



In situ measurement of electrical conductivity of Zircaloy oxides and their formation mechanism under electron irradiation

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Abstract

In situ electrical conductivity of Zircaloy-2, improved Zircaloy-2 and Zircaloy-4 oxide films has been measured with 1 MeV electron irradiation using gold, copper and zirconium electrodes during beam-on and -off in the temperature range of 296–680 K in order to find the rate controlling factor of oxidation of the alloy. Current–voltage characteristics of all oxides during irradiation show almost ohmic behavior for Zircaloy-2 and Zircaloy-4 oxides, and non-ohmic for improved Zircaloy-2 oxide where the current is electronic in nature and may be associated with ohmic and Schottky and/or Poole–Frenkel processes, respectively. The electrical conductivity of such films under irradiation, called radiation induced conductivity (RIC), is proportional to the irradiation flux and it is predominantly due to electronic excitation. Subsequent subsection of the specimens under irradiation with beam-on and -off shows RIC by electron excitation from the valence to conduction band and annealing of the conductivity at temperature, respectively. It is concluded that the electron motion dominates the electrical conductivity of Zircaloy oxides. Therefore, the slow-diffusing negative oxygen ions control the oxidation process of Zircalloys. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

After a long operation experience of fission reactors, it is unnecessary to elaborate the application of Zircalloys in light water reactors where they are being used as fuel cladding and channel box materials [1]. With the increasing consumption of energy, the optimization of fuels in fission reactors and the difficulties of making new kind of reactors such as fusion reactors, the long life time of fuel cladding is essential. Achievement of long life time of this core component is inhibited under irradiation because of corrosion/oxidation degradation of such elements [1]. Generally, the corrosion or oxidation reaction in Zircalloys is unlikely to proceed unless elec-

trons are transferred from the metal to water and oxygen ions are diffused in the opposite direction of electrons. Thus the diffusion of oxygen ions and the movement of electrons are indispensably important in oxidation, with the slower migrating species acting as the rate controlling process. In order to understand the oxidation mechanism of Zircalloys, several studies have been performed under various conditions with and without irradiation [2–8]. A complex behavior of current in Zircaloy-2 oxides was found by placing the specimens in molten salt where the electronic and ionic current followed the Schottky emission and Tafel relationship, respectively [2]. It was concluded that both electrons and ions were equally important as the rate controlling process. A subsequent study by Shirvington [3] has argued Schottky type electronic conduction takes place through intermetallic precipitates in the Zircaloy-2 oxide films. Ramasubramanian [4] had indicated that the

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electron transport occurs through intermetallic precipitate sites of Zircaloy-2, Zr–Cr, Zr–Ni, and Zr–Fe binaries during corrosion by measuring I – V behavior with gold or aluminum evaporated counter-electrodes on to the sample. This author also postulated that the oxidation electron current for those alloys can not be represented by a single process. Photo current measurements of Zircaloy oxides showed positive current which is consistent with electron movement from the oxide surface to the metal substrate [5]. In addition, the comparative study of oxides of different composition alloy elements such as Zr, Sn, Cr, Ni and Fe with various depth showed that the electrical conductivity of the Zr–Sn–Fe oxide is the lowest among all alloys. Shirvington [6] has studied the electrical characteristics of two types of Zircaloy-2 oxides grown in oxygenated water in the fast neutron flux of 1.5×10^{13} n/cm² s with fluoride contamination (in reactor oxide) and in the steam of micro-autoclave (out reactor oxide) environments found electron conduction which is not affected by oxidation environments. Gamma irradiation at 29.2 Gy/s on Zircaloy-2 oxide has no significant effect on electron transport [7]. However, although from the beginning of the operation of fission reactors the oxidation phenomenon of Zircalloys has drawn attention of many researchers, no single study has confirmed the species controlling the oxidation. The present authors have previously measured the I – V behavior and the unirradiated electrical conductivity of the same specimens as used in this study. They have shown the dominant electronic conductivity of Zircaloy oxides and concluded that the negative oxygen ions were controlling the oxidation process of Zircalloys. A complete investigation of the Zircaloy oxide films before, during and after irradiation was, however, considered necessary to give a decisive conclusion on the rate controlling process of Zircaloy oxide films. It was also noted that the rate controlling species of Zircaloy oxidation is always associated with the slower species in the conductivity measurements [8]. Thus the purpose of the present study is further to interpret the oxidation mechanism of Zircalloys by determining the rate controlling factor and to relate the conductivity with oxidation resistance through in situ measurements of electrical conductivity of Zircaloy-2, improved Zircaloy-2 and Zircaloy-4 oxide films under electron irradiation.

