Letter to the Editors

Metal and oxygen mobilities during Zircaloy-4 oxidation at high temperature

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Abstract

Oxidation experiments have been carried out on Zircaloy-4 samples in water at 633 K and 200 bars and in dry oxygen at 633 K and 1 atm, in order to study the mobility of species in the growing oxide films. The transport of metal and oxygen was studied by using the inert gas implantation and the Rutherford backscattering spectrometry (RBS) techniques. For oxide thickness lower than the transition ones, both in water and in dry oxygen environment, the oxide thickening occurs only by oxygen migration. Nevertheless a substantial amount of Xe marker was lost during reoxidation in case of corrosion experiments made under high temperature water. This behaviour may be explained by the presence at the surface of the sample of a hydrated layer in which Xe diffusion is accelerated, specially in pressurised water. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Migration of species across an oxide film (oxygen, metal) is required for the mechanism of oxide growth to go on. Ion injection into a growing oxide occurs at the metal–oxide interface for cations and at the oxide–gas interface for anions. Ionic migration processes into the growing oxide film have then a great importance concerning oxidation mechanism.

In the case of oxidation of Zy-4 in high temperature water, it has never been clearly established that oxygen is the most mobile species although it is generally accepted [1]. The transport mechanism responsible for oxide film growth on metals, i.e., whether growth occurs by metal or oxygen migration or both, can best be measured by the use of inert markers. These markers are placed on, or just beneath the surface of the specimen, and any change in their location, due to subsequent oxidation, is directly related to the transport mechanism involved. Concern-

ing zirconium, inert gas techniques have already been used [2,3] but only in the case of anodic oxidation. Using beta ray spectroscopy and radiotracer techniques, it has been shown that the thickening of the anodic oxide in pure zirconium target proceeds almost by oxygen migration [2]. Implantation of Xe and Kr markers and analysis by a precision sectioning technique have been used by Whitton [3] to measure the mode of anodic oxide formation on pure Zr. They also conclude that oxygen species are almost the only mobile species. Nevertheless, anodic oxidation and pure zirconium are in question in these papers and it is hazardous to extend these results to oxide grown in high temperature water, where defects are more numerous, and to zirconium alloys, where oxidation kinetics are different. The aim of this study was to determine the nature of the mobile species in the case of high temperature oxidations. Therefore, we used oxidation in high temperature water (633 K and 200 bars) and also in high temperature dry O_2 (633 K and 1 atm). Comparison of these two experiments may allow a better understanding of the behaviour of Zy-4 oxidised in high temperature environment.

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2. Experimental methods

2.1. Oxidation

The specimens used in the present work were machined from a sheet of Zircaloy-4 (1.5 wt% Sn, 0.2 wt% Fe, 0.1 wt% Cr). They were $6 \times 15 \times 2$ mm^3, giving an area of 2.64 cm^2. Before being oxidised the samples were mechanically polished first with SiC paper of 800 and 1000 and then with diamond paper (and solution SPM from Presi). Then they were ultrasound cleaned in a solution of 50% ethanol – 50% acetone.

Autoclaves were deoxygenated with Ar + H$_2$ prior to performing the corrosion experiments. The samples were exposed to demineralised water at 633 K and 200 bars. Exposure periods varied from 2 days to 52 days. After corrosion, the specimens were removed from the autoclave and dried with a nitrogen flux. The furnace used for corrosion experiments in oxygen at 1 atm was first vacuum pumped. Then specimens were oxidised at 633 K in oxygen passed through a desiccated silica gel. Exposure period varied from 8 h to 34 days.

