

HYDROGEN SUPERSATURATION EFFECTS IN ZIRCONIUM AND ITS ALLOYS DURING ELECTROCHEMICAL HYDRIDING*

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الخلاصة :

أثناء الدراسات على الهدرجة الإلكتروليتية لمعدن الزركونيوم وسبائكهم رقم ٢ و ٤ في محلول مائي معياري لحمض الكبريتيك قمنا بحسابات للقيمة (H_m) وهي نسبة الجزئ الغرامي للهيدروجين لكل جزئ غرامي من المعدن. تزداد قيم (H_m) إزداداً خطياً مع زمن معالجة الكاثود الى أن تصل الى هضبة تتوقف قيمة فيها عن الإزداد وتصل قيمة (H_m) فيها الى ٩,٥. هذا الرقم العالي لقيمة (H_m) لا يمكن تفسيره بافتراض الهدرجة لوحدها وبدل أن ظواهر الإشباع تلعب دوراً هاماً يجعلها ذات منفعة عملية لتخزين الهيدروجين.

ABSTRACT

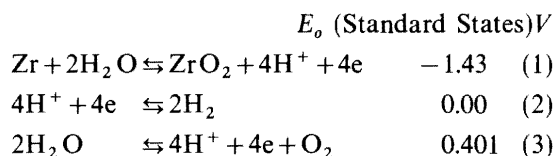
During electrochemical investigations on the hydriding behavior of zirconium, zircaloy 2, and zircaloy 4 in 1.0 N H₂SO₄ aqueous solution, calculations were made on the ratio of gram atom hydrogen to gram atom metal (H_m). H_m values increased linearly with time of cathodic treatment and finally tended to attain a plateau, with H_m values as high as 9.5. This value is much higher than can be explained if only hydride formation is assumed to take place, and indicates supersaturation effects which may be significant for application in the use of metals for hydrogen storage.

*This is a section of work done at Nuclear Technology Laboratories, Imperial College, London.

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INTRODUCTION

Zirconium and its alloys find application as cladding materials in nuclear reactors to encase nuclear fuel and arrest the flow of fission products. Zirconium has a combination of mechanical, chemical, and nuclear properties which particularly suit it for such a use in water nuclear reactors. In an aqueous medium, zirconium corrosion can be attributed to the following reactions:



Some of the hydrogen released by reaction (2) may dissolve in zirconium, become bound in the metal and thus hydride it, and this causes embrittlement of the metal.

During electrochemical investigations on the hydriding behavior of zirconium and its alloys[1], hydrogen supersaturation has been observed and it is this effect that forms the basis of this paper.

Metal hydrides have already been proposed as hydrogen energy storage media[2]. The reactions involved in the formation and decomposition are rapid enough to consider using such materials in many types of devices. Will[3] has patented a lanthanum nickel anode in alkaline electrolyte. Recent work at Centre National de la Recherche Scientifique[4] has led to a series of $LaNi_5$ based alloys by partially substituting other elements for lanthanum and nickel for use as hydrogen storage electrodes in alkaline batteries. Belkbir and co-workers[5] determined the kinetic rules of formation and decomposition of the hydrides derived from $LaNi_5$ type compounds.

This paper describes a simple aqueous electrochemical technique for hydriding zirconium and its alloys, and the observed hydrogen supersaturation effects which may be significant for application in the use of metals for hydrogen storage.

