CORROSION OF ZIRCALOY SPENT FUEL CLADDING IN A REPOSITORY

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Prepared for:
NRC Contract No. FIN A-4171
U.S. Nuclear Regulatory Commission
Office of Nuclear Material Safety and Safeguards
Washington, DC 20555

July 1989
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Corrosion of Zircaloy Spent Fuel Cladding in a Repository

I. INTRODUCTION

Zircaloy's corrosion behavior is of particular interest in applications such as nuclear fuel cladding and in subsequent long term nuclear waste storage are of particular interest. The zirconium alloys termed Zircaloy were developed for use in the nuclear industry. Zircaloy cladding, which is tubing with a wall thickness of less than 1 mm, is a container for UO₂ nuclear fuel pellets during the time when the fuel is in reactor service, in temporary storage and in long term nuclear waste storage.

The Environmental Protection Agency (EPA) has promulgated environmental radiation protection standards for management and disposal of spent nuclear fuel high-level and transuranic waste. The Nuclear Regulatory Commission (NRC) requires that nuclear waste containment shall be substantially complete for a period of 300 to 1000 years. The NRC also requires that thereafter no more than one part in 10² of the inventory of radionuclides present at 1000 years after closure may be released annually from the engineered barrier system of a geologic repository. The Department of Energy (DOE) describes general guidelines for the recommendation of sites for nuclear waste repositories.

Determinations of Zircaloy durability and whether credit can be allowed for Zircaloy cladding acting as a barrier against radionuclide release must include considerations of the specific Zircaloy, its metallurgical condition, its corrosion resistance and its history in service and storage. Corrosion initiation and behavior will be affected by the type of reactor and exposure of the cladding, the composition of the crud which was present on the fuel rods and how the fuel rods were cleaned. Some aspects of corrosion behavior of Zircaloy and requirements for nuclear waste storage have been discussed previously. It has been concluded that with intact cladding no radionuclide release occurred, and that radionuclide release increased with increased exposed area of the spent fuel. The question regarding whether Zircaloy cladding can be given any credit for acting as a barrier to radionuclide release, however, remains to be answered. An increased understanding of the corrosion behavior of Zircaloy would contribute to this assessment.

A. Purpose

This is a review of selected aspects of the corrosion and technology of zirconium (Zr) and Zircaloy. Information is provided that can be used for gaining a better understanding of the durability of Zircaloy spent fuel cladding.
B. Scope

Zirconium and Zircaloy corrosion resistance and reactions in various environments will be discussed along with selected forms of corrosion. Information on environments other than those expected in the repository is provided to give a better understanding of the corrosion of Zircaloy. Zircaloy is more than ninety eight percent Zr so the corrosion behavior of Zr and Zircaloy are similar. Small differences in corrosion behavior will be discussed. Some background information will be given on the metallurgical aspects of zirconium which relate to corrosion resistance and mechanical durability of the Zircaloy.

Zirconium attains its corrosion resistance through the presence of a surface oxide film, and some information on the oxidation of zirconium will be given. There are many references relating to Zircaloy corrosion in the nuclear power industry, and only a few are cited in this brief review. This paper discusses Zircaloy cladding corrosion only, and oxidation of spent fuel and solubilities of U and UO₂ are not addressed.

II. BACKGROUND

A. Zirconium

Zr has properties which make it an attractive material for the nuclear industry. Its crystalline structure and properties are affected by increasing temperature and alloying.

1. History

Zirconium was discovered in 1789 by Martin Heinrich Klaproth when he was studying semiprecious stones from Ceylon. Klaproth, in 1794, found another new element which he named titanium, but titanium had been discovered in 1791 by Gregory and called Menachin. Zirconium is generally less corrosion resistant than titanium.

Zirconium accounts for 0.028 percent of the earth's crust and is the 19th most abundant element. It is found as ZrSiO₄ in beach sand in regions throughout the world and as ZrO₂ and ZrSiO₄ deposits in Florida, California, Oregon, Idaho, Brazil, Australia and India. Berzelius produced impure zirconium in 1824, and van Arkel and de Boer produced high purity zirconium in 1925 using an iodide decomposition process. The Kroll process for producing zirconium involves magnesium or sodium reduction of ZrCl₄ and was developed in 1946 by the U. S. Bureau of Mines in Albany, Oregon.

2. Properties

Zirconium is pyrophoric, and small pieces with a large surface to volume ratio will ignite easily. Large pieces are oxidation resistant at high temperatures.
Some properties of Zr are given in the following table. It is suitable for use in high temperature, high mechanical strength and ductility applications.

