TASCC-P-95-27

PREPRINT

tascc

***ELASTIC RECOIL DETECTION (ERD) OF LIGHT
ELEMENTS IN THE NEAR-SURFACE REGION OF
Zr AND ITS ALLOYS FOLLOWING CORROSION***

J.S. Forster and R.L. Tapping

AECL, Chalk River Laboratories, Chalk River, Ontario K0J 1J0, Canada

J.A. Davies, R. Siegele and S.G. Wallace

Accelerator Laboratory, McMaster University,
Hamilton, Ontario L8S 4M1, Canada

Submitted to
Surf. and Coatings Techn.

NOTICE

This report is not a formal publication; if it is cited as a reference, the citation should indicate that the report is unpublished. To request copies our E-Mail address is **TASCC@CRL.AECL.CA**.

Physical and Environmental Sciences
Chalk River Laboratories
Chalk River, ON K0J 1J0 Canada

1995 August

5w9544

Elastic Recoil Detection (ERD) of Light Elements in the Near-Surface Region of Zr and Its Alloys Following Corrosion

J.S. Forster and R. L. Tapping

AECL, Chalk River Laboratories, Chalk River, Ontario, Canada K0J 1J0

J.A. Davies, R. Siegele and S. G. Wallace

Accelerator Laboratory, McMaster University, Hamilton, Ontario, Canada L8S 4M1

Abstract

The use of very heavy ion beams in elastic recoil detection (ERD) measurements makes ERD a semi-universal technique capable of measuring all elements from hydrogen to elements with mass ≥ 100 . We have used this technique to profile light elements in the near-surface region of thin foils of Zr-2.5wt%Nb which had been exposed to a corrosive solution of 0.1% NH_4HF_2 in D_2O . We present results for H,D,C,N,O and F in the near-surface region of such foils and demonstrate the power of ERD for such studies.

INTRODUCTION

The ingress of hydrogen isotopes into Zr and its alloys is a critical issue since it can seriously degrade the physical properties of components made from these materials [1]. In recent years we have studied deuterium ingress into zirconium and its alloys [2-4] using an electrochemical cell and in-situ ion-beam analysis. Thin (1-4 μ m) cold-rolled foils were mounted on a compact cell, placed in a vacuum chamber, and exposed to a 0.1% NH_4HF_2 in D_2O solution. The deuterium which was taken up by the foil as a result of this corrosive reaction was measured both in-situ and, subsequently, ex-situ (with the foil dried and the original liquid side facing the beam) using the $\text{D}({}^3\text{He},\text{p}){}^4\text{He}$ nuclear reaction.

The foils studied in Ref. [4] were subsequently analyzed for fluorine content [5] using the ${}^{19}\text{F}(\text{p},\alpha\gamma){}^{16}\text{O}$ nuclear reaction to determine the correlation, if any, between deuterium and fluorine uptake. We found that the fluorine uptake was essentially independent of deuterium uptake. A major problem in these studies was that the D and F measurements were carried out in separate experiments using very small beam spots (~ 0.5 mm) so that there was considerable uncertainty that the ${}^3\text{He}$ and p analyzing beams sampled the same regions of the foils.

We have made further corrosion studies and in this work we report the use of heavy-ion ERD to simultaneously measure all elements from H to F in the near-surface region of Zr-2.5wt%Nb foils subjected to corrosion and demonstrate the capability of ERD for such studies.

EXPERIMENT

Thin ($\sim 4\mu\text{m}$) foils of Zr-2.5wt%Nb were prepared by cold rolling. To ensure that the starting material for the experiments had similar microstructure we stress-relieved the foils by annealing them in vacuum at 580 °C for twenty four hours. The foils were then mounted on a compact electrochemical cell and placed in a vacuum chamber. The foils were exposed to a 0.1% NH_4HF_2 in D_2O solution for 10 minutes and then flushed with H_2O . Measurements were then made of the deuterium uptake both in-situ and ex-situ (with the original liquid side of the foil dried and mounted facing the beam) using the $\text{D}({}^3\text{He},\text{p}){}^4\text{He}$ nuclear reaction as described previously [2-4]. The foils were subsequently removed from the cell and elements in the near-surface region measured by ERD.