2. Experimental procedure

The Zircaloy oxide films used in this study were produced on both sides of polycrystalline Zircaloy plates of Zircaloy-2, improved Zircaloy-2 and Zircaloy-4 by inserting them in steam of an autoclave, first, for 8 h at 680 K and then for 16 h at 780 K at a pressure of 10.3 MPa. The chemical composition (wt%) of the Zircalloys

used in the present study is given elsewhere [8]. The thickness of oxide films was 3 μ m. Specimens of 5.5 mm diameter were taken from the oxidized plates by using an ultrasonic cutter and the bottom side of oxide films was removed by polishing paper. The total thickness of the specimen including Zircaloy metal after polishing on one side was reduced to about 200 μ m. A center electrode of 2 mm diameter and a guard electrode of 4.5 and 3.5 mm outer and inner diameter, respectively were formed separately by gold, copper and zirconium vacuum deposition to the top of the specimen. The abraded metal side of the specimen (bottom side) acted as the base electrode. In situ measurements of electrical conductivity and I – V were performed in a high voltage electron microscope (HVEM) under irradiation with 1 MeV electrons during beam-on and-off conditions over the temperature range of 296–680 K. During the measurements of electrical conductivity an electric field of 1.7 MV/m (potential of 5 V) was continuously applied to the base electrode with a Hewlett-Packard 4339A high resistance meter and the specimen current was also recorded every two minutes using the same device. On the other hand, for I – V measurements the voltage applied is indicated in the graph. Irradiation was done only to the center electrode region of the specimen in the vacuum pressure of 10^{-5} Pa. The ohmic behavior of specimens at different temperatures during irradiation was checked with varying applied voltages in the forward and backward directions. Details of the experimental procedure and the specimen holder used are illustrated elsewhere [8,11].

3. Results and discussion

3.1. I – V Characteristics

The I – V characteristics of (a) Zircaloy-2 with (i) gold (Au), (ii) copper (Cu), and (iii) zirconium (Zr) electrodes, (b) improved Zircaloy-2 and (c) Zircaloy-4 oxides with copper electrodes under a 1 MeV electron irradiation flux of 1.4×10^{18} e/m² s (7.6×10^4 Gy/s) is shown in Fig. 1. Albeit the I – V and the electrical conductivity measurements of Zircaloy-2, improved Zircaloy-2 and Zircaloy-4 oxide specimens were done with three kinds of electrodes, we will concentrate on the results with one electrode material, emphatically Cu electrodes since all three types of electrodes showed similar behavior (compare Fig. 1(a) (i), (ii) and (iii)). The specimen current increases by almost two orders of magnitude compared to that without irradiation in all specimens regardless of electrode type, and the I – V behavior of Zircaloy-2 and Zircaloy-4 oxides is approximately ohmic at various temperatures. Unlike Zircaloy-2 and Zircaloy-4 oxides, the I – V behavior of improved Zircaloy-2 specimen is non-ohmic with

