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CORROSION FATIGUE OF ANNEALED ZIRCALOY-2 IN AQUEOUS SOLUTIONS AT 575 K

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INTRODUCTION

Zircaloy components in CANDU (CANada Deuterium Uranium) nuclear reactors are subjected to fluctuating stresses. Fatigue tests have been performed on Zircaloy-2 in conditions normally encountered in the coolant water. In CANDU reactors the coolant water has a pH of 10 and contains deuterium to remove any oxygen in the coolant. The pH is controlled by LiOH in pressurized water reactors and NH_4OH in boiling water reactors. The effect of possible contaminating ions such as Cl, F^- and NO_3^- on the fatigue has been studied. The chloride and fluoride ions can be leached from Teflon valve packing and nitrate ions are formed by the radiolysis of ammonia. Some of the Zircaloy-2 components are fabricated with a hard 40 mm thick zirconium oxide surface layer for wear resistance [1] and fatigue specimens were tested with a similar oxide layer.

EXPERIMENTAL PROCEDURE

Tests were performed on two Baldwin SF-4 fatigue machines adapted for this programme by the addition of specimen capsules through which was circulated an aqueous solution at a pressure of 10.5 MPa and a test temperature of 575 K. A sinusoidal tensile load was applied to all specimens at a frequency of 60 Hz.

All specimens were made from Zircaloy-2 made to AECL specification MET-52 Issue 6, and annealed at 975 K before machining. Three types of specimens were tested.

1. Round bar 4.1 mm gauge diameter.
2. Round bar 4.1 - 5.0 mm gauge diameter at the base of a notch with 0.13 mm root radius and a stress concentration factor K_t of 3.
3. Round bar 3.9 - 4.9 mm gauge diameter under a 50 μm oxide layer prepared by heating in air at 925 K for 24 hours.

If specimens elongated due to creep, the load was automatically adjusted to maintain a constant stress cycle. Static (mean) and dynamic (alternating) loads were chosen such that the stress ratio (R) equalled 0.1.

$$R = \frac{\text{minimum stress}}{\text{maximum stress}} = 0.1$$

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Stress was calculated for the cross section at the base of the notch and the section beneath the oxide layer, where applicable.

For comparison purposes, stresses were normalized to the ultimate tensile strength of the unnotched bar and were reported as the ratio

$$\frac{\text{maximum stress}}{\text{ultimate tensile strength}} .$$

The fatigue ratio is defined as

$$\frac{\text{fatigue limit}}{\text{ultimate tensile strength}} .$$

The effective notch concentration factor K_f is defined as

$$\frac{\text{fatigue strength of an unnotched specimen}}{\text{fatigue strength of a notched specimen}} .$$

Reference fatigue curves were first determined in two standard solutions, which represent typical environments in CANDU reactors:

1. ammoniated water of pH 10 containing 10 - 20 ppm hydrazine to remove oxygen to simulate oxygen free reactor coolant,
2. lithiated water of pH 10 containing 10 - 20 ppm hydrazine.

Specimens were then tested in contaminated solutions at the approximate fatigue ratios determined in the uncontaminated solutions (Tables 1 and 2).

RESULTS

Fatigue Tests

The reference curves for the three types of specimens in uncontaminated solutions are shown in Figures 1 and 2. The fatigue life of unnotched specimens in ammoniated water is lower than in lithiated water. Oxidation reduced the fatigue ratio to the same level in both solutions. In ammoniated water the oxide layer had a detrimental effect greater than that of the notch. However, in lithiated water the oxide layer and the notch both lowered the fatigue life by the same amount for cycles below approximately 2×10^6 while for lower stresses and higher cycles, the notch was more detrimental than the oxide.

Oxidized specimens were tested at the fatigue ratio in solutions contaminated with up to 10,000 ppm chloride ions (Tables 1 and 2). It was found that a reduction in fatigue life occurred at 2,000 ppm Cl^- in ammoniated water and at 10,000 ppm Cl^- in lithiated water (Figure 3).

