



Letter to the Editors

Supercharging of Zircaloy-4

G. Domizzi *, L. Lanzani, P. Coronel, P. Bruzzoni

Departamento Materiales, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Av. del Libertador 8250, Buenos Aires 1429, Argentina

Received 5 September 1996; accepted 8 May 1997

Abstract

During service, nuclear components of low thickness made of Zr alloys may reach hydrogen contents above the terminal solid solubility, being the excess hydrogen precipitated as uniformly distributed particles (supercharging). This phenomenon can produce alloy embrittlement. To evaluate the behaviour of the hydrided material, it is necessary to obtain similar hydride distributions in the laboratory. In the present work, two hydriding methods have been tested: (1) corrosion in LiOH solution; (2) gas phase charging on samples coated with Cu. The latter requires a relatively short hydriding time, does not affect the microstructure and allows a simultaneous measurement of hydrogen content. © 1997 Elsevier Science B.V.

1. Introduction

Zirconium alloys employed in nuclear reactors undergo corrosion in water at high temperature and pressure, with a simultaneous hydrogen uptake. After some years in service, thin wall components may reach hydrogen concentrations well above the terminal solid solubility (TSS) at the operation temperature. The excess hydrogen appears as precipitated hydrides in a nearly homogeneous distribution. This process is known as supercharging and may cause alloy embrittlement.

In order to assess the behaviour of the hydrided material, it is necessary to develop laboratory hydriding techniques which reproduce the hydride distributions found in service, without affecting the microstructure usually found in Zircaloy-4 reactor components (recrystallized or deformed α phase). The Zr–H equilibrium diagram presents a eutectoid reaction at 550°C and so this temperature must not be surpassed during hydriding.

Moreover, supercharging is attained when the hydrogen absorption rate is lower than some critical value [1,2], otherwise a solid hydride layer is formed on the material surface. Several researchers achieved this objective through different methods: accelerated corrosion in LiOH solutions

[3,4], thermal cycling of samples coated with a hydride layer [5,6], gas phase charging in the presence of an oxide film [7–9]. Although these methods are effective, they are too slow or they produce an undesirable film of oxide on the material surface, or they do not provide a direct measurement of hydrogen concentration.

In our laboratory a method was developed to obtain supercharging of Zry-4 by gas phase charging. A copper film was electrodeposited on the specimen surface to limit the hydrogen influx. The features of this method are: precise in situ measurement of the hydrogen concentration, high hydrogen concentrations achieved in a relatively short time and negligible oxide film formation.

Hydriding tests in LiOH solutions were carried out in order to evaluate and compare the hydride distribution results obtained by gas phase charging.

2. Experimental details

2.1. Material

Zircaloy-4 specimens were cut from a 0.2 mm thick foil, which contained 18 $\mu\text{g/g}$ of hydrogen from fabrication. The specimens were 6–7 cm long and their total surface area was 12 cm^2 .

The microstructure of the alloy consists of equiaxed α grains with an average diameter of 10 μm and uniformly

* Corresponding author. E-mail: domizzi@cnea.edu.ar.

distributed Zr(Fe/Cr)₂ precipitates (diameter of less than 0.5 μm). The presence of microstresses in the material was detected by the X-ray diffraction line broadening method.

2.2. Hydriding methods

2.2.1. Gas phase hydriding

Before hydriding, the specimens were ground with SiC abrasive papers down to 1200 mesh, cleaned with trichlorethylene and coated with an electrodeposited Cu film. The film thickness, as calculated from weight increase results, ranged from 1.8 to 2.7 μm.

The gas-phase hydriding tests were carried out in a closed chamber. This chamber consisted of a quartz tube connected to a pressure measurement device and an electrolytic hydrogen gas generator. Prior to hydrogen charging, the system was evacuated with a mechanical pump, heated and kept at 200°C for 5 min to allow degassing.

Hydrogen was introduced into the chamber at room temperature, then the chamber was heated up to the hydriding temperature (*T*) for 10–15 min. The temperature of the chamber could be kept uniform at ±1°C within a length of 6 cm. During hydriding, the chamber temperature increased continuously at a rate lower than 1°C/h because of furnace drift. After hydriding, the chamber was quickly cooled (5 min) to room temperature.

Hydrogen concentration in the specimens was calculated (assuming ideal gas behaviour) from the difference between the initial and final pressures measured at room temperature.

An air leak into the chamber was measured in the range 0.4×10^{-3} – 2.3×10^{-3} Pa dm³ s⁻¹, with or without hydrogen in the chamber. While oxygen is assumed to be absorbed due to the oxidation reaction, nitrogen is not absorbed and accumulates inside the chamber. This causes an apparent decrease in the amount of absorbed hydrogen in the range 0.6×10^{-3} – 1.1×10^{-3} μg/s which was considered in the calculation of the hydrogen concentration.