Oxidation kinetics determined from the weight change of the specimens are presented on Fig. 1. Each experimental point corresponds to an unique sample, which is not put back in the autoclave or in the furnace for a longer exposure period. In this manner, adding errors along the kinetic curve is avoided. Moreover a cross section of a sample oxidised 29 days has been analysed by scanning electron microscopy. This direct measurement of the oxide thickness confirms our indirect results obtained from weight gain measurements. Fig. 1 shows kinetics of oxidation obtained by weight gain measurements, in good agreement with results already published [4].
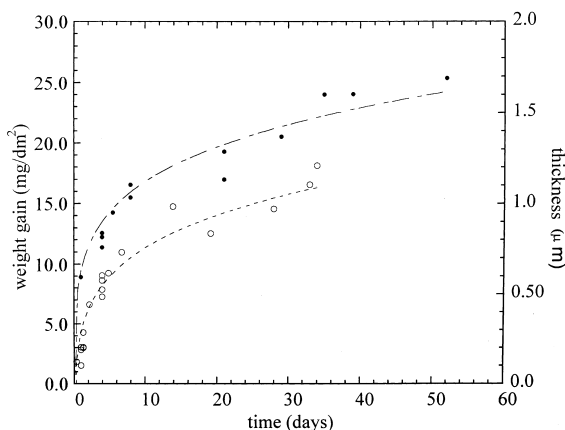

Fig. 1. Kinetics of oxidation. The conversion used was 1 μm for 15 mg/dm^2. The data are that of autoclave experiments (633 K and 200 bars) (●) and from oxidation in dry oxygen (633 K, 1 atm) (○).

2.2. Implantation

Ideal inert marker atoms have to be uncharged, large in size, so they do not diffuse significantly within the oxide lattice, and present in trace amount so that the macroscopic properties of the tagged oxide remain unaltered. Xe markers atoms, which have the required properties were chosen because they have a large atomic number and consequently they can be easily discerned from the zirconium peak in RBS spectra. They were implanted into preoxidised Zy-4 samples, to act as a marker surface layer. The marked samples were then reoxidised in autoclave environment or in dry O$_2$ and the thickness of the oxide so formed was followed by weight gain measurements. The position of the Xe ion layer before and after this second oxidation was obtained by RBS analysis techniques. The migration behaviour of the metal cations and oxygen anions can then be deduced from the change of the position of the Xe peak.

Xenon marker atoms were ion-implanted into the pre-formed oxide at an energy of 150 keV and at a dose of about $1–1.3 \times 10^{16}$ at/cm^2. The xenon implantation energy and dose were selected in such a way that the Xe peak before and after reoxidation could be analysed by RBS technique. According to TRIM simulation, with this energy into bulk zirconia, the mean 'projected' range of the distribution of the Xenon markers is located at a depth of about 25 nm.

2.3. Analysis

Rutherford backscattering spectroscopy (RBS) is used to determine the film composition versus depth, and also the implanted Xe position. Each sample is analysed at 165° backscattering angle, with 1 MeV He$^+$ ions from a 1 MV van de Graaff accelerator, at normal incidence. The energy calibration is obtained on an oxidised silicon reference and a very thin gold layer sputtered on silicon.

Concentration profiles obtained thanks to RBS spectra can only be fitted by successive simulations [5] of the spectra corresponding to hypothetical descriptions of the target and iterative improvement of these description. This iterative method used for profile reconstitution is devised in order to reach up to the best resolution allowed by experimental data, without forcing the profile to obey any user-defined shape. At each iteration, for any change in the concentration profile imposed to improve the fit, the resulting energy loss, energy dispersion and trajectory of the ion are computed. Such a technique is very efficient since it avoids empirical fit of parameters of a hypothetical type of profile, but it computes the concentration profile without any restrictive initial assumption and with maximal accuracy [6].

3. Results and discussion

Main results are summarised in Table 1. For the first series of samples, the preoxidation exposure period was chosen rather long. Indeed, as it has been already explained, during the second oxidation the change in the marker position is directly related to the transport mechanism involved. Then if growth occurs only by metal migration, the change in the marker position is equivalent to the thickness of the oxide formed during the reoxidation. Since the xenon marker position is determined by RBS, simulation of the spectrum has shown that the penetration depth of the xenon ions could not exceed about 100 nm. Thus the thickness of the second reoxidation has to be very thin (about 40 nm) and it was necessary to be on the plateau of the kinetic curve. The first experiments were then made with pre-formed oxide of about 1.4 µm, corresponding to a treatment of 29 days, a xenon-implanted preoxidised specimens were reoxidised for a short time (1–2 days).

Afterwards, since almost no zirconium diffusion occurs, oxides exposed during 4 days were always used as preformed oxide. The post-oxidation periods varied from 21 to 52 days for samples exposed to water and from 18 to 29 days for samples exposed to dry oxygen.

