ATOM-PROBE ANALYSIS OF ZIRCALOY

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Abstract - Zirconium based alloys in the Zircaloy series have been analysed with atom-probe field-ion microscopy. During specimen preparation an anodic layer is formed, containing about 50% oxygen. In preliminary analyses of the matrix all the minor elements Fe, Ni, Cr and O were detected, and it appears possible to determine with the atom-probe whether any particular heat treatment causes matrix depletion.

I - INTRODUCTION

Zirconium alloys are used as fuel cladding materials in nuclear reactors because of their low neutron absorption at reactor operating temperatures. In particular the alloys Zircaloy-2 and Zircaloy-4 are widely used in boiling water reactors (BWR) and pressurized water reactors (PWR), respectively. The Zircaloys contain tin and small amounts of iron and chromium. Zircaloy-2 also contains some nickel.

The corrosion properties of these zirconium alloys has attracted increased interest during the last few years because of the current trend in using higher fuel burn-up before reprocessing (or direct deposition) than originally envisaged.

The most important corrosion mechanism is not the same in PWR and BWR environments. In water (PWR) "general corrosion" dominates. This type of corrosion appears to be cyclic in nature: the oxide consists of layers, a few micrometers thick, and the corrosion rate decreases continously during the formation of each layer and increases again suddenly as the next layer begins to form /1/.

In a BWR, where the oxygen content of the water and steam is higher than in a PWR, "nodular corrosion" is the life determining mechanism. In this case, after some time of general corrosion, large oxide nodules appear on the outer surface of the cladding tube. The nodules grow at a much higher rate than the general corrosion layer and soon cover most of the tube surface /2/. Eventually the whole fuel element has to be removed from the reactor core at a much earlier time than expected from the general corrosion rate.

It is known that the heat treatment given to the material during the manufacturing process affects the corrosion properties considerably /3/. The heat treatment of Zircaloy tubes usually involves quenching from about 1050°C (beta quench) before cold rolling and intermediate and final annealing at about 500°C (alpha anneal) followed by furnace cooling. This heat treatment brings about precipitation of intermetallic compounds such as $Zr(Cr,Fe)_2$ and $Zr_2(Ni,Fe)$.

A possible consequence of this precipitation is that the matrix gets depleted of the minor alloying elements, Fe, Cr and Ni. However, it has been very difficult to

measure the matrix composition with more conventional methods of microanalysis since the concentration levels are low and good spatial resolution is required to avoid analysing the precipitates. We have therefore tried to use atom-probe microanalysis to study the zirconium alloys. In the present paper the first results from this work are presented.

II - EXPERIMENTAL

The compositions of the two alloys studied, Zircaloy-2 and 4, are given in Table 1. The Zircaloy-2 material had been beta quenched at an intermediate stage and given a final anneal at 565 °C for 2 h. This material exhibited good corrosion properties when autoclave tested in 500 °C high pressure steam.

Of the Zircaloy-4 material two varieties were studied: "Standard", which was conventionally heat treated, and "Experimental", which was beta quenched in an intermediate stage and processed with low temperatures in subsequent intermediate anneals. Both varieties were given a final stress relieving anneal at about 500 °C. This heat treatment procedure gives rise to different corrosion properties in high temperature steam autoclave testing, with the "Standard" variety showing better corrosion properties.

From heat treated Zircaloy tubes, square bars were cut out and electropolished to needle-shaped specimens in a solution of 5% perchloric acid in methanol at room temperature. Uniform polishing was obtained at a voltage of 12 V. After forming a neck the bar was polished off at 7 V in an electrolyte of 5% perchloric acid and 35% n-butanol in methanol, using an automatic circuit breaker. It was found to be important to avoid interrupting polishing before drop off occurs, since the thin black anodic film that is formed when polishing is started disturbes the process. Fortunately, this film peels off after a short time of electropolishing.

Atom-probe analysis was performed at a pressure of less than 60 nPa using a specimen temperature of 90 K and an evaporation pulse amplitude of 15% of the specimen high voltage. Neon gas was used for field-ion imaging.

III - RESULTS

A transmission electron micrograph of a Zircaloy specimen is shown in Fig. 1. A thin layer of an anodic film is seen, about 6 nm thick and seemingly containing crystallites some 3-4 nm in width. All specimens prepared were found to have such a film on their surface.

Field-ion imaging first gives a rather faint image because of the surface film. After some field evaporation metallic zirconium appears with normal image brightness (Fig. 2). Atom-probe analysis of surface films showed that they were zirconium oxide (Fig. 3), but their oxygen content was only about 50%, whereas the common oxide ZrO_2 should contain about 67% oxygen (Table 2). The major peaks in the mass spetra from the oxide films are those from the oxide ions ZrO^{2+} and ZrO^{3+} . From

TABLE 1 Composition of Alloys Studied

Material	Composition (at%)					
	Sn	Fe	Cr	Ni	O	Zr
Zircaloy-2	1.13	.21	.19	.09	.72	bal.
Zircaloy-4	1.16	.37	.16	-	.63	bal.

the metallic matrix, all metal atoms evaporate as 2+ ions. Zirconium also appears with threefold and fourfold charge. Oxygen, which actually is an intentionally present alloying element in the Zircaloys, evaporates mainly as molecular ZrO ions. A large amount of hydrogen is also seen, both as H^+ and as ZrH^{2+}.

