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CORROSION AND FAILURE CHARACTERISTICS OF ZIRCONIUM ALLOYS IN
HIGH PRESSURE STEAM IN THE TEMPERATURE RANGE 400-500 °C (a)

MASTER

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Paper for presentation at the ASTM Symposium, "Application-Related Phenomena in Zirconium and Hafnium Alloys," Philadelphia, Pennsylvania, November 5, 6, and 7, 1968.

- (a) This paper based on work performed under United States Atomic Energy Commission Contract AT(45-1)-1830.
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ABSTRACT--A nuclear fuel failure phenomenon prompted a study of the corrosion properties of the Zircaloy-2 fuel cladding. The principal studies were conducted at 400, 450, 475 and 500 °C in steam at 1700 psig. Materials tested were: five lots of Zircaloy-2; one lot of Ozhennite (Zr-0.2Sn-0.1Fe-0.1Ni-0.1Nb) and one lot of crystal bar zirconium. As-fabricated Zircaloy-2 underwent a rapid approach to failure in tests at 475 and 500 °C. The attack involved nucleation of nodular oxide which spread across the surface, finally resulting in an accelerated, relatively uniform attack. Ozhennite was resistant to the attack. Heat treatments (α and β anneals) suppressed the nodular attack on Zircaloy-2 but not on crystal bar zirconium.

KEY WORDS--zirconium alloys, catastrophic corrosion, high-temperature corrosion, fuel cladding.

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INTRODUCTION

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Part 2 REV

A nuclear fuel failure phenomenon prompted a study of the corrosion characteristics of the Zircaloy-2 fuel element cladding, since there was evidence that high local temperatures contributed to the failure. Details of the failure are classified, but aspects of the associated out-of-reactor corrosion characterization study are presented in this paper.

Zircaloy-2 has generally performed well as a reactor component material. Flux-enhanced corrosion is observed (1-4), but complete penetration of a fuel cladding would not be expected, even under the highest known rates of flux-enhanced corrosion (2). Therefore, other aspects of Zircaloy-2 failure characteristics were investigated. Kass (5) reported poor corrosion resistance for Zircaloy-2 at 510 °C. Similarly, Bourgeois and Chirigos (6) reported that alpha annealed Zircaloy-2 formed a non-adherent white oxide after one day at 510 °C; beta-quenched specimens were more resistant, but 0.080-in thick specimens failed completely between 15 and 21 days. Weinstein and Holtz (7) found that Zircaloy-2 disintegrated in steam at 480 °C within 97 hr. Zircaloy-2 exposed in other studies in high-pressure steam has generally shown poor corrosion resistance above ~480 °C (8-13).

In this study, corrosion tests included high pressure steam exposures at 500 °C to induce and characterize the failure. Other characterization runs were performed at 400, 450 and 475 °C to determine the general corrosion behavior of the cladding and to determine how far down the temperature scale the catastrophic failure could be induced on the Zircaloy-2 fuel cladding. Ozhemnite was included in the autoclave study as a material being considered for in-reactor corrosion studies and as fuel cladding for a set of experimental fuel elements. Crystal bar zirconium was exposed in a 500 °C test in alpha

and beta fast-cooled conditions to compare failure tendencies of unalloyed material with the behavior of Zircaloy-2.

This paper describes the mode of catastrophic failure which was observed on as-fabricated Zircaloy-2 in the high-temperature autoclave tests. Substantial differences in the corrosion behavior of different Zircaloy-2 lots were observed; however larger contrasts were observed in the behavior of Zircaloy-2, crystal bar zirconium, and Ozhennite. Significant differences in corrosion behavior also were observed for a given Zircaloy-2 lot exposed in alpha and beta annealed and as-fabricated conditions.

EXPERIMENTAL

Autoclave tests on Zircaloy-2 fuel cladding required retrieval of cladding from unexposed fuel elements. Samples of cladding were obtained by dissolution of the associated metallic uranium in nitric acid. The fuel clad was etched in 67% H_2O - 30% HNO_3 - 3% HF ^(Vol %), vapor blasted on both sides, and etched again. The entire finishing process removed approximately 0.002 in. of cladding per surface. To assure that contaminated surface layers were not a factor in the accelerated corrosion, some specimens were etched to remove up to 0.008 in. of cladding per surface. Failure characteristics at 500 °C were not altered significantly by the severe etch.