EXPERIMENTAL

A polarization cell shown in Figure 1, and similar to

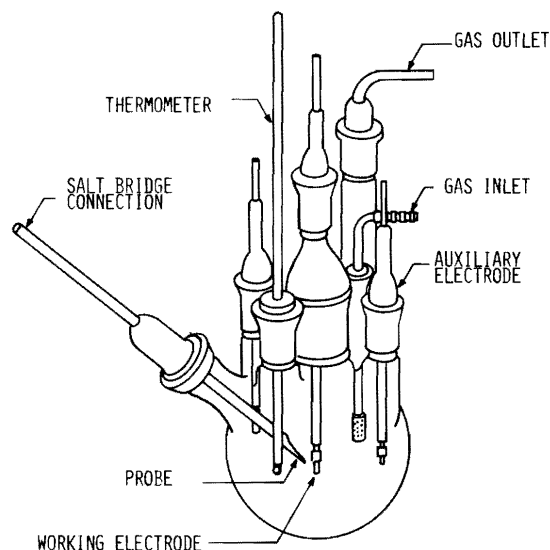


Figure 1. Polarization Cell

that described by Greene [6] is used in this work. It is filled with electrolyte solution ($1.0NH_2SO_4$), a cylindrical auxiliary electrode of platinized platinum, and a working electrode of the metal to be investigated are inserted into it. The reference electrode is a saturated calomel electrode connected to a luggin probe by a bridge of cell solution. Hydrogen gas from a gas cylinder is passed through a catalytic recombiner to remove traces of oxygen, and is bubbled continuously through the test solution.

The electrode potential is controlled using a potentiostat (Wenking PCA 72) and may be scanned at a desired scan rate using a potential scan generator (Wenking SMP 72). The potential maintained and the logarithm of the current flowing are recorded on an X-Y recorder with a logarithmic amplifier on one axis (Bryans 26000). The polarization cell was heated on an electric mantle for scans above room temperature.

Materials

Zirconium metal and its alloys were supplied by IMI Ltd. All solutions used in this work were made from analytical grade reagents and distilled water from an all glass still.

Procedure

After filling the cell, purging with hydrogen was

begun and the heater turned on. At least 2 hours elapsed between temperature equilibration and the start of an experiment, and gas purging was continued throughout. Electrode preparation (0.6 cm², thickness 0.2 cm) was done by abrading respectively with 240, 300, 400, and 600 grade silicon carbide paper. The electrode was then rapidly washed with distilled water and inserted into the cell. Measurements were begun after a fixed interval of 2 minutes after immersion. The measuring procedure was to start controlling the electrode potential at the value prevailing and start immediately to scan the potential. The potential maintained and the logarithm of the current flowing were recorded on an X-Y recorder with a logarithmic amplifier on one axis (Bryans 26000).

For hydriding experiments, prior to anodic treatment the electrodes were hydrided by subjecting to cathodic polarization at a rapidly increasing scan rate of 0.100 V/s. The voltage increase was stopped at a preset overpotential, η , and held for a definite time, t , s, for hydriding to take place. At the end of hydriding time the reverse scan was immediately performed and current density, i , was plotted as a function of η . The specimen passed through an open circuit potential into the anodic region. New electrodes were used for each hydriding experiment.

RESULTS AND DISCUSSION

Figures 2(a) and (b) show anodic and cathodic currents with zircaloy 2 as a function of an overpotential of 1000 mV with respect to a standard calomel elec-

trode (-0.236 V). The anodic current density increased with applied potential. The voltage-current plots are represented by:

$$i_a = i_0 e^{\eta/b_a} \tag{4}$$

$$i_c = i_0 e^{-\eta/b_c} \tag{5}$$

In these equations i_a is the anodic current density, i_c is the cathodic current density, b_a and b_c are Tafel constants, and i_0 is the exchange current density.

For anodic currents (Equation (4)), the metal rapidly passivates by oxide film formation and when film formation is complete i_a is sharply limited by diffusion of oxygen ions through the oxide. As the voltage is increased the film thickens to balance the current increases and the following equation holds for the limiting current i_L [7]:

$$i_L = \frac{FZ\rho r}{E_0 M} \tag{6}$$

- where F = The value of the Faraday.
- Z = The number of electrons transferred in the formation of ZrO_2 from Zr .
- ρ = The density of oxide film.
- E_0 = Field strength in the oxide (V/cm).
- M = Molecular weight of oxide.
- r = The rate of voltage increase (V/s).

If the metal is subjected to cathodic treatment, i.e. the voltage is reduced with respect to open circuit potential, cathodic current flows and hydrogen is generated on the zirconium surface in accordance with Equation (2) and some hydrogen enters the metal.