Specimens were tested in both ammoniated and lithiated water with fluoride concentrations of 100 ppm without failure (> 20×10^6 cycles) (Tables 1 and 2). Severe corrosion had occurred over the surface of the specimen and large craters were formed with zirconium hydride at their bases.

100 ppm of chloride and nitrate in ammoniated water did not affect the fatigue life (Table 1). No tests were run in lithiated water since radiolysis of ammonia is the only source of nitrate in a CANDU primary heat transport system.

Fractography

Two stage replicas of the fracture surface of specimens were examined using transmission electron microscopy. All the fractures examined showed three types of fracture modes, occurring sequentially from the point of initiation to final separation:

1. feather cleavage (at the point of fracture initiation only),
2. brittle fatigue,
3. ductile fatigue.

Figure 4 shows the typical fractographs.

Feather cleavage is typical of normal fatigue crack initiation but brittle fatigue can occur in two forms:

a) fine straight striations with sharp changes in elevation between fracture plateaus,
b) fine curved striations with cleavage steps or river patterns normal to them.

Type (b) is indicative of corrosion fatigue but only type (a) was observed on the specimens examined. The region of brittle fatigue was largest on the specimens which had a reduced fatigue life in the aqueous solutions containing chloride ions.

DISCUSSION

Figures 1 and 2 show that the oxidized layer reduced the fatigue life of annealed Zircaloy-2. The oxide layer is brittle and the first few stress cycles crack the oxide which effectively forms a notch. The notch then propagates through the oxygen rich layer under the oxide. Thus the oxide layer can be regarded as a fatigue crack starter.

Mann [2] reported that in boiling water the chloride ion concentration at porous coatings would be the bulk concentration multiplied by a factor of 10^3 - 10^5 and a crevice would have less effect. In CANDU reactor systems, it is our opinion that a factor of less than 10^3 should be applied to a bulk concentration of less than 1 ppm and we would expect approximately 100 - 1000 ppm chloride ions in crevices. Thus the concentration of chloride ions required to reduce the fatigue life of oxidized Zircaloy-2 is much greater than would be expected in an operating reactor. Although high concentrations of chloride ions reduce the fatigue life of Zircaloy-2, the resulting behaviour does not have all the characteristics of corrosion fatigue. The fracture surfaces do not show the brittle fatigue normally associated with corrosion fatigue and the S-N curve exhibits a fatigue limit which does not occur in most examples of corrosion fatigue. However, since the environment does reduce the fatigue life in some cases it must be assumed that corrosion fatigue is occurring.

The region of brittle fatigue was normally small but in the specimens which had a reduced fatigue life in chloride solutions this region covered almost half the fracture surface.

The addition of 100 ppm chloride and nitrate ions does not affect the fatigue life, consequently radiolysis of ammonia is not an important consideration.

CONCLUSIONS

1. In the environments tested, an oxide coating reduces the fatigue life of annealed Zircaloy-2 by at least as much as a notch with a stress concentration K_t of 3 or an effective notch concentration factor K_f of 1.2 for ammoniated water and 1.9 for lithiated water.

2. Chloride ion concentration of 2,000 ppm in ammoniated water and 10,000 ppm in lithiated water reduces the fatigue ratio of oxidized Zircaloy-2.

3. Fluoride ions and nitrate ions in the concentrations tested do not affect the fatigue limit of oxidized Zircaloy-2.

4. Corrosion fatigue of oxidized Zircaloy-2 is not expected to be a problem in ammoniated or lithiated reactor waters contaminated by expected concentrations of chloride or fluoride ions or by chloride plus nitrate ions in the case of ammoniated water.

