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Iodine Stress Corrosion Cracking of Zircaloy-4 Tubes

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K A I S

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Abstract

In this paper, it is attempted to investigate the phenomena of iodine stress corrosion cracking of Zircaloy-4 cladding failures in reactor through the results of similar out-of-pile test in iodine vapour.

The main result of this experiment is a finding of the relation between the threshold stress which can lead to iodine stress corrosion cracking of Zircaloy-4 tube and the iodine concentration. The values of critical stress and the critical iodine concentration are also obtained.

A model which relates failure time of Zircaley-4 tube to failure stress and iodine concentration is suggested as follows:

$$\log t_F = 5.5 - (3/2)\log c - 4\log\sigma$$

where t_F: failure time, minutes

c: iodne concentration, mg/cm^3

σ: stress, 10^4psi

요 약

원자로 가동시, 정상상태에서 벗어나 갑작스럽게 출력이 바뀔 때 발생하는 응력의 집중과 핵 분열시 발생하는 요오드의 부식에 의해서 생기는 피복물질의 응력부식파괴현상을 이해하기 위하여, 이번 실험에서는 지르칼로이-4(Zircaloy-4)관을 사용하여 요오드응력부식 실험을 원자로 안의 상태에 가깝도록 300°C의 상태아래서 행하였다.

요오드 농도에 따라서 지르칼로이-4, 관(Tube)의 응력부식에 한 파괴시간을 구했고, 응력부식을 일으킬 수 있는 임계요오드 농도 및 임계접선방향의 응력을 구하였다.

요오드에 의한 응력부식이 화학적인 반응이라기 보다는 기계적인 반응성격을 갖기 때문에 응력부식을 파괴역학적인 관점에서 설명하고자 응력과 파괴시간을 함수관계로 다음과 같이 표시해 보았다.

$$\log t_F = 5.5 - (3/2)\log c - 4\log\sigma$$

t_F : 파괴시간(〃)

c : 요오드농도(mg/cm^3)

σ : 응력(10^4psi)

I. Introduction

After the Kroll process[1] was developed in 1945, zirconium became a very important material in the nuclear industry and particularly in respect of its use in the core of reactors.

However, the occurrence of low ductility cladding failures under power ramp conditions has been recognized as serious problem. These fuel rod defects are attributed to pellet-cladding interaction strains induced by thermal distortion of UO_2 pellets and probably assisted by fission product species.

In mainly CANDU reactors, it was shown that most of their power ramp related failures involve indine assisted stress corrosion cracking[2]

A study of the interaction of iodine with Zircaloy-2 tubes subjected to tensile stress at 350°C, was first reported in 1966 by Rosenbaum[3]

Thereafter the susceptibility of Zircaloy to iodine stress corrosion cracking (SCC) has been established through out-of-pile test by a number of investigators (3-14). They have studied the SCC susceptibility of many zirconium alloys in their relation to test temperature, iodine concentration, texture, cold work, residual stress, oxygen effect, and neutron flux, using a test method that utilized split ring or ioternally pressurized tube specimens.

So the main purpose in the present study is to understand the effect of iodine gas on the fracture of Zircaloy-4 tubes stressed by means of thermal expansion of Al-7075-T_6 mandrels at 300°C and to find the relation between the threshold stress which can lead to SCC of Zircaloy-4 tube and the iodine concentration.

Also here on the bais of elastic fracture mechanics, a model which relates the failure time of Zircaloy-4 to rupture stress is suggested.

II. Experimental Method and Materials

2.1 Materials

The specimens have been prepared from 50% cold-worked and stress relieved Zircaloy-4 tubes. The stress relieving has been carried out by heat-treatment at 500°C for four hours. Specimens have dimension of 15mm long, 9.65mm inner diameter and 0.04mm wall thickness. The alloy composition is given in Table 1.