**Table 1. Properties of Zirconium**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>1930°C (3506°F)</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>6.53 g/cc</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>110 MPa (16 ksi) at 427°C (800°F)</td>
</tr>
<tr>
<td></td>
<td>552 MPa (80 ksi) at room temp.</td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>9.9 x 10⁴ MPa (14.4 x 10³ ksi)</td>
</tr>
<tr>
<td>Shear modulus</td>
<td>3.6 x 10⁴ MPa (5.25 x 10³ ksi)</td>
</tr>
</tbody>
</table>

Zirconium has a low neutron scattering cross section. This, combined with its high temperature mechanical properties, adequate thermal conductivity, and the stability of these properties after irradiation, makes it a good material for nuclear reactor applications.

Nuclear grades of zirconium are free of hafnium. Hafnium has many properties similar to zirconium and usually is found associated with zirconium, and zirconium sponge could contain a few percent of hafnium. The hafnium is undesirable for most nuclear applications because hafnium has a high neutron cross section.

3. Crystal Structure of Zirconium and Zirconium Alloys

Zirconium has a close-packed-hexagonal (cph) crystal structure (alpha Zr) at room temperature and undergoes an allotropic transformation to a body-centered-cubic structure (beta Zr) at 870°C (1600°F). Some elements, including Al, Sb, Sn, Be, Pb, Hf, N, O, and Cd, are alpha stabilizers and raise the transformation temperature of alpha to beta. Other elements, such as Fe, Cr, Ni, Mo, Cu, Nb, Ta, V, Th, U, W, Ti, Mn, Co and Ag, are beta stabilizers and have the opposite effect and lower the alpha to beta transformation temperature.

Zirconium and its dilute alloys can exhibit strong anisotropy. In the wrought form, these materials have a preferred crystallographic orientation. Orientation textures develop during processing of metals to wrought form and the resulting texture will cause mechanical properties to vary with rolling and transverse directions.

Most of the alloying elements form intermetallic compounds with Zr, and the distribution, size and properties of these phases are important to corrosion resistance in steam or hot water. The main precipitate which is present in Zircaloy-4 is Zr(Fe,Cr)², while Zr(Fe,Cr)² and Zr²(Fe,Ni) are present in Zircaloy-2. Zircaloy-2 and Zircaloy-4 usually are forged in the beta region, then solution treated at 1065°C (1950°F) to increase
the amount of alloying elements going into solid solution, and this is followed by a water quench. The uniform distribution of fine intermetallic compounds produced by heat treating and quenching, is preserved by hot working in the alpha region below 790°C (1472°F)\(^8\).

B. Zircaloy

1. General Information

Zircaloy-2 and Zircaloy-4 were developed for the nuclear industry, and are used as fuel cladding in power boilers. Both alloys are more than ninety eight percent Zr.

Alloys used for fuel cladding in the nuclear industry are primarily Zircaloy-2 for boiling water reactors (BWR) and Zircaloy-4 for pressurized water reactors (PWR)\(^1\), with Zr-2.5Nb being used in smaller amounts. Compositions of these three zirconium alloys are given in Table 2.

| Table 2. Composition of Selected Zirconium Alloys |
|-------------------|---|---|---|---|---|
| Alloy             | Sn | Fe  | Cr  | Ni  | Nb |
| Zircaloy-2        | 1.5| 0.12| 0.10| 0.05| Bal. |
| Zircaloy-4        | 1.5| 0.20| 0.10| 0.005| Bal. |
| Zr-2.5Nb          |    |      | 2.5 |     | Bal. |

2. Corrosion Resistance

Corrosion resistance of these dilute zirconium alloys is slightly diminished but very similar to that of zirconium. One instance in which zirconium alloys can have superior corrosion resistance to the base zirconium metal is in high temperature water or steam. Alloying with small amounts of Sn, Fe, Cr and Ni improves resistance to high temperature water corrosion. The Zr-2.5 Nb is less corrosion resistant than the Zircalloys except in steam at temperatures above 400°C (750°F), and it is used for pressure tubing in some reactors.

C. Welding

The high reactivity of zirconium and Zircaloy necessitates that welding be carried out in a vacuum or as a second choice, in an atmosphere of argon or helium. Studies involving effects of impurities in H\(_2\)SO\(_4\), on corrosion resistance of zirconium showed that corrosive effects due to impurities were greater in welded areas\(^1\). Contamination with hydrogen, oxygen or nitrogen should be avoided by argon purging during welding to prevent embrittlement of the welded area\(^1\).
III. REPOSITORY ENVIRONMENT

The repository environments for locations involving basalt, salt and tuff were reviewed previously\(^{14}\) and conditions were given in some detail. Some of the information from this reference relating to the tuff repository is presented here. The tuff repository is located in the state of Nevada and is in the Topopah Spring Member of the Paintbrush Tuff at Yucca Mountain. The tuff is in unsaturated devitrified zones with twelve percent porosity and contains five volume percent water\(^{14,15}\). Oxygen is expected to be present. Water flow has been stated to be 6 to 8 mm per year, but this could change.

