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The electrical conductivity of zircaloy oxide films

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Abstract

The electrical conductivity of Zircaloy-2, improved Zircaloy-2 and Zircaloy-4 oxide films has been measured using gold, copper and zirconium electrodes over the temperature range of 296–723 K. No notable discrepancies among the temperature dependence of electrical conductivity in the oxide films obtained from all electrodes were found. Depending on the activation behavior it is thought that the conductivity corresponds to the thermal excitation of electrons. The current–voltage characteristics of all oxide films show non-Ohmic behavior where the bulk current (electronic in nature) is associated with the Schottky and/or the Poole–Frenkel processes. On the basis of these results, it is concluded that the electron motion dominates the electrical conductivity of zircaloy oxide films. Therefore the slow-diffusing negative oxygen ions control the oxidation process of zircaloys. © 1998 Elsevier Science B.V.

1. Introduction

Zircaloy-2 and Zircaloy-4 are being used in light water reactors as fuel cladding and channel box materials. Under such circumstances, enhancement of corrosion or oxidation is one of the critical problems for confirming their high burnup capability [1]. The formation of oxides can be simply explained using the model shown in Fig. 1. It is very clear from this figure that the dissociation of water generates negative oxygen ions which diffuse towards the metal side through oxide and the ionization of zirconium produces electrons which transfers opposite to oxygen ions. The reaction between zirconium and negative oxygen ions results in zirconium oxide. Thus, the oxidation of zircaloys is unlikely to happen unless electrons are transferred from the metal to water with the diffusion of negative oxygen ions to the opposite direction of electrons. In other words, the oxidation process is due to the diffusion of negative oxygen ions and the movement of electrons with one acting as the rate controlling species. However, even though many researchers pay attention to the oxidation phenomenon of zircaloys because of its practical importance for the stable operation of fission reactors, no agreements have been achieved to specify the controlling species of the oxidation. Cox found a complex behavior of current in Zircaloy-2 oxides when the specimens were placed in molten salt and showed that the electronic current fits a Schottky emission process whereas the ionic current follows the Tafel relationship [2]. He also argued that the electronic conductivity was controlled by minor alloying elements by comparing the characteristics of unalloyed and alloyed oxides. He concluded that both electrons and ions were equally important in the rate controlling process. A subsequent study by Shirvington [3] has proposed Schottky type electronic conduction takes place and passes through intermetallic precipitates in the Zircaloy-2 oxide films. Inagaki et al. [4] have done photo current measurements of zircaloy oxide films and found positive current which is consistent with electron movement from the oxide surface to the metal substrate. In addition, they have studied the effects of different alloying elements such as Zr, Sn, Cr, Ni and Fe on the oxidation process and suggested that the electrical conductivity of the oxide of Zr–Sn–Fe elements is the lowest among all alloys.

Thus, the review of the literature indicates no agreement, suggesting the probable reasons for this conflict to be due to different impurities as well as the discrepancies

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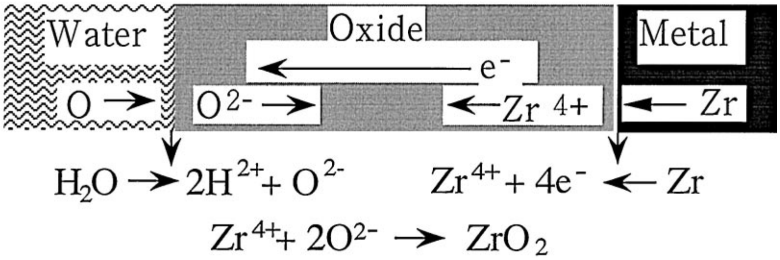

Fig. 1. A schematic diagram showing the formation of oxide film on zirconium and the reactions during oxidation.

of electrode materials. These conflicting results/hypotheses lead us to do experiments of electrical conductivity and current–voltage (*I*–*V*) measurements of zircaloy oxide films using several electrode materials. It is not necessary to mention the importance of the electrical conductivity measurements which is a good way to clarify the controlling species depending on the activation process. Because the current flowing through oxide (corrosion) films may consist of ionic and electronic current. By analyzing the pronounced species of conductivity, it is possible to find the rate controlling species of zircaloys responsible for oxidation. It should be noted that the rate controlling species of oxide film growth is always associated with the slow species in the conductivity measurements. So if the electrical conduction through zirconium oxide film is predominantly due to electrons then the rate controlling process should be negative oxygen ions. A complete treatment of the zircaloy oxide films before and during irradiation is, however, indispensable to give any definitive conclusions on the rate controlling process of zircaloy oxide films. Thus the objective of the present study is to find the controlling species of oxidation of zircaloys and the relationship between the electrical conductivity of zircaloy oxide films and the corrosion of zircaloys.