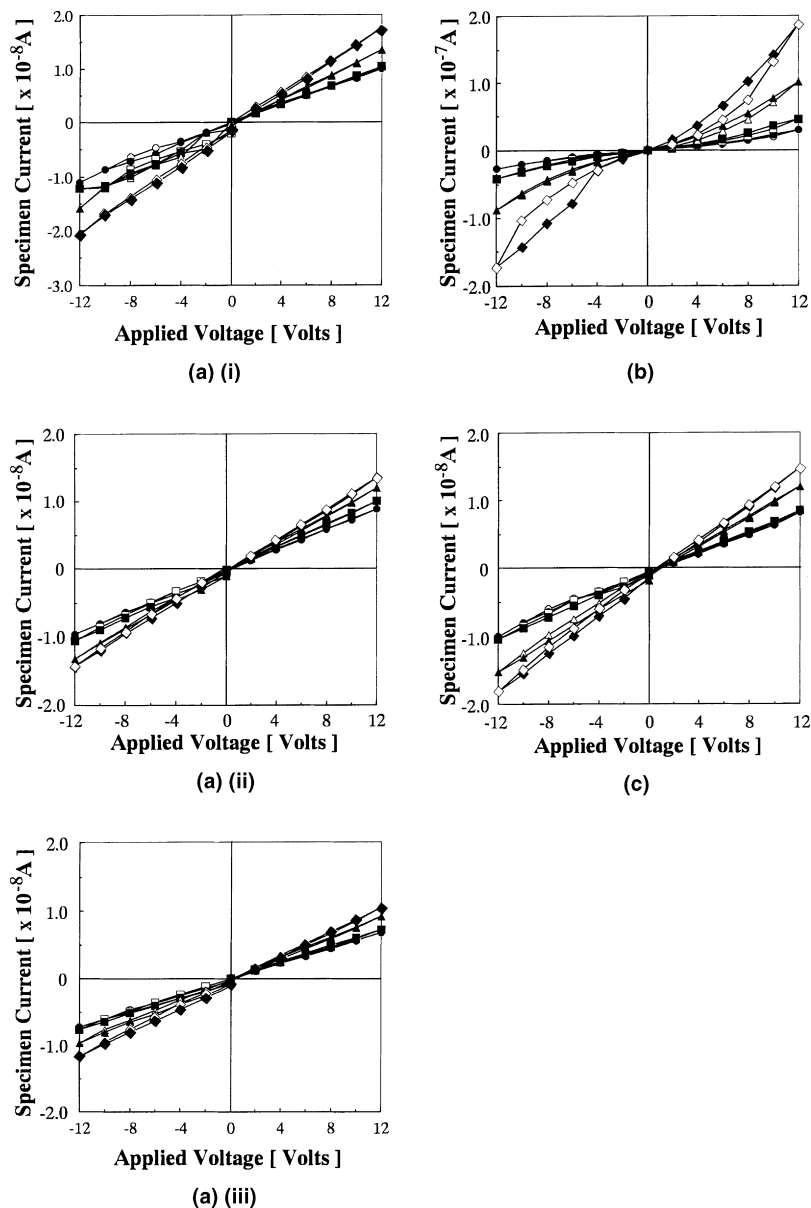


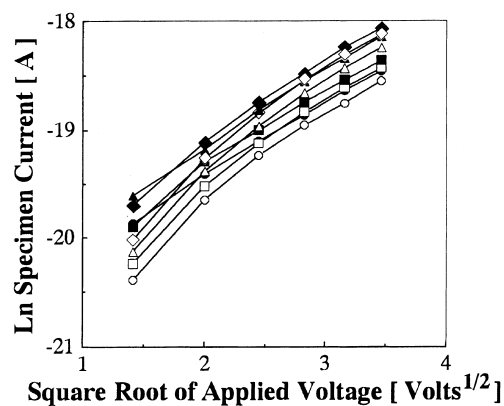
Fig. 1. I - V relationships of (a) Zircaloy-2 with (i) gold, (ii) copper, and (iii) zirconium electrodes, (b) improved Zircaloy-2 and (c) Zircaloy-4 oxides with Cu electrodes under irradiation with a 1 MeV electron flux of 1.4×10^{18} e/m² s at temperatures of about (○) 296 K, (□) 426 K, (△) 575 K and (◇) 675 K. The open and filled symbols correspond to the increasing and decreasing applied voltage, respectively.

significant hysteresis. The degree of hysteresis of improved Zircaloy-2 oxide increases with increasing irradiation temperature. It should be noted here that the I - V characteristics of Zircaloy-2 and Zircaloy-4 oxides before irradiation was non-ohmic, where the experiments had been carried out inside a bell jar with the same experimental conditions except irradiation. The changing of non-ohmic behavior of Zircaloy-2 and