Radiation present will be gamma and will be approximately \(10^4\) rads per hour. This repository probably will not pressurize after closing, and the water will boil off leaving a residue of salts which may or may not redissolve.

Water taken from the Jackass Flats J-13 Well in the tuff repository area contains a number of ions in small concentrations including Li\(^+\), Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\), Be, Al\(^{3+}\), SiO\(_2\), F\(^-\), Cl\(^-\), CO\(_3\)\(^{2-}\), HCO\(_3\)\(^-\), SO\(_4\)\(^{2-}\), NO\(_3\)\(^-\), PO\(_4\)\(^{3-}\). The pH of the water has been reported to be 7.1 but could go more basic depending on the ion concentration. The water pH could shift to the acidic range due to radiolysis of N\(_2\)/O\(_2\)/H\(_2\)O mixtures. Analytical work still is needed to show whether pore water in the tuff has the same composition as the J-13 water.

Calculations of repository temperatures over extended times involve a given repository design and assumptions used, such as the absence of packing material, and are subject to change. Calculated temperature versus time profiles for a tuff repository are given in reference 14 and show a fuel centerline temperature of 330°C which decreases to 100°C after 300 years. Some other calculations showed that centerline temperatures were in excess of 350°C\(^{15}\). The calculated temperature at the canister was approximately 245°C and decreased to 80°C after 200 years.

IV. TYPES OF CORROSION

Corrosion processes within the tubing due to reactions of the cladding with the nuclear fuel and its environment must be considered as well as corrosion behavior of the outer surface of the cladding which is exposed to environments of reactor service, temporary storage and permanent storage. Most cladding failures reported until now appear to have initiated at the inner tubing wall. Causes of these failures include clad collapsing, pellet cladding interactions, hydriding, fretting and some failures due to unknown causes. The problem of collapsing was corrected by pressurizing the clad fuel. Causes of failure on the outside of the cladding include water side corrosion and crud-induced localized corrosion. A discussion of the forms of corrosion and the corrosion behavior of zirconium in various media are given in references 7 and 8. Discussions of Zircaloy cladding corrosion under repository type conditions and effects on radionuclide containment are given in reference 14. Selected information on corrosion behavior is given in the following sections.
A. General Corrosion

General corrosion, also known as uniform corrosion, may be described as an electrochemical attack covering the entire surface of the exposed metal. Metals and alloys subject to uniform corrosion become thinner or completely corrode as a result of this uniform attack over the surface. Zirconium and Zircaloy are resistant to uniform corrosion due to the protective oxide layer which forms on the surface. Uniform corrosion and subsequent thinning of either material would become a problem only if the protective surface oxide film underwent a transition to the thicker, nonprotective oxide described in the section on oxidation.

Some uniform corrosion data on zirconium are tabulated in reference 14 and the part relating to the tuff environment was taken from reference 17. These data were calculated using the formula\(^6\) for weight gain after the transition in oxide film growth,

\[
\Delta W = 1.12 \times 10^8 \exp \left[-\frac{12529}{T(K)}\right]t
\]

where \(\Delta W\) is weight change in mg/dm\(^2\)/day, \(T\) is the absolute temperature and \(t\) is time. Some of the results are shown in Table 3.

<table>
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<tr>
<th>Temperature °C</th>
<th>Environment</th>
<th>Thickness Loss (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>Aqueous</td>
<td>0.02</td>
</tr>
<tr>
<td>250</td>
<td>Air or Steam</td>
<td>0.008</td>
</tr>
<tr>
<td>300</td>
<td>Aqueous</td>
<td>0.2</td>
</tr>
<tr>
<td>300</td>
<td>Air or Steam</td>
<td>0.1</td>
</tr>
<tr>
<td>350</td>
<td>Aqueous, Air or Steam</td>
<td>1.0</td>
</tr>
<tr>
<td>400</td>
<td>Aqueous</td>
<td>4.4</td>
</tr>
<tr>
<td>400</td>
<td>Air or Steam</td>
<td>6.3</td>
</tr>
</tbody>
</table>

