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Deformation Characteristics of Zircaloy-4 Fuel Cladding due to Oxidation in Environment of High Temperature and Steam

Sung-Hoon Jung and Kyung-Soo Suh
Korea Advanced Energy Research Institute

In-Sup Kim
Korea Advanced Institute of Science and Technology
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고온, 수증기 속에서 산화된 질칼로이-4 핵연료 피복관의 변형 특성에 관한 연구

정 성 훈 · 서 경 수
한국에너지연구소

김 인 섭
한국과학기술원
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Abstracts

Studies were conducted to determine the extent of oxidation and same of the mechanical property changes of Zircaloy-4 fuel cladding after it was exposed to hot steam environment. The purpose of these tests was to provide some informations on the embrittlement behavior of CANDU type fuel cladding, which could be experienced under the loss-of-coolant accident conditions. The Zircaloy fuel cladding tubes were exposed in a steam environment at the temperature of 900°C, 1,000°C. The growth of the ZrO_2 layer combined with an oxygen rich α-phase layer into the Zircaloy tube material was found as a function of time t and temperature of steam exposure, $E=1.1\sqrt{Dt}+0.002$, where D is a temperature dependent diffusion coefficient. The tensile strength of the specimens exposed for a short period increased but decreased continuously with further exposure. The circumferential elongation was drastically changed with the exposure time while the hoop strength did't decrease greatly. The X-ray measurement of preferred orientation of the Zircaloy tube material indicated that grains in the as received tube were oriented such that the poles of the basal(0001) planes were predominantly radial, while the poles of the basal plane in the tube materials heat-treated at 1,000°C were oriented tangentially. It appears that this reoriented texture may contribute to lessening the decrease of the hoop strength of the heat treated Zircaloy tube material.

요 약

가상적인 냉각재 상실 사고시의 조건하에 일어날 수 있는 취약화 현상에 대한 자료를 얻기 위하여

고온의 수증기 분위기에서 Zircaloy-4 핵연료피복관의 산화거동과 기계적성질 변화에 대한 연구를 수행하였다. 시편은 캔두형핵연료 피복관으로 사용되는 질칼로이 튜브를 사용하였으며 냉각재 상실 사고시 야기될 수 있는 수증기 분위기속 900°C와 1,000°C에서 유지시간을 변경하여 가면서 산화시켰다. 질칼로이 피복관의 표면과 내부에서 ZrO_2 및 α상의 형성속도 E는 온도와 시간의 함수인 $E=1.1\sqrt{Dt}+0.002$로 나타났다. 여기서 D는 온도에 의존하는 확산계수임. 시편에 대한 인장강도, 후프강도 및 연신율을 측정한 결과 단시간 산화된 시편의 인장강도는 원래의 피복관에 비해 처음에는 약간 증가하다가 계속되는 유지 시간에 따라 감소하였다. 후프강도는 유지 시간에 따라 많이 감소하지 않았으며 외경 방향의 인장율을 급격히 감소하였다. 피복관의 선택 방위 측정 결과 원래의 피복관 입자는 대부분이 기저면(0001)에 대한 극축이 외경 방향에 평행하게 놓였었으나 1,000°C에서 열처리한 경우는 극축이 외경 방향에 수직으로 변경됨을 알 수 있었으며 이러한 결정면의 방위분포 결과가 후프강도의 유지에 기여하는 것으로 추측되었다.

I. Introduction

One of the possible consequences of a loss-of-coolant accident (LOCA) in a water cooled reactor is rapid heat up of the fuel tubes in a steam environment. During the period when the cladding is exposed to steam at elevated temperatures, several investigators reported[1~4] that an oxide film on the cladding surface and an oxygen gradient into the cladding matrix are formed by reaction of the Zircaloy with the steam.

Since the ductility of Zircaloy is a function of oxygen content, and the oxygen content is a function of time and temperature of steam exposure[5], a study of the embrittlement phenomena under a LOCA necessitates the examination of specimens exposed to specific temperatures for given lengths of time in a steam environment. The temperature considered in this study were 900°C and 1,000°C. The reaction of steam with the Zircaloy cladding firstly results in dissociation of steam into oxygen and hydrogen, and then the oxygen reacts with zirconium according to the relation; $Zr+O_2 \longrightarrow ZrO_2$.