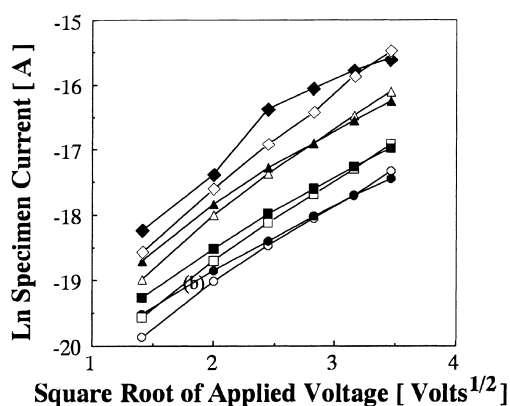
Zircaloy-4 oxides into almost ohmic during irradiation is most likely due to irradiation effect. The non-ohmic Schottky effect usually forms after making contact with an electrode having a different work function from that of Zircaloy oxides. The Schottky barrier assists flowing electrons with one polarity in the specimen. On the other hand, at reverse polarity, the Schottky barrier hinders the electron current [8]. The interpretation of this

behavior might be very complicated; however, at least it can be said that irradiation with 1 MeV electrons changes (lowers) the Schottky barrier between oxide and electrode. A previous study of the electrical characteristics of in reactor and out reactor Zircaloy-2 oxides [6] found that a current on the order of micro-ampere flowed through the specimen at zero potential at 295°C which is very unlikely in our study. One drawback of Ref. [6] is that the electric contact from the oxide was taken by platinum electrode through dipping the specimen into eutectic salt which may give different interpretation of the whole study. Shirvington could not find any reasonable difference in the conductivity between in-reactor and out-reactor oxidized specimens. In fact the oxides of in reactor specimens should be more thicker than that of out reactor control because oxygen ions are more enhanced under irradiation. Therefore, there should be a difference in the conductivity between in-reactor and out-reactor specimens. The transport of electrons or diffusion of oxygen should be affected differently during oxide formation under irradiation compared to out-of-reactor controls, producing different rates of oxidation growth. If one wants to see the discrepancy between in-reactor and out-reactor specimens, one should do in-situ measurement of conductivity and in that case one may see the difference.

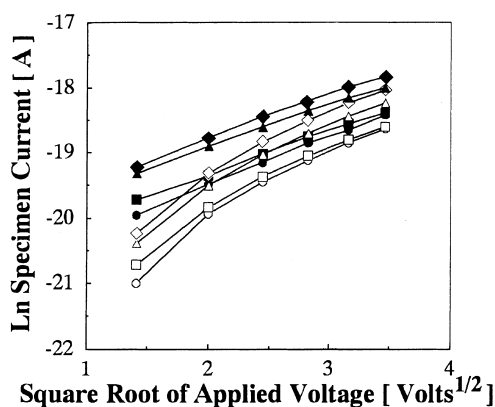
Although the I - V behavior of Zircaloy-2 and Zircaloy-4 oxides are almost ohmic, suppose the I - V behavior of all types of specimens with all electrodes are associated with Schottky emission and Poole-Frenkel model and are redrawn in accordance with modified Schottky emission and Poole-Frenkel model ($\ln I$ versus $V^{1/2}$) [8]. The semi log plot of current of all the specimens with copper electrode against the square root of applied voltage is shown in Fig. 2. Linear lines within experimental error are obtained only for improved Zircaloy-2 oxide. The non-linear curves in Fig. 2 for Zircaloy-2 and Zircaloy-4 oxides suggest the Schottky emission and Poole-Frenkel model are not applicable for Zircaloy-2 and Zircaloy-4 oxides during irradiation. Conversely, either Schottky emission or the Poole-Frenkel model may be the conduction process in improved Zircaloy-2 oxide. The current at zero potential is obtained by extrapolating $\ln I$ versus $V^{1/2}$ curves and plotted $\ln(I_0/T^2)$ versus $1/T$ for the Schottky model. The $\ln(I/V)$ versus $V^{1/2}$ plot is plotted for Poole-Frenkel model from 296 to 680 K (Fig. 3) in order to differentiate between the Schottky and Poole-Frenkel mechanisms and to know which mechanism is better fitted by the curves. However, due to the non-linearity of those curves it is not clear which conduction mechanism is present in the improved Zircaloy oxide. This can be a consequence of either one or both mechanisms involved in the conduction process of improved Zircaloy-2 oxide. As mentioned before [8], in the previous study the I - V measurement was done before irradiation



(a)



(b)



(c)

Fig. 2. $\ln I$ - $V^{1/2}$ relationships of the (a) Zircaloy-2, (b) improved Zircaloy-2 and (c) Zircaloy-4 oxides curves with Cu electrodes of Fig. 1 which are redrawn in accordance with the modified Schottky and Poole-Frenkel models. The open and filled symbols correspond to the increasing and decreasing applied voltage, respectively.