The spectrum of a 29 days pre-oxidised sample after xenon implantation is shown in Fig. 2. Using the iterative method for profile reconstitution, it is possible to determine the exact position and the width of the xenon profile. By this process, we obtain the concentration profiles of the different species shown in Fig. 3 and the final spectrum simulation, in great agreement with the experimental one (Fig. 2). Using a similar process, we have determined the xenon marker distribution for each sample before and after the second oxidation. By comparison of these 2 spectra (as for example on Fig. 4), it is

then possible to get information about the growth mechanism of the oxide. The mean depth position of the xenon profile is in all cases close to 20 nm as forecast by TRIM simulations.

The Xe concentration profiles obtained from spectra of samples preoxidised 4 days in high temperature water are compared with the profiles obtained after reoxidation of the same samples during 21 and 52 days, which corresponds to a thickness variation of, respectively, 508 and 971 nm (Fig. 4). The same comparison was made for samples oxidised in dry O_2 environment (Fig. 5). Here two exposure periods of reoxidation were explored, 17.8 and 29 days, corresponding, respectively, to 372 and 577 nm of thickness variation.

As can be seen from Figs. 4 and 5, the cationic transport fraction is equal to zero. That means that in the case of corrosion experiment of Zy-4 in high temperature environment (water and dry oxygen at 633 K), for exposure periods lower than the breakaway, i.e. when the transition is not reached, the thickening of the oxide must proceed entirely by oxygen migration. Indeed, the most important result of this study is the proof that oxidation of Zy-4 in high temperature environment proceeds only by oxygen migration, at least for thicknesses lower than 1.7 µm. This conclusion confirms the results obtained from previous experiments in anodic oxides [2,3].

In the case of gas experiments, the final location of the Xe markers was the same as the initial one, which indicated that the Xe markers did not move during the reoxidation in dry oxygen at 1 atm. On the other hand, experiments made in pressurised water have shown a loss of xenon during the reoxidation which indicated that Xe markers moved in the growing oxide, from the oxide to the water.

The second important result of this study is the observation that a substantial amount of Xe was lost

Table 1
Results summary

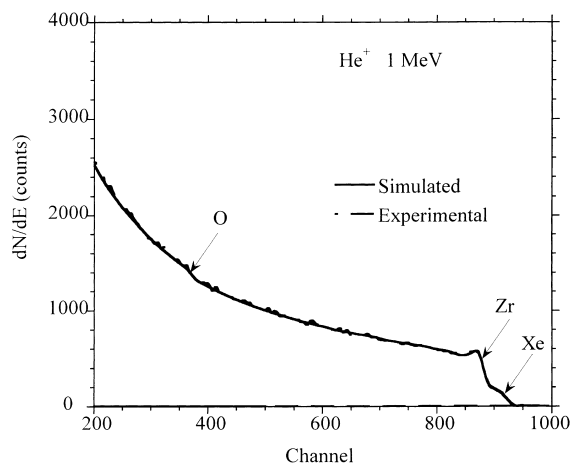| Exposure periods			Xe position Variation (nm)	Implantation dose measured by RBS (10^{16} atm/cm^2)		
First oxidation (days – nm)	Second oxidation (days – nm)	Variation (nm)		Before second oxidation	After second oxidation	Loss of xenon (%)
Autoclave						
29 – 1167	2 – 1328	161	0	1.20	0.72	40
29 – 1138	2 – 1333	195	0	1.16	0.72	38
29 – 1288	7.5–1515	227	1	1.35	0.75	44
4 – 730	21 – 1238	508	0	0.96	0.50	48
4 – 880	35 – 1603	723	0	1.09	0.32	71
4 – 1003	52 – 1974	971	2	0.94	0.17	82
4 – 626	34 – 626 (vacuum)	0	1	1.43	1.39	2
Gas						
1.3 – 284	17.8 – 904	620	0	1.2	1.3	0
1.3 – 199	17.8 – 794	595	4	1.3	1.3	0
4 – 483	29 – 1027	544	3	1.0	0.8	20
4 – 604	29 – 1181	577	3	1.0	0.9	10

