

An apparatus for rapid measurements in aqueous electrolytes at high temperatures and pressures

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An apparatus is described to measure the initial polarization of freshly prepared surfaces of zirconium and its alloys in water under controlled conditions at high temperatures and pressures. The main feature is a working electrode capable of being pneumatically inserted into a replenished autoclave at high temperature and pressure. The autoclave is fitted with an external reference electrode at ambient temperature and pressure. Using this, the hydrogen electrode in 0.1 M NaOH has been shown to give an apparent temperature coefficient of about $1.0 \text{ mV } ^\circ\text{C}^{-1}$ over the range 20–200°C.

1. Introduction

The apparatus described in this note was developed to study the anodic polarization of zirconium and its alloys in water at high temperatures and pressures. A previous study was made on the behaviour at ambient temperatures [2].

At ambient temperatures, measurements were made in a glass cell similar to that described by Greene [1]. The reference electrode was a saturated calomel electrode (SCE), connected to a Luggin probe in the cell by a bridge of the experimental solution, terminated at the reference electrode by a slow leak and salt bridge.

The auxiliary electrodes were cylinders of platinized platinum mounted using Stern-Makrides gaskets mounted either in a PTFE holder with a compression seal, or in a mount cast of epoxy resin.

Hydrogen from a gas cylinder was passed through a catalytic recombiner to remove traces of oxygen and bubbled continuously through the test solution.

The electrode potential was controlled using a potentiostat (Wenking PCA72) and scanned in steps using a motor potentiometer (Wenking SMP69). 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).

Typical results obtained in 0.1 N NaOH at

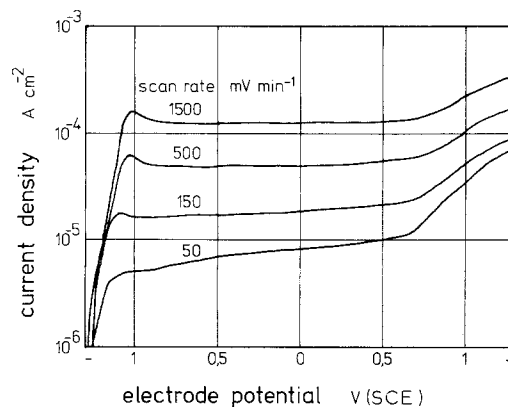


Fig. 1. Anodic polarization curve.

20°C are shown in Fig. 1. The initial Tafel line and peak in these curves were identified with the formation of an oxide film, and the subsequent plateau was identified with a thickening of the film. This work was repeated over the temperature range 20–85°C. From the slope of the Tafel line, the height of the peak, and from the voltage at which it occurs, it was possible to calculate apparent values of an activation energy for a surface reaction. Also from the limiting current in the plateau region it was possible to estimate a value for the average field strength in the oxide layer [2].

No comparable estimates could be made at the slow scan rates where no peak or plateau current could be discerned. Here the film was inferred to

be formed at a faster rate than the measurements were made. At a scan rate of 500 mV min^{-1} the plateau current is reached after scanning 0.25 V i.e. in about 30 s.

In order to continue these measurements at higher temperatures it was necessary to construct an appropriate autoclave. However, the warm-up time of an autoclave with a static test electrode would be so long that the early polarization behaviour shown on the experiments at ambient temperatures would not be observed at the higher temperatures. Bacarella [3] using a static zirconium test electrode at temperatures up to 300°C did not observe similar early polarization behaviour.

The apparatus described here was designed with the main requirement that it should be possible to insert a freshly abraded, or chemically polished, electrode into an aqueous solution at the experimental temperature (up to 330°C) in less than 30 s, with little or no exposure to the air in the process.

In order to ensure reasonably constant solution chemistry, the design was to include a once through circulation system.

2. Apparatus

2.1. Overall Layout

A schematic flow sheet of the apparatus is shown in Fig. 2. A large pressure vessel provides a reser-

voir of experimental solution at working pressure and ambient temperature. The solution is passed slowly through the test cell, which is at the experimental temperature. The anodic polarizations are performed in this cell. Above the test cell is a pneumatic ram assembly to allow the insertion and removal of the test electrode.

