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Review of the Oxidation Rate of Zirconium Alloys

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Abstract

The oxidation of zirconium alloys is one of the most studied processes in the nuclear industry. The purpose of this report is to provide in a concise form a review of the oxidation process of zirconium alloys in the moderate temperature regime. In the initial “pre-transition” phase, the surface oxide is dense and protective. After the oxide layer has grown to a thickness of 2 to 3 μm 's, the oxidation process enters the “post-transition” phase where the density of the layer decreases and becomes less protective. A compilation of relevant data suggests a single expression can be used to describe the post-transition oxidation rate of most zirconium alloys during exposure to oxygen, air, or water vapor. That expression is: Oxidation Rate = $13.9 \text{ [g/(cm}^2\text{-s-atm}^{-1/6}) \exp(-1.47 \text{ eV/kT}) \times P^{1/6} \text{ (atm}^{1/6})]$

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1. Introduction

The oxidation of zirconium alloys is one of the most studied processes in all of the nuclear industry. As an example, keying in the words "Zircaloy" and "oxidation" in the Los Alamos Science Search Plus web site yields over 800 references. While many of these reports are written to address the reaction of fuel and steam with Zircaloy in the case of a nuclear accident, there are still a substantial number of reports dealing with the oxidation of Zircaloy at temperatures of 800 K and below. The purpose of this report is to present as briefly as possible a working knowledge of the chemistry and kinetics of the oxidation of zirconium alloys at moderate temperatures. In addition, a single equation describing the oxidation rate of Zircaloy as a function of temperature and oxygen (or water vapor) pressure is given.

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2. Review

Regardless of the type of oxidant (oxygen, water, water vapor, CO, etc) to which zirconium or its alloys such as Zircaloy-2 and Zircaloy-4 are exposed, the general behavior of the process is more or less the same [1-8]. Due to relatively low diffusivity of oxygen in zirconium [9,10] and due to the chemical affinity of zirconium for oxygen, the formation of the oxide occurs immediately upon contact even at the lowest pressures of the oxidant. While a small quantity of oxygen may actually be in solution in the Zircaloy beyond the oxide layer, upon formation of even the thinnest oxide layer, all future uptake of oxygen is then controlled by the migration of the oxygen through the oxide layer. The initial oxidation process is referred to as “pre-transition” [1-8]. The pre-transition phase of zirconium oxidation lasts until the oxide layer reaches a thickness of approximately 2 to 3 μm 's. While there is some disagreement about the exact time dependence of the oxidation, most of the researchers agree that the initial weight gain of the oxide is parabolic (proportional to $t^{1/2}$), changing over to cubic (proportional to $t^{1/3}$), then changing over to the “post transition” linear oxidation. Figure 1 shows a typical oxidation curve for temperatures in the range of 600 K. While the very first part of the parabolic phase can be thought of as the time when the near surface sites on the zirconium are being filled, the subsequent transition from parabolic to cubic is described by Yoo et al. [1] as being driven by the chemical and stress gradients across the narrow oxide layer. During the pre-transition phase, the oxide is quite dense and protective, containing an appreciable amount of tetragonal zirconia. At this early stage of the oxidation, the stable phase of the zirconia should be monoclinic. According to Yoo et al. [1], it is the compressive stress in the oxide layer that stabilizes the tetragonal phase. Because the oxide layer is a mixed ionic electronic conductor, the oxygen migration through the oxide layer proceeds via a coupled diffusion of the charged components O^{2-} and electrons e^- . Once the thickness of the oxide reaches a critical level, the stress in the outer region of the layer is no longer sufficient to stabilize the tetragonal phase, and a monoclinic phase begins to form over the top of the tetragonal phase. Eventually, the larger volume of the monoclinic phase puts sufficient tensile stress on the underlying tetragonal phase, causing it to crack. Yoo claims this is the beginning of the post-transition phase. The remainder of this report will only consider the longer term, post-transition phase.

