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Journal of Nuclear Materials 298 (2001) 291–296

journal of nuclear materials

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Dissolution of oxygen-enriched Zircaloy-2

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Received 6 March 2001; accepted 4 July 2001

Abstract

When metal is removed from oxidised Zircaloy specimens in order to study the morphology of the oxide at the metal–oxide interface needle-like features are frequently observed. Since similar features are not observed in cross-section TEM examinations it has been questioned whether or not the needles are a result of the dissolution process. In particular it has been proposed that reprecipitation of oxide may take place when the metal is enriched with oxygen. In the present work oxygen-enriched Zircaloy has been dissolved and the resulting structures examined. The results indicate that the needles are in fact artefacts of the specimen preparation procedure. However, there are no significant differences between oxygen-enriched and normal Zircaloy below an oxide layer grown in steam at about 400 °C. In view of the differences between the needle structure observed after metal removal with bromine or by electropolishing and removal by HF–HNO_3 pickling solution it is speculated that the needles consist of a hydrous zirconium oxide which is unstable in the pickling solution. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

A good corrosion resistance is one of the most important factors behind a long lifetime of the cladding tube and therefore a large effort has been spent on developing an understanding of the oxidation mechanism for zirconium alloys. To achieve this knowledge a large number of different techniques have been used to study the formed oxide. Electron microscopy, electrochemical impedance spectroscopy, secondary ion mass spectroscopy and light optical microscopy are examples of used techniques. It is well established that the oxide growth takes place at the metal–oxide interface. In order to get information on the microstructure of the growing oxide at the interface, cross-sectional TEM is commonly used. Another technique is to remove the metal and study the backside of the oxide at the interface [1,2]. In the latter case a needle-like oxide structure has been reported to develop after a certain exposure time [2]. However, no features reminiscent of these needles are seen at the interface during cross-sectional TEM investigation [3–5]. The discrepancy between the two techniques is illustrated in Fig. 1. A Zircaloy-2 sample was oxidised in steam at 400 °C and 10 MPa for 3 days. The sample was prepared for cross-sectional TEM according to [3] and the micrograph is given in Fig. 1(a). To prepare the sample for the SEM study of the oxide surface at the interface the metal was chemically dissolved in 15% bromine and 85% methanol solution. The oxide remains intact during the metal stripping. A rather rough oxide surface often described as a cauliflower type of surface can be seen in both TEM and SEM, see Fig. 1. However, in the SEM image a finer degree of surface roughness is also seen, which has no correspondence in the TEM image. This finer degree of surface roughness has been described as needles [2]. The origin of these needles has been discussed along two lines, either as artefacts from the sample preparation [6,7] or as a true feature of the metal–oxide interface [2,8].

Earlier studies of the oxide layer in TEM involved removal of the metal in bromine [6]. From these studies it was reported that 'Experience has shown that the bromine attack results in a fibrous and often a dendritic appearance of the film. Film specimens showing these features were rejected'. It is in this context interesting to