The Zr-2.5wt%Nb foils were bombarded by a 230 MeV beam of ${}^{209}\text{Bi}$ ions from the tandem accelerator of the TASCC (tandem accelerator superconducting cyclotron) facility at Chalk River. The foils were pressed flat and glued onto an aluminum disk which was mounted on a two-axis goniometer with x- and y-translation. The target was positioned at 35° to the beam direction and recoils were detected in a large solid-angle ionization counter positioned at 45° to the beam. The detector, which is very similar to the one described by Assmann et al. [6,7], is described in detail elsewhere [8]. Briefly, the detector is an ionization chamber in which the cathode is split in two halves in a "backgammon" shape. Signals from the left (l) and right (r) sides provide the x-coordinate by $x = (l-r)/(l+r)$. The ratio $(l+r)/E$, where E is the total energy signal from the anode, gives the y-coordinate since the magnitude of the cathode signal depends on the distance of the ionizing particle from the Frisch grid. Since the detector subtends $\pm 1.6^\circ$ about its centre we are able to correct the total energy signal to a common angle using the position information

and thus compensate for kinematic broadening of the energy signal.

The anode is subdivided into two sections of length 12 cm. and 18 cm. The first section gives ΔE and the second section gives the remaining energy E_R thereby allowing us to carry out particle identification using standard $\Delta E - E$ techniques. Since elements lighter than boron give a very low ΔE signal in the gas counter, a silicon, surface-barrier detector, 300 mm² and 300 μ m thick, is placed at the rear of the counter. The surface-barrier detector solid angle is 23% of the solid angle of the gas detector which is 3.0 msr.

The entrance window on the gas detector consists of a 70 μ g/cm² thick stretched polypropylene foil which is supported by a 92% transmission stainless steel mesh. Isobutane, at 30 Torr pressure, was used as the counter gas and operated at a reduced field E/p of 1 V/cm-Torr.

RESULTS

Figure 1 shows a plot of ΔE versus E_R for an unetched foil which had been stress-relieved by heating in vacuum. Inspection of figure 1 shows that we clearly resolve C, N and O and the Zr signals. In figure 2 we show total energy spectra for C,N,O and F which have been kinematically corrected as described above, for windows on the various elements in figure 1. Also shown, in the lower panel, is the spectrum from the silicon counter which gives the spectrum of hydrogen in the foil. The H,C and N spectra show that these elements are confined to the surface region. There is also a surface peak for O although we see that some O has diffused into the foil as a result of the heating to stress relieve the foil. Finally, there is little or no D or F in the unetched foil.

Figure 3 shows the ΔE versus E_R plot for a corroded foil and here it can be clearly seen that fluorine from the 0.1% NH_4HF_2 in D_2O etch has been incorporated into the foil. The same

spectra as shown in figure 2 are shown in figure 4 but for an etched foil. Inspection of figure 4 shows clearly that D also has entered the foil as a result of the etch. Although we do not have particle identification for particles that only give a signal in the silicon surface-barrier detector we can easily separate H and D from the energy of the recoil since, in ERD the energy E_2 of a recoil of mass M_2 is given by:

$$E_2 = 4 M_1 M_2 / (M_1 + M_2)^2 E_1 \cos^2 \theta \quad (1)$$

where E_1 is the energy of the beam of mass M_1 and θ is the angle between the beam direction and the detector. In our case, where $M_1 \gg M_2$ this can be rewritten as:

$$E_2/M_2 \approx 4E_1/M_1 \cos^2 \theta \quad (2)$$

and, thus, the energy of the recoils is roughly proportional to their mass as i.e. D recoils have twice the energy of the H recoils. Further, we know from earlier measurements [2-5] that both D and F are confined to the near-surface region and this is confirmed by the shape of the D and F spectra in figure 4.