The lower temperature data indicate no significant amount of corrosion due to general corrosion, but the higher temperature data indicate amounts of corrosion which exceed the thickness of the cladding wall in less than 300 years. Zircaloy corrosion is sensitive to increases in temperature. These data indicate that additional high temperature oxidation data and knowledge of the repository storage temperature and environment would be needed to make a prediction of the effects of uniform corrosion.
B. Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a complex form of localized corrosion that occurs in the presence of a corroding environment and a tensile stress. SCC can occur without warning and can be catastrophic. SCC is discussed in reference 19. Factors important in determining mechanisms of SCC include chemical composition, electrochemical reactions, mechanical properties and condition of the material. Anodic dissolution at the crack tip and a concentrated stress at the crack tip can lead to failure. Adsorption of ionic species in the strained area of the crack tip can also lead to failure. Some SCC failures appear to result from a series of brittle fractures. There are other mechanisms, related to these, which can lead to SCC failure. The U-bend test, consisting of a rectangular specimen bent around a predetermined radius and maintained under constant strain during corrosion exposure, or other similar tests can be applied to determine whether a metal undergoes SCC, but since SCC can develop over time without showing indications of this problem, the absence of SCC failure does not mean that the material is immune. Metals which are susceptible to SCC can appear sound for extended times can fail suddenly due to SCC. Additional information on a materials susceptibility to SCC can be obtained from slow strain rate testing.

Zirconium and its alloys are resistant to SCC in seawater, most aqueous environments and some sulfate and nitrate solutions. SCC of Zircaloy can occur in concentrated methanol, solutions containing heavy metal chlorides, ferric chloride solutions, copper chloride solutions, organic solutions with chloride, gaseous iodine or fused salts. Liquid metal embrittlement has been reported for zirconium in contact with molten cesium and with liquid sodium or cadmium.

Data show that if the electrode potential of Zircaloy-2 is raised to a value which is slightly more positive than its corrosion potential in neutral dilute sodium chloride solutions at 25°C, SCC will occur. SCC from the fuel side of the cladding can result from effects of fission products such as iodides.

The estimated in-reactor failure rate for LWR fuel cladding is 0.01 percent. Earlier in-reactor failure rates in BWRs were as high as one percent. Less than 0.002 percent of Zircaloy fuel rod failures, under reactor conditions, are caused by waterside corrosion. During in-reactor service, there is some creepdown of the cladding and also expansion of the fuel occurs causing localized stress regions in the cladding.

The hoop stress, \( s \), defined as \( s = \frac{pr}{t} \), where \( p \) is pressure in MPa, \( r \) is the radius of the tube in meters and \( t \) is the wall thickness of the tube in meters, can be an important factor in failures initiating from the inside of the cladding. The importance of the hoop stress increases when the ratio of the tube diameter to the tube wall thickness is greater by a factor of ten. Approximate measurements for Zircaloy-2 and Zircaloy-4 are an outside diameter of 12 mm with a wall thickness of 0.9 mm and an outside diameter of 11 mm and a wall thickness of 0.9, respectively.
Calculations of the minimum hoop stress necessary for SCC due to iodine gave values of 200-220 MPa at 400°C\textsuperscript{21} and 216 MPa at 300°C\textsuperscript{25,26}. Hoop stresses in rods stored below 60°C have been estimated to be in the range of 1.7 MPa to 3.7 MPa with some having a hoop stress of 5.4 MPa\textsuperscript{27,14}. In late 1978, General Electric began He pressurizing BWR fuel rods to 0.3 MPa, and Westinghouse began He pressurizing PWR fuel rods to 3 or 3.4 MPa\textsuperscript{14}. The estimate then for the hoop stress in a BWR rod was 3.1 MPa at 100°C and 9.2 MPa for a PWR fuel rod\textsuperscript{28,14}.

Calculations of the hoop stress during the containment period at 300°C result in approximately 22.7 for BWR rods and 82.5 for PWR rods\textsuperscript{14,17}. These hoop stresses are much lower than the 200 – 220 MPa described as necessary to produce SCC, but the total considerations regarding whether SCC from inside the cladding will occur must also include inner tube wall surface defects, local stresses, texture of the inner surface, localized chemical inhomogeneities either in or on the surface, whether hydriding has occurred and whether the fuel rod was pressurized. Inner surface texture can affect susceptibility to SCC\textsuperscript{29}, and this effect can be reduced by modifying the texture\textsuperscript{30}.