2. Experimental procedure

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 in the pressure of 10.3 MPa. The chemical composition (wt%) of zircaloys used in the present study is shown in Table 1. The thickness of oxide films was 3 μm. 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. Precautions were taken at the time of using ultrasonic cutter for preventing any cracks in the oxide films. The total thickness of the specimen including zircaloys after one side polishing was reduced to about 200 μm. On the oxide films at the top side of specimens, a center electrode of 2 mm diameter and a guard electrode of 4.5 and 3.5 mm outer and inner diameter, respectively, were made by vacuum deposition of gold, copper and zirconium, having a work function of 4.8, 4.4 and 3.9 eV, respectively, in order to differentiate the role of electrode materials (Schottky effect) with the bulk behavior in a vacuum pressure of 10^{-4} Pa. The abraded zircaloy metal side of the specimen (bottom side) served as base electrode. The electrical conductivity and *I*–*V* measurements were performed in a vacuum bell jar at a pressure of 10^{-4} Pa over the temperature range of 296–723 K. An electric field of 1.7 MV/m (applied voltage was 5 V) was continuously applied to the base electrode during the measurements of temperature dependence of electrical conductivity with a Hewlett–Packard 4339A high resistance meter and the specimen current was recorded every two minutes using the same device. The *I*–*V* behavior of specimens at different temperatures was checked by changing applied voltages in the forward and backward directions. The specimen current was measured about 30 s after applying a voltage with 2 V increments in order to get a stable reading of the specimen current in the *I*–*V* measurements. However, at the time of zero voltage it is delayed more than 2 min for getting more accuracy of the specimen current at different temperatures. More details of the experimental procedure and the specimen holder used are illustrated elsewhere [5].

Table 1
Chemical composition (wt%) of zircaloys used in the present study

	Sn	Fe	Cr	Ni	Zr
Zircaloy-2	1.32	0.17	0.10	0.07	balance
Improved Zircaloy-2	1.48	0.23	0.10	0.09	balance
Zircaloy-4	1.29	0.21	0.11	–	balance

3. Results and discussion

Fig. 2 shows the *I*–*V* behavior of Zircaloy-2, improved Zircaloy-2 and Zircaloy-4 oxides with copper electrode at indicated temperatures as an example of sequentially treated oxides with various electrode materials. The *I–V* characteristics of zircaloy oxide films was more Ohmic at lower temperatures than that of higher temperatures and the degree of hysteresis is more pronounced at higher voltages and temperatures. The specimen current is almost proportional to the voltages but differs with an amplitude which might be due to the function of the interface between oxide and metal layers. However, the difference between the magnitude of the specimen current with voltage at the base and the center of specimen can be explained by using the band structure of the metals and the semiconductors. Generally, it is known that if the Fermi level of semiconductors is higher than that of metals, depending on the work function of the electrode materials, the electrons will flow from semiconductors to metals. This flowing of electrons results in a decrease in electron density which bends the band of semiconductor and make an energy barrier for transferring of electrons from metals to semiconductors. This is called a Schottky barrier [6]. Thus, the Schottky barrier acts differently with applying voltage at base and center electrodes. However, the specimen current of zircaloy oxide films with voltage at the base and the center is more or less directly controlled by the Schottky barrier. In the case of gold electrode, although the specimens current generally increases and decreases with increasing and decreasing applied voltage, respectively, the shifting current of Zircaloy-2 specimen in the negative quadrant is higher than that of improved Zircaloy-2 and Zircaloy-4 specimens. Abrupt increasing in the specimen current occurs when temperature is raised from ∼ 500 to 700 K in all specimens with all types of electrodes. However, the dielectric strength, i.e. the ability to withstand a large field of improved Zircaloy-2 oxide films, was lower than that of the Zircaloy-2 and Zircaloy-4 oxide films and it occurred at the early stage in the case of the gold electrode. The non-Ohmic behavior may be due to the difference in the work function of the electrode material and the zircaloy. Finally, we used zirconium electrodes (work function is 3.9 eV) to make a more definitive comparison of the effects of work function of electrode materials on *I–V* curves of zircaloy oxides. The *I–V* behavior of oxides with zirconium electrode is quite similar to that of other electrodes. It is seen that the current passing through all specimens at zero potential is not negligible even though it is small amount. For the precise interpretation of the specimens current at zero potential it is necessary to make the *I–V* plots in the same scale. When it is done, no notable difference in the zero-voltage specimens current among all specimens is found. In all *I–V* measurements, the specimen currents were rather time dependent at lower voltage (less than 2 V) and at lower temperature and it is