While there is contradictory evidence of whether the Zircaloy alloys have a faster oxidation rate than pure zirconium [11-14], there is no evidence of significant differences between the oxidation rates of Zircaloy-2 and Zircaloy-4 [11,15,16]. For that reason, data points shown in the tables and figures below do not differentiate between the two different alloys. Also, from the AERE Reference [12], we know that the oxidation rates for oxygen and water vapor are identical. Table 1 gives the compilation of data [3,6,7,9,12-14] on post-transition oxidation rates for Zircaloy as a function of pressure and temperature.

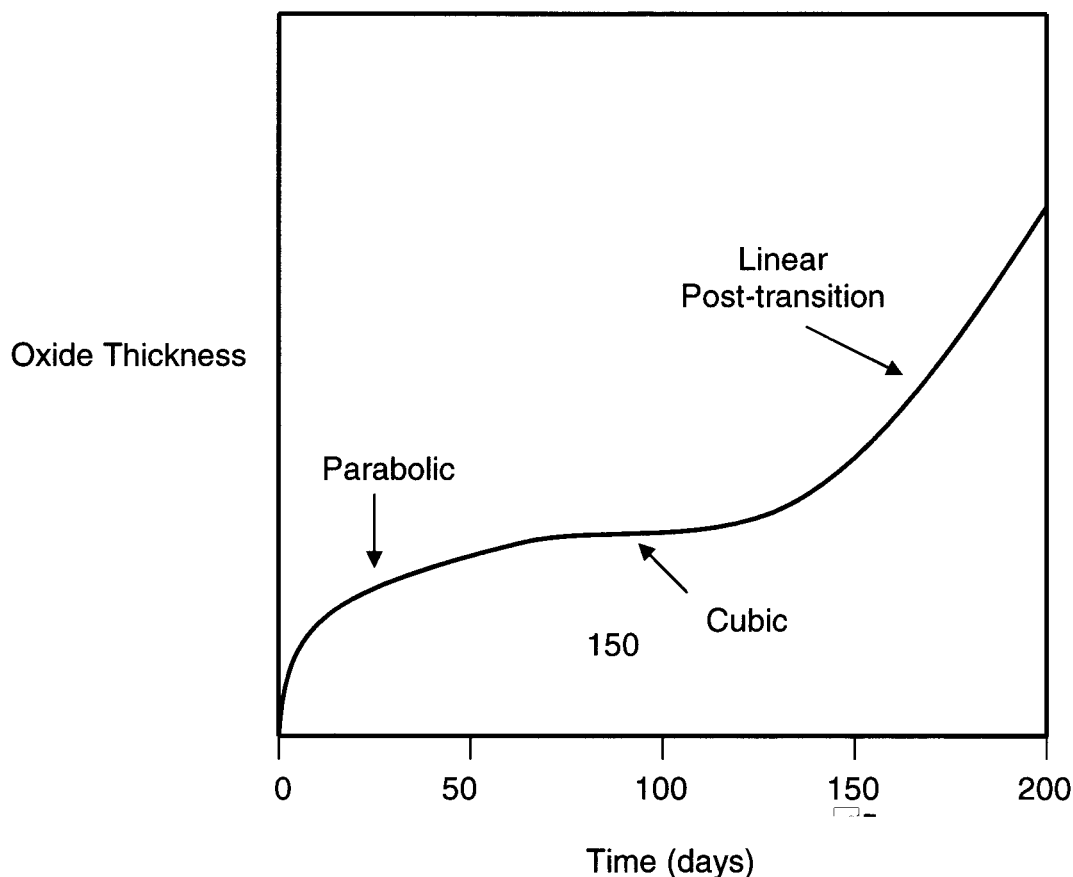


Figure 1. Typical oxidation curve for Zircaloy

Before examining results from the literature on the pressure dependence of Zircaloy oxidation, we will first examine the overall oxidation reaction and how pressure might possibly affect it. As mentioned above, in post-transition oxidation the oxide consists of two different phases. There is the outer, cracked, monoclinic layer. Inside this layer is the dense tetragonal layer, perhaps also containing some cracks or porosity, where oxygen transport is controlled primarily by the number of oxygen vacancies. Three different groups [7,13,17] have studied the oxygen or water vapor pressure dependence of the oxidation of Zircaloy. In 1963 Cox [17] examined the effects of pressure on the oxidation of Zircaloy-2 in steam and oxygen. He reported the post-transition equilibrium oxidation rate to be relatively insensitive to pressure. He did note that pressure changes during post-transition oxidation had a strong, temporary effect. Cox claimed that an outer oxide layer whose density is proportional to the oxygen pressure could explain this behavior. An outer layer formed at low oxygen pressure would have a low density, and would temporarily allow a high