In order to give high stress to the Zircaloy-4 tube, aluminum mandrels have been empleyed, because its higher coefficient of thermal expansion has rendered it more suitable for tests. The specific material of aluminium mandral is Al 7075-T6 made by Sam Sun Industry Co. Although Al-7075-T6 has been hot extruded, its thermal coefficients of expansion have shown significant directionality. Then machining has been done to the direction of extrusion. The direction of mandrel axis coincides with that of extrusion. The mandrels havebeen prepared in various eters. The iodine crystals containing a trace amount of impurities of 0.02% non-volatile material, 0.02% sulfate, 0.005% chlorine and bromines have been employed as a cor-

Table 1. Composition of Zr-4 tube (17)

Element	ppm	Element	ppm
Sn	15500	Hf	41
Fe	2250	H	10
Cr	1050	Mn	25
Ni	35	N	33
Al	46	O	1100
B	0.2	Si	50
C	145	Ti	25
Cd	0.2	W	25
Co	10	U	1.0
Cu	16	Zr	balance

rosion agent.

2. 2 Procedure

SCC tests have been conducted on Zirealoy-4 tubes inserted Al-7075-T6 mandrels.

The Zircaloy-4 tubes are stressed in the iodine atmosphere as a results of thermal expansion of fitted internal mandrel.

The developed hoop tensile stress depends on the initial diameter clearance. The negative clearance at room temperature imparts a higher stress to the specimens. The clearances between tube and mandrel have been arranged to be a fairly tight pushfit in the tests, but on occasion, an oversize mandrel has been cooled in liquid nitrogen before insertion in the tubing.

Before loading the Pyrex capsules have been cleared by cleaning solution (13g of $Na_2Cr_2O_7$ per 100m*l* of distilled water, and 85m*l* of concentrated H_2SO_4) and throughly dried.

After cleaning and drying, the specimens have been placed in Pyrex capsules of capacity about 65cm^3 with known amount of iodine which had been weighted by balance.

Each capsules have been evacuated with rotary pump to remove extraneous gases and moisture from the system. To provide better vacuum condition and thereby better control of the I_2 atmosphere, isolation cold trap has been used.

The vapour pressure of I_2 is 0.03 torr, while that of H_2O is 4.6 torr at 0°C. The I_2 placed in tube, is believed to be free of H_2O. The isolation cold trap has been cooled by dryice and aceton. The moisture and some of the I_2 have been accumulated in the isolation trap which has been held at −55°C. The iodine crystal which have been placed inside at one end of the tube, had been cooled with dryice (−55°C) to prevent its loss by evaporation. The vacuum have been obtained at $\sim10^{-3}$ torr.

The sealed capsules have been placed in an electric thermal bath at the temperature 300°C. The experiments have been done during 100 hours at most.

III. Results and Discussion

The experimental data are expressed in terms of iodine concentration. The failure time means the time duration required for cracking in furnace. It is expressed in hour unit. The amount of iodine also is expressed as mg/cm^2 (iodine mass per unit surface of Zr-4), because this parameter is invariant.

The mark "o" means a failure specimen.

The mark "x" means no failure specimen.

The mark "*" means that experiment data is the expected value.

The stress value is the hoop stress of Zircaloy-4 tube. The mark "O_2" in parenthesis of Table 3 and 4 means that experiment was carried out with specimen contained oxide layer. This oxide layer occured before loading in the Pyrex capsule.

The relations between hoop stress of Zr-4 tube and iodine concentration are shown in

Table 2. 0.2mg/cm^3

stress \ concentration	1.1mg/cm^2	1.8mg/cm^2	1.91mg/cm^2
8.79×10^{4}psi		0(19hrs)	
8.20×10^{4}psi		x	
7.62×10^{4}psi	o(11hrs)	x*	x
7.03×10^{4}psi	x	x*	x
6.45×10^{4}psi	x	x*	x

Table 3. 0.55mg/cm^3

stress \ concentration	3.18mg/cm^2	2.44mg/cm^2
7.62×10^{4}psi	x(O_2)	x(O_2)
7.03×10^{4}psi	0(2hrs)	0(3hrs)
6.45×10^{4}psi	x	x
5.28×10^{4}psi	x*	x*