The error in the mass of absorbed hydrogen was calcu-

lated from the errors in: temperature, chamber volume, pressure and air leak rate.

These hydriding tests were performed at 800 Pa < *P*_{H₂} < 5000 Pa and 400°C < *T* < 420°C.

For comparison, the hydrogen concentration of two specimens was determined with a LECO™ hydrogen analyzer.

2.2.2. Hydriding in LiOH solution

The accelerated corrosion tests were performed in two stainless steel autoclaves, one of them having a stainless steel liner and the other a titanium liner. The tests were performed in 1 M LiOH solution at 343°C and 13.2 MPa. The extent of the corrosion reaction was controlled by the exposure time.

Prior to the test, each specimen was abraded with SiC papers down to 600 mesh, rinsed in bidistilled water, dried with acetone, measured and weighed. After the test, the cleaning and drying procedures were repeated. Finally, the weight gain was evaluated.

The thickness of the oxide films, formed by the corrosion reaction, was measured by optical microscopy of cross-sectioned samples. Previously, the specimens were mounted in Araldit D epoxy resin to minimize oxide spalling. Then they were abraded with SiC papers down to 1000 mesh and polished with 7 μm diamond paste during a short time to reduce rounding of the edges.

The hydrogen concentration was determined with a LECO™ hydrogen analyzer.

2.3. Hydride distribution analysis

After hydriding, the specimens were cut in several sections in order to verify that the hydride distribution was uniform throughout the sample. The sections were mounted in Araldit D resin and etched in a solution of 45 ml of acetic acid, 45 ml of concentrated HNO₃ and 4 ml of concentrated (70%) HF. Then, they were observed by optical microscopy.

Table 1
Gas phase hydriding of copper electroplated specimens

Specimen no.	No. of cycles	Total charging time (h)	H ₂ concentration (μg/g)	Hydride distribution
G1	1	8.0	1560 ± 80	inner clusters (Fig. 1a)
G2	1	6.6	1230 ± 70	inner clusters
G3	2	1.5	530 ± 50	no clusters
G4	2	8.0	1000 ± 90	no clusters
G5	2	3.3	1078 ± 70	no clusters
G6	2	7.8	1480 ± 90, 1475 ^a	no clusters (Fig. 1b)
G7	5	13.5	2680 ± 190	no clusters
G8	5	12.8	2960 ± 170, 2964 ^a	no clusters (Fig. 1c)
G9	6	12.8	3190 ± 180	no clusters
G10	8	16.6	3730 ± 300	no clusters

^a Determined by LECO analyzer.

3. Results and discussion

3.1. Gas phase hydriding

The copper film was effective in limiting the initial hydrogen absorption rate in the range 0.5×10^{-8} – 1.5×10^{-8} g cm⁻² s⁻¹. Because of the air leak into the chamber, an oxide film (less than 0.1 μm in thickness) was formed on the specimen surface. This oxide film caused a continuous decrease of the hydrogen absorption rate.

The fact that nitrogen is not absorbed by Zircaloy-4 in the present experimental conditions was confirmed by chemical analysis of nitrogen in the non-hydrided foil and in the specimen G2, which yielded 46 and 28 μg/g, respectively. The air leak during hydriding of specimen G2 was 0.8×10^{-3} Pa dm³ s⁻¹ and the hydriding time was 6.6 h. If nitrogen from the air leak had been absorbed by the specimen, its concentration would have increased as much as 260 μg/g.

Two specimens were supercharged in only one cycle of heating, hydriding and cooling. The rest of the specimens were subjected to 2–8 cycles. Table 1 shows the number of cycles, the total hydriding time and the final hydrogen concentration.

The observation of the different sections of each specimen showed that no surface hydride layer was formed and uniform hydride distribution (supercharging) was attained throughout each specimen (Fig. 1).

The specimens hydrided in only one cycle showed some clusters through their thickness (Fig. 1a), while in the cycled specimens a more uniform hydride distribution was found (Fig. 1b and c).

In the cycled specimens the first cooling was carried out when the hydrogen concentration slightly exceeded the solid solubility for dissolution (TSSD = 217 μg/g at 420°C [10]). This first cooling was fast enough to produce the precipitation of fine and uniformly distributed hydride particles. During the following cycle, the small hydride particles were not completely dissolved and they acted as nuclei for the subsequent hydride growth. In this way no clusters were formed.

The X-ray diffraction line broadening was quantified through the integral width B (°) of the {10.5} peak. In both the as received material and a non-hydrided sample treated at 420°C for 8 h, the B value was 0.312. On the other hand, in a non-hydrided sample treated at 530°C for 2 h, the B value was 0.265. These results show that residual microstresses are present in the as received foil and that hydriding at temperatures up to 420°C does not affect this state of microstresses.