C. Effects of Hydrogen

Failures due to hydrogen pick-up by a material are due to the combination of the embrittling effects caused by hydride formation or hydrogen adsorption and the presence of stress. Other factors such as temperature and chemical environment also play a role in this type of failure. Hydrogen embrittlement failures have an induction period as does SCC and crack propagation is similar in hydrogen embrittlement and SCC. Crack initiation mechanisms for SCC and hydrogen embrittlement are different, and cathodic protection methods which can be applied to prevent or delay SCC can be sources of hydrogen and are not appropriate for use against hydrogen embrittlement.

Zircaloy-2 is somewhat more subject to hydrogen pick-up than is Zircaloy-4. Examples of cladding failures attributed to hydrogen adsorption from hydrogen produced during corrosion have been reported\textsuperscript{28}. An earlier source of hydrogen was water left in the fuel inside of the cladding, but this was eliminated by drying the fuel.

The solubility of hydrogen in Zircaloys is approximately 60 ppm at 300°C and is 1 ppm at 20°C\textsuperscript{15,33,34,35}. Exceeding this solubility will result in the formation of brittle hydrides. The hydrogen content of spent fuel claddings has been reported to be in a range of 80 to 150 ppm and also less than 50 ppm\textsuperscript{33}. Sources of hydrogen available to the cladding include hydrogen generation by corrosion processes, hydrogen present in the reactor cooling water and other possible sources. A general or uniform corrosion rate in excess of 3 mils (0.003 in. or 0.076 mm) per year would result in embrittlement except in oxidizing environments\textsuperscript{13}. 
D. Pitting

Pitting is a severe form of localized corrosion. In some cases, the full extent of the damage to the structure is not obvious by visual inspection of the surface. Pitting occurs at sites of breakage in the protective surface film, defects in the material and at other discontinuities. The initiation of the pit occurs when the disparity at the pit site permits the exposure of the metal to the chemical ions. There is an electrode potential difference between the pit site and the remainder of the protected metal surface. Once the exposure has occurred, a pit develops as is shown in Figure 1.

The small area of the pit (acting as the anode) compared to the larger area of the remaining surface (acting as the cathode) results in a high corrosion current density at the base of the pit. As pitting occurs, metal ions can react with the environment to form precipitates which in some cases, may cause a film to cover the top of the pit. As pitting progresses, corrosion products, such as metal ions and hydrogen, within the pit, cannot escape. These corrosion processes within the pit lower the pH into a more acid region and pitting is accelerated.

Cathode:

\[ 2H + 2e^- \rightarrow H_2 \]
\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]
\[ Me^{+2} + 2H_2O \rightarrow Me(OH)_2 + 2H^+ \]

Anode:

\[ \text{Metal} \rightarrow Me^{+2} + 2e^- \]

Figure 1. Schematic drawing showing anodic and cathodic areas and some reactions of pitting corrosion.
Materials can be tested for susceptibility to pitting, and a method for this test is described in ASTM F-746\textsuperscript{36}. Techniques for pit propagation measurements also have been described\textsuperscript{37}. A method of pitting evaluation is described in ASTM G46, Standard Recommended Practice for Examination and Evaluation of Pitting Corrosion\textsuperscript{38} and involves locating the pits, then determining the density and depth. The pitting factor is used to show the damage of some pits and can be described as

\[
Pitting \ Factor = \frac{Deepest \ Metal \ Penetration}{Average \ Metal \ Penetration}.
\]

This shows that, in the case of a pitting factor of one, uniform or general corrosion is occurring.

Zirconium surface films readily reform if broken, but zirconium is not completely immune to pitting. Pitting does occur in hydrochloric acid solutions which contain ferric or cupric ions and possibly in other environments. Fluorine, chlorine, bromine and iodine in aqueous or gaseous forms could cause pitting to occur.

E. Crevice Corrosion

Crevice corrosion is a form of localized corrosion which occurs at occluded areas such as gaskets, threads, overlaps and places which are deprived of the surrounding environment. Damaging ionic species can become concentrated in creviced areas causing conditions similar to those developed in pitting. Zirconium is resistant to crevice corrosion since a protective surface film forms; nevertheless, crevice corrosion could occur.

F. Nodular Corrosion and Crud Induced Localized Corrosion

Nodular corrosion and crud induced localized corrosion were found in the late 1970's. These forms of fuel cladding corrosion have been described in detail in reports from the General Electric Company\textsuperscript{39,40,41}. Nodular corrosion was first observed in 1979, and it was determined to be related to crud-induced localized corrosion (CILC) which was observed by the same authors in 1978. Although CILC was found first, the explanation of the mechanism indicates that it is preceded by nodular corrosion.