ACKNOWLEDGEMENTS

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REFERENCES

1. WATSON, R. D., Report AECL-2542, Atomic Energy of Canada Limited, March, 1966.
2. MANN, E. M. W., CERL-RD/L/N124/75.

Table 1 Effect of Contaminants on Corrosion Fatigue of Annealed Zircaloy-2 in Ammoniated Water at 575 K and 10.5 MPa

Bar Type	No. of Tests	Contaminant*	Maximum Stress / UTS	Cycles	Comments
Plain	--	--**	0.59	> 50 x 10^6	Estimated Fatigue ratio is 0.59
	3	25 ppm Cl$^-$	0.57 - 0.59	15 - 36	No Failure
	3	100 ppm Cl$^-$	0.59 - 0.61	20 - 25	No Failure
Oxidized	--	--**	0.41	50	Estimated Fatigue ratio is 0.41
	3	25 ppm Cl$^-$	0.40 - 0.42	20 - 30	No Failure
	3	50 ppm Cl$^-$	0.42	15 - 21	No Failure
	3	100 ppm Cl$^-$	0.42	20 - 30	No Failure
	1	500 ppm Cl$^-$	0.42	15	No Failure
	1	2000 ppm Cl$^-$	0.42	0.32	Failed
	1	5000 ppm Cl$^-$	0.42	0.16	Failed
	1	100 ppm F$^-$	0.42	25.7	No Failure. Pitting. Oxide flaked off.
	2	100 ppm Cl$^-$ +100 ppm NO$_3^-$	0.42	15 - 21	No Failure

* Primary Solution Ammoniated Water pH 10 + 15 - 20 ppm Hydrazine

** Cl$^-$ Determined 0 - 20 ppm

Table 2 Effect of Contaminants on Corrosion Fatigue of Annealed Zircaloy-2 in Lithiated Water at 575 K and 10.5 MPa

Bar Type	No. of Tests	Contaminant*	Maximum Stress / UTS	Cycles	Comments
Oxidized		--**	0.42	> 20 x 10^6	Fatigue ratio 0.42
	3	100 ppm Cl$^-$	0.42 - 0.44	20 - 26	No Failure
	2	500 ppm Cl$^-$	0.42	15 - 30	No Failure
	2	1000 ppm Cl$^-$	0.42	26	No Failure
	1	2000 ppm Cl$^-$	0.42	15	No Failure
	1	5000 ppm Cl$^-$	0.42	20	No Failure
	1	7500 ppm Cl$^-$	0.42	15	No Failure
	1	10000 ppm Cl$^-$	0.42	∿ 0.3	Failed
	1	100 ppm F$^-$	0.42	29.6	No Failure. Pitting. Oxide Flaked Off.
	1	100 ppm F$^-$	0.42	42.5	Fractured. Severe Corrosion. Oxide Flaked Off.

* Primary Solution Lithiated Water pH + 15 - 20 ppm Hydrazine

** Cl$^-$ Determined 0 - 11 ppm

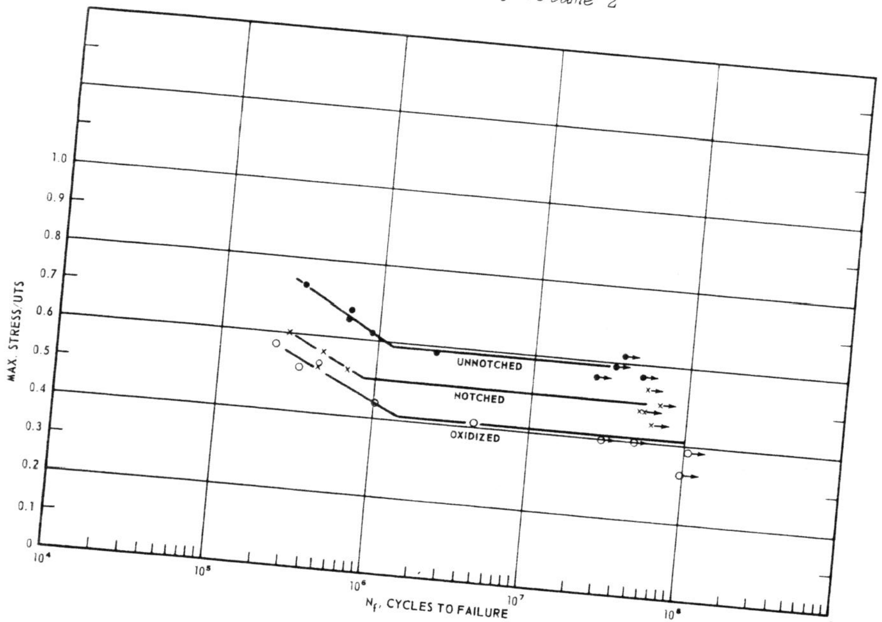


Figure 1 Reference Fatigue Curves for Annealed Zircaloy-2 in Ammoniated Water at 573 K