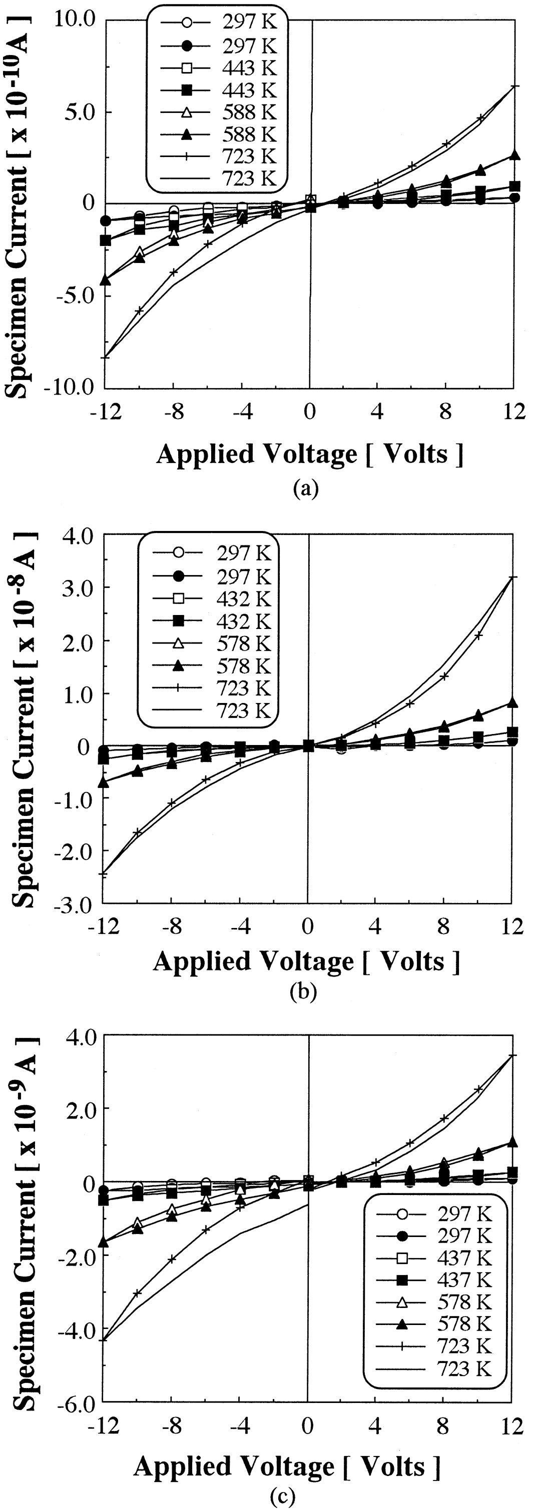

Fig. 2. *I–V* relationships of (a) Zircaloy-2, (b) improved Zircaloy-2 and (c) Zircaloy-4 oxide films with copper electrode at indicated temperatures. The unfilled and filled symbols correspond to the increasing and decreasing applied voltage, respectively.

believed to be due to a space-charge buildup in the electrode [7]. Shirvington [8] et al. have mentioned that the current flowing at zero potential represents the oxidation ionic current which is exactly equal to electronic current. We have come to know [9] that the work function of Zircaloy-4 oxide is 3.9 eV which is exactly same as that of zirconium electrode. This suggests that the interface between oxides and electrodes may not have effect on the specimen current. So probable reasons for flowing current through specimen at zero applied voltage might be due to the reduction of oxygen and the effect of interface between zircaloy metal and oxide film. In fact, however, no substantial dependence of the specimens current on the electrode materials has been found.