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PII: S0022-3115(01)00649-3

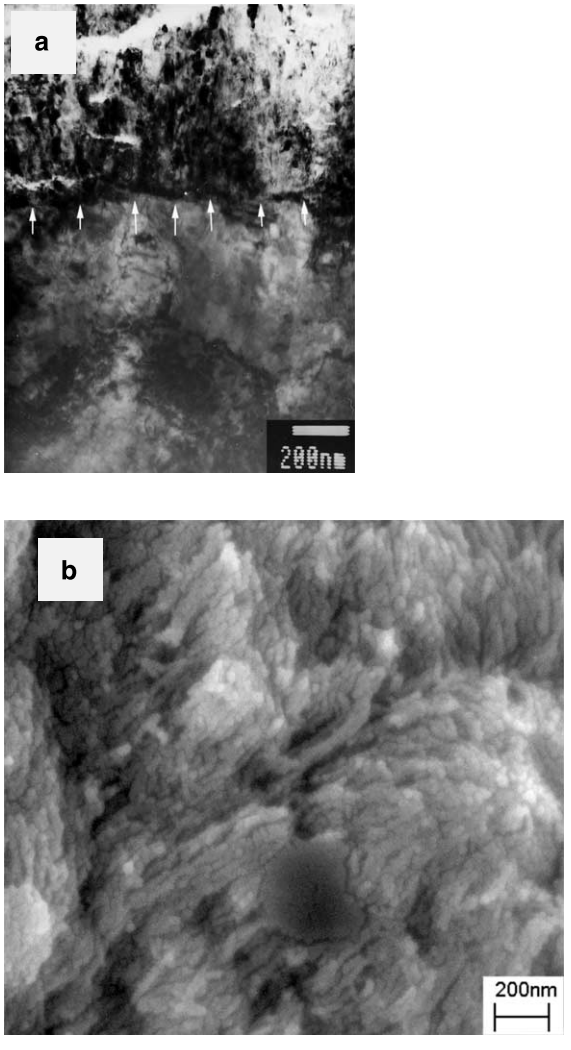

Fig. 1. Zr-2 sample oxidised in steam at 400 °C and 10 MPa for 3 days, investigated by: (a) Cross-sectional TEM showing the oxide/metal interface (arrows indicate interface). (b) SEM micrographs showing the surface of the oxide at the interface, after the metal has been removed in 15% Br–85% methanol solution.

note that the needles also appear after electropolishing in a perchloric acid based electrolyte [8]. Since the method of metal removal was electropolishing islands of metal were left on the oxide surface. To determine if the needles were a specimen preparation effect the specimen was subjected to a $HF–HNO_3$ pickling solution, which removed the metal islands. On inspection of the surface after pickling it was observed that the needles had been attacked. They had decreased in numbers and looked less well defined. On the surfaces where metal islands had been present before pickling needle-like features emerged from the oxide surface as if they had grown out of the oxide but they were by no means as well-developed needles or as numerous as the needles observed after electropolishing. Clearly one possible explanation to this observation is that the needles are a true feature of the metal–oxide interface which is preserved in electropolishing but destroyed by the more aggressive pickling solution. However, it appears equally possible that these needle-like features are an artefact from the sample preparation as proposed by Cox [7]. The difference between electropolishing and pickling is then that the pickling solution has a higher solubility of oxide than the electropolishing solution and for that matter also the bromine–methanol solution. Such a difference seems also to be evidenced by the change in the needle structure when it is immersed in the pickling solution. Cox has also proposed that oxygen/hydrogen dissolved in the metal during oxidation is not soluble in the bromine/methanol and that the needles are formed by the precipitation of these elements (See [2, Discussion]).

2. Results and discussion

To test the hypothesis by Cox [2] a sample of standard Zr-2 tube (~3 cm) was oxidised in air at 400 °C, and a 30 μm thick oxide layer was formed. The oxidised tube was then placed in an evacuated glass tube and heat-treated at 550–600 °C for nearly 6 months until all oxygen was dissolved in the Zr(O) sample. After the oxidation the sample was completely black, and when the tube had received a metal lustre again the heat-treatment was stopped. Compared with a non-oxidised sample the oxygen-enriched sample was somewhat less lustrous. SEM investigation of the sample after heat-treatment showed a surface with cracks and these are memory effects from the cracks formed in the oxide layer, see Fig. 2(a). EDS-analysis of the surface was performed and the result is given in Table 1. The oxygen content is fairly high (8 at.%) and due to the air oxidation also nitrogen was found in the sample. X-ray diffraction analysis of the sample showed the existence of only metal, result given in Fig. 2(b). The increase of oxygen content in the metal increases the lattice parameters of the zirconium crystal. It is mainly in the basal plane that the increase is observed but some increase also takes place in the *c*-direction. An X-ray analysis of the reference sample was performed to compare the result with the result from the oxygen-enriched sample.

A 1 cm long tube piece of the Zr(O) sample was partly chemically dissolved in bromine–methanol solution. The remaining part of the tube was examined in SEM, see Fig. 3(a). EDS-analysis was performed in points according to the figure and the result is given in Table 2. Point 1 is from the remaining metal and the fraction of oxygen and nitrogen is in parity with that found before the dissolution treatment. Point 2–4 is