permeation rate when the pressure was increased. Eventually, the higher pressure would cause the density of the layer to increase, and the permeation would then decrease back to the lower, equilibrium rate. In his measurements, Cox varied the oxygen pressure from a low of 6.58×10^2 Pa (5 torr) up to 6.58×10^4 Pa (500 torr). As the pressure was increased by two orders of magnitude, the oxidation rate increased by a factor of 2.6. This change would give an oxidation rate that varies approximately as the pressure raised to the $1/5^{\text{th}}$ power. In his work, Westerman [13] began by comparing the oxidation of Zircaloy-2 in air to that in water vapor. He reported the behavior of the Zircaloy to be almost identical in the two different oxidants. He went on to show that the post-transition oxidation rate of Zircaloy does depend on pressure, but did not calculate the actual pressure dependence. In their experiments, Nakamura et al. [7] varied the oxygen pressure by almost four orders of magnitude (20 Pa up to 10^5 Pa). The post-transition oxidation rate was seen to be proportional to $P^{0.15}$. As a compromise between the results of Cox [17] and the results of Nakamura et al. [7], we will assume the post-transition oxidation of Zircaloy to be proportional to $P^{1/6}$.

Having now come up with a reasonable way to account for the pressure dependence of the Zircaloy oxidation rate, we can use that pressure dependence to correct all of the data given in Table 1 to a single pressure. Figure 2 shows the oxidation rates from Table 1 plotted versus $1/T$ where the data has been corrected to a pressure of 10^5 Pa. The least-squares fit of the data gives the following expression for the oxidation rate of Zircaloy in the absence of radiation:

$$\text{Oxidation rate [gm/(cm}^2\text{-s)]} = 13.9 \text{ [g/(cm}^2\text{-s-atm}^{-1/6}) \exp(-1.47 \text{ eV/kT)} \times P^{1/6} \text{ (atm}^{1/6})$$

As can be seen from the figure, the deviation of the data points, as recorded by the various research groups, from the calculated formula is quite small. This small deviation adds credibility to both the temperature and pressure dependence of the derived equation.

Table 1. Oxidation Rate (gm/cm²-s) for Zircaloy as a Function of Temperature and Pressure

	623 K	633 K	673 K	723 K	773 K	803 K	Ref. #
2.0x10 ¹ Pa					6.9x10 ⁻¹⁰		7
2.0x10 ² Pa					1.3x10 ⁻⁹		7
1.3x10 ³ Pa						5.0x10 ⁻⁹	3
1.0x10 ⁴ Pa	1.7x10 ⁻¹¹						6
1.0x10 ⁴ Pa			1.6x10 ⁻¹⁰				6
1.0x10 ⁴ Pa				7.2x10 ⁻¹⁰			6
1.0x10 ⁴ Pa					3.2x10 ⁻⁹		6
2.0x10 ⁴ Pa					2.1x10 ⁻⁹		7
9.0x10 ⁴ Pa					2.6x10 ⁻⁹		7
1.0x10 ⁵ Pa	1.7x10 ⁻¹¹						12
1.0x10 ⁵ Pa	2.3x10 ⁻¹¹						9
1.0x10 ⁵ Pa			2.8x10 ⁻¹⁰				12
1.0x10 ⁵ Pa					5.0x10 ⁻⁹		12
3.4x10 ⁶ Pa	2.6x10 ⁻¹¹						12
1.9x10 ⁷ Pa		4.1x10 ⁻¹¹					16
2.0x10 ⁷ Pa	2.8x10 ⁻¹¹						9