and the specimen current was almost proportional to the voltage but differed with an amplitude due to the

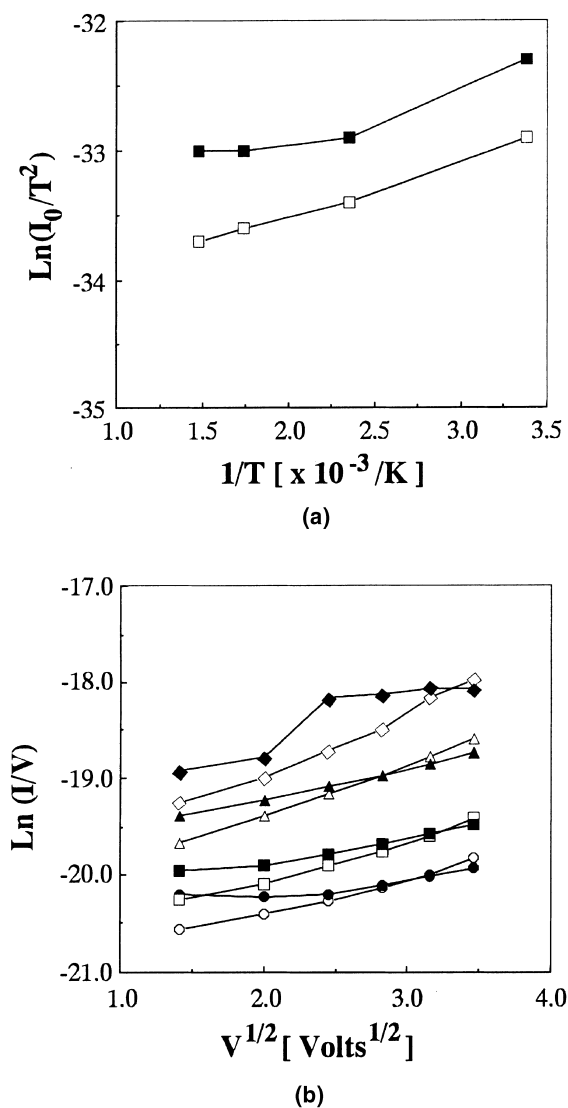


Fig. 3. (a) $\ln(I_0/T^2)$ at zero potential as a function of reciprocal temperature and (b) $\ln(I/V)$ versus square root of potential at temperatures of (○) 296 K, (□) 426 K, (△) 575 K and (◇) 675 K for improved Zircaloy-2 oxide films with Cu electrodes for discriminating Schottky and Poole–Frenkel processes. The open and filled symbols correspond to the voltage applied at the base and the center electrodes, respectively.

function of the interface between oxide and metal layers. It was also argued that the specimen current of Zircaloy oxide films with voltage at the base and the center was more or less directly controlled by Schottky barrier. However, the electrode effect might be changed under electron irradiation. Thus the specimen current of Zircaloy oxides with positive voltage and negative voltage at base is more or less controlled by Schottky barrier and changes with irradiation.

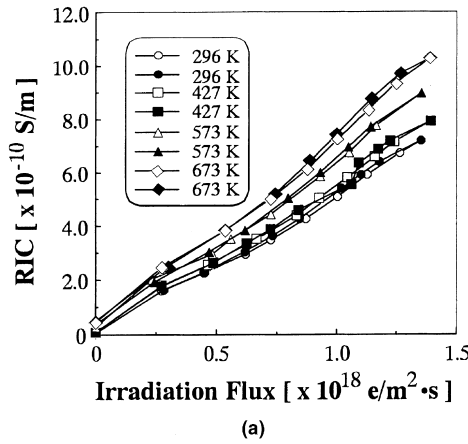
3.2. Irradiation flux dependence

Fig. 4 shows the irradiation flux dependence of RIC of Zircaloy oxides having copper electrode under 1 MeV electrons irradiation with increasing and decreasing beam intensity at various temperatures. The electrical conductivity proportionately increases with increasing irradiation flux and irradiation temperature for all specimens regardless of electrode material. No substantial difference between the conductivity during increasing and decreasing beam intensity is found in Zircaloy-2 and Zircaloy-4 oxides. But in the case of improved Zircaloy-2 oxide, the conductivity for increasing beam intensity is rather lower than that for decreasing beam intensity. Also the linearity of RIC of improved Zircaloy-2 oxide with irradiation flux becomes non-linear at higher temperatures, similar to the I – V behavior during irradiation. Temperature sensitivity of improved Zircaloy-2 oxide is the highest among all specimens, indicating the presence of more trapping level than Zircaloy-2 and Zircaloy-4 oxides. However, the strong irradiation flux dependence might be explained in terms of electronic excitation from valence band to conduction band [9] with 1 MeV high energy electrons because of good insulating behavior of Zircaloy oxides.