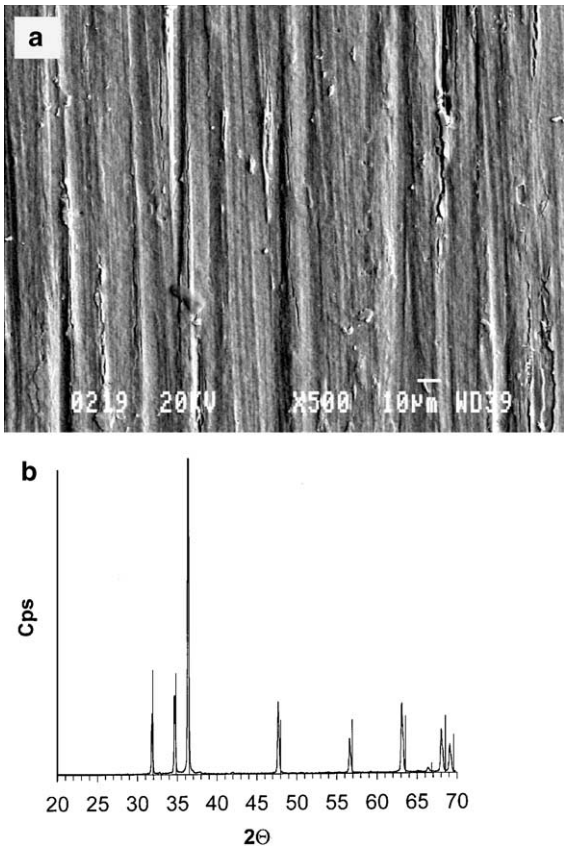

Fig. 2. Zircaloy-2 sample oxidised in air at 400 °C to form a 30 μm thick oxide layer and then heat-treated in evacuated glass tube for nearly 6 months at 550–600 °C until all oxygen was solved in the solid solution: (a) SEM micrographs showing the metal surface after oxidation and heat-treatment in evacuated glass tube, sample Zr(O). (b) X-ray analysis of sample Zr(O), with the standard reflections for zirconium.

Table 1
EDS-analysis of sample Zr(O) (at.%)

N	6.8
O	8.2
Zr	82.6
Sn	2.4

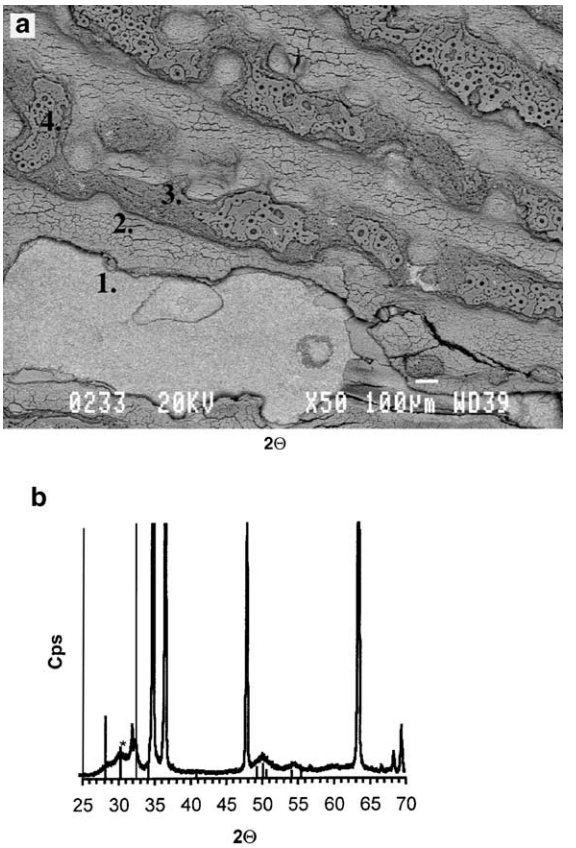

Fig. 3. The Zr(O) sample partly dissolved in 15% Br-85% methanol solution: (a) SEM micrograph, point 1 is located in the remaining metal, while point 2–4 is on precipitated layers. (b) X-ray diffraction, with the standard reflections for δ-hydride (fine line), monoclinic ZrO_2 (bold line) and tetragonal ZrO_2 (*).

Table 2
EDS-analysis of sample Zr(O) after dissolution in bromine–methanol (at.%)

	1	2	3	4
N	8.4	8.7	9.7	6.6
O	6.8	15.8	20.9	17.1
Br	0.8[a]	2.8[a]	12.1	9.3
Zr	82.3	71.1	57.0	67.2
Sn	1.7	1.6	0.3[a]	−0.2[a]

Analysis performed according to Fig. 3.
[a] $<2\sigma$.

from EDS-analysis of the precipitated layers. An enrichment of oxygen is found in this area. The remaining piece has also been investigated with X-ray diffraction, see Fig. 3(b). Both monoclinic and tetragonal zirconiumdioxides were detected together with some δ-zirconiumhydride, but the main signal is from the metal. The presence of a high fraction of tetragonal phase indicates a precipitation process. The bromine–methanol solution with dissolved zirconium was held in a funnel with a filter paper inside. The black deposit that was found on the filter paper was investigated in SEM. A photo from one precipitate is given in Fig. 4 and the EDS-analysis from this area is given in Table 3. The result of the EDS-analysis of the precipitate is in parity with the analysis of the precipitated layer on the partly dissolved Zr(O) sample, see Table 2. The microstructure shows no needles, however the surface is rather wave-formed.