A field evaporation profile through the oxide layer and into the metal is shown in Fig.4. The results of matrix analyses are given in Table 3.

IV - DISCUSSION

Oxide layer

The anodic oxide layer that formed during electropolishing was in all cases found to contain about 50% oxygen, i.e. considerably less than the normally occurring oxide, ZrO_2 (zirconia). Thick oxide layers on Zircaloy tubes are known to consist of zirconia, but close to the oxide-metal interface, both amorphous oxide and the suboxide ZrO have been observed /4/. The present results are in agreement with these observations.

More iron was recorded from the oxide layer (about 1% of the metal content) than would be expected from bulk analysis. By contrast, no chromium at all was found in the oxide.

Oxide-Metal Interface

The composition of oxide-metal interfaces was found to lie between that of the oxide and of the metal. Thus, no element appears to be enriched to or depleted from the interface region.

TABLE 2 Atom-Probe Analysis of Anodic Oxide

Material	Variety	Composition (at%)					
		Sn	Fe	Cr	Ni	O	Zr
Zircaloy-2		1.28±.37	.63±.25	-	.61±.31	53.8±1.9	43.7±1.6
Zircaloy-4	Standard	.52±.21	.35±.17	-	-	45.3±1.5	53.8±1.5
Zircaloy-4	Experimental	.65±.21	.72±.23	-	-	46.6±1.3	52.0±1.3

TABLE 3 Atom-Probe Analysis of Zircaloy Matrix

Material	Variety	Composition (at%)					
		Sn	Fe	Cr	Ni	O	Zr
Zircaloy-2		1.43±.20	.23±.08	.06±.04	.25±.10	.68±.14	bal.
Zircaloy-4	Standard	1.11±.30	.08±.08	.24±.14	-	.48±.19	bal.
Zircaloy-4	Experimental	.82±.27	.18±.13	.37±.18	-	.55±.22	bal.

Matrix composition

As seen from Table 3, the contents of the minor alloying elements Fe, Cr, Ni and O all lie within the expected range of composition. Zircaloy-2 appears not to be depleted of alloying elements, and it is possible that there exists a difference in alloying element content between the two varieties of Zircaloy-4. However, due to the small number of ions recorded in these first analyses (about 1000) it is not possible to draw any definite conclusions, other than that it appears to be possible to make accurate analyses of these materials with the atom-probe. It is encouraging that the oxygen content (mostly from zirconium oxide ions) is in good agreement with the bulk composition. The large amount of hydrogen recorded was probably introduced during electropolishing. Zirconium has a high affinity for hydrogen, and small hydride precipitates are frequently seen in the transmission electron microscope.

V - CONCLUSIONS

1. Methods to image and analyse Zircaloy specimens in the atom-probe field-ion microscope have been developed.

2. The anodic oxide on Zircaloy specimens contained about 50 at% oxygen.

3. No enrichment or depletion of any element was found in the oxide-metal interface.

4. It appears possible to detect any large scale matrix depletion of the minor alloying elements in Zircaloy with atom-probe analysis.

ACKNOWLEDGEMENTS

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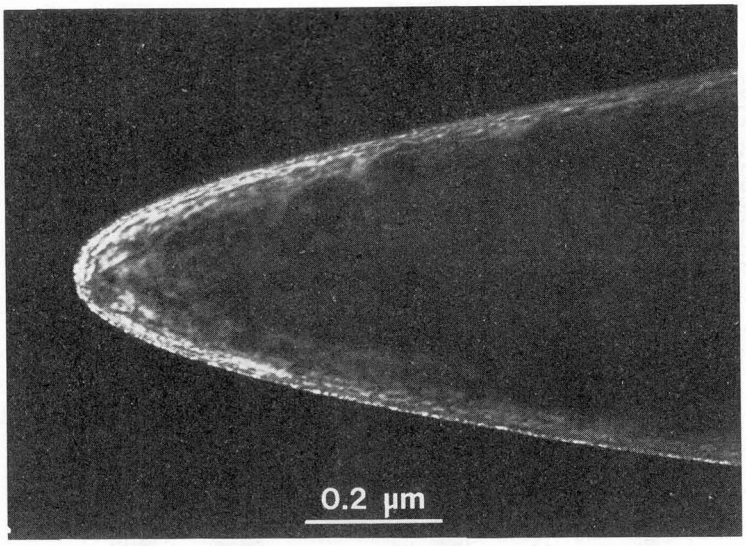

Fig. 1 - Field-ion specimen of Zircaloy-2, as polished. A thin layer of anodic oxide is present on the surface. Dark field transmission micrograph.