Table 4. 2mg/cm³

concentration / stress	8.86mg/cm²	13.26mg/cm²	14.01mg/cm²
$.62\times10^4$psi	x(O_2)	x(O_2)	x(O_2)
7.03×10^4psi	o(1hr)		x
6.45×10^4psi	x	o(1/3hr)	x*
5.28×10^2psi	x	x	x*

Table 5. 10mg/cm³

concentration / stress	44.04mg/cm²	59.35mg/cm²	66.85mg/cm²
7.62×10^4psi	0(1/2hr)	0(1/4hr)	
7.03×10^2psi	0(5hrs)		0(1/3hr)
6.45×10^4psi	x	x	0(2/3hr)
5.28×10^4psi	x	x*	x

Table 6. 20mg/cm³

concentration / stress	143.24mg/cm²
6.45×10^4psi	0(1/3hr) (O_2)
5.28×10^4psi	0(1/3hr)
4.12×10^4psi	0(1/3hr)

Table 7. 40mg/cm³

concentration / stress	224.4 mg/cm²	224.4 mg/cm²	250² mg/cm	408.7 mg/cm²
2.85×10^4psi	x	0(1/2hr)	x x	0(1/6hr)
1.78×10^4psi	x	x	x x	x

Table 2~7.

The values (mg/cm²) are obtained from that total iodine amount in pyrex tube be divided by total surface of Zr-4 specimen in Pyrex tube.

The values (mg/cm³) are obtained from that total iodine amount in Pyrex tube be divided by total volume of Pyrex tube.

Date in Tables can be plotted as Fig. 1.

The photographs of specimens are shown in Fig. 2 and 3.

Threshold stress means the minimum stress of Zr-4 which can lead to cracking at constant iodine concentration.

Thereshold behavior as function of iodine concentration can be divided into three region.

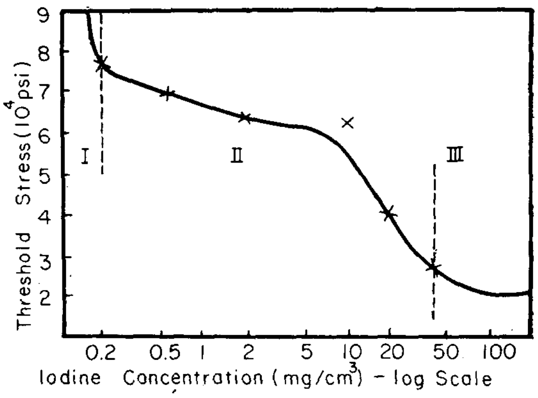

Fig. 1. Relationbb etween threshold stress and iodine concentration.

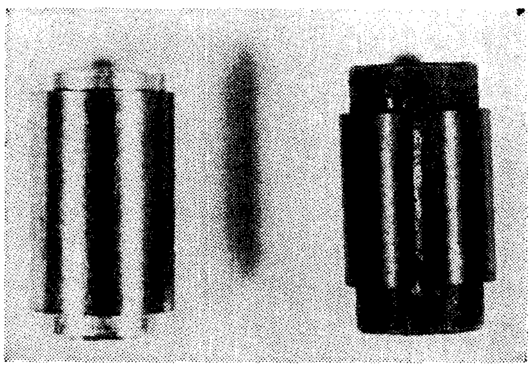

Fig. 2. left; Before loading specimen Right; Iodine stress corroiion cracking specimen

Specimens in pyrex tube
Fig. 3. The first (from left to right) is the cracked specmen.

It should be noted that in region I, iodine concentration does not depend on the threshold stress. Crack behavior is expected to have similarity to the overstrained cracking. It is to be thought that the phenomenon of SCC can be shown in region II, the primary reaction seems to be chemical corrosion

3.1 Experimental Method

The mandrel method for giving a stress has been adopted in the present experiment. The first reason is that the mandrel load has its simplicity and facility and it provides uniform stress over a large area of the tube.

It is a suitable method for SCC testing as recommended in ASTM SUP 425.[20]

The second reason is that it has the advantage of good approximation of pellet-cladding mechanical interaction taking place at high reactor power.

The third reason is that this method has the property of biaxial or trial stress tension.