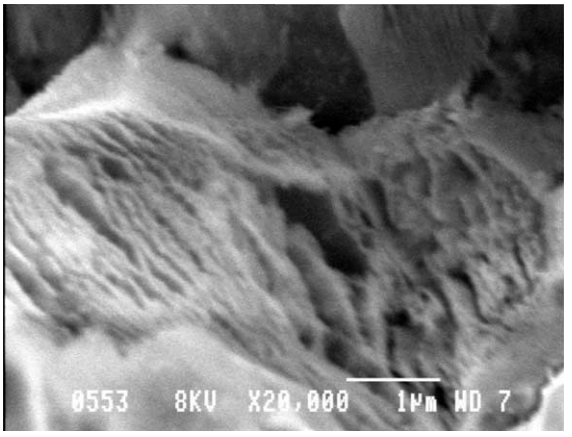

Fig. 4. SEM micrograph showing precipitate found on filter paper.

Table 3
EDS-analysis of precipitate found on filter paper (at.%)

N	9.0
O	18.8
Br	9.2
Zr	62.0
Sn	1.0

To investigate the appearance of needles further new samples were prepared for chemical dissolution of the metal. The investigated materials were the Zr(O) sample and a reference Zr-2 sample, i.e., the same alloy with and without oxygen enrichment. The samples were prepared in two ways before chemical dissolution:

I. Coating of the surface with a special varnish, not soluble in the chemical solution used for dissolving the metal.

II. Oxidation of the two materials for 3 days at 400 °C and 10 MPa.

The oxidation rate for the two materials was different, being higher for the Zr(O) sample. Cross-sectional TEM investigation showed that the oxide thickness for the Zr(O) sample is ~5 μm and for the reference sample ~1 μm. A micrograph of the reference sample is shown in Fig. 1(b). The oxidised and the varnish-coated samples were mechanically thinned to ~200 μm before dissolution of the metal. Two methods of removing the metal were tested:

1. Electrochemical dissolution in 10% $HClO_4$–90% ethanol solution at 25 °C and 14 V.
2. Chemical dissolution in 15% Br–85% methanol solution.

Not all of the metal was removed and the examination in the SEM was localised to the edge of the remaining metal, i.e., the investigated area is from newly released oxide/varnish-coat. On the varnish-coated samples a deposit of small particles was found as shown in Fig. 5. This is quite a thin layer. An EDS analysis of the layer showed the presence of Zr and Au. The Au is explained by the sputter coating used to make the specimen conductive for examination in the SEM. Inspection of other parts of the Al stub on which the sample was mounted, but which also had the same Au coating, showed no particle deposit. We conclude that some zirconium compound deposits on surfaces under the removed metal. There were no significant differences observed between the four different samples of varnish under the removed metal.

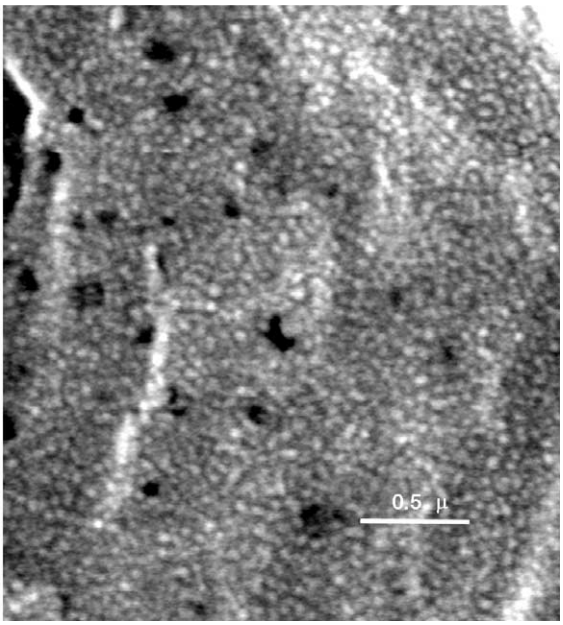

Fig. 5. SEM micrograph showing precipitates found on the varnish-coated sample.