The remarkable coincidence in the results of I–V curves using gold, copper and zirconium electrodes (not in amplitude but in qualitative behavior), again inspired us to perform the temperature dependence of electrical conductivity measurements of zircaloy oxide films with all electrode materials. Cox [2] has mentioned the necessity of the measurements of electrical conductivity of zircaloy oxides as a function of temperature. In order to understand the process involving in the transport species of zircaloy oxides, a series of temperature dependence of electrical conductivity will be presented. The temperature dependence of electrical conductivity of zircaloy oxide films using copper deposited electrodes is shown in Fig. 3. The temperature was changed at the rate of ~ 3 K/min at the moment of increasing and decreasing temperature. The conductivity was measured at every 5 K with the applied voltage of 5 V for all oxides (applied electric field is 1.7 MV/m) at the base electrode. The electrical conductivity increases and decreases with increasing and decreasing temperature, respectively and there is no sign of saturating the conductivity with increasing temperature. The hysteresis during increasing and decreasing temperatures with copper electrode is almost alike except the difference between the conductivity at the lower temperatures which is about a factor of three. The visual hysteresis of the conductivity may be due to the variation of the oxygen in the zirconium oxide matrix during measurements inside the bell jar. The tendency for increasing of activation energies is observed at higher temperatures for all of the specimens. If the electrical conductivity of zircaloy oxide films is considered simply a process of thermal activation, the estimated activation energy of all oxide films is in the range of 0.20 ± 0.05 eV which is supposedly corresponding to the thermal excitation of electrons. Charlesby [10] measured the electrical current of zirconium oxide film at different temperatures and estimated the activation energy of 0.375 eV and argued for electronic conductivity. The investigation of electrical conductivity of reduced stabilized zirconia shows that when the electronic conductivity is dominant, the activation energy is changed from about 1 eV to a value from 0.03 to 0.06 eV at temperatures up to 570 K [11], which is very compatible with this study. Those values of activation energy are analogous to our results regardless of oxide types and electrode materials. Comparisons of the activation energy among all types of oxide films show that the activation energy of improved Zircaloy-2 oxide decreases at the time of decreasing temperature at higher temperature than that of increasing temperature.

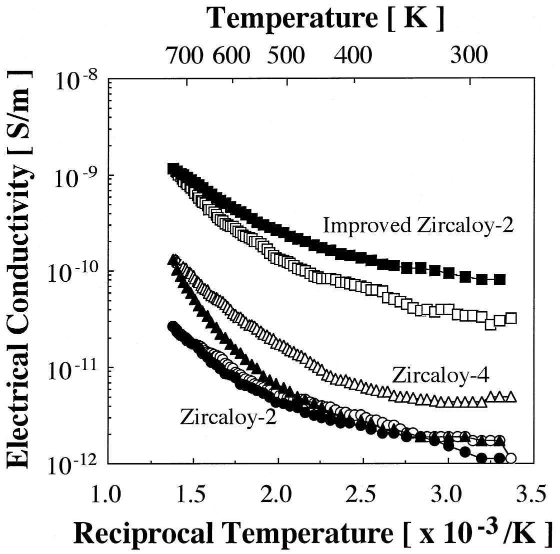

Fig. 3. Temperature dependence of electrical conductivity of Zircaloy-2, improved Zircaloy-2 and Zircaloy-4 oxide films with copper electrode in an applied electric field of 1.7 MV/m. The unfilled and filled symbols correspond to increasing and decreasing temperatures, respectively.

Further analysis is made to calculate the energy difference between the trap level and the bottom of the conduction band through the temperature dependence of electrical conductivity and found that it is identical to the activation energy. The magnitude of the electrical conductivity of Zircaloy-4 and Zircaloy-2 specimens is almost equivalent and lower than that of improved Zircaloy-2 specimen. Almost overlapping behavior in the electrical conductivity with gold electrode is found in Zircaloy-2 and Zircaloy-4 oxide films which is lowered from improved Zircaloy-2 oxides by two orders of magnitude. The conductivity of improved Zircaloy-2 oxide films at the moment of decreasing temperature is always higher than that of the increasing temperature over the whole temperature range which is just opposite to the cases of Zircaloy-2 and Zircaloy-4 oxide films. No remarkable slope change is found in all oxides. Kumar et al. [12] have measured the electrical conductivity of zirconium oxides and made the plots of log conductivity versus reciprocal temperature and log conductivity times temperature versus reciprocal temperature for the electronic conductivity and ionic conductivity, respectively. They showed that although the ionic conductivity prevailed at temperatures lower than 923 K, the electronic conductivity was always greater than the ionic conductivity above 973 K. What we would like to emphasize here is that the specimens exhibiting electronic conduction may prior to the ionic conduction up to this temperature range (< 723 K). Thus it is reasonable to hypothesize that the ionic conductivity may be pronounced at higher temperatures. Cox [2] has mentioned that surface diffusion at the oxide-environment interface is most likely associated with the process of surface conduction of electrons. It suggests that the measurements of bulk conductivity of zircaloy oxide films have rather surface conductivity effect. In fact in our experiments, standard electric guarding technique has been used in order to avoid surface current effect. So even if there exist any surface leakage currents, they would not have affected our electrically guarded measurements of the bulk specimen current.