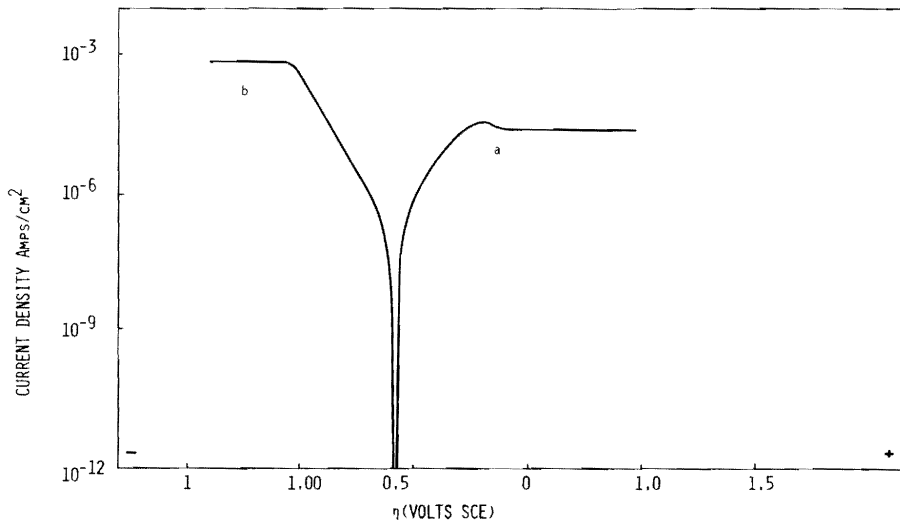


Figure 2. Current Density versus Potential (Volts SCE)

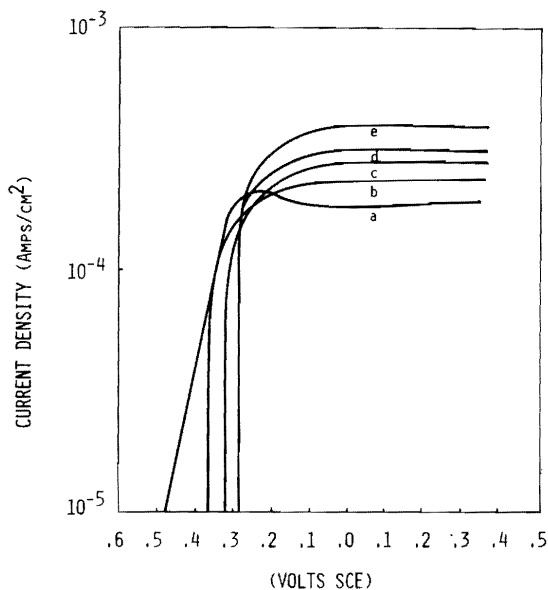


Figure 3. Limiting Current for Anodic Oxide Growth on Zircaloy 2 Pretreated with Cathodic Polarization. Times for Pretreatment ($n=1000$ mV): $a=0$, $b=600$, $c=1200$, $d=2400$, $e=3600$ s

Figure 3 shows the plot of anodic current i for the zircaloy 2 specimen with an increasing cathodic treatment time t s at 20°C , and a cathodic overpotential of 1000 mV. At the end of time t , the reverse scan was performed and current density i was plotted as a function of η . The specimen passed through an open circuit potential into the anodic region where the metal rapidly became passive. The limiting passive