The surface of the oxide at the interface of samples (I and II), after the metal has been removed, was also investigated in SEM and the micrographs are shown in Fig. 6(a)–(d). The higher oxidation rate for the Zr(O) samples results in an interfacial roughness, causing the off-focus in some part of the micrographs. As can be seen in the micrographs the appearance of the oxide is different between samples with different types of oxide removal. The oxides where the metal has been removed by electropolishing are quite similar, as are the oxides where the metal has been removed by bromine–methanol solution. However, there is no correlation between the observed structures at the interface oxide surface in SEM studies and the observed appearance of the metal/oxide interface during cross-sectional TEM studies, i.e., the appearance of needles in the SEM micrographs is not seen in TEM. It is also interesting to note that there is no big difference between the structure of the oxide of

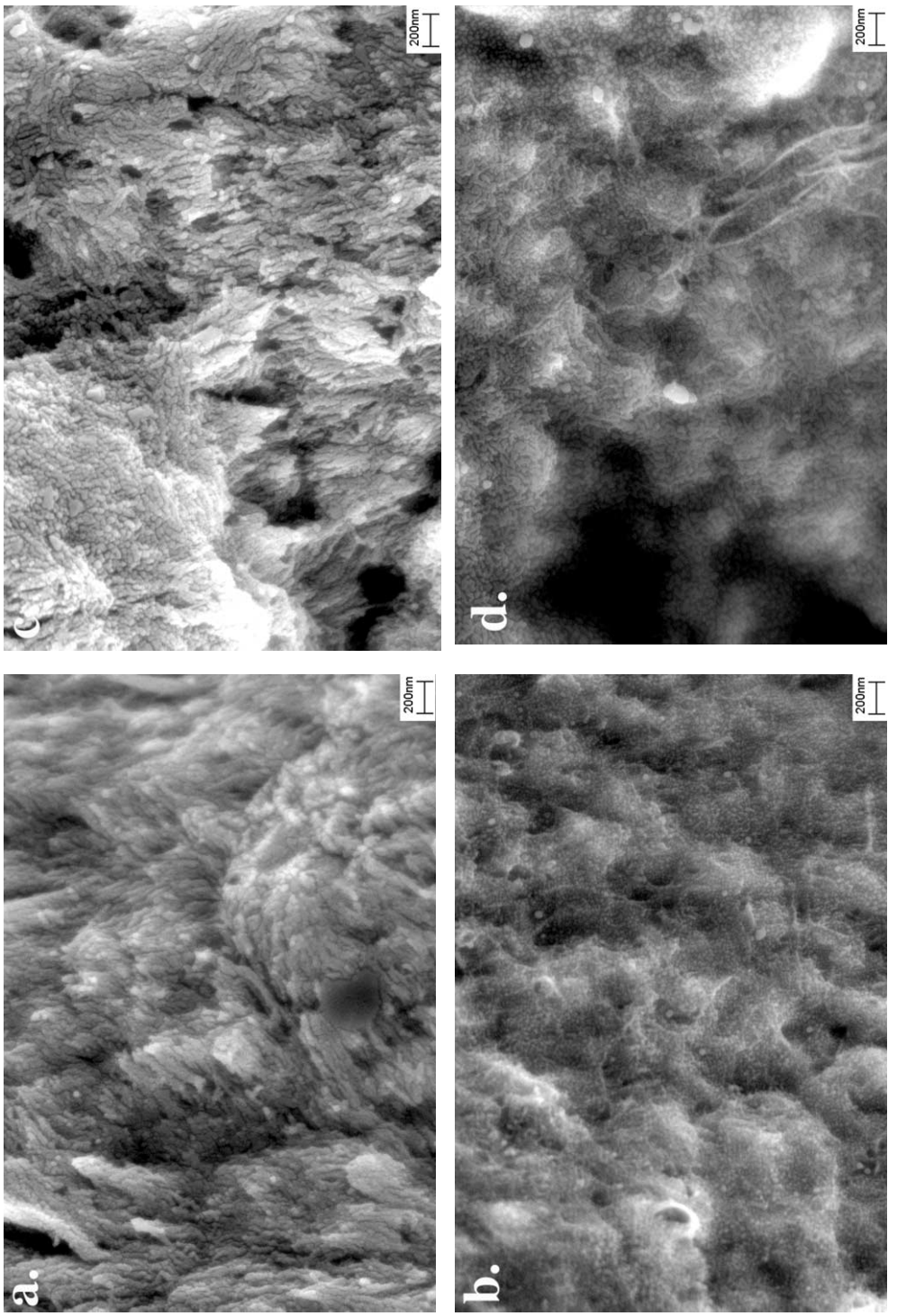

Fig. 6. FEG-SEM micrographs showing the surface of the oxide at the interface, after the metal has been removed (samples oxidised for 3 days at 400 °C and 10 MPa before investigation): (a) Reference sample, the metal electrochemical dissolved in 10% $HClO_4$–90% ethanol solution at −25 °C and 14 V. (b) Reference sample, the metal chemical dissolved in 15% Br–85% methanol solution. (c) Sample Zr(O), the metal electrochemical dissolved in 10% $HClO_4$–90% ethanol solution at −25 °C and 14 V. (d) Sample Zr(O), the metal chemical dissolved in 15% Br–85% methanol solution.

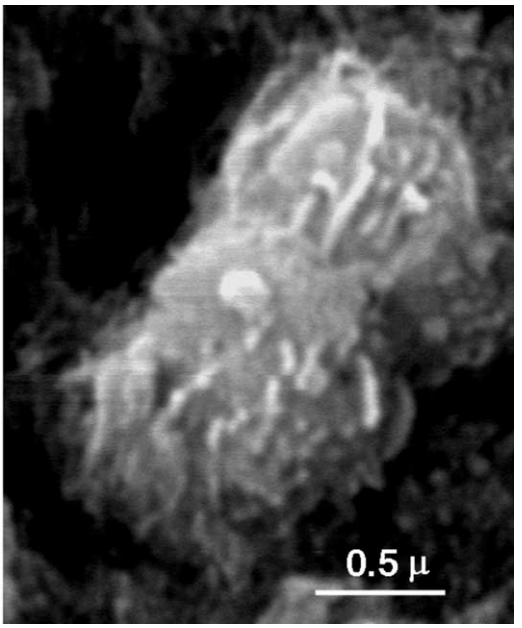

Fig. 7. Same as Fig. 6(c), but from examination in an old SEM.

the reference sample and the oxide of the oxygen-enriched sample.

Another source of experimental uncertainties is whether the image shows the true features of the surface. The pictures in Fig. 6 were taken in a modern field emission gun (FEG) SEM. These structures have also been examined in an older SEM. One example is shown in Fig. 7 from a specimen of Zr(O) with the metal removed by electropolishing. It has some of the features observed in previous investigations and is quite unlike the structure seen in Fig. 6(c) of the same specimen observed in the FEG-SEM.