Diffusion reaction of oxygen can be expressed in terms of $\sqrt{Dt}$, where D is a temperature-dependent diffusion coefficient and t is time of exposure.

In the present study attemps are made to interprete mechanical property changes of Zircaloy cladding material that result from exposure to a high temperature steam through measurement of formation of the oxide and α-phase layer of the Zircaloy cladding, which could be expressed as a function of the temperature and time of the exposure in steam.

Tensile strength and hoop strength are measured and discussed in relation to the degree of oxidation of the Zircaloy material.

Also, the strength variations are evaluated with respect to the deformation mechanism concerned with the texture changes on the thermal effect.

II. Experimental Procedure

II. 1 Specimens and Apparatus

Zircaloy-4 tubes of the size used in the CANDU reactor were obtained from Mannsesmann Co., in West Germany. The test specimens had dimensions the 13.08mm outside-diameter by 0.42mm wall-thickness and 240mm length. Nominal chemical composition of the as received specimen is presented in Table 1 and a photomicrograph of the cross section of the specimen is shown in Fig. 1.

Zircaloy samples were placed in the quartz tube to maintain a stagnant steam environment. Direct Zircaloy clad resistance heating method was used to raise the temperature of the fuel rod cladding.[6~7]

Table 1. Chemical Composition of Zircaloy-4 Cladding

Alloying Elements	Contents
Tin	1.20~1.70 Wt%
Iron	0.18~0.24 Wt%
Chromium	0.07~0.13 Wt%
Total Fe+Cr	0.28~0.37 Wt%
Carbon	80~300 ppm
Oxygen	900~1,500ppm
Zr+Permitted Impurities	Balance

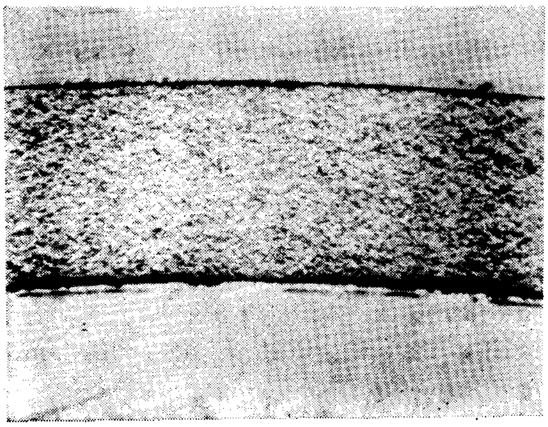

Fig. 1. Microstructure of Zircaloy-4 Fuel Cladding

Both ends of the Zircaloy tube specimen were clamped with pure copper grippers which were connected with a SCR controlled AC power supplier. To maintain the uniform steam environment on the whole surface of the Zircaloy tube specimen, a steam shower method was used for the axial length of the Zircaloy tube: Fig. 2 shows the schematic of Zircaloy tube oxidizing apperatus consisting of SCR controlled power supply, steam supply system, and temperature—control instrumentation. Two of type S (Pt—Pt 10%Rh) thermocouples (0.1 mm dia) were spot welded directly to the tube specimen to check and maintain the desired temperature. As for the fuel rod condition in the reactor, the steam with a flow rate of 6cc/ min, was supplied only to the outside of the Zircaloy tubes and the inside of the tubes was purged with argon gas.

II. 2 Test Procedure

The Zircaloy tubes were directly heated up to 900°C and 1,000°C for a period of 10 sec to 600 sec and then allowed to cool down to room temperature. The heating rate was 50°C/sec and cooling rate was maintained about 25°C/sec. Metallurgical samples were prepared from the section of the Zircaloy tube specimen and photomicrographs were made to determine the zirco-