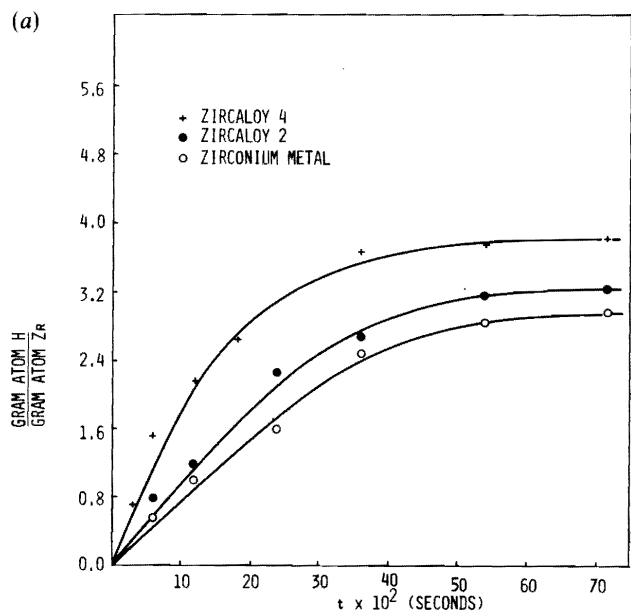
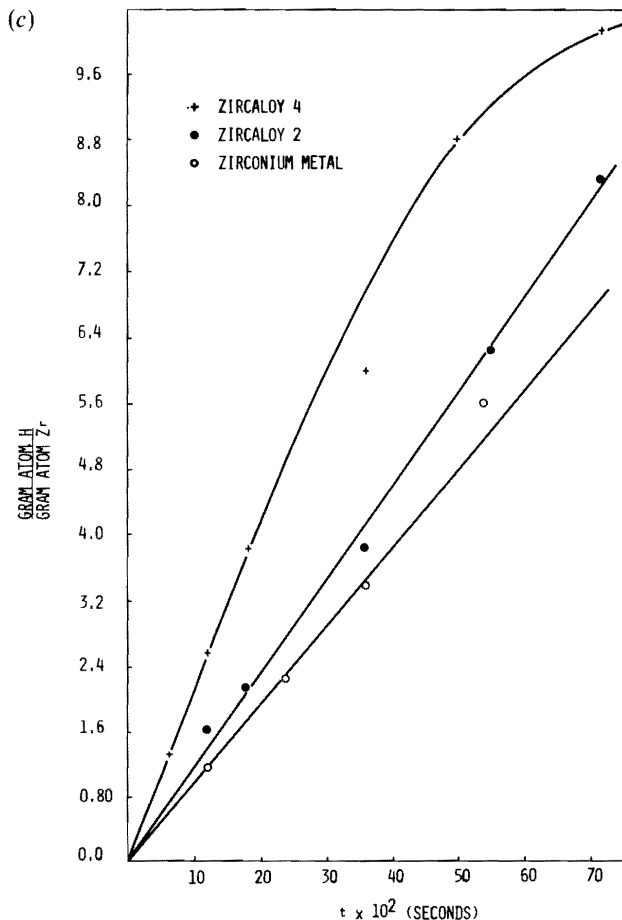
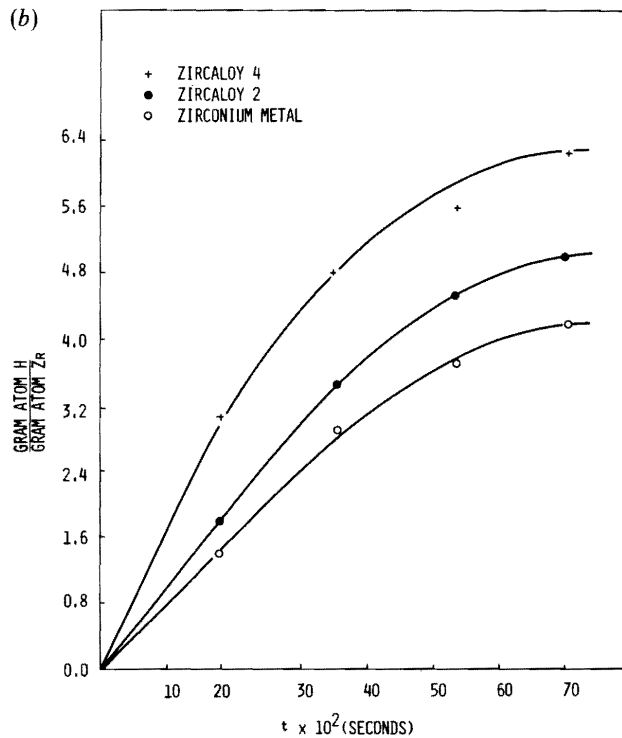
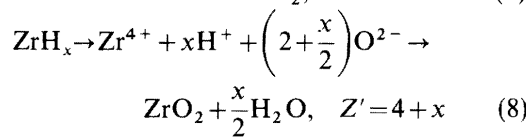
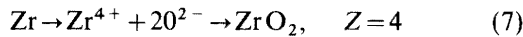