Our final attempt was to perform the conductivity measurements using the same work function as that of the major element of the alloy. With all kinds of electrodes, the conductivity in the improved Zircaloy-2 oxide is higher than that of Zircaloy-2 and Zircaloy-4 oxides. Though the increasing and decreasing conductivity behavior with temperature having zirconium electrode is similar to that of other electrode materials, the range of conductivities of all specimens varies with a magnitude of 10 which is believed due to the difference in the alloy composition. An important conclusion to be drawn from the temperature dependence of electrical conductivity results is that the highest electrical conductivity of the improved zircaloy oxide, indicating the role of (higher amount of Sn and Fe) solutes in this alloy. It is well known that the band gap energy of zircaloy oxides is around 6.5 eV which is much higher than the activation energy. Thus the lower activation energy rejects the possibility of electron excitation from the valence to the conduction bands. Therefore the presence of donor centers and trapping centers in the forbidden band is reasonable which can excite electrons thermally at field assisted condition [13]. This idea is analogous to the proposal proposed by Harrop and Wanklyn [14] that the carrier mobility of semiconductors and insulators tends to decrease markedly with increase of temperature of a given substance through the measurements of electrical conductivity of zirconiums and Zircaloy-2 oxide films.

We have already understood that the conductivity of zircaloy oxide films is electronic in nature. Due to the non-Ohmic behavior of zircaloy oxides, it is essential to clarify whether the current of oxides is passed through bulk or is controlled by electrodes. Several researchers [3,15–17] have investigated behavior of metallic oxides by using the well known Schottky emission and Poole–Frenkel models. The current flow based on the modified