The hydrogen concentration was measured by LECO in two separate samples of specimen G6; the values obtained were 1468 and 1482 μg/g. Four samples were cut from specimen G8 to carry out LECO analysis, three of them were obtained from one end of the specimen and the

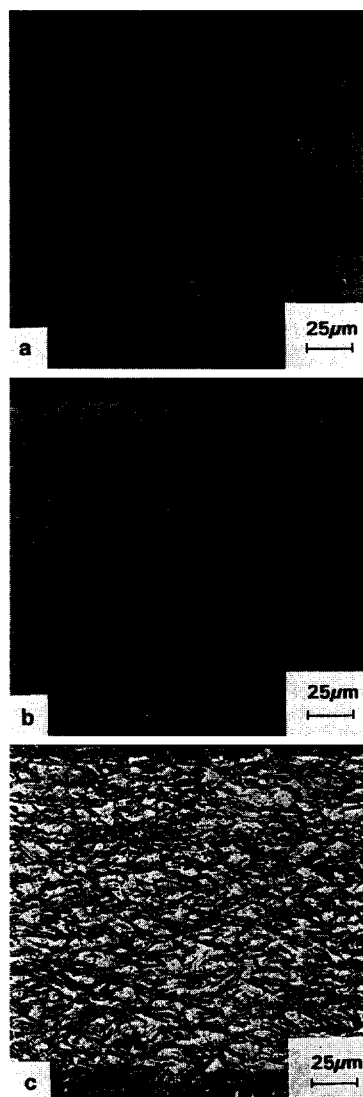


Fig. 1. Hydride distribution in Cu electroplated specimens charged in gaseous H₂. Charging time and hydrogen concentration are reported. (a) Specimen G1, 8 h, 1560 ± 80 μg/g. (b) Specimen G6, 2.7 h + 5.1 h, 1480 ± 90 μg/g (1475 μg/g by LECO). (c) Specimen G8, 1.5 h + 5.1 h + 1 h + 3 h + 2.1 h, 2960 ± 170 μg/g (2964 μg/g by LECO).

measured values were 2960, 2540 and 2971 μg/g. The fourth sample, cut from the other end of specimen G8, gave 2958 μg/g. These results are in good agreement with the hydrogen concentration measured by the pressure difference method used in the present work (1480 ± 90 μg/g in sample G6 and 2960 ± 170 μg/g in sample G8), with the only exception of the 2540 μg/g value that falls out of the error band. The LECO results also show the uniformity of the hydrogen concentration throughout each specimen.

Table 2
Autoclave hydriding

Specimen no.	Time (h)	Weight gain (mg dm^{-2})	Oxide film thickness (μm)	$C_{\text{H,max}}$ ($\mu\text{g/g}$)	C_{H} ($\mu\text{g/g}$)	Hydride distribution
A1	62	243.5 ^a	16.3	4712	3000	inner clusters (Fig. 2b)
A2	17	49.1 ^b	3.3	951	630	inner clusters
A3	11 + 19	86.3 ^b	5.3	1517	1432	inner clusters (Fig. 2a)
A4	12 + 27	94.6 ^b	6.2	1794	1609	inner clusters

$C_{\text{H,max}}$ and C_{H} are defined in text.

^a Test in stainless steel liner (corrosion rate $4 \text{ mg dm}^{-2} \text{ h}^{-1}$).

^b Test in titanium liner ($2\text{--}3 \text{ mg dm}^{-2} \text{ h}^{-1}$).

3.2. Hydriding in LiOH solution

The results of the hydriding tests in the autoclave are shown in Table 2. Exposure time, weight gain, oxide thickness, the upper limit for the hydrogen content ($C_{\text{H,max}}$) and the measured hydrogen content (C_{H}) are reported. $C_{\text{H,max}}$ was calculated from the measured oxide thickness, assuming that 100% of the hydrogen produced in the corrosion reaction is absorbed by the alloy.

Several authors studied the corrosion of Zry-2 and Zry-4 in LiOH aqueous solutions at high pressure and temperature [3,4,11]. They proved that both corrosion and hydrogen absorption follow a linear kinetics for weight gains above 30 mg dm^{-2} . In agreement with these results,

under the present experimental conditions, it was verified that the corrosion rate is approximately constant. Under this linear behavior it is valid to calculate an average hydriding rate from the measured hydrogen content and the testing time; the results obtained in this way ranged from 6×10^{-10} to $9 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$. The hydrogen absorption rate in corrosion tests is one order of magnitude lower than in gas phase tests.