Figure 4. Surface Hydrogen and Time of Cathodic Treatment (Overpotential 1000 mV): (a) 20°C , (b) 50°C , and (c) 70°C



current was higher than for the unhydrided metal because of the hydrided surface. If the metal surface contains more hydrogen, more electrons will be released in the production of H^+ . The effective value of Z for a hydrided surface, Z' , is expected to be higher than for the pure metal as shown in the following equations:



The higher value of the effective Z results in an increase in the limiting current i'_L for the hydrided surface (see the Appendix). Figures 4(a), (b), and (c) show plots of the hydrogen to metal ratio H_m versus hydriding time at various temperatures. H_m values increase with time of hydriding. The rate of uptake of hydrogen is faster for zircaloy 4 than for zircaloy 2 and the pure zirconium metal, and saturation is seen to occur at high levels. At the plateau level the rate of hydride formation equals the rate of escape of hydrogen from metal surface [1]. At higher temperatures, the hydriding effect is enhanced (Figures 4(a), (b), and (c)), zirconium and its alloys can become supercharged with hydrogen as shown by the high H_m values, and the phenomena of hydrogen supercharging in zircaloy has also been mentioned by Marino [8]. The ratio of hydrogen to metal in the surface increases to values greater than the limits of stable forms of zirconium hydride at $ZrH_{1.5}$. In the case of zircaloy 4 at $70^\circ C$ the ratio of hydrogen to metal increases to a value of 9.5.

During cathodic treatment hydrogen is delivered to the surface at effectively high overpressure. Most of the hydrogen delivered to the sample at high overpressure during cathodic polarization can be seen bubbling off the surface. The hydrogen that is absorbed in the metal supersaturates and can be seen to be emitted as bubbles after cathodic treatment is stopped. If the subsequent anodic treatment is delayed, the enhanced plateau observed immediately after hydriding disappears, as shown in Figure 5.

CONCLUSIONS

There is an indication that zirconium and its alloys can supersaturate with hydrogen. However, it is difficult at this stage to predict the nature of the attachment between hydrogen and zirconium. Further investigations on surface and sub-surface changes are recommended as these could reveal useful information.