The pipework uses $\frac{1}{8}$ in. high pressure fittings supplied by Autoclave Engineers Inc., the gauges were supplied by Budenberg Gauge Co. Ltd. and the electrical heating, control and temperature measurement instruments by Pye Ether Ltd. The rest of the equipment was constructed in the workshops of the Chemical Engineering Department at Imperial College.

2.2. Reservoir vessel

The reservoir vessel is shown in Fig. 3. It has a capacity of approximately 6 l. It is made of 316 stainless steel. The pressure seal of the cap is effected by a Viton O ring. The gas handling system allows for de-gassing the solution after filling, purging and pressurizing. The gas is supplied from standard gas bottles. The vessel has been hydraulically tested to 300 bar. For the experiments currently in progress, a gas pressure of 1 bar of hydrogen with an overpressure of about 100 bar of argon is used. The electrolyte is 0.1 M NaOH . Both the reservoir vessel and the test cell are enclosed in a safety case of $\frac{1}{2}$ in. steel plate to protect against

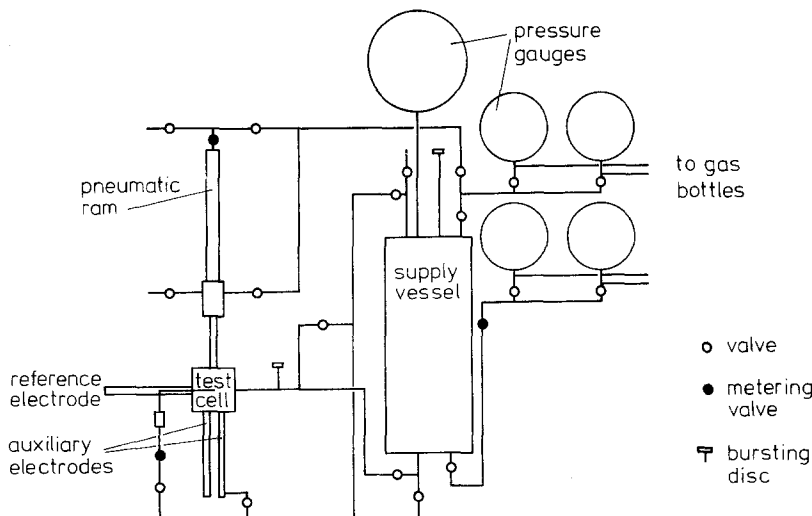


Fig. 2. Schematic layout.

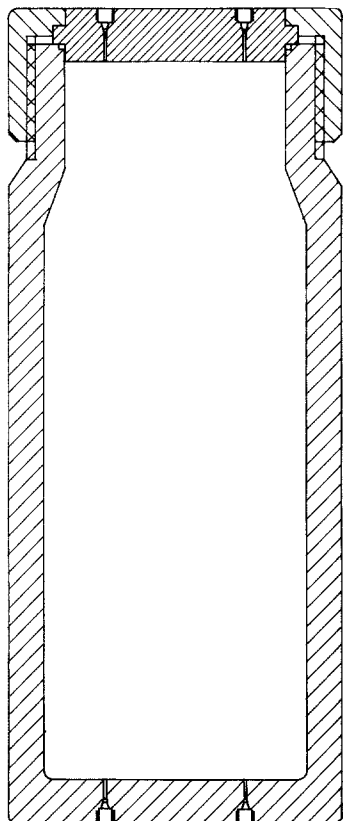


Fig. 3. Supply Vessel.

the possible ejection of faulty fittings. Both are fitted with bursting discs rated at 4000 psi (about 270 bar) to protect against accidental overpressure.

2.3. Test cell

The test cell itself is shown in Fig. 4. The cell is made of titanium and provided with seven access ports. The top, single, port is used for the test electrode. The bottom two ports carry two auxiliary electrodes of blacked platinum. Two of the side ports carry the solution flow, one carries a thermocouple well and the last carries a reference electrode probe. The cap of the test cell is secured to the body by eight set screws. The pressure seal is by a titanium sealing ring lapped and polished in to the cap and the body.

The test cell is heated electrically and each of the access tubes are made of titanium. They are cooled at the ends distant from the cell. All the metal parts in contact with hot solution are of titanium (except for the electrodes).