The following materials were included in the high temperature steam tests:

- Four lots of Zircaloy-2 from fuel cladding - 42-0, 42-i, 47-0, 47-i
- Ozhennite 0.5 (0.2Sn-0.1Fe-0.1Ni-0.1Nb)
- One lot of Battelle-Northwest standard Zircaloy-2 (Lot 1021)
- Crystal bar zirconium

Lots 42-0 and 47-0 came from the same Zircaloy-2 billet, but were extruded separately under essentially the same conditions. Analyses of the three Zircaloy-2 cladding materials, 1021 Zircaloy-2, and Ozhennite are given in Table 1. The Zircaloy-2 cladding materials were extruded, while 1021 Zircaloy-2 and Ozhennite were received in the cold rolled condition.

The tests were conducted in standard stainless steel autoclaves. The standard test pressure was 1700 psig; however, conditions in one test were 4000 psig at 450 °C. The autoclaves were operated at a low refreshment rate (0.3 gal/hr); the autoclave volume is 1.6 gal.

Autoclaves were filled and vented as startup proceeded. Feed water was deionized and deoxygenated. To investigate effects of nitrogen, tests at 500 °C were run with and without a helium sparge on the feedwater. A test to investigate possible effects of dissolved nitrogen was conducted at 450 °C using feed water sparged with nitrogen at ambient temperature (~18 ppm N₂ at saturation in water at 25 °C and one atmosphere N₂ pressure).

To investigate the possibility that stress centers acted as nucleation sites, selected specimens were indented before and after annealing and etching. Specimens prefilmed at 360 °C were included in one 500 °C test. Certain as-etched specimen surfaces were contaminated with localized smears of aluminum and iron.

RESULTS

Weight gains as a function of temperature, time and alloy appear in Figure 1 for a series of autoclave experiments in steam at 1700 psig. The plotted data include only two of the four Zircaloy-2 cladding lots, viz., those showing the highest (42-0) and lowest (42-i) weight gains. Weight gains for

Lot 1021 Zircaloy-2 reference stock and for Ozhennite also are given in Figure 2.

The 500 °C test produced high weight gains and disintegration of some specimens during the 24 hr. exposure. Specimen appearance after the 500 °C test is shown in Figure 2. Appearances of duplicate specimens were remarkably similar, but weight gains and appearances varied from one Zircaloy-2 lot to another. Lot 1021 was the most resistant Zircaloy-2 material at 500 °C. The localized attack precludes interpretation of the kinetics of the reaction from the weight gain data. However, the results establish some limits for maximum penetration rate, since specimens ~0.030 in. thick were essentially penetrated in one day at 500 °C and in five days at 475 °C. Ozhennite was resistant to the nodular attack, in agreement with favorable high temperature corrosion resistance reported by Ambartsumyan, et al (14) and Klepfer (15).

The rapid failure was characterized by nucleation and propagation of oxide nodules (Figure 3a and 4a). Diameters of the nodules were generally greater on the Zircaloy-2 cladding materials than on 1021 Zircaloy-2 at comparable exposures. The nodule in Figure 4a rises approximately ten mils above the original plane of the metal and has a maximum vertical span of 21 mils. Zirconium oxide of theoretical density (5.7 g/cc) expands approximately 1.5 times over the volume of the original metal. The volume of the oxide in Figure 4a is approximately 1.8 times the volume of the original metal. The fact that the indicated density is lower than the theoretical density is consistent with the highly cracked appearance of the oxide. The nodules were hard and resisted spalling in early stages. In later stages, the nodules began to spall.

The nodules finally agglomerated, producing a more uniform, but highly accelerated attack (Figure 3b and 4b). The branching attack in Figure 3b

probably occurred near the end of the exposure, after the embrittled metal cracked from stresses generated by the oxidation. At 475 °C, oxide nodules nucleated after 24 hr on two of the Zircaloy-2 cladding lots (42-0 and 47-0) and on Zircaloy-2 lot 1021. An additional exposure to a total of 5 days at 475 °C produced rapid approach to failure on several specimens. Ozhenite resisted the nodular attack and rapid failure. Specimens of a Zr-2.5Nb alloy exposed four days at 475 °C performed similarly to Ozhenite.

At 450 °C the nodular attack was not observed in exposures to 59 days. However, unexpected behavior of 1021 Zircaloy-2 was observed at 450 °C; a pronounced transition occurred after ~3 days, finally resulting in weight gains approximately a factor of two higher than weight gains on the cladding lots. However, the attack was uniform and resulted in a light gray oxide. Again, Ozhenite weight gains were the lowest in the test.

At 400 °C, the four cladding lots underwent early transition. Early transitions also were observed in 400 °C, 1500 psig steam tests on other Zircaloy-2 material from extruded tubes (2). Ozhenite underwent a transition in the 400 °C test, resulting in weight gains higher than the Zircaloy-2 weight gains. The nodular attack did not occur on any specimens in the 400 °C test in maximum exposures of 63 days. Lot 1021 was not exposed at 400 °C; however, previous exposures at 400 °C in 1500 psig steam resulted in transition after 40 days at weight gains of ~40 mg/dm².