The final question to be addressed for the oxidation of Zircaloy in nuclear applications is that of the effect of radiation damage. McDougall et al. [18] examined the oxidation rate of pre-oxidized Zircaloy-2 samples in the NRU research reactor at 568 K with water containing lithium impurities. They reported the oxidation rate to be increased by factor of 3-5 depending on the oxide thickness. Asher et al. [19] examined the effects of fast neutron and gamma radiation on the oxidation rate of Zircaloy-2. The effect of the gamma radiation on the oxidation rate was seen to be minimal. For fast neutron fluxes of 3×10^{13} n/cm²-s, the oxidation rate of the Zircaloy-2 samples was increased by a factor of 8 at 573 and 613 K, but no enhancement was seen at 673 K and above. The authors concluded that the enhancement in the oxidation rate was the result of radiation damage to the oxide layer or the underlying metal. Ittis et al. [20] did not measure the rate of oxidation in his neutron irradiated Zircaloy-4 samples, but did note changes in the oxide layers of those samples compared to unirradiated ones. Irradiated samples were seen to have areas of nanocrystals of random orientation in the area of the metal-oxide interface. These nanocrystals were thought to originate with the crystallization of amorphous oxide. Additionally, grain growth in the neutron irradiated samples suggested the activation of irradiation-induced grain boundary migration. In their work, Bossis et al. [21] reported an enhanced oxidation rate in neutron irradiated Zircaloy-4 due to a highly perturbed metal-oxide interface and oxide layer. The oxide layer was seen to contain several populations of cracks not seen in the unirradiated samples. The authors proposed the increased cracks and defects to be due to the degradation of the tetragonal oxide layer in the radiation field. Comparing their