2.4. Auxiliary Electrodes

The test cell with all access tubes attached is shown in Fig. 5. One of the two identical auxiliary electrodes is shown in Fig. 6. The electrode itself is a blacked platinum cylinder 30 × 5 mm diameter. It is mounted on a tube of recrystallized alumina. Electrical contact is by 6 BA studding running through the alumina tube. A pressure seal of the 'unsupported area' type is made between the alumina tube and the platinum by carefully lapping the electrode onto the tube using diamond abrasive paste, finishing at 1 μm grade.

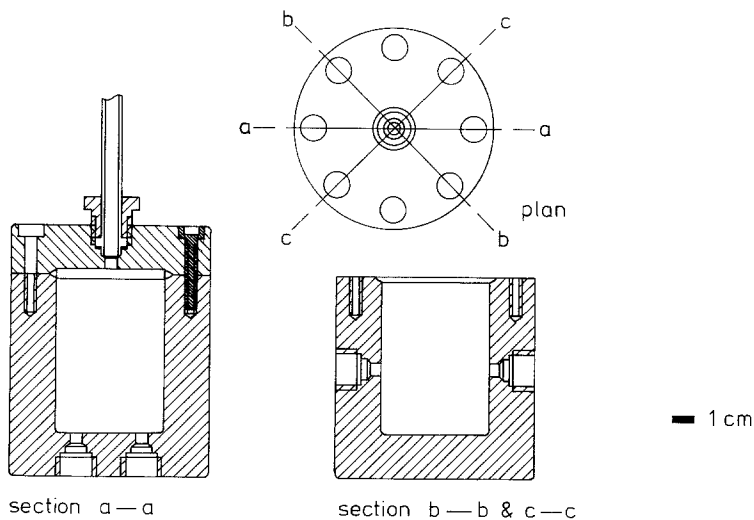


Fig. 4. Test cell.

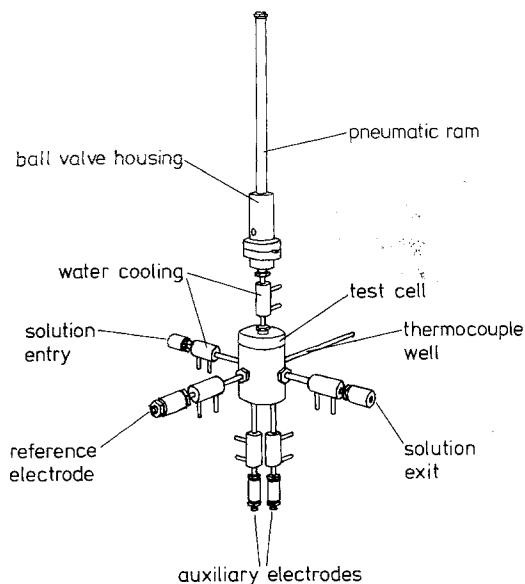


Fig. 5. Test cell assembly.

The alumina tube runs through a cooled access tube, of titanium, and is sealed against pressure by a circumferential Viton O ring at the cold end. The titanium access tube is sealed at both ends by a metal to metal seal effected by a gland nut's bearing on a collar welded onto the tube. In operation

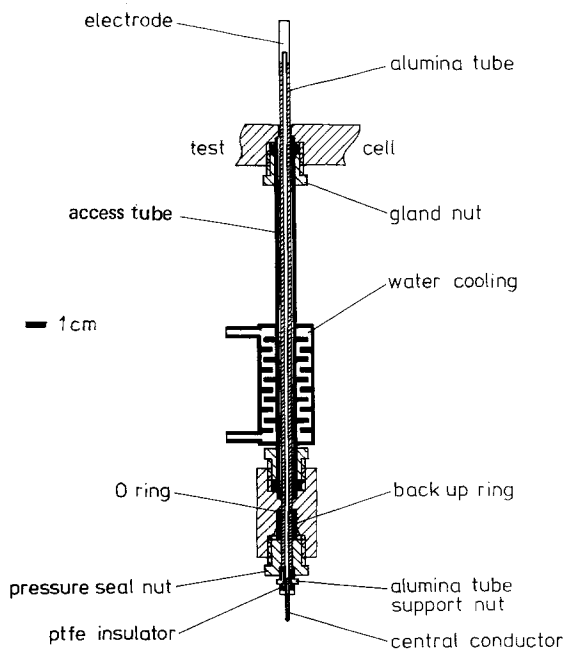


Fig. 6. Auxiliary electrode.

the two auxiliary electrodes can be checked one against the other for a stable and consistent rest potential.

