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HAL Id: jpa-00229949
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Submitted on 1 Jan 1989

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ATOM PROBE ANALYSIS OF THIN OXIDE LAYERS ON ZIRCALOY NEEDLES

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Abstract Thin oxide layers have been grown on atom probe needles of Zircaloy in order to study the oxide-metal interface. The oxide was formed during one to thirty days in dry air, as well as during 5 s in boiling water. Atom probe analysis was performed of oxide layers thinner than 10 nm. These layers were found to contain low amounts of oxygen, less than stoichiometric ZrO. Transmission electron microscopy of equally treated specimens showed that the oxide was partially amorphous and contained small crystallites 5-10 nm in size.

1. Introduction

Zirconium alloys have been used as fuel claddings in nuclear reactors for more than thirty years. In this environment, the oxidation of the fuel claddings normally decides the service lifetime of the fuel elements. The oxidation of Zircaloys can be divided into two stages: a pre-transition oxidation showing a parabolic weight gain behaviour, and a subsequent post-transition oxidation where the weight gain is linear with time. Due to the development of a network of cracks and pores the oxide layer loses its adherent nature, and the oxygen transport through the oxide layer is promoted. In pressurised water reactors the transition normally begins at an oxide thickness of about 0.5-1 μm.

In crystalline oxide layers on Zircaloys oxygen diffusion is presumed to be grain boundary diffusion. Although several investigations of the oxide microstructure have been undertaken, the oxygen transport into the metal and the exact microstructure of the oxide-metal interface are not known. In pre-transition oxide layers, grown in water and steam, Sabol et al /1/ concluded that the oxide crystallite size increased with increasing oxide thickness. The initially formed oxide scale contained crystallites of 5 nm size, while the grain size at the oxide-metal interface was about 20 nm. According to Sabol, small crystallites grow in preferred orientations, until a limiting crystallite size is obtained. At this stage, nucleation of small crystallites starts at the oxide-metal interface.

Moseley and Hudson /2/ studied cross-sections in TEM of the metal close to oxide layers formed in 350 °C steam on Zircaloy-2. They observed a square electron diffraction pattern which was interpreted as cubic ZrO, and a corrosion model was proposed in which the oxidation
proceeds as $\text{Zr}_3\text{O}_4 \rightarrow \text{ZrO}_2$. Urquart and Vermilea /3/ performed TEM studies of oxide layers grown on Zircaloy-2 in dry oxygen at 600 °C. They found that the post-transition oxide consisted mainly of monoclinic $\text{ZrO}_2$, with small parts of cubic $\text{ZrO}_2$ and an intermediate, unidentified fcc phase. In oxide layers thinner than 0.4 μm grown in oxygen at 250 - 450 °C, Douglass and Van Landuyt /4/ observed oxide crystallites that seemed to grow in a partially amorphous film. The crystallinity of the film increased with increasing film thickness.

This work contains a preliminary investigation by the atom probe technique of pre-transition oxide films. As the temperature and the pressure used in the experiments are lower than in an actual reactor environment, the resemblance of the oxide to that formed "in-reactor" can only be partial.

2. Experimental

From a Zircaloy-4 material with the composition Zr-1.65%Sn-0.12%Mn-0.2%Fe-0.1%Cr, atom probe specimens were prepared using either of the two electro-polishing methods described in /5-6/. In the method described by Hadjadj et al., the electrolyte is pumped along the specimen to reduce passivation. This method is preferred since it provides a more uniform anodic oxide layer and a reduced risk of specimen failure due to field evaporation of thick oxide flakes.