Table 1 gives a summary of the D content in the near-surface region of the foils as obtained from NRA and ERD analyses. Also shown is the analysis of F in the near-surface region of these foils. Overall, there is reasonable agreement for the D uptake as determined by the two methods especially considering that the beam spot size in the NRA measurement was a 0.5 mm diameter beam spot and in the ERD measurements the beam spot was 1 mm wide by 3 mm high. We also note that there is little variation in the F content which is consistent with the earlier measurements [5].

CONCLUSIONS

We have presented ERD measurements of light elements in the near-surface region of thin foils of Zr-2.5wt%Nb which had been subjected to corrosion. We have compared the analysis of the uptake of deuterium by this method and compared it to results using nuclear reaction analysis; both methods are in reasonable agreement. We have also shown that the fluorine uptake during etching is relatively constant as was observed in earlier measurements using nuclear reaction analysis [5]. Finally, we have demonstrated that ERD is capable of measuring all elements from hydrogen to fluorine simultaneously and is a valuable technique for studies of this type.

It is a pleasure to thank the CANDU Owners Group (COG) for support of this work.

REFERENCES

1. H.R. Gray, M.G. Nelson, R.E. Johnson, W.B. McPherson, F.S. Howard, and J.H.S. Wisher, *Int. J. Hydrogen Energy* 3(1978)105.
2. J.S. Forster, D. Phillips, T.K. Alexander, R.L. Tapping, T. Laursen and J.R. Leslie, *Nucl. Instr. and Meth.* B48(1990)489.
3. J.S. Forster, T.K. Alexander, D. Phillips, R.L. Tapping, T. Laursen and J.R. Leslie, *Nucl. Instr. and Meth.* B56/57(1991)821.
4. J.S. Forster, R.L. Tapping, T.K. Alexander, D. Phillips, T. Laursen and J.R. Leslie, *Nucl. Instr. and Meth.* B64(1992)403.
5. J.R. Leslie, T. Laursen, J.S. Forster and R.L. Tapping, *J. Nucl. Mater.* 218(1995)314.
6. W. Assmann, P. Hartung, H. Huber, P. Staat, H. Steffens and Ch. Steinhausen, *Nucl. Instr. and Meth.* B85(1994)726.
7. W. Assmann, H. Huber, Ch. Steinhausen, M. Dobler, H. Glückler and A. Weidinger, *Nucl. Instr. and Meth.* B89(1994)131.
8. J.S. Forster, P.J. Currie, J.A. Davies, R. Siegele, S.G. Wallace and D. Zelenitsky, to appear in the proceedings of "4th European Conference on Accelerators in Applied Research and Technology", Zurich, 29 August-September 4, 1995.

TABLE 1

Deuterium and Fluorine Concentrations in the Near-Surface of Etched Zr-2.5wt%Nb Foils

Sample	$D_{\text{NRA}} (\times 10^{17} / \text{cm}^2)$	$D_{\text{ERD}} (\times 10^{17} / \text{cm}^2)$	$F_{\text{ERD}} (\times 10^{16} / \text{cm}^2)$
1	2.53	3.05	4.9
2	1.87	0.94	4.4
3	0.16	0.24	5.2
4	2.44	2.80	5.3

FIGURE CAPTIONS

- Figure 1 ΔE versus E_R for recoils from a stress-relieved, unetched Zr-2.5wt%Nb foil.
- Figure 2 Kinematically corrected total energy spectra for the major elements shown in figure 1 i.e. C,N,O and F. The lower plot for H is from the silicon, surface-barrier detector.
- Figure 3 Same as for figure 1 but for a foil which had been etched with a 0.1% NH_4HF_2 in D_2O solution.
- Figure 4 Same as for figure 2.

Fig. 3