Other tests, conducted to identify the factors causing nucleation of the nodular attack, are discussed in the following sections.

Effect of Nitrogen

Effects of dissolved nitrogen on the nodular attack were investigated in autoclave tests at 500 °C, 1700 psig, using air-saturated nitrogen feed water

(~18 ppm N_2) in one test and helium-sparged feed water in a comparison test. A similar mild nodular attack occurred on the as-fabricated lot 1021 test alloy in both 24-hr exposures. Thus, nitrogen in the steam was eliminated as the cause of the nodular attack. A 72-hr test at 450 °C in steam, using nitrogen-sparged feed water, also failed to induce a nodular attack.

Effect of Pressure

Pressure surges in a small constrained region were considered as a possible factor inducing rapid fuel cladding corrosion in the reactor system. An autoclave test was conducted at 450 °C in 4000 psig steam to investigate the possibility that an increase in steam pressure would lower the nucleation temperature for the nodular attack. No evidence of the nodular attack was observed after 17 days at 4000 psig steam pressure.

The possible role of pressure in nucleating the nodular attack is interesting, since work at low pressures (~25 torr and 1 atm water vapor) have generally shown well-behaved kinetics over considerably longer exposures than those nucleating the failures at high pressures (15). Kass presented evidence of a pressure effect on the catastrophic attack in tests at 625 °C (5). Wanklyn, et al (13) also observed pressure effects on the steam corrosion of zirconium and several of its alloys at 500 °C. Klepfer (8) conducted tests at 1000 psig for up to 356 hr at 480 °C without observing failures on Zircaloy-2, while Weinstein and Holtz (7) observed failure after 97 hr (pressure not specified). However, variations in corrosion behavior as a function of Zircaloy-2 lot, heat treatment and pressure enter into comparisons of results from different laboratories.

Effect of Heat Treatment and Surface Preparation

To arrive at a better understanding of the nucleation of the nodular attack, a set of specimens was prepared which included the Zircaloy-2 cladding lot

with the highest corrosion rates (42-0), Zircaloy-2 lot 1021 and crystal bar zirconium. Each material was exposed in alpha and beta annealed (fast-cooled), conditions; in addition, the Zircaloy-2 lots were tested in the as-received condition. The specimens were exposed 24 hr at 500 °C in 1700 psi steam, followed by an additional 60-hr exposure in the same environment.

Results of the tests are summarized in Table 2.

Results from Table 2 may be summarized as follows:

- Nodular attack occurred on as-fabricated Zircaloy-2 (both lots) but did not occur on corresponding as-etched alpha and beta annealed (fast-cooled) specimens.
- Prefilming at 360 °C did not suppress the nodular attack.
- Abrading with emery paper induced a rapid attack on alpha annealed specimens but not on beta annealed, fast-cooled specimens.
- Crystal bar zirconium having had alpha and beta heat treatments failed within 24 hr.

The nodular attack was initiated in 24 hr in the test described in Table 3, but the failure did not propagate to the extent observed in the first 500 °C test (Figure 2). The factors influencing the propagation of the failure after the nuclei form have not been identified.

Wanklyn, et al (13) observed rapid failure of α -annealed zirconium at 500 °C in steam at 1500 psi in 24 hr; failure did not occur in steam at one atm. A pustule attack was observed on zirconium specimens exposed at the lower pressure in the tests reported by Wanklyn, et al.

Attack at Indents

Sets of indents were formed on as-fabricated and beta annealed, fast-cooled Zircaloy-2 (lots 42-0 and 1021). The indents were approximately 0.040 in.

in diameter at the top and 0.020 in. deep. Indents were formed at three stages in sample preparation: a) before anneals; b) after anneals, before final etching; and c) after anneals and final etching.

Type a and type b indents did not initiate nodular or white oxide on either Zircaloy-2 lot. However, nodules and white oxide were observed around type c indents on as-fabricated specimens on both lots, though the attack was more pronounced on lot 42-0. The indenter surface was carefully cleaned before use. Evidence presented later suggests that metal smears from the indenter were not responsible for the accelerated attack around and in the indents. Residual stress from the distorted metal is suspected to have caused the attack on unetched indents. Etching or annealing apparently removed the regions of high stress. Nucleation of nodules at specimen edges and at stamped numbers also suggested that stress promotes formation of the nodular oxide. However, nodules also formed away from obvious stress locations. Cox (16) observed that the first occurrence of white oxide following transition is usually at specimen edges, with subsequent spreading of the white oxide over the specimen surface.