2.5. Reference electrode

An external SCE is used, which is at ambient temperature and pressure. The reference electrode probe is an alumina tube passing through one of the titanium access tubes. A pressure seal is made on the outside of the alumina tube, at the cold end, by a Viton O ring. The solution pressure inside the tube is dropped across a wooden plug. This arrangement is shown in Fig. 7. A salt bridge connects the atmospheric pressure side of the wooden plug to the reference electrode. The seepage rate of electrolyte through the plug is about 2 ml in 24 h.

The relative position of test and auxiliary electrodes is shown in Fig. 8 — a schematic horizontal section of the test cell at its mid point.

2.6. Test electrode

The materials used for the present series of experiments are zirconium, zircaloy 2 and zircaloy 4 in sheet form. Rectangular electrodes are fabricated and mounted on a zircaloy 2 stud by argon arc welding. The stud is lapped on to the end of an alumina tube to provide a pressure seal in similar fashion to the auxiliary electrodes. A heavy oxide coating on the stud ensures that it does not provide a significant part of the experimentally measured current. The whole mounting and movement assembly for the test electrode is shown in Fig. 9. The mode of operation and procedures used are as follows.

The test electrode F, and the ram tube D are initially separated from the ball valve assembly E. The electrode is prepared by abrasion or chemical polishing, rapidly washed and the whole assembly connected to the ball valve housing E. Argon is flushed through the pressure connection B, keeping the electrode in an inert atmosphere. (The preparation could, if necessary, be performed under an inert gas flooded hood, but this has not been found necessary in the current experiments).

The argon at entry B is from the same pressure supply that pressurizes the reservoir and test cell. The pressure at B is, after flushing, allowed to

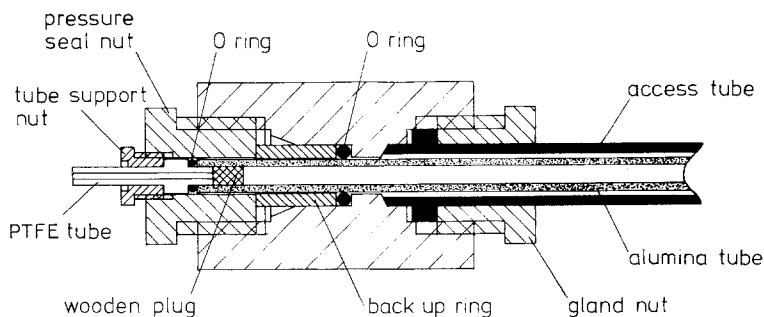


Fig. 7. Reference electrode probe.

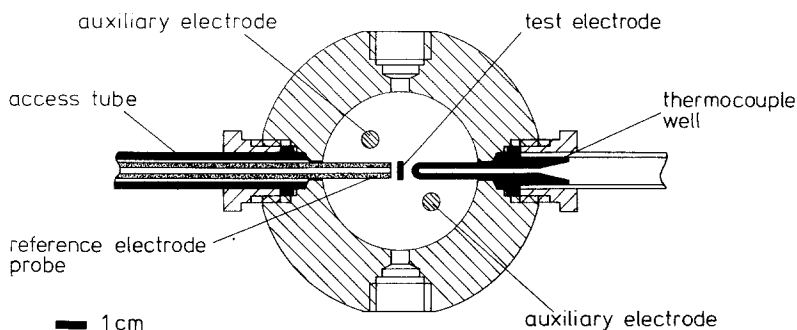


Fig. 8. Test cell – section at midpoint.