In summary, the results obtained in this investigation show that the needles are artefacts from the sample preparation, which is in accordance with the work by Cox [7]. Comparison of an oxidised reference sample with an oxidised sample of Zircaloy enriched with oxygen did not indicate that dissolved oxygen plays a role in the precipitation reaction. The observed structures at the metal–oxide interface are virtually identical, the major difference being that the interface is rougher for the more rapidly oxidising Zircaloy enriched in oxygen. It thus seems likely that the needles are the result of a precipitation reaction in connection with the dissolution of the metal. One possibility is that it is a type of hydrous zirconium oxide, which is known to have a higher solubility than a well-crystallised oxide [9]. In fact, the needle structure was partially dissolved in the HNO_3–HF pickling solution [8]. This further underlines that the needles consist of precipitated oxide, especially in the light of the statement made by Cox [7], that the oxide scale on zirconium is quite stable in the pickling solution with a dissolution rate less than 0.2 nm/min. The particles found on the varnish also indicate that a precipitation reaction is involved. However, it must be noted that the structure on the varnish is not as complex as that on the oxide surfaces and the amount of material does not appear to be as large. An explanation may be that the pre-existing oxide surface provides nucleation sites from which the hydrous oxide can grow. Thus, there may be more precipitated material on the oxide surface than there is on the varnish for the simple reason that the precipitation reaction can start earlier on the oxide than on the varnish where the nucleation must occur in the solution. In addition the restricted agitation within pores formed during the dissolution process will increase the concentration of solved zirconium and enhance the amount of precipitated oxide.

Acknowledgements

Financial support from the Swedish Nuclear Power Inspectorate (SKI) is gratefully acknowledged. This work was carried out as a part of the Swedish research programme for the understanding of Zircaloy corrosion and hydriding mechanisms, funded by ABB Atom AB, Barsebäck Kraft AB, OKG AB, and Vattenfall.

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