CILC was found to occur in systems which had copper present\textsuperscript{39}. The most frequent type of crud found on cladding in BWR service is mostly Fe\textsubscript{2}O\textsubscript{3}, which is fluffy, loosely adherent, has a low density and has good heat transfer in boiling conditions. If copper is present in the system, even in small amounts, the crud or scale deposits are mostly a combination of Fe\textsubscript{2}O\textsubscript{3} and CuO. Such deposits are tightly adherent, have a high density and low thermal conductivity under boiling conditions. Fifty percent of the cation content in these deposits is copper as opposed to ninety percent iron in the more usual crud. These copper bearing cruds flake off. They also have been found between layers of white ZrO\textsubscript{2} on the
cladding surface. The protective form of ZrO₂ is black and covers the surface as a thin layer. Reactions of the oxide with copper result in severe local corrosion or pits in the regions 20 to 40 inches and occasionally at 80 to 100 inches from the lower end of the fuel rod. CILC failures are associated with soluble copper in the water which could come from corrosion or wear of tubing or other parts containing copper. CILC failures occur more frequently in (U,Gd)O₂ rods but failure can occur in UO₂ rods. The power exposure threshold must be sufficient to produce fuel failure. These failures occur in only a small fraction of the rods.

These damaging crud deposits are most commonly found on top of the protective oxide and are associated with white oxide nodules. The protective film formed on Zircaloy in Boiling Water Reactor (BWR) service is a black oxide. Figure 2 is a schematic drawing of Zircaloy cladding with possible surface oxides or crud coatings.

Some localized lens-shaped white oxides also develop, and these nodules grow faster than the adherent uniform black oxide film. The nodules are not as adherent or protective and are sites for scaling or other reactions. Nodular corrosion has been studied and variables which affect it have been discussed. The nodules do not form at these precipitate sites or at grain boundaries as might be expected. Both alloys become more resistant to nodule formation after heat treating in the alpha-beta or beta phase regions above 830°C. This increased resistance is attributed to a redistribution of solute elements in the Zircaloy. A mechanism is given based on the effects of the solute depletion on the composition and structure of the black uniform surface oxide.

Zircaloy cladding wall

Nuclear Fuel

Zircaloy cladding wall

Thin (2um to 3 um) protective oxide

Thick nonprotective oxide

Crud of variable composition

Figure 2. Zircaloy Cladding Section Showing Oxides and Crude Layers on Outer Surface.

Detrimental effects of the presence of copper on nodular corrosion have been described. Effects of other elements on nodular and uniform corrosion in steam at 400°C and 500°C have been studied, and results showed that iron and nickel improved both uniform and nodular corrosion resistance of Zircaloy but both increased the amount of hydrogen pick-up. Tin decreased the nodular corrosion resistance, and niobium improved nodular corrosion resistance and improved resistance to hydrogen pick-up.
V. OXIDATION OF ZIRCONIUM

Zirconium forms a visible oxide film at 200°C (400°F) which is protective but at a temperature of 425°C (800°F), a thicker, loose white scale develops which is not protective. Oxidation rates for zirconium in various media at different temperatures are tabulated\(^7,8\). Zirconium and its alloys usually show a decreasing corrosion rate in high temperature water which may be followed by a rapid linear rate of attack. Film growth in the early stages of zirconium oxidation (pretransition) have been described as following cube root kinetics\(^{11,32,43}\). This is shown schematically in Figure 3. At a critical thickness, dependent on environmental factors, such as temperatures of 280°C and above, the kinetics change, and a transition to linear growth, with time, occurs. The post transition, thicker film is not protective, and a protective film rapidly reforms to begin a new cycle of film growth. It has been shown that in water at 360°C, these repeated cycles of cube root and linear kinetics occur\(^4,44\). In studies of Zircaloy-2 corrosion in high temperature water, it was postulated that oxygen diffuses through the corrosion film by easy paths such as grain boundaries or other discontinuities\(^{45}\). Experiments conducted at 355°C to study transport of oxygen and hydrogen (as deuterium) in growing corrosion films showed oxygen diffusion at grain boundaries and other short circuit diffusion pathways\(^{45}\). High concentrations of hydrogen also were observed in these studies. Other high temperature studies, with an applied tensile stress, showed a 1.2 to 2 fold increase in the corrosion rate of Zircaloy-2 in steam at 400°C to 475°C over that at 300°C\(^{46}\).

![Figure 3. Oxidation of Zirconium](image-url)
The oxidation rate in the pretransition region is enhanced by reactor radiation and is related to the fast neutron flux\textsuperscript{47}. Pretransition oxidation curves for zirconium in water or steam, fused salt or air at 350°C are essentially the same\textsuperscript{11}. The structure of the initial oxide film in terms of grain boundaries and other defects appears to be important in the further oxidation or growth of the oxide film.

