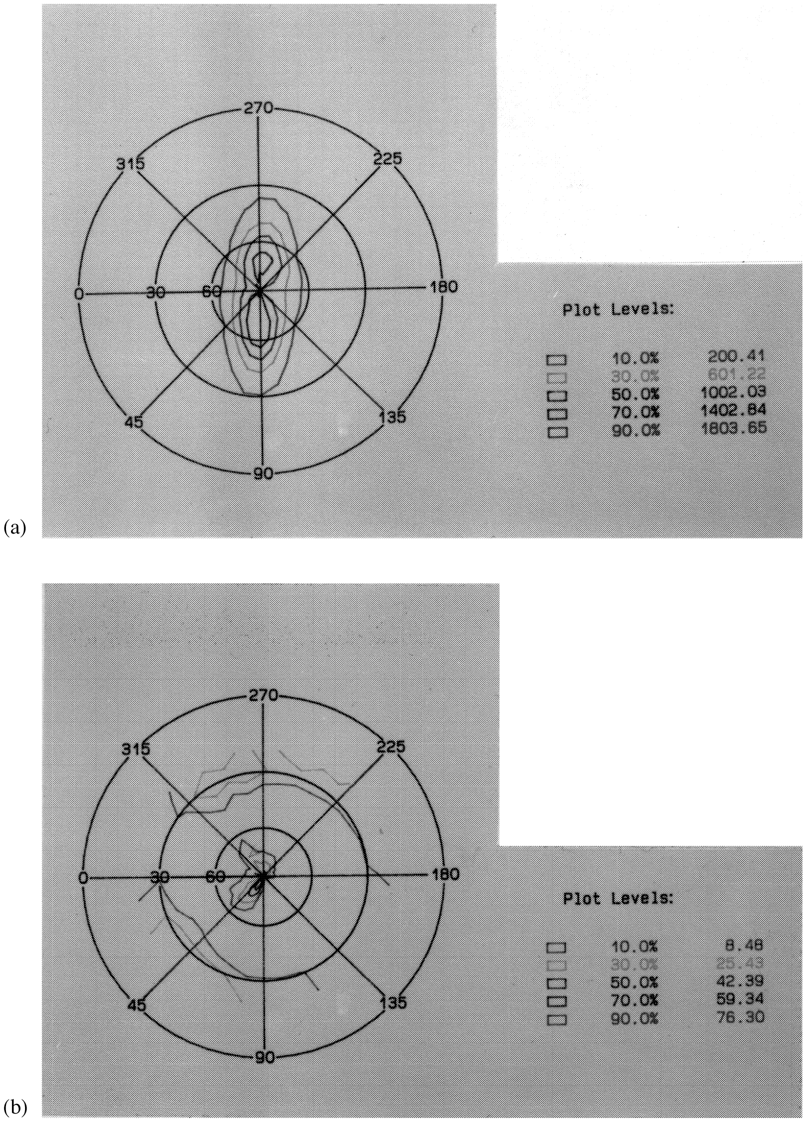

Fig. 5. Basal pole figures of Zircaloy-4 cladding tube used in this study along (a) radial and (b) longitudinal direction.

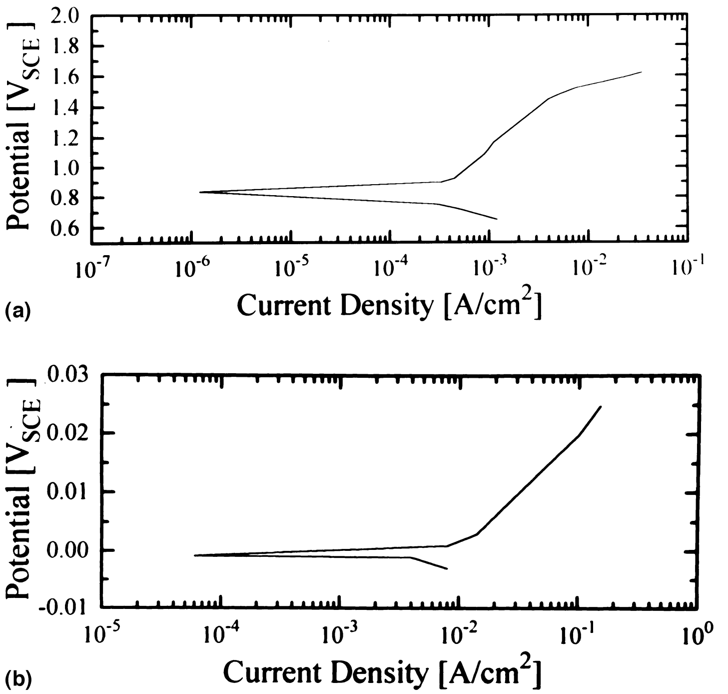

Fig. 6. Potentiodynamic polarization curves for Zircaloy-4 in (a) deaerated 90% HNO_3 and in (b) deaerated 40% HCl + 500 ppm $FeCl_3$ at 25.

Table 5
Corrosion potentials of Zircaloy-4 cladding tubes in various acid solution at room temperature

Environment	Corrosion potential (mV$_{SCE}$)	
	As-received Zircaloy-4	Hydrided Zircaloy-4
90% HNO_3	+920	+823
40% HCl + 500 ppm $FeCl_3$	−3	−12

HCl + 500 ppm $FeCl_3$ at 25°C. Table 5 shows the corrosion potentials of the alloys with and without large amount of hydride in various corrosive environments. The corrosion potentials of the hydrided alloy were lower than those of as-received alloy in corrosive environments. The corrosion potential of the material in the nitric acid solutions is +823 mV$_{SCE}$. The potential is dramatically reduced to −12 mV$_{SCE}$ in the 40% HCl + 500 ppm $FeCl_3$. Although zirconium has relatively good corrosion resistance against general attack in nitric acid, as shown in Fig. 5, the corrosion potential of the alloy is reduced when it is in the solution containing hydrochrolic acid with small amounts of ferric ions. It is well known that stability of an passive oxide film on the metal is sustained by its solid state properties such as molar volume and density [14]. For the zirconium oxide, ZrO_2, which has strong metal-oxygen bonding energy of 6.16 eV per equivalent, disruption and dissolution occur at sites where atomic defects are present. One of the reasons for the defect formation is the incorporation of foreign ions from the electrolyte during the growth of oxide film. The break of passive film causes the reduction of corrosion potential. Therefore, the corrosion potential drop observed in Fig. 5 results in the strong oxidant affecting the stability of the passive film. This agrees well with the observation by Heakel [15].

4. Conclusions

1. The high temperature cathodic hydrogen charging method is one of the most effective techniques to generate hydrides in zirconium alloys.
2. The optimum conditions for charging more than 1000 ppm of hydrogen in the material were

0.4 A/cm^2 for 24 h at 150 ± 0.5°C in electrolyte containing hydrobisulphate ions.

3. The observed hydride in this study were δ-hydride ($ZrH_{1.6}$) and γ-hydride (ZrH).
4. After vacuum annealing at 400°C for 3 h, thin platelet shaped hydrides were formed inside the alloy and preferentially oriented along circumferential direction, which is related to the texture of the material.
5. The corrosion potentials of the alloy containing the hydride were +830 mV_{SCE} in 90% HNO_3 and −12 mV_{SCE} in 20% hydrochloric acid solution containing small amount of ferric ion at 25°C, respectively. The corrosion potentials of the hydrided alloy were lower than those of as-received alloy in the corrosive environments.

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