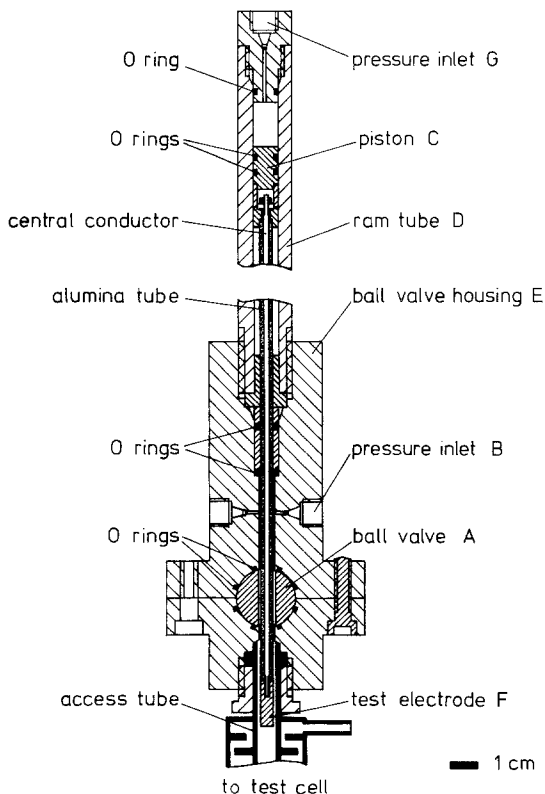


Fig. 9. Pneumatic ram.

reach test pressure. The ball valve A can then be opened, leaving a straight through access from test electrode to cell. The same gas pressure is now applied at the pneumatic ram inlet G. The difference in area between the ram piston C and the alumina electrode mounting tube is such that the piston moves down the ram tube and forces the electrode into the cell. A fine control metering valve is fitted to enable accurate control of the rate of descent. Electrical contact with the test electrode is maintained by a fine wire running along the inside of the pneumatic ram tube in the section at ambient pressure. This wire is tensioned over a pulley attached to the ram tube just above the ball valve assembly. The movement of the tensioning weight also provides an indication of ram position.

When familiar with the procedures, it is possible to perform the whole series of operations from finishing the preparation of the electrode to starting electrochemical measurements in about 30 s, or within about 2 or 3 s of contacting the experimental solution.

The electrode is withdrawn by reversing the procedures. When the pneumatic ram connection

G is slowly vented the pressure inside the test cell forces the electrode to withdraw, the ball valve can be closed and the electrode and ram tube removed. The alumina tubes used throughout are a standard item (Thermal Syndicate Ltd.). For use in the ram tube it was found necessary to polish the outside of the alumina tube with diamond paste to ensure the smooth travel of the ram.

3. Results

The apparatus is being successfully used for studies on the early stages of oxide film formation on zirconium and some alloys. So far the maximum temperature used has been 240°C. A full presentation and discussion of the high temperature results is in preparation.

3.1. Apparent temperature coefficient of the hydrogen electrode

Measurements are reported here on the potential of the platinum black electrodes relative to the external calomel electrode.

The system used to connect the external electrode introduces two imponderables into the measured potential difference: the thermal junction potential due to the temperature gradient along the probe, and the streaming potential due to pressure differences and fluid flow through the wooden plug. For example, in a solution of 0.1 M NaOH saturated with hydrogen at atmospheric pressure, the mean potential difference between the internal platinum black electrode at 20°C and 100 bar pressure, and the external calomel electrode at 20°C and 1 bar was -0.989 V compared to the calculated value of -1.004 V. The latter value was observed when the pressure was equal for both electrodes. With the system isothermal throughout this difference of 15 mV is attributed to the streaming potential across the wooden plug.

The observed effect of temperature on the hydrogen electrode potential with 1 atm of H₂ and 0.1 M NaOH electrolyte is as shown in Fig. 10.