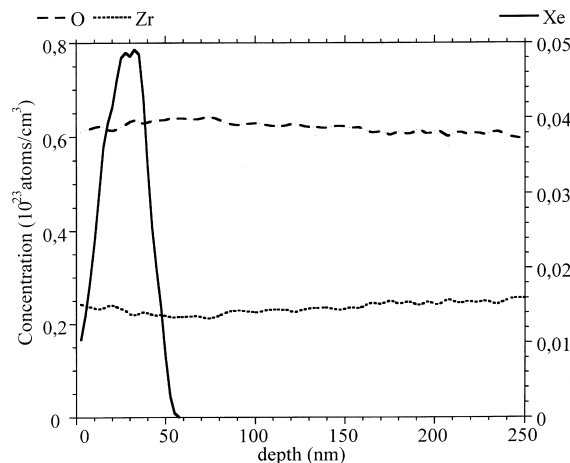Fig. 2. RBS Spectrum of a sample pre-oxidised 29 days after a Xe implantation.

Fig. 3. Profiles of the different species obtained from the spectrum of a 29 days pre-oxidised sample after Xe implantation thanks to PERM simulation [6].

Fig. 4. Comparison of the Xe concentration profile obtained from RBS spectra of samples before reoxidation (——), after a 21 days reoxidation (– – –), and a 52 days reoxidation (- - -) in high temperature water. The depth is calculated with the hypothesis of a homogeneous ZrO_2 layer with a density of 5.826.
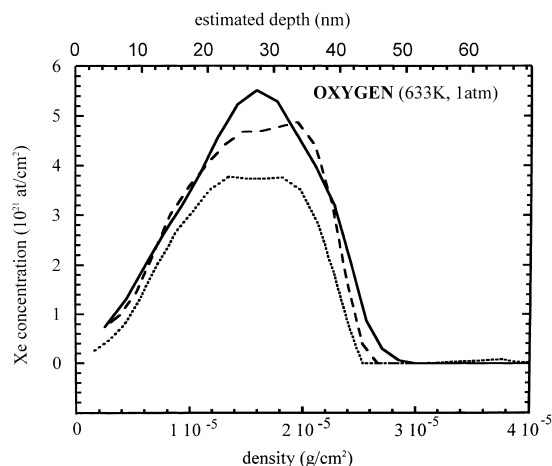
Fig. 5. Comparison of the Xe concentration profile obtained from RBS spectra of samples before reoxidation (——), after a 17.8 days reoxidation (– – –), and a 29 days reoxidation (- - -) in high temperature dry oxygen. The depth is calculated with the hypothesis of a homogeneous ZrO_2 layer with a density of 5.826.

during the reoxidation in water environment, whereas Xe atoms are almost completely retained in oxide grown in dry gas. The reason for this significant loss is not yet well understood. Nevertheless some hypothesis may explain the behaviour of Zy-4 in high temperature water.

Thanks to experiments made in high vacuum, it can be concluded that xenon atoms do not diffuse into the oxide at 633 K. Indeed, a sample oxidised 4 days in autoclave, where 1.2×10^{16} at/cm^2 Xe atoms were implanted, was annealed during 34 days in a high vacuum furnace (2×10^{-8} Torr). No loss of xenon was observed here. Although the Xe atoms do not diffuse in the static oxide, they could diffuse in the growing oxide under high temperature water.

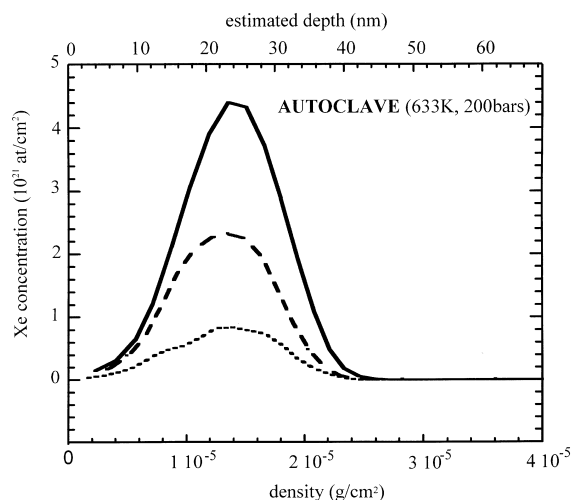It is well known that when exposed to the atmosphere, and moreover to water, the surface of most oxide systems becomes covered by a hydrated layer that builds up to compensate at least in part the coordinative unsaturation of the surface ions. This surface hydrated layer is normally made of hydroxyl groups belonging to the coordination sphere of one or more surface cations, and of undissociated water molecules coordinated to surface cations. On metal oxides, water may absorb in either molecular or dissociative form. Water may also