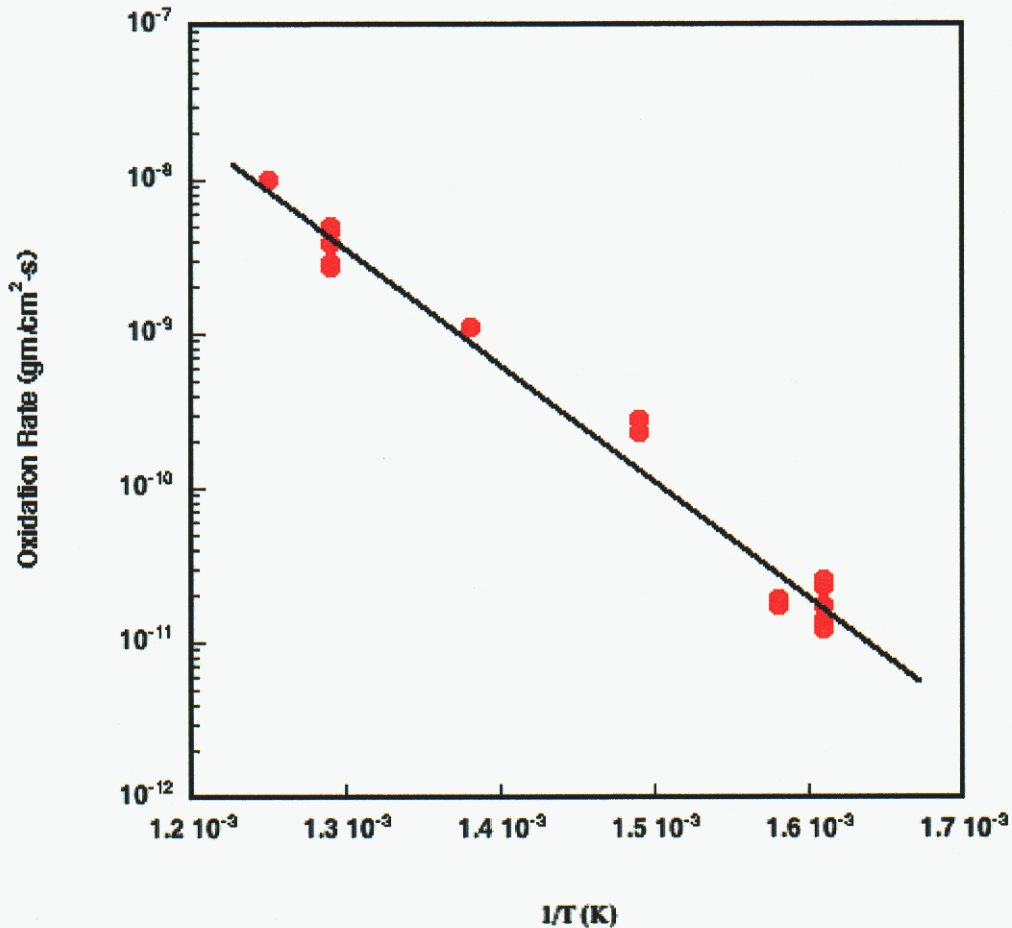


Figure 2. Oxidation rate for Zircaloy as a function of temperature

measured oxidation rate for neutron irradiated Zircaloy-4 at 576 K to that predicted by the formula given above, an enhancement in the oxidation rate by 4.3 is calculated. In A.B. Johnson's work in EPRI NP-5132 [11], it was also concluded that the primary effect of neutron irradiation on Zircaloy oxidation was the degradation of the protective oxide layer. A report of micronodules and corresponding microcenters of porosity was given, suggesting development of porosity as the primary effect. There was confirmation in this report that radiation effects are enhanced by dissolved oxygen in the water as well as by chemistry changes to the water. In fact, the oxidation rate of both Zircaloy-2 and Zircaloy-4 at 633 K in water with dissolved oxygen was increased by almost an order of

magnitude by neutron irradiation. On the other hand, the oxidation rate of the same two alloys at 633 K in low oxygen water was not significantly increased by the neutron irradiation. For samples pre-oxidized to give a preexisting thick oxide layer, oxidation rates in the neutron field again substantially exceeded those outside of the reactor. A pre-film thickness of approximately 10 μm was required to get the radiation enhancement.

The overall effect of neutron irradiation on the oxidation rate of Zircaloy is much easier to qualify than quantify. For water with oxygen added, there is a substantial increase in the oxidation rate, at least for temperatures below about 700 K[11]. There is also an increase in the oxidation rate due to neutron irradiation if the film thickness is greater than about 10 μm 's [18]. For relatively thin films and water without dissolved oxygen, the enhancement in oxidation rate due to neutron irradiation appears to be minimal. The effect of the added oxygen in the water is difficult to understand. Without the addition of neutron irradiation, other researchers [12] have found no differences in oxidation rates between samples exposed to water vapor or air. It can be speculated that oxygen is more readily able than water molecules to penetrate microcracks in the oxide layer generated by the irradiation.

3. Summary

In summary, in the absence of neutron irradiation, the overall oxidation of zirconium and its alloys is fairly well understood. The oxidation rate depends upon the pressure of the oxygen or water vapor, and scales approximately with pressure to the 1/6th power. For Zircaloy-2 and Zircaloy-4, the oxidation rate in the absence of neutron irradiation is given by:

$$\text{Oxidation rate [gm/(cm}^2\text{-s)]} = 13.9 \text{ [g/(cm}^2\text{-s-atm}^{-1/6}) \exp(-1.47 \text{ eV/kT)} \times P^{1/6} \text{ (atm}^{1/6})$$

Data points needed to generate this equation came from experiments where the temperature was varied between about 573 and 823 K and pressures between 20 and 2×10^7 Pa. When neutron irradiation is included, the error bars on the quantification of the oxidation rate may increase somewhat, depending upon the actual temperature of the irradiation. The enhancement in the oxidation rate in the presence of fast neutrons depends upon neutron intensity, temperature, water chemistry, dissolved oxygen in the water, and oxide layer thickness. Still, if all of the conditions to which the Zircaloy is going to be exposed is included in the analysis of the oxidation rate, it should be possible to predict the post-transition rate within a factor of 2 to 4.

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