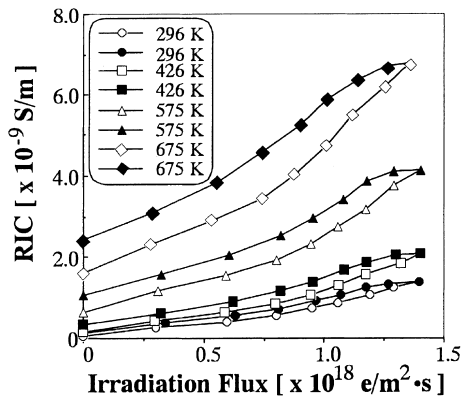
Usually the electrical conductivity (σ) of ceramic insulators during irradiation is expressed [10] by the equation $\sigma = \sigma_0 + kR^\delta$, where σ_0 is the conductivity in the absence of radiation, k a material dependent constant, R the irradiation flux and δ the irradiation flux exponent. The temperature dependence of the δ values for all oxides during increasing of beam intensity was obtained from Fig. 4 and it is shown in Fig. 5. It is evident that the δ value decreases slightly with increasing temperature. The values of δ are near unity, indicating the formation of point defects which act as trapping centers. With irradiation temperature and time, the trapping and recombination centers are produced and pronounced at higher flux region [11]. At higher irradiation temperatures, the amount of electron recombination increases, thereby retarding excitations which causes a decrease in the irradiation flux exponent.

3.3. Conductivity with beam-on and -off

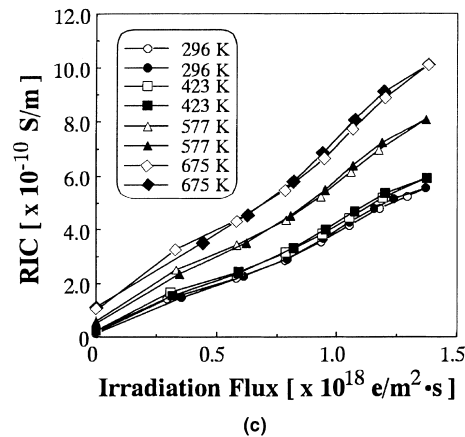
The electrical conductivity of Zircaloy-2, improved Zircaloy-2 and Zircaloy-4 oxides with Cu electrodes irradiated with a 1 MeV electron flux of 1.4×10^{18} e/m² s (7.6×10^4 Gy/s) at beam-on and -off conditions in an applied dc electric field of 1.7 kV/m is shown in Fig. 6. The specimens were exposed before, during and after irradiation for a constant time increment of 1200 s at different temperatures, which increased by about 130 K at each step from 296 to 673 K. The conductivity measurements were initiated five minutes after each increase



(a)



(b)



(c)

Fig. 4. RIC of (a) Zircaloy-2, (b) improved Zircaloy-2 and (c) Zircaloy-4 oxides having Cu electrodes under 1 MeV electron irradiation with increasing and decreasing beam intensity in a dc electric field of 1.7 kV/m at different temperatures. The open and filled symbols correspond to the increasing and decreasing of beam intensity, respectively.

in annealing temperature to allow the specimen to reach thermal equilibrium. In the absence of irradiation, the