bond in dissociated form, in which case the driving force is formation of metal–hydroxyl bond. The quantity of reversibly absorbed water increases with the relative humidity and with time in the case of atmospheric corrosion [7].

It is the presence of the hydrated layer and its formation during the oxide growth that may induce a xenon flux from the surface sample to the high temperature pressurised water. In the case of anodic oxidation of zirconium, Khalil et al. [8] have studied the absorption of water by using isotope ^{222}Rn of the noble gas radon as an inert marker. This latter emits α-particles (5.486 MeV) which loose energy at a predictable rate on passing through matter. Because of the presence of this hydrated layer at the samples surface, the mass of matter traversed by α-particles increases. The extra energy loss is due to absorbed water. Indeed, this energy loss has been shown to increase as water is absorbed and to decrease when samples were dried. Thanks to this technique, a $Zr(OH)_4$ layer of about 10 nm thick has been measured on these anodic zirconium samples. Moreover Ardizzone et al. [9] have observed water chemisorbed at the surface of ZrO_2 sample powders. It has been shown that during a long ageing of about one year in a closed glass container, a dehydroxilated ZrO_2 powder slowly adsorbs water from the environment. So it is clear that zirconium alloys exposed to high temperature water develop on their surface a hydrated layer. Some XPS experiments allow us to conclude that this layer exists on our sample oxidised in autoclave [10]. To our knowledge, no direct quantitative measurement of the thickness of this $Zr(OH)_4$ layer has been made yet for samples oxidised in pressurised water. Analysis of H ex situ may be an indirect way to approximate this thickness. According to Elmoselhi et al. [11] it is reasonable to assume that a hydroxide layer like $Zr(OH)_4$ of at least 20 nm thickness at the outer surface of our sample builds up during oxidation in autoclave. Indeed it has been shown that exposing Zr–2.5%Nb and Zircaloy-2 to D_2O vapour (573 K) during at least 4 h resulted in a near-surface overconcentration of deuterium. Near-surface concentration was considered here as the concentration at the outer layer of the oxide up to 20 nm from the oxide surface [11].

Xe atoms were then implanted into a hydroxide rather than an oxide compound. The structure of this surface hydrated layer may be gel-like in the case of oxidation under high temperature water. We may assume that Xe diffusion is accelerated due to the presence of this particular structure, a fortiori in autoclave where water was under pressure and high temperature. This explains the loss of Xe atoms during reoxidation in autoclave, whereas in case of reoxidation in dry O_2, no significant loss of Xe atoms was observed. This hypothesis is confirmed by another results. As a matter of fact, some samples first oxidised 4 days in dry oxygen were then reoxidised during 29 days in pressurised water after implantation of 2×10^{16} atm/cm^2 Xe atoms. During the second oxidation, oxide growth develops this gel-like surface structure. RBS analysis shows on these samples a loss of about 40% of implanted Xe atoms, whereas in the case of first and second oxidation with the same exposure periods in dry oxygen the Xenon loss is only 10%. This means that the mechanism of oxidation in high temperature water carries away the Xe atoms. We explain this significant loss by the accelerated diffusion of Xe atoms in this hydrated layer during oxidation.

4. Conclusion

The corrosion of Zircaloy-4 in high temperature environment occurs by oxygen migration trough the corrosion film, with the formation of new oxide at the metal–oxide interface. This result, obtained by using the inert gas implantation and the RBS analysis techniques, was accurate in the case of oxides thickness lower than the transition ones.

It has also been observed a migration of the Xe markers from the oxide to the water during reoxidation in autoclave. The presence of a hydrated surface layer on these samples may induce an accelerated diffusion of the Xe atoms in the growing oxide. This hypothesis explains the loss of the Xe markers observed by RBS analysis.

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