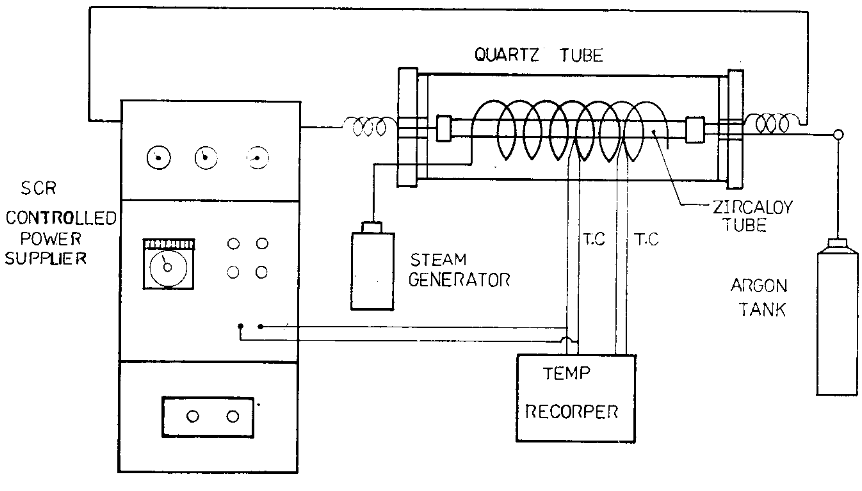

Fig. 2. Schematic of Zircaloy Tube Oxidizing Apparatus

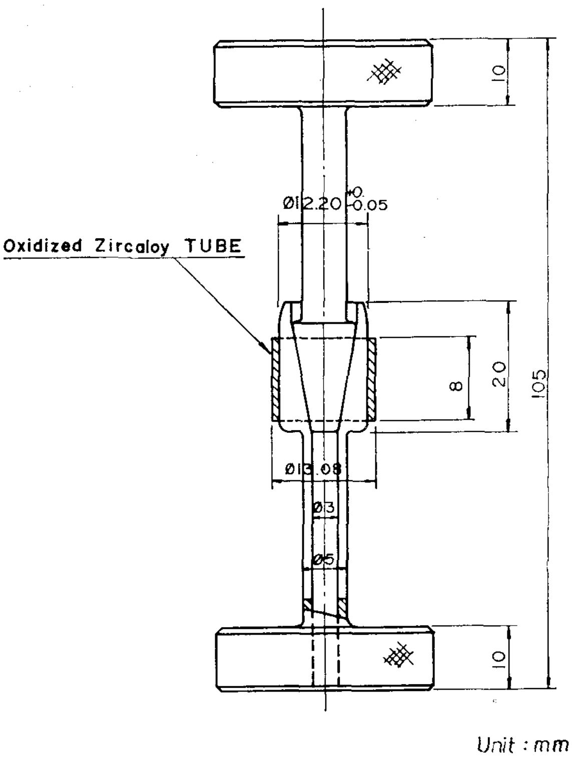

Fig. 3. Dimensions of Ring Expanding Tool

nium-oxide and oxygen-rich α-phase layer thickness. The embrittlement of the Zircaloy tube specimen were determined by the axial tensile test and ring expansion test. Tensile tests were conducted according to ASTM E8 at room temperature in air using an INSTRON universal testing machine to measure the ultimate tensile strengh of oxidized Zircaloy specimen. Ring expansion tests were also conducted the same way as tensile tests but attached a special tool[8] (Fig. 3) to the INSTRON to measure the hoop stress of the oxidized specimens. The cross head speed of the testing machine was 0. 1mm/min for both tests.

II. 3 Measurement of Crystallographic Texture

The texture of the Zircaloy-4 cladding was determined using the inverse pole figure technique.[9,10] Composite specimens from each tube were prepared for the radial, tangential and axial direction. Each specimen was mounted in a diffractometer (Philips Noreco) and scanned using a Cu $K\alpha$ target. The area under the(hk.l) reflection peak was used to calculate the texture coefficient values from the equation

$$T.C(\text{hk.l}) = \frac{I(\text{hk.l})/I_0(\text{hk.l})}{\frac{1}{n}\sum_{0}^{n} I(\text{hk.l})/I_0(\text{hk.l})}$$

Where I=measured integrated intensity of a given hk.l reflection

I_0=intensity of the same hk.l reflection produced by a powder sample of random orientation

n=total number of reflections measured

$T.C$=Texture coefficient

III. Results and Discussion

III. 1 Microstructual Characteristics of Oxidized Zircaloy Tube.

The as-received microstructure of the Zircaloy tube used in these tests was shown in Fig. 1. The Zircaloy tube specimens meet the requirements for reactor grade Zircaloy-4 tubing as specified in ASTM B-353. The tubes exhibited a very small grain size of less than 10μm in as-received condition. Exposure to a high temperature steam environment caused change in the microstructure of the Zircaloy tubing as shown in Fig. 4. The structure of the exposed material