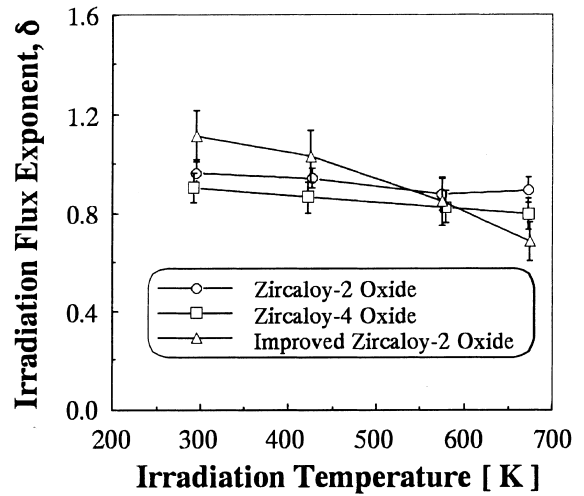


Fig. 5. Temperature dependence of irradiation flux exponent (δ) of electrical conductivity (σ) based on $\sigma = \sigma_0 + kR^\delta$ with the experimental data shown in Fig. 4, where the significance of parameters is written in the text.

conductivity is dependent on temperature but not on time. At each step after turning on the electron beam, the specimen conductivity promptly increases to a certain value approximately two orders of magnitude higher than the pre-irradiation value and then sublinearly increases with time in improved Zircaloy-2 specimen and monotonously changes or decreases with time in Zircaloy-2 and Zircaloy-4 specimens. Upon turning off the beam, most of the RIC is immediately reduced near to the unirradiation value at the respective temperatures. Even though substantial difference between the beam-on and -off conductivity is found in all specimens, the time-dependent degradation behavior exists only in improved Zircaloy-2 specimens. This may be due to the generation of more trapping levels in improved Zircaloy-2 than that of Zircaloy-2 and Zircaloy-4 oxides [12]. Analysis of the conductivity data during beam-on and -off shows that the activation energy is reduced by two to three times when the specimens are being irradiated. The reduction of this activation energy during irradiation may indicate the generation of new trapping level for electrons closer to the conduction band [13,14]. The investigation of electrical conductivity without irradiation of reduced stabilized zirconia shows that when the conductivity is electron dominant, the activation energy is in the value from 0.03 to 0.06 eV at temperatures up to 570 K [15], which is compatible with this study. Kang and his co-workers [16] irradiated ZrO₂-10%Gd₂O₃ specimen with ⁶⁰Co Gamma rays (4.3 Gy/s) with beam-on and -off at 723 K and found increasing of RIC with time during irradiation and a monotonic decrease of postirradiation conductivity with time. The enhancement of conductivity was interpreted in terms of

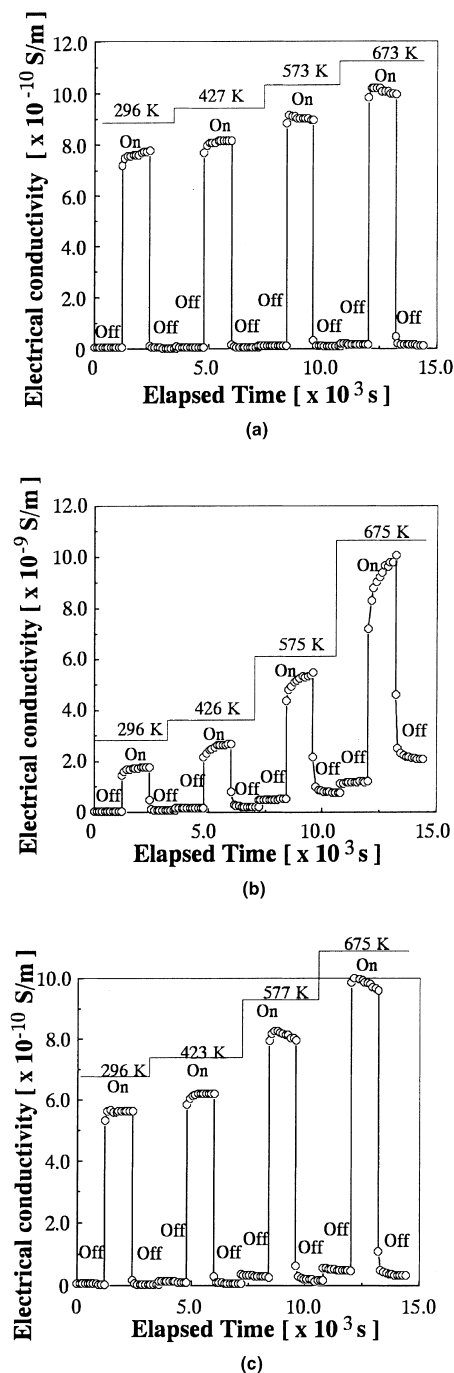


Fig. 6. Time dependence of electrical conductivity for (a) Zircaloy-2, (b) improved Zircaloy-2 and (c) Zircaloy-4 oxides having Cu electrodes under irradiation with a 1 MeV electron flux of 1.4×10^{18} e/m² s at beam-on and -off conditions.