The polished needles were inserted in the atom probe where the anodic oxide was field evaporated from the tip of the specimens. This sequence was followed by field ion microscopy, using Ne as image gas at a temperature of 90 K. The specimens were field evaporated until the tip surface appeared to be free from oxide. This was verified by atom probe analysis. The specimens were then heated to room temperature in vacuum and in nitrogen gas and subsequently stored in dry air. In the case of the oxides formed in water, the specimens were immediately dipped in boiling distilled water for 5 s, and then reinserted into the atom probe. To analyse the oxide, a temperature of 60 K and a pulse fraction of 15 % were used. These conditions are the same as for matrix analysis of Zircaloy /7/. However, in order to maintain the field evaporation of the oxide layer as uniform as possible, the field strength was kept somewhat lower.

Specimens stored in dry air 48 h, 312 h and 672 h, as well as the water oxides, were analysed by atom probe. A set of specimens which were subjected to the same oxidation treatment as the atom probe specimens were prepared for TEM examinations in a JEOL 2000 FX transmission electron microscope. This was done in order to avoid contamination which usually occurs during electron microscopy prior to atom probe analysis. In the case of the water oxides, the TEM specimens were dipped for 60 s in water, compared to the 5 s for the atom probe specimen since a thinner oxide layer was preferred for atom probe analysis.

3. Results

TEM micrographs of Zircaloy specimens oxidised in dry air are shown after 48 h in Fig. 1 (a), and after 672 h in Fig. (b-d). At the tip of the specimen the oxide crystallite size was approximately 5-10 nm. In the specimen stored for 672 h, two types of oxide were observed: a partially crystalline layer approximately 10 nm thick at the oxide-metal interface, and; an outer, thicker amorphous layer at the sides of the specimen. The thick amorphous layer had grown from the anodic oxide which formed during specimen preparation. In the 48 h oxide
layer, only a small amount of crystallites was present in the oxide layer, and the layer thickness was about 6 nm. In both specimens, a glassy phase surrounding the crystallites was imaged by centered dark field imaging using diffuse scattered electrons. This film was thinner in the specimen stored 48 h.

The diffraction patterns from TEM were calibrated against the α-Zr matrix reflections, and atomic plane distances of the oxide crystallites were calculated. These were in agreement with the monoclinic \( \text{ZrO}_2 \) phase. Some atomic plane distances of the matrix and the crystallites were very close. This fact, together with the microcrystalline structure of the oxide layer made it difficult to isolate specific reflections for dark field imaging of crystallites. This explains the existence of Moiré patterns seen in the centered dark field image in Fig. 1 c).

Table 1(a)-(c) shows the results from atom probe analysis of the oxide layers formed in air. As can be seen, the oxygen content was around 46 atomic percent and was lower than the zirconium content in all cases. This implies that \( \text{ZrO}_2 \) was not the major constituent of the analysed oxide layer.

Water oxide specimens which had been dipped in boiling water for 60 seconds are shown Fig. 2. As in the oxide formed in air both an amorphous and a partly crystalline part could be observed. The thickness of the partly crystalline region was about 8 nm. In Fig. 2 a), an amorphous layer is clearly visible even at the tip of the specimen, where the anodic oxide had been field evaporated. As is shown in Table 1(d), atom probe analysis of two specimens with thinner oxide layers formed in water during 5 s, gave differing results. In one analysis the oxygen content was as low as 34 atomic percent, whereas in another shorter analysis the oxygen content was approximately the same as in the oxide formed in air, i.e. 46 atomic percent.

The amount of collected ions during atom probe analysis is too low for analysis of the concentration of the alloying elements Fe and Cr in the oxide layer. As measured by atom probe, the matrix content of both Fe and Cr is 0.01 weight %.

Composition profiles based on the atom probe analyses did not show any large variations in oxygen concentration in the oxide layer. In the approximately 1 nm thick interface the oxide content decreased to less than 1 at. %. The oxygen content remained at this level during the subsequent analysis of the metal. This is consistent with the bulk composition of the alloy, 0.7 at. %.