Surface Contamination

Metallic aluminum and iron were smeared on selected surfaces of the two Zircaloy-2 lots (42-0 and 1021) having alpha and beta heat treatments. Nodules did not initiate in or around the smeared areas.

Electron Microprobe Analysis

One of the large oxide nodules (Figure 4a) was scanned with an electron microprobe to see if impurities or alloy segregations were detectable. No alloy segregations or impurities were found.

Hydrogen Absorption in the Autoclave Environments

Table 3 summarizes hydrogen absorption as a function of temperature, alloy, and Zircaloy-2 lot. In terms of mg/dm^2 , hydrogen absorption was lowest for Ozhenite, because of the relatively low corrosion rates. However, percentage hydrogen absorbed in Ozhenite was comparable to the highest Zircaloy-2 values. Percentage hydrogen pickup was similar for the two Zircaloy-2 lots. There were no consistent trends in percentage absorption as a function of temperature. Substantial hydriding occurred on some Zircaloy-2 specimens, resulting in absorption of up to 2900 ppm of hydrogen (Lot 42-0 after 5 days, 475 °C, 1700 psig steam).

Table 3--Hydrogen Absorption in Autoclave Tests

Specimen	mg/dm^2				Percent ^a			
	400°C	450°C	475°C	500°C	400°C	450°C	475°C	500°C
Test Duration, days	63	59	5	1	63	59	5	1
Lot 42-0 Zircaloy-2	0.2	22.7	43.5	<u>b</u>	2	42	25	<u>b</u>
Lot 1021 Zircaloy-2	-	42.3	15.2	18.4	-	32	34	19
Ozhenite	4.7	7.6	3.9	2.8	35	46	28	40

^a Percent of corrosion hydrogen absorbed.

^b Specimens in advanced stage of failure.

DISCUSSION

The high temperature corrosion behavior of zirconium alloys has been studied, but the nature of the accompanying accelerated attack is not well-characterized. The most significant aspect of Zircaloy-2 corrosion in this study was the nucleation of a catastrophic failure phenomenon. Since the corrosion kinetics at low pressures are reasonably well-behaved, high pressure appears to be a factor in the failure mechanism. Heat treatment has been shown

to enter in. The attack varies greatly from one alloy to another, but also varies as a function of Zircaloy-2 lot (Figure 2). Response to in-reactor corrosion also varied as a function of Zircaloy-2 lot (2). The corrosion behavior of Ozhenite shown in Figure 1 was in good quantitative agreement with the results of Boulton at 450 and 500 °C, but the results of this study at 400 °C were high (17). The reason for the unusual behavior of Ozhenite at 400 °C is not clear, but the explanation probably lies in a selective sensitivity of Ozhenite to an undetected impurity in the 400 °C autoclave environment. An example of selective sensitivity to impurities is given by LeSurf and Bryant (3); the out-of-reactor corrosion of the Zr-2.5Nb alloy is sensitive to dissolved oxygen in the coolant, while Zircaloy-2 corrosion is essentially unaffected in the same environment.

The shapes of the nodules in Figures 3a and 4a suggest that the attack proceeded from a point of nucleation. The suppression of the nodular attack by heat treatments indicates that the nuclei are provided by the metal or oxide structure and not by contamination from surface preparation or from the environment. Hydrides are a potential source of nuclei; however, Cox (16) reported that hydride contents up to 3000 ppm did not significantly effect Zircaloy-2 corrosion at 500 °C.

In a previous study (2), extruded Zircaloy-2 lots exhibited accelerated corrosion at 400 °C. The corrosion resistance was improved when the stringer-like second phase was redistributed in a fine, relatively uniform precipitate. The correlation between good corrosion resistance and a uniform distribution of fine second phase particles is well-known (10, 18). Gross second phase stringers present possible sites for nucleation of the nodules. However, Armand, et al (18) observed blistering of the oxide in areas of second phase depletion. The poor corrosion performance of crystal bar zirconium at 500 °C

also provides evidence that the rapid attack nucleates in zones where the alloying agents are depleted and not at gross second phase precipitates.

The proposed sequence of the nodular attack is: a) the generation of a small region of nonprotective oxide, surrounded by protective oxide; b) the rapid propagation of the nonprotective oxide, perhaps by an autocatalytic mechanism; the volume expansion of the oxide and the opposing constraint of the metal lifts the nucleus and surrounding oxide above the plane of the metal; c) the agglomeration of nodules, finally resulting in a relatively uniform but accelerated attack, which may rapidly consume the specimen (Figures 3b and 4b).