the enhancement of oxygen ions. Contrary to Kang et al. [16], RIC abruptly increases by a few orders of magnitude when the beam is turned on and then slowly in-

creases or decreases with time in this study, representing excitation of electrons and/or interaction of excited electrons with new generated trapping levels. Harrop and his co-workers [7] have irradiated Zircaloy-2 oxide anodic and corrosion films under gamma irradiation of dose rate of 29.2 Gy/s with beam-on and -off conditions and found very puzzling and contrasting results to this study as well as to Kang et al. [16]. They examined the conductivity during beam-on and -off and did not observe any notable difference between them other than a slight beam heating effect, although the conductivity did not revert to the virgin state after irradiation. They also failed to observe any electrical properties change after a gamma irradiation dose of 2.5×10^3 Gy whereas Kang et al. found 17% change of RIC after an accumulated dose of 3.1×10^4 Gy. On the other hand, if one looks at the numerical amplitude of conductivity of these data, one can see that the conductivity of the virgin specimen increases by at least one order of magnitude after subjecting specimen to an irradiation dose of 9.2×10^7 Gy. For instance, the value of electrical conductivity of Zircaloy-2 with copper electrode before irradiation is 3.4×10^{-12} S/m and the in-beam conductivity became 7.2×10^{-10} S/m for a dose rate of 7.6×10^4 Gy/s at 300 K and clearly exhibited an irradiation flux effect (Fig. 4), representing RIC resulting through excitation of electrons from the valence to conduction band. But if we consider the absolute value of the conductivity before and after irradiation during beam-off at a constant temperature and time, we can see that the conductivity is recovered (Fig. 6). Depending on the beam-on and -off conductivity characteristics, it is concluded that energetically excited electrons and thermally excited electrons take part as a major contributor to the electrical conductivity under beam-on and -off conditions, respectively [9,10,14]. The difference of the electrical conductivity of Zircaloy-2 and -4 vs. improved Zircaloy-2 oxides at beam-on condition at different temperatures again indicates stronger dependence of improved Zircaloy-2 oxide on irradiation flux and temperature. This effect may be explained by the difference of type of precipitates and of interface between oxide and metal of Zircaloy oxides [17]. However, the discrepancy in the electrical conductivity at beam-on and -off [8], of all oxides was not due to the variation of electrode materials (Au, Cu, Zr). It may be summarized from Zircaloy oxides data that the ionic conductivity is negligibly small compared with that of the electronic conductivity in Zircaloy oxide specimens up to 680 K. According to the model of the oxidation of Zircaloy [8], since electrons are the conduction species then the rate of oxidation reaction is controlled by the diffusion of negative oxygen ions because of maintaining the charge equilibrium of the oxidation process. Recently, Nowotny and his co-workers [18] have also found the negative oxygen ions are the rate controlling factor of oxidation of Zircaloy

which are equivalent to the transport of oxygen vacancies. The electrical conductivity of improved Zircaloy-2 oxide is comparatively higher than that of Zircaloy-2 and Zircaloy-4 oxides. In fact, the superior corrosion behavior of improved Zircaloy-2 is not evident from this study because of the ionic rate controlling factor of Zircalloys. Further experiments with and without irradiation are necessary to re-examine the results obtained in this study.

4. Conclusions

No substantial electrode effects are found. The I - V characteristics of Zircaloy-2 and Zircaloy-4 oxide films are approximately ohmic and in the case of improved Zircaloy-2 oxide film are non-linear. The current is electronic in nature in all cases, and is apparently associated with ohmic and Schottky and/or Poole-Frenkel processes, respectively. The results presented here show that the electrons motion dominates the electrical conductivity of Zircaloy oxides both with and without ionizing radiation. Hence, it is very likely that the diffusion of negative oxygen ions controls the oxidation process of Zircalloys. The mechanism responsible for the superior corrosion behavior of improved Zircaloy-2 is not evident from this study.

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