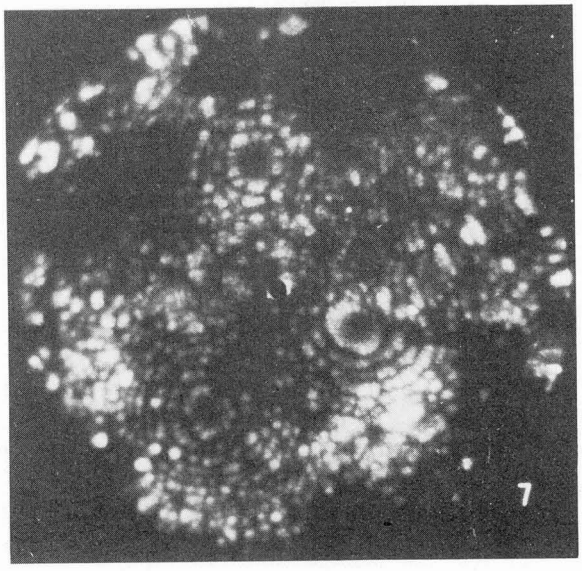

Fig. 2 - A specimen of Zircaloy-4, after that most of the oxide layer has been field evaporated away. Some areas (dark) are still covered with oxide. Neon field-ion micrograph.

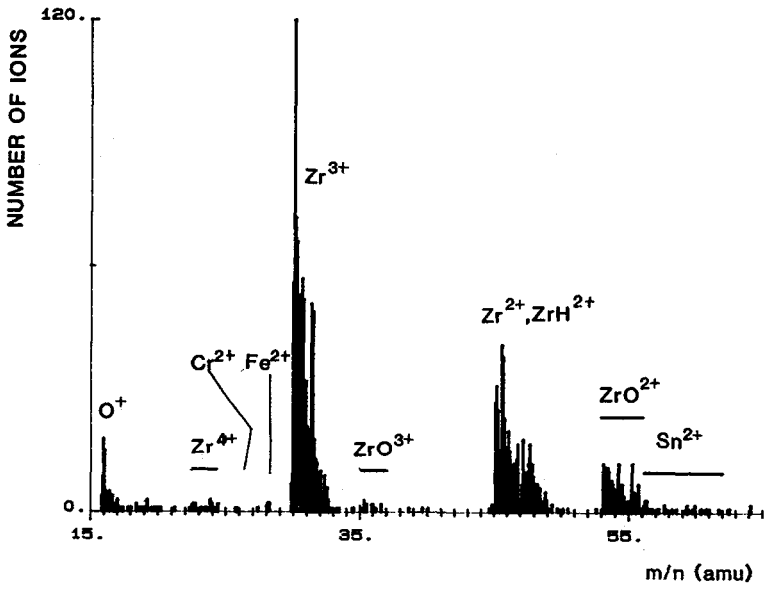

Fig. 3 - Atom-probe spectrum from the interface region between oxide and metal. Both zirconium ions and zirconium oxide molecular ions are seen.

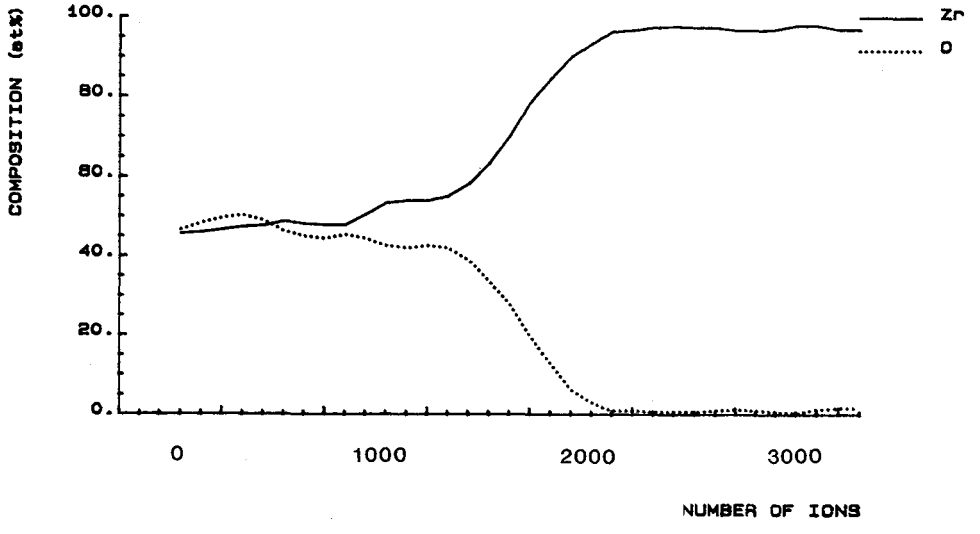

Fig. 4 - Field evaporation profile from the oxide layer, through the oxide-metal interface and into the metallic matrix. The total depth of analysis is about 4 nm.