Frequency 60 Hz R = 0.1
● Unnotched Specimens
○ Oxidized Unnotched Specimens

Ammoniated Water
x Notched Specimens K_t = 3
→ No Failure

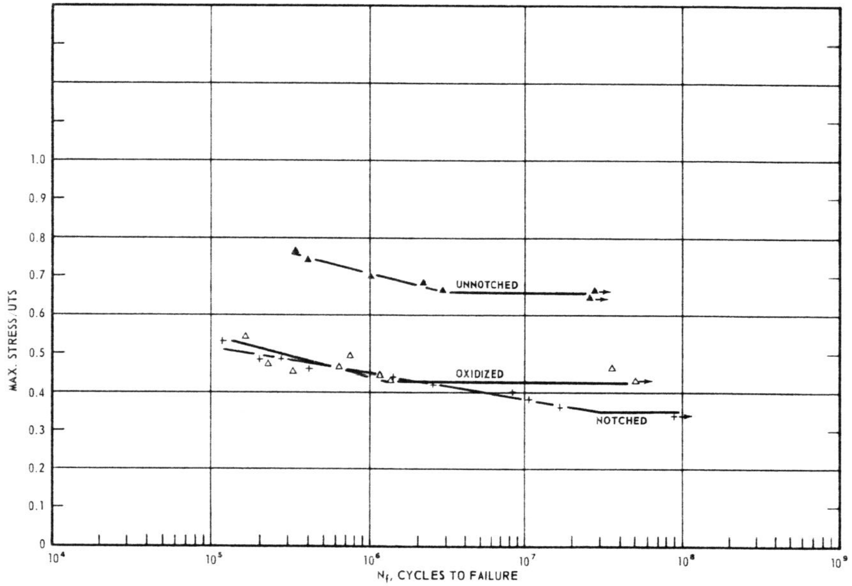


Figure 2 Reference Fatigue Curves for Annealed Zircaloy-2 in Lithiated Water at 573 K