Calculations based on weight gain at a temperature of 180°C for 10,000 years show depths of oxidized Zircaloy ranging from 4 μm to 53 μm, and it was concluded that at this temperature and below, failure of the Zircaloy due to oxidation should not occur\textsuperscript{32}. Results of other corrosion tests based on oxidation and weight gain are given in reference 14. Some of these data indicate that the cladding would fail. If the water temperature is below about 250°C when the water reaches the Zircaloy cladding, the oxidation mechanism could change and the rate could become considerably lower as is indicated in the post transition region of Figure 3.

Information on the condition of spent fuel and spent fuel cladding is available from reports developed by the Materials Characterization Center (MCC). The Approved Testing Material (ATM) - 106\textsuperscript{48} is a high burn-up, high fission gas release material from a PWR and is one of five ATMs which are representative of different fuel types and reactor conditions. Metallographic characterization indicated that the oxide layer or reaction product on the interior surface of the cladding was uniform and ranged in thickness from 4 μm (0.004 mm) to 9 μm (0.009 mm). The exterior cladding surface oxide was thicker in the middle of the rod than at the bottom of the rod. The top of the rod was not analyzed. The exterior oxide in the middle of the rod has a thickness ranging from 11 μm (0.011 mm) to 15 μm (0.015 mm) and was multilayered with the outside layer being loosely held. Further microstructural analysis indicated that increased hydriding could be correlated with increased cladding oxide thickness. Not all spent fuel has a uniform surface oxide, and ATM-103, representing a moderate burn-up, low fission gas release, material had localized corrosion products with the remaining surface relatively bare.

VI. AQUEOUS CORROSION RESISTANCE OF ZIRCONIUM/ZIRCALOY

Zirconium readily oxidizes to form a protective surface film and is resistant to strong acids, alkalis and to organic acids. Carbon and nitrogen impurity contents of 40 and 300 ppm, respectively, increase the corrosion rate of zirconium. Zircaloy-2 has less than 0.006 percent nitrogen. The addition of tin to Zirconium counteracts detrimental effects of absorbed gas on corrosion resistance\textsuperscript{7,8}.

Zirconium is attacked by fluoride ions, wet chlorine, aqua regia, concentrated sulfuric acid, hydrofluoric acid, ferric chloride and cupric chloride. An extensive table showing corrosion rates of zirconium in various media is given in reference 7 which indicated that the information should be used only as a guide and that further tests, in situ, should be conducted to verify the corrosion resistance in a given medium. A table,
showing corrosion rates in various media, is included in reference 7. Much of the information on reactions in acids and alkalies is taken from references 7 and 8, but it is verified in numerous other references.

A. Sulfuric Acid

Zirconium is corrosion resistant in sulfuric acid in concentrations up to 60% up to boiling temperatures, and concentrations of 80% at room temperature. This resistance is lower for welded material and heat affected zones even at lower acid concentrations. This resistance is the result of a protective cubic ZrO₂ film with a small amount of a monoclinic zirconium oxide phase present. Corrosion resistance in concentrations of sulfuric acid above 70% is strongly temperature dependent and is affected by the formation of a looser less protective film, Zr(SSO₄)₂.4H₂O and also the formation of hydrides. These films, consisting of zirconium sulfate, zirconium hydrides and small zirconium metal particles, can be pyrophoric. Impurities in the sulfuric acid such as Fe³⁺, Cu²⁺, Cl⁻, NO₃⁻ and seawater, have detrimental effects on Zircaloy corrosion resistance to sulfuric acid.

B. Nitric Acid

Zirconium is resistant to nitric acid in concentrations up to 65 wt. percent and at a stress limit of 150 MPa up to temperatures of 120°C. Other studies showed high corrosion resistance for zirconium in 70 percent nitric acid at room temperature and little effect on the SCC susceptibility by the presence of FeCl₃, seawater, NaCl and corrosion products released from stainless steel. Fluoride ions should be avoided and chlorine in the gaseous phase should be avoided as well as high stresses at elevated temperatures in 70 percent HNO₃.

C. Hydrochloric Acid, HCl; Phosphoric Acid, H₃PO₄; Alkalies; Saline Solutions

Zirconium is resistant to all concentrations of hydrochloric acid to temperatures above boiling. Zirconium is resistant to phosphoric acid at concentrations up to 55 percent and at temperatures above boiling. Zirconium is resistant to alkalies. It is resistant to saline solutions to temperatures of boiling except for solutions containing FeCl₃ and CuCl₂.