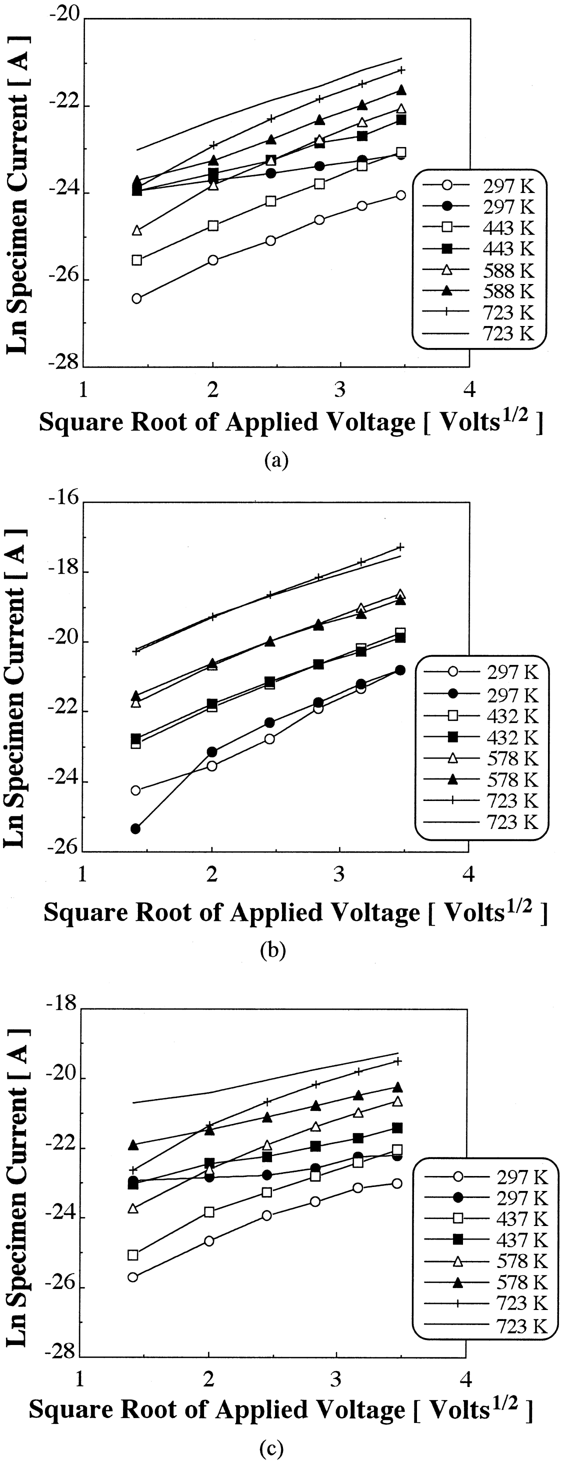

Fig. 4. Ln $I - V^{1/2}$ relationships of (a) Zircaloy-2, (b) improved Zircaloy-2 and (c) Zircaloy-4 oxide films with copper electrode at indicated temperatures. Here, I and V represent specimen current and applied voltage, respectively. The unfilled and filled symbols correspond to the increasing and decreasing applied voltage from zero voltage, respectively.

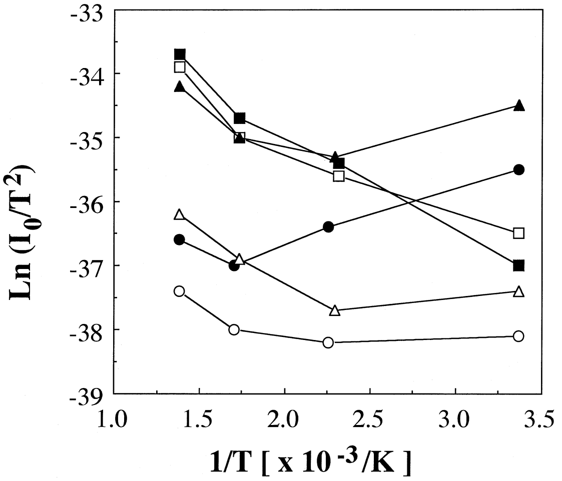

Fig. 5. Ln (I_0/T^2) as a function of $1/T$ for (○) Zircaloy-2, (□) improved Zircaloy-2 and (△) Zircaloy-4 oxide films with copper electrode. Here, I_0 and T represent specimen current at zero potential and temperature, respectively. The unfilled and filled symbols correspond to the voltage applied at the base and the center electrodes, respectively.

Schottky emission and the Poole–Frenkel mechanisms is, respectively, expressed [15] by

$$J = AT^2 \exp\left(\frac{e^{3/2}V^{1/2}}{kT\sqrt{\pi\varepsilon d}} - \frac{\Phi}{kT}\right) \tag{1}$$

and

$$J = G_0\left(\frac{V}{d}\right)\exp\left(\frac{2e^{3/2}V^{1/2}}{kT\sqrt{\pi\varepsilon d}} - \frac{\chi}{kT}\right), \tag{2}$$

where A is the Richardson constant, T the temperature, e the charge on the electron, V the voltage, k the Boltzmann's constant, ε the dielectric constant, d the thickness of the insulator, ϕ the work function, G_0 a constant with the dimension of the conductivity and χ the energy difference between the trap level and the bottom of the conduction band.

When the specimens current from the I–V characteristics of our results is plotted in accordance with both the Schottky emission and the Poole–Frenkel models (ln I versus $V^{1/2}$) [3,15,16] linear lines within the experimental error are obtained. For instance, the plot of the logarithmic current of the specimens with copper electrode against the square root of applied voltage is shown in Fig. 4. Then the values of current are extracted at zero potential by extrapolating $\ln I$ versus $V^{1/2}$ curves and plotted $\ln(I_0/T^2)$ versus $1/T$ according to the Schottky emission (Fig. 5). On the other hand, ln(specimen current divided by potential) as a function of the square root of the applied voltage is plotted at a constant temperature of 723 K according to the Poole–Frenkel model (Fig. 6). The purpose of this plotting of the two curves is to differentiate between the two mechanisms by checking which mechanism is better fitted to the curves. However, both curves deviate from linearity. So it is not clear at present which conduction mechanism is followed by the current of the specimen.