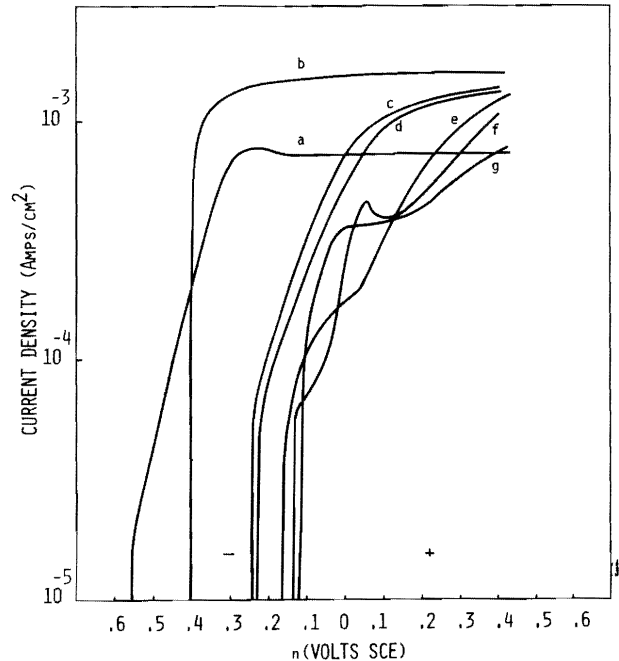


Figure 5. Loss of Supersaturated Hydrogen from Cathodically Treated Zircaloy 4, $70^\circ C$, Exposure 60 min, Overpotential 1000 mV: (a) No Hydriding. (b) Cathodic Treatment 60 min. (c) Cathodic Treatment 60 min. Anodic Treatment Delayed 20 s. (d) Cathodic Treatment 60 min. Anodic Treatment Delayed 2 min. (e) Cathodic Treatment 60 min. Anodic Treatment Delayed 5 min. (f) Cathodic Treatment 60 min. Anodic Treatment Delayed 20 min. (g) Cathodic Treatment 60 min. Anodic Treatment Delayed 40 min.

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APPENDIX

The amount of hydrogen in the hydrided metal can be estimated from the knowledge of limiting currents:

$$i_L = \text{limiting current for unhydrided metal,}$$

$$i'_L = \text{limiting current for hydrided metal,}$$

$$\frac{i_L}{i'_L} = \frac{Z}{Z'}$$

It is assumed that metal density and field strength in the oxide are independent of the amount of hydrogen in the metal:

$$Z' = \frac{i'_L}{i_L} Z, \quad \Delta Z = Z' - Z = Z \left(\frac{i'_L}{i_L} - 1 \right).$$

Now assume that each atom of hydrogen is associated with one electronic charge, then the amount of hydrogen in g-atom/cm³ metal is given by

$$H_m = \frac{\Delta Z \rho}{M} = \frac{\rho Z}{M} \left(\frac{i'_L}{i_L} - 1 \right).$$

Now,

ρ = density of hydrided metal = 6.49 g/cm³,

M = Molecular weight of metal $M = 91.22$,

$Z = 4$.

Therefore,

$$\begin{aligned} H_m &= 0.284 \left(\frac{i'_L}{i_L} - 1 \right) \frac{\text{g-atom H}}{\text{cm}^3 \text{ metal}} \\ &= 4 \left(\frac{i'_L}{i_L} - 1 \right) \frac{\text{g-atom H}}{\text{g-atom Zr metal}}. \end{aligned}$$

REFERENCES

[1] G. N. Walton, S. M. Ali, and M. Rashid, 'The Hydriding of Zirconium and its Alloys in Electrochemical Corrosion', *Second International*

Conference on Water Chemistry of Nuclear Reactor Systems, 13-17 October (1980), Bournemouth, England.

[2] F. E. Lynch and E. Snape, 'The Role of Metal Hydrides in Hydrogen Storage and Utilization', *Proceedings of 2nd World Hydrogen Energy Conference*, Zurich, Switzerland, 21-24 August (1978).

[3] F. E. Will, 'Hermetically Sealed Secondary Battery with Lanthanum and Nickle Anode', *U.S. Patent*, 3, 874, 928, 1 April (1975).

[4] A. Percheron, J. C. Achard, J. Louviers, M. Bonnemay, B. Bronoel, J. Sarradin, and L. Schalapbach, 'French Patent Specifications', 75-16160, 21 May (1975).

[5] L. Belkbir, N. Gerard, A. Percheron-Guegen, and J. C. Achard, 'Kinetics of Hydrogen Absorption and Desorption by Ternary LaNi₅ Type Intermetallic Compounds', *Proceedings of the 2nd World Hydrogen Energy Conference*, Vol. 5, Zurich, Switzerland, 21-24 August (1978).

[6] N. D. Greene, 'Experimental Electrode Kinetics', Rensselaer Polytechnique Institute, Troy, N. Y. (1966).

[7] M. L. Brown and G. N. Walton, 'A Comparison of the Polarization Behavior of Zirconium and its Alloys', *Journal of Nuclear Materials*, **58** (1975), p. 321.

[8] G. P. Marino, 'Hydrogen Supercharging in Zircaloy', *Material Science and Engineering*, **7** (1971), p. 355.

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