D. Water and Steam

Corrosion resistance of Zircaloy-2 and Zircaloy-4 in high temperature water and steam is superior to that of unalloyed zirconium. Corrosion resistance of Zr-2.5Nb is generally less than that of the Zircaloy but in steam, at temperatures in excess of 400°C (750 F), Zr-2.5Nb has superior corrosion resistance. The corrosion resistance of Zr-2.5 Nb can be improved by heat treating.
VII. SUMMARY

Zirconium is a reactive metal which becomes highly corrosion resistant to various media due to the formation of a protective surface oxide film. Low alloy zirconium alloys, such as Zircaloy-2 and Zircaloy-4 which are used for nuclear fuel cladding, essentially maintain this corrosion resistance under specified conditions. Zircaloy-2 and 4 are resistant, within limits, to acids, alkalis and organic acids. Corrosion of Zircaloy in water and steam is increased with temperature and with carbon and nitrogen impurity contents. Zirconium is not corrosion resistant to fluoride ions, wet chlorine, aqua regia, concentrated acids and ferric chloride and cupric chloride.

Additional electrochemical and corrosion data are needed for predicting Zircaloy corrosion behavior in a long term nuclear waste repository. Temperatures may range from 330°C to 100°C for the first 300 years, and general corrosion might not be a problem under these conditions. However, additional information on mechanisms of oxidation and passivity, along with effects of ions present and other environmental factors, would be useful for relating to the occurrence of localized corrosion.

Zircaloy may be subject to stress corrosion cracking initiating from the inside of the cladding or from the outside of the cladding. Hydrogen embrittlement and metal embrittlement may occur, and there is possibility of pitting occurring. Ions such as those of the halides, especially iodine, would be suspect for causing SCC. Ions such as those of copper or iron may react with the surface oxide film and eliminate the film's protection at a local site. The literature contains many references of research carried out to address these localized corrosion problems in reactor service. Research is needed now to address conditions of nuclear waste storage, including environmental and material variations which could occur over time.

The oxidation rate in the pretransition region of oxide film formation on Zircaloy is increased by radiation. Existing data need to be coordinated and more data are needed to determine effects of radiation and temperature on the oxide thickness and transition temperature.

Metallurgical conditions of the cladding including orientation textures, defects, impurities and histories in reactor service and storage should be established and catalogued. These factors, also, will affect the corrosion and durability of the cladding.

Solubility of the spent fuel will be a factor in the amount and type of radionuclides released, and oxidized fuel has increased aqueous solubility. Oxidation of the spent fuel could occur at rates greater than those previously predicted. This increased oxidation could be due to a lower activation energy for oxygen diffusion at grain boundaries in the spent fuel. Spent fuel volume expansion resulting from oxidation could cause stress cracks in the Zircaloy cladding.
VIII. RECOMMENDATIONS

Aspects of Zircaloy corrosion which need further study include the effects of repository conditions on the following topics:

1. Structure of the oxide film, its stability and transition, and how this film and, also passivity, are affected by temperatures, wetting, drying and other conditions of the repository.

2. Stress corrosion cracking and other mechanical and corrosion failures in which surface crystallographic texture has an important role.

3. Susceptibility of Zircaloy to stress corrosion cracking using various tests including slow strain rate or other appropriate measurements.

4. Susceptibility to pitting or other localized corrosion in environments containing ferric chloride, cupric chloride, fluorine and under conditions of varying pH.

5. Welding integrity and localized and general corrosion of welded areas.

6. Effects of previous service history, especially relating to hydrogen uptake and hydrogen embrittlement cracking and other localized corrosion.

7. Projected stability of initial condition of cladding at time of repository storage using data obtained from characterization of spent fuel approved testing materials (ATMs).

IX. REFERENCES


50. Yau, Te-Lin, Zirconium for Nitric Acid Solutions, ibid. 57-


X. ACKNOWLEDGEMENTS

Support from the U. S. Nuclear Regulatory Commission (U.S. NRC) under FIN A-4171-9 and helpful suggestions of Charles H. Peterson, Engineering Branch, U. S. NRC are gratefully acknowledged.
Corrosion of Zircaloy Spent Fuel Cladding in a Repository

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This is a brief review of selected aspects of corrosion and technology of zirconium and Zircaloy. Corrosion of zirconium and Zircaloy in various media is discussed as well as the susceptibility of these materials to various forms of corrosion. Recommendations are given for some areas of Zircaloy corrosion pertinent to the durability of spent fuel cladding that need further study.

corrosion, Zirconium, Zircaloy, spent fuel, nuclear waste, cladding

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