Hartman et al. [15] have concluded through identical calculations for silicon oxide films that the conduction mechanism is most likely neither due to Schottky emission nor Poole–Frenkel effect but rather due to bulk limited conduction mechanism. An extensive analysis of I–V curves of Zircaloy-2 oxide films was made by Shirvington [3] where he plotted a series of I–V curves such as I–V, I–V^2, I–V^3, log I–V or log I–$V^{1/2}$ and concluded that the electron was the conduction species mechanized either by Schottky emission or by Poole–Frenkel model. As we failed to discriminate between Schottky emission and Poole–Frenkel model, there is a possibility of involving, either one or both mechanisms, in the conduction process of the specimens current. Simmons [13] proposed a conduction model for insulators on the basis of shallow neutral traps and deep donors and concluded bulk conductivity associated with Schottky effect. It is reported that the applied voltage dependence of the specimens current represents the bulk conduction described by the Poole–Frenkel mechanism [18]. Shirvington [3] has argued that the conduction mechanism of Zircaloy-2 oxides is either by Schottky emission or Poole–Frenkel excitation through a thin ZrO_2 layer over the intermetallic precipitates. The current flows due to the Schottky effect might not be the controlling process during oxidation because of the major portion of the current flows through bulk effect [2]. Due to the strong dependence of the specimen current on applied voltage regardless of electrode materials, it may be con-

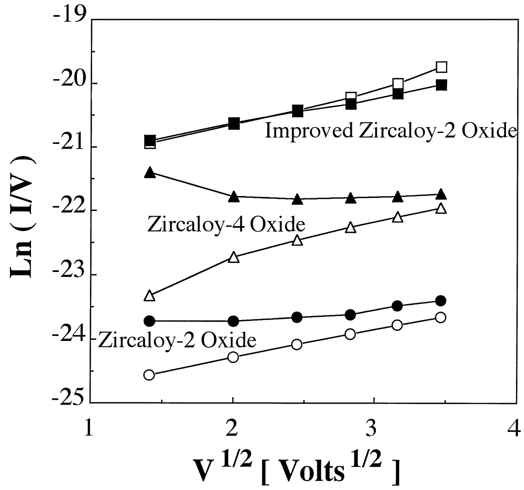

Fig. 6. Ln (I/V) as a function of $V^{1/2}$ for (○) Zircaloy-2, (□) improved Zircaloy-2 and (△) Zircaloy-4 oxide films with copper electrode at 723 K. Here, I and V represent specimen current and applied voltage, respectively. The unfilled and filled symbols correspond to the voltage applied at the base and the center electrodes, respectively.

cluded that the current flows through bulk of zircaloy oxide films which is electronic in nature. In the case of improved Zircaloy-2 oxide, the hysteresis is higher than that of Zircaloy-2 and Zircaloy-4 oxides i.e. the effect of applied voltage is highest and its resistance is lowest. Also the estimated highest energy difference between the trap level and the bottom of the conduction band (0.25 ± 0.01 eV) occurred for improved Zircaloy-2 oxide, manifesting stronger electronic conduction takes place in improved Zircaloy-2 oxides because the trap depth is identified with the thermal activation energy [15]. In addition, the stronger temperature dependence of I–V curves as well as electrical conductivity in improved Zircaloy-2 oxides is believed to be due to a higher amount of Ni and Fe which have anti-corrosive behavior thereby improving the corrosion resistance in improved Zircaloy-2 [4]. In our study, however, it is concluded that only electrons contributed to the conduction process, indicating that the negative oxygen ion is the controlling factor of zircaloy oxidation.

4. Conclusions

No visible effects of electrode materials on the specimen current of zircaloy oxides are found. The I–V characteristics show non-Ohmic behavior and the current is electronic in nature which passes through bulk associated with the Schottky and/or the Poole–Frenkel processes. Results of zircaloy oxides show that the electron motion most likely dominates the electrical conductivity of zircaloy oxides. Therefore the slow-diffusing negative oxygen ions control the oxidation process of zircaloys. The electrical conductivity of improved Zircaloy-2 oxide is strongly temperature dependent and is comparatively higher than that of Zircaloy-2 and Zircaloy-4 oxides. Although the electronic conductivity of improved Zircaloy-2 oxide is highest, it is not compatible to the oxidation behavior of improved Zircaloy-2 because of the ionic rate controlling process of zircaloys.

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