The major stress is acting in the hoop direction and minors are the radial stress and axial stress which depends upon frictional forces between mandrel and tube.

The experimental results of Rosenbaum[3] and Bob[11] showed that complex stress systems are more likely to produce SCC than is simple uniaxial stressing. But the disadvantage of this method is in uncertainty of the value of stress generated in the tube. So that, the interally pressurized method is a very suitable for SCC of Zircaloy-4 tube, i.e., the interally pressurized tube with inert gas is available for good estimating stress.

However the sealing of inert gas is extremely difficult to handle in a ordinary laboratory.

3.2 The Stress

Under condition of elastic behavior of the tube and the mandrel, the stress is estimated by the following equation which is derived from Lame's quation.

$$\sigma_t = \frac{[(\alpha_{Al}-\alpha_{Zr})(T_t-T_0)-d/R]E_{Zr}}{1+\frac{hE_{Zr}}{RE_{Al}}+\frac{h}{R}\nu_{Zr}-\frac{hE_{Zr}}{RE_{Al}}\nu_{Al}}$$

α_{Al}: Aluminum thermal expansion coefficient
α_{Zr}: Zircaloy-4 thermal expansion coefficient
E_{Al}: Young's Modulus of Aluminum
E_{Zr}: Young's Modulus of Zircaloy-4
T_t: test temperature (300°C)
T_0: room temperature (20°C)
h: tube wall thickness
R: tube radius
d: diameter cleararance
ν_{Al}: poission's ratio of Aluminium
ν_{Zr}: possion's ratio of Zircaloy-4

The stress values in Table 2 to 7, have been obtained by this equation. But it should be noted that this equation does not show plastic deformation effect and creep effect in long duration experiment, which is a defect in this treatise.

3·3 SCC Susceptibility of Zircaloy-4

Zirconium alloys are always covered with an oxide film after exposure to oxygen containing environment at room or reactor operating temperatures. It is possible that the growth of Zirconium oxide may be modified by the presence of iodine to give a porous rather than compact layer. The data which have the mark of "O_2" in Table 3 and 4 has been obtained from the experiments which have been performed under special condition. It has been carried out after the tube specimens had been oxidized to form an oxide layer. If the surface of tubes stressed in tension stays covered by the thick oxide layer, cracking will not occur. The data in Table 3 and 4 also stows that oxide layer on Zircaloy-4 tube plays a protective role against iodine vapor. The above physical phenomena describe the time dependency of

SCC.

In reactor, when the final power is high, SCC starts with mechanical crack in ZrO_2 film of the cracking Zr-4 surface. After ZrO_2 film break down, cracking proceeds to notch formation at a grain boundary or to surface pit. Thus the cladding should be in a metalllurgical state that is susceptible to SCC.

3·4 Influence of Stress

From the results of expericment that are shown in Tables, it tan be estimated qualitatively that threshold stress for iodine-induced cracking is dependent on the available initial amount of iodine. Threshold stress is decreased as iodine concentration is increased. If the amount of iodine is inceased as much as possible, it can be thought that the thresshold stress would go to a critical value. The critical stress. exists in this SCC process, i. e. ; below which the Zircaloy-4 tube would have no possibiliy of SCC, even if the iodine concentration is high. In fuel failure, hoop stress must exceeds the critical stress for SCC.

3. 5 Influence of Iodine Concentration

In order to maximize the amount of observing data with a minmum number of speciemens, the SCC behavior has been examined at iodine concentrations of 0. 2, 0. 55, 2. 10, 20, 40 mg/cm^3. Some corrosive effect results from the reduction of the failure time and the stress when iodine concentration is high as shown in the region II (Fig. 1).

The lowest iodine concentration that could lead to cracking is induced to 0. 2mg/cm^3 from the experimental data. So when the iodine available to Zircaloy-4 surface is less than 0. 2mg/cm^3, failures do not result.