The hydrogen pickup evaluated as: $C_{\text{H}}/C_{\text{H,max}}$ ranged from 0.60 to 0.80. The corrosion rate, hydrogen pickup and hydriding rate are in good agreement with the data presented in literature [3,4].

Some micrographs of specimens tested in the autoclave are shown in Fig. 2. The hydride distribution is nearly uniform across the section. There are some clusters of higher particle concentration, which cannot be eliminated by intermediate coolings (Fig. 2a). In the autoclave the cooling rate was slow (16 to 56°C/h); in this way hydrogen diffusion to the existing hydride particles was favored, so no new nuclei were generated during cooling as it happened in fast cooled gas phase charging. These observations agree with those of Murgatroyd and Winton [3], who found aligned coarse platelets when the specimens were slowly cooled; instead, when specimens were quenched, random fine and coarse particles were seen. The former precipitated during cooling and grew with further hydrogen addition.

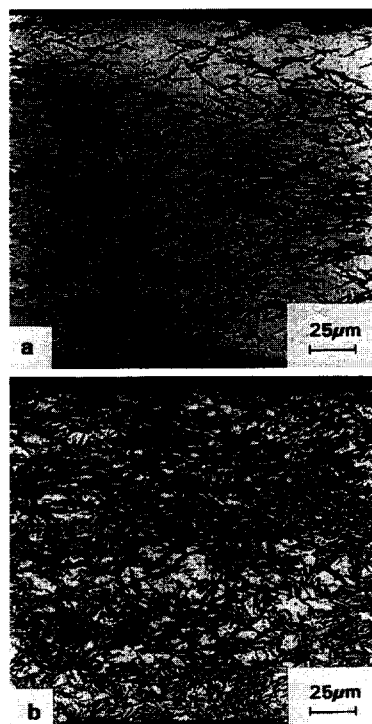


Fig. 2. Hydride distribution in autoclaved specimens. Charging time and hydrogen concentration are reported. (a) Specimen A3, 11 + 19 h, $1432 \mu\text{g/g}$. (b) Specimen A1, 62 h, $3000 \mu\text{g/g}$.

4. Conclusions

- Supercharging was accomplished in 0.2 mm thick Zry-4 foil by: (1) electroplating with Cu (Cu thickness $\approx 2 \mu\text{m}$) and hydriding in gaseous H_2 at $800 \text{ Pa} < P_{\text{H}_2} < 5000 \text{ Pa}$ and $400^\circ\text{C} < T < 420^\circ\text{C}$ and (2) autoclaving in 1 M LiOH solution at 343°C and 13.2 MPa.

- The advantages of the gas phase charging technique are: (1) supercharging is achieved in relatively short times; (2) microstructural properties, including microstresses, are not affected at 420°C ; (3) individual specimens can be charged with simultaneous and precise measurement of the hydrogen concentration and (4) the thickness of the oxide film formed on the specimen surface is lower than $0.1 \mu\text{m}$.

- Autoclave hydriding requires longer exposure times,

a thick oxide film is formed on the specimen surface and the hydrogen concentration measurements must be carried out in a separate equipment.

● Hydriding in one step, either in gas phase charging or in LiOH autoclave tests, produced similar hydride distributions with inner clusters formed through the foil thickness. Intermediate coolings from test temperature to room temperature lead to a more uniform hydride distribution throughout the specimen thickness, when the cooling rate was high as in gas phase charging. In LiOH solution tests the cooling rate was too slow to produce such effect.

Acknowledgements

The authors thank J. Ovejero García, M. Ipohorski and R. Mizrahi for their important comments and suggestions and D. Hermida for the X-ray diffraction measurements.

References

- [1] G.P. Marino, *Mater. Sci. Eng.* 7 (1971) 335.
- [2] M.P. Puls, *J. Nucl. Mater.* 165 (1989) 128.
- [3] R.A. Murgatroyd, J. Winton, *J. Nucl. Mater.* 23 (1967) 249.
- [4] S. Kass, *Corrosion* 25 (1969) 30.
- [5] R. Westerman, *J. Nucl. Mater.* 18 (1966) 31.
- [6] D.G. Westlake, S.T. Ockers, *J. Nucl. Mater.* 37 (1970) 236.
- [7] J.H. Huang, S.-P. Huang, *Mater. Sci. Eng. A161* (1993) 247.
- [8] J.-H. Zhang, Commissariat à la Energie Atomique Report, CEA-R-5634, 1993.
- [9] J. Bai, C. Prioul, D. François, *Metall. Trans.* 25A (1994) 1185.
- [10] G.F. Slattery, *J. Inst. Met.* 95 (1967) 43.
- [11] S.G. McDonald, G.P. Sabol, K.D. Sheppard, Zirconium in the Nuclear Industry, 6th Int. Symp., ASTM STP, Vol. 824, 1984, p. 519.