Areas of stress accentuated the nucleation of nodules on as-fabricated specimens. However, etching after indentation tended to suppress the effect of the stress, suggesting that only the more severe stresses were active in promoting the attack.

The varying morphology of the nodules as a function of Zircaloy-2 lot suggested a difference in the character (primarily size) of the nuclei producing the nodules.

The beneficial effect of heat treatments to extend the integrity of Zircaloy-2 in high-temperature ($>480^{\circ}\text{C}$), high-pressure steam is indicated in this study, in agreement with earlier observations (5, 6, 8, 10, 11).

CONCLUSIONS

1. A nodular mode of attack occurred on five Zircaloy-2 lots at 500°C and on two of the lots at 475°C . The nodular attack led to a rapid approach to failure on some specimens. The nodular attack did not occur at 400 and 450°C in exposures to 360 days.

2. The nodular attack was observed on as-fabricated Zircaloy-2, but did not occur on alpha annealed and beta fast-cooled specimens in exposures to 84 hr at 500 °C.
3. Corrosion behavior in the range 400-500 °C varied considerably with Zircaloy-2 lot and greatly as a function of alloy. Susceptibility to failure was highest for crystal bar zirconium; the nodular attack did not occur on Ozhemnite.
4. Stressed areas promoted the attack on as-fabricated specimens, but not on annealed specimens, even when stress was introduced after the anneal.

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FOOTNOTES

Page 1.

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Table 1--Analysis of Alloys - Weight Percent^a

Lot 42-i	Sn-1.51; Fe-0.15; Cr-0.09; Ni-0.06; Al-0.0027; C-0.01; Hf-0.0068; Si-0.0046; H-0.0004; N-0.0052; O-0.12.
Lot 47-i	Sn-1.67; Fe-0.15; Cr-0.10; Ni-0.05; Al-<0.0020; C-0.0098; Hf-0.013; Si-<0.0030; H-0.0005; N-0.0048; O-not given.
Lots 42-O and 47-O	Sn-1.49; Fe-0.1; Cr-0.10; Ni-0.056; Al-0.0050; C-0.018; Hf-0.0082; Si-0.0075; H-0.0007; N-0.0064; O-not given.
Lot 1021	Sn-1.34; Fe-0.14; Cr-0.16; Ni-0.050; Al-0.0050; C-0.041; Hf-0.009; Si-0.003; H-0.0010; N-0.0043; O-not given.
Ozhennite	Sn-0.21; Fe-0.10; Cr-0.0045; Ni-0.10; Al-0.0064; C-0.0096; Si-0.0053; H-0.0005; N-0.0055; O-0.094; Nb-0.10.
Crystal Bar Zirconium	Sn-<0.001; Fe-0.022; Cr-0.0044; Ni-0.0010; Al-0.0045; C-0.0050; Hf-0.0072; Si-<0.0040; H-0.0004; N-0.0025; O-0.013.

^a The highest values from top, middle and bottom analyses from the respective ingots are reported.

Table 2--Heat Treatment and Surface Preparation Effects
on Corrosion at 500 °C, 1700 psig Steam

Specimens	Condition	Corrosion Response
Zircaloy-2 Lot 42-0	As-Fabricated	Nodules initiated after 24 hr
	Alpha Anneal:	
	Etched both sides:	Uniform gray-black oxide
	Etched one side	Rapid attack on etched and polished surfaces
	Polished one side:	
	Beta Anneal:	
	Etched both sides:	Uniform gray-black oxide
Zircaloy-2 Lot 1021	As-Fabricated	
	Etched	Nodules initiated after 24 hr
	360 °C Prefilm	Nodules initiated after 24 hr
	Alpha Anneal:	Uniform gray-black oxide
	Beta Anneal:	
	Etched both sides:	Uniform gray-black oxide
	Etched one side	Uniform gray-black oxide
	Polished one side:	
Crystal Bar Zirconium	Alpha Anneal	Failure almost complete after 24 hr
	Beta Anneal	Failure almost complete after 24 hr

Figure 2. Zirconium Alloys Autoclaved 24 Hr., 500 °C, 1700 psig steam.

250X
24 Hr 500 °C 1700 psig steam

250X
135 Hr 475 °C 1700 psig steam

Figure 3. Early and Advanced Stages of Accelerated Corrosion on Zircaloy-2, Lot 1021.

75X
500 °C 12 Hr 1700 psig steam

75X
500 °C 24 Hr 1700 psig steam

Figure 4. Early and Advanced Stages of Accelerated Corrosion on Zircaloy-2 Lot 42-0.