Frequency 60 Hz R = 0.1
▲ Unnotched Specimens
△ Oxidized Unnotched Specimens

Lithiated Water
+ Notched Specimens K_t = 3
→ No Failure

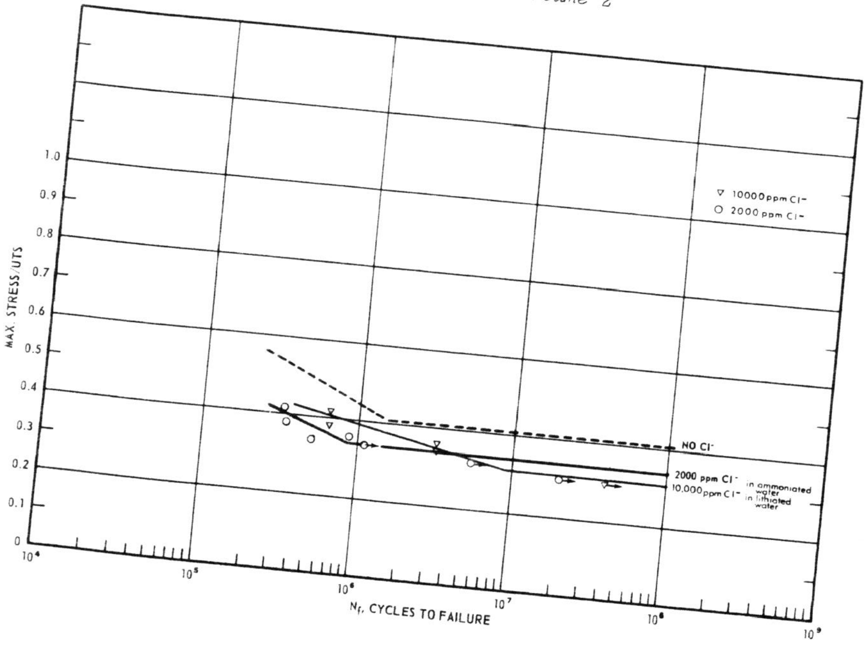


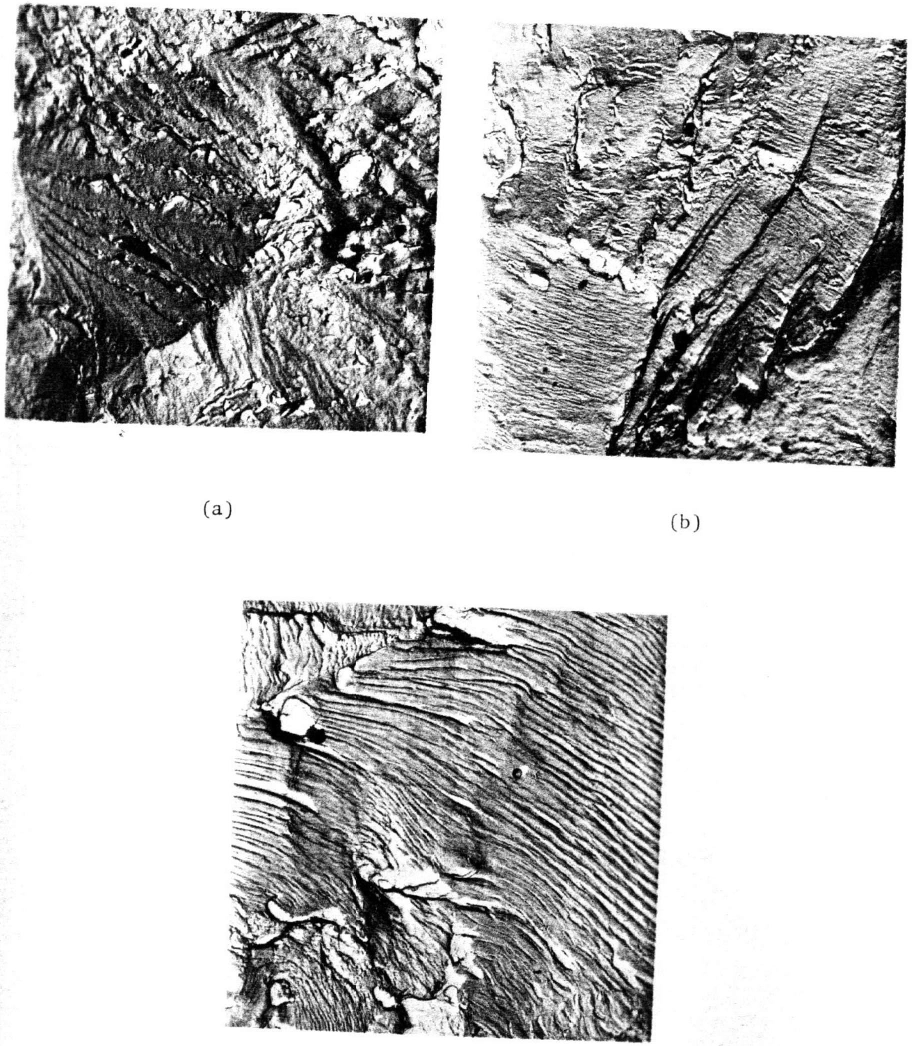
Figure 3 Fatigue Curves for Oxidized Unnotched Zircaloy-2 Showing the Effect of 2000 ppm Cl^- in Ammoniated Water and 10,000 ppm Cl^- in Lithiated Water at 573 K

Frequency 60 Hz R = 0.1

—○ Ammoniated Water + 2000 ppm Cl^- --- Ammoniated Water

—▽ Lithiated Water + 10,000 ppm Cl^-

→ No Failure



(a)

(b)

(c)

Figure 4 Fracture Surfaces of Zircaloy-2 Specimens Fatigued in Aqueous Solutions Containing Chloride Ions 5000X

(a) Feather Cleavage
(b) Brittle Fatigue
(c) Ductile Fatigue