De Bethune *et al.* [4] derive a temperature coefficient of $0.640 \text{ mV } ^\circ\text{C}^{-1}$ for a hydrogen electrode at 1 atm H₂ in 0.1 M HCl, over the range 25–60°C. For this range the value from Fig. 10 is approximately $0.8 \text{ mV } ^\circ\text{C}^{-1}$. The activity coef-

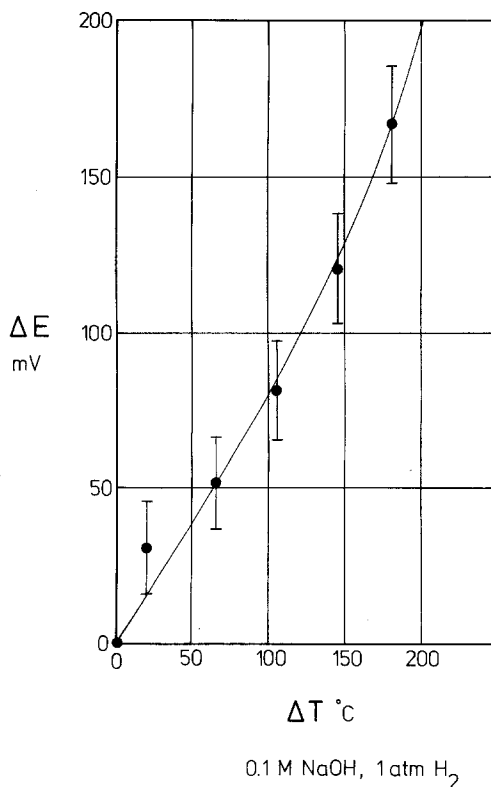


Fig. 10. Hydrogen electrode — potential shift versus temperature.

ficients of NaOH and HCl are similar at 0.1 M, so the values might be expected to be comparable.

Up to 200°C the variation in potential is similar to that deduced for the NHE by McKie [5].

3.2. Alumina insulators at high temperatures

Over 200°C the rate of attack of high pH solutions on the alumina electrode supports is appreciable. For work in high pH solutions at higher temperatures, a slightly different system of electrode support is at present being used, where the electrodes are supported on titanium tubes and insulated by a thin PTFE gasket between electrode and support tube.

4. Discussion

4.1. Ram loaded electrode

Operation has proved the utility of the design enabling electrodes to be inserted into and with-

drawn from the system operating at high temperature and pressure. For the studies on zirconium currently in progress the early stages of film formation have been observed. Also, the system enables experimental data to be rapidly acquired, since there is no need to cool and depressurize the autoclave between experiments. Fresh solution is flushed through from the reservoir after one experiment and another undertaken almost immediately.

4.2. Hydrogen electrode temperature coefficient

Two causes of temperature variations in measured potentials are, effects at the electrode studied and thermal liquid junction potential (Soret diffusion) in the electrolyte bridge. In the case of an external reference electrode these are compounded with streaming potential effects due to fluid flow in the porous plug.

The results reported here on the hydrogen electrode temperature coefficient are in good agreement with McKie's findings [5] but differ significantly from the calculated values reported by de Bethune [4]. McKie's measurements involved the electrolyte with a temperature gradient but no porous plug. This suggests that any effect of the porous plug streaming potential is relatively constant with temperature and that the differences between the calculated and observed potentials are

due to the Soret effect. However it is possible that compensating variations have masked the effects in question.

5. Conclusions

(1) A ram loaded working electrolyte has been designed which enables electrodes to be rapidly measured and changed in high temperature water.

(2) For dilute electrolytes (0.1 M) and a constant pressure drop, an isothermal porous plug can be considered to add a constant streaming potential to experimentally measured potential differences for temperature differences up to 200°C.

(3) Over this temperature range, the hydrogen electrode in 0.1 M NaOH, 1 atm H₂ has an apparent temperature coefficient of about 1.0 mV °C⁻¹.

References

- [1] N. D. Greene, 'Experimental Electrode Kinetics' Rensselaer Poly. Institute, Troy N.Y., (1965).
- [2] M. L. Brown and G. N. Walton, *J. Nuclear Materials* **58** (1975) 321.
- [3] A. L. Barcarella and A. L. Sutton, *J. Electrochem. Soc.* **112** (1965) 546.
- [4] A. J. de Bethune, T. S. Licht and N. Swendeman, *ibid.* **106** (1959) 616.
- [5] A. S. McKie, Proceedings 1st Int. Conference High Pressure & High Temperature Electrochemistry, University of Surrey 1972. (In press.)