3. 6 Mechnaism

The Zircaloy-iodine vapour system is unusual because cracks apparently propagate in the absence of an electrolyte. Since electrolytic theories do not seem to be applicable, thus it is attempted to relate the Ziircaloy-iodine cracking behavior to fracture meclamics. [5] It is thought that Zr-I reaction at the crack-dip reduces the energy reguired to break a Zr-Zr bond by creating intermediate weaker Zr-I-Zr bonds. W. D. Robertson and A. S. Tetelman[21] proposed that dislocations generated during plastic deformation were piled up against obstacles, probably grain boundaries in the case of intergranular failures. the normal stress in acting at the head of a disllocation queue tended to open up a crack and this process was facilitiated by simultaneous chemical attack to remove the reactive material adjacent to the obstacle.

3. 7 SCC Model

SCC is typified by stress below which no failure occcurs. Delayed failure of structural components subjected to an aggressive environment may occur under statically applied stress well bolow the yield strength of material. Failure of structural component under these condition, is mainly caused by SCC. The traditional approach to study SCC susceptibility of a material in a given environment, is based on the time required to cause failure of smooth or mildly notched specimens subjected to different stress levels,

In SCC, slow crack growth may occur constant stress over a period of time, when certain materials are subjected to particular environments. The crack growth rate approach to study SCC behavior of environment-material systems involves the measurement of the rate of crack growth per unit time, as a function of the instantaneous stress-intensity factor. By this method, P. H Kreyms, G. L. Spahr, and J. E. Mc Cauley[15] obtained equation. ①

$t_F = B\sigma^{-4}$ ··· ①

t_F: failure time for SCC

σ: hoop stress

B: proportionality constant

Taking logarithm both side of Eq. ① and arranging it,

$\log t_F = B(T, C) - 4 \log \sigma$

This expression is the relation between the failure time and the hoop stress. B (T, C) is a function of temperature and iodine concentration.

Then the empirical reaction rate is given below:

$w^n = k_p \cdot t + \text{constant},$ ······························ ③

where

W: weight gain per unit area

k_p: reaction rate constant

t: exposure time

So the exposure time is obtained from Eq. ③

$t = \left(\frac{1}{k_p}\right. W^n + \text{constant}$

Taking logarithm both side

$\log t = n \log W + \text{constant}$ ························ ④

In case that the stress and the temperature are constant, B(T, C) can be expressed as following on the analogy of Eq. ④:

$B(T, C) = n\log C + \text{constant}$

If the value of n is obtained by fitting of experimentel data, failure time can be expressed below:

$\log t_F = 5.5 - \frac{2}{3} \log C - 4 \log \sigma,$

where

t_F: failure time, minutes

C: iodine concentration, mg/cm^3

σ: stress, 10^4psi

The control parameters for SCC are corrosive environment, sustained stress, and susceptible metallugial structure. The corrosive environment is iodine vapour in SCC on Ziroaloy-4 tube. The amount of iodine produced by irradiation of UO_2 fuel is well reported[11]. About 15% of total fission products formed by U, are iodine isotopes. Only one isotope, I^{129}, is stable and 0.8% of total fission products.

On the other hand, there is still a different argument that mechanical overstraining of the low-ductility-irraiated cladding might be the primary mechanism for fuel failure. The causes of the low ductility failures have not always been pinpointed, but there is an evidence[2,3,18,19,22,23] to suggest that a number of these failure results from fission product iodine SCC.

IV. Conclusion

A) Threshold stress to cause the SCC of Zircaloy-4 tube depends on iodine concentration. The critical stress levels below which SCC is not observed for the test time up to 100 hrs, are in the range of 1.78×10^4 psi to 2.95×10^4 psi.

B) The critcal iodine-concentration that can iniitiate cracking of Zircaloy-4 tube, is 0.2 mg/cm^3 (1.1mg/cm^2)

C) The failure time depends on the iodine concentration and the hoop stress of Zircaloy-4 tube. It can be described as $\log t_F = 5.5 - \frac{3}{2} \log C - 4 \operatorname{cog} \sigma$.

D) The oxide layer on the surface of Zircaloy-4 tube, plays a protective role against iodine vapour. But at the high concentration, its role is negligible. Because the stress would be sufficient to rupture the protective ZrO_2 layer that exists on the Zircoaloy-4 surface.

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