4. Discussion

The low oxygen concentration of the oxide, as measured by atom probe analysis, was much lower than in a stoichiometric \( \text{ZrO}_2 \). If the oxide crystallites were monoclinic \( \text{ZrO}_2 \), the low concentration could be due to analysis of amorphous parts of the oxide. The observed thick amorphous layers grown on anodic oxide were not likely to be analysed by atom probe, but the crystallites at the tip of the needles were embedded in a thin amorphous film. The low oxygen content could also be an artefact due to losses in the analyses. During the analyses, the last of our four timer channels was filled during at most 1 % of the events, which means that some heavy ions were lost. These could possibly be oxygen, as most of the oxygen was detected as heavy \( \text{ZrO}_2 \) ions. However, this fact cannot explain a loss as great as 20 atomic percent, which would be the case if the oxide layer was entirely crystalline \( \text{ZrO}_2 \). The measured oxygen contents was not
significantly altered by the use of pulse ratios of 25%. The difference in oxygen contents between the two water oxides, according to atom probe analysis, could be the result of analysing different types of amorphous oxide.

It the oxide grown on the tip of the specimens, the crystallites were small, and did not have any apparent growth direction. The oxide crystallites at the sides of the specimens were larger in size, apparently up to 50 nm. In the crystalline oxide region, although the layer thickness increased with oxidation time, the size of the crystallites was not observed to vary significantly.

The results from this work can be compared with atom probe analysis of anodic oxide formed during electropolishing at room temperature /8/. The anodic oxide layer contained 54 atomic percent oxygen, and TEM studies revealed 3-4 nm crystallites in an approximately 6 nm thick oxide layer.

The TEM studies in this work were performed in order to determine which kind of oxide was analysed in the atom probe. However, the geometry of the atom probe specimens used, a needle entirely covered with oxide, was not satisfactory for microstructural investigation by TEM. Therefore, in the future cross-sections of oxidised thin Zircaloy layers will be produced and used to determine the crystal structure of the metal-oxide interface.

5. Conclusions

- Atom probe analysis has been performed of thin oxide layers grown on atom probe specimens of Zircaloy-4. Analysis was performed at 60 K using a low field evaporation rate.

- Oxide layers formed in air during 48 to 672 h contained about 46 atomic percent oxygen. TEM studies of similarly treated specimens suggested that the analysed oxides consisted partly of an amorphous oxide layer less than 10 nm thick. These layers contained crystallites 5-10 nm small in diameter. From diffraction patterns of the crystallites, atomic plane distances were calculated which agree with those of monoclinic \( \text{ZrO}_2 \).

- According to atom probe analysis, oxide layers formed in water at 100 °C during 5 s contained 37-46 atomic percent oxygen, TEM studies of thicker oxide layers formed during 60 s in water showed the same types of crystallites and amorphous oxide layer as the oxides which had been formed in air.

6. References

Figure 1. Centered dark field TEM micrographs of oxide layers formed in dry air. 1(a) Oxide crystallites in an oxide layer formed during 48 h. 1 (b)-(c) Oxide grown for 672 h, with crystallites close to the metal, and an outer amorphous oxide layer. 1 (d) Image formed with reflections from both matrix and oxide crystallites. Arrow indicates a columnar structure of crystallites in the inner oxide layer.
Figure 2. Two specimens oxidised for 60 s in boiling water. 2(a) TEM micrograph of a sharp needle, covered with a thick amorphous oxide layer at the sides of the specimen. 2(b) Centered dark field micrograph of oxide crystallites on a blunter specimen. Here, the amorphous layer was thinner, and a smaller amount of crystallites were present than in the oxide formed in air after 672 h.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>(a) Air, 48 h</th>
<th>(b) Air, 312 h</th>
<th>(c) Air, 672 h</th>
<th>(d) Water, 5 s</th>
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<tr>
<td></td>
<td>(at. %)</td>
<td>(at. %)</td>
<td>(at. %)</td>
<td>(at. %)</td>
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<td>C</td>
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<td>2.13 ± 0.44</td>
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<tr>
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<td>—</td>
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<tr>
<td>Cr</td>
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<td>—</td>
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<td>—</td>
<td>—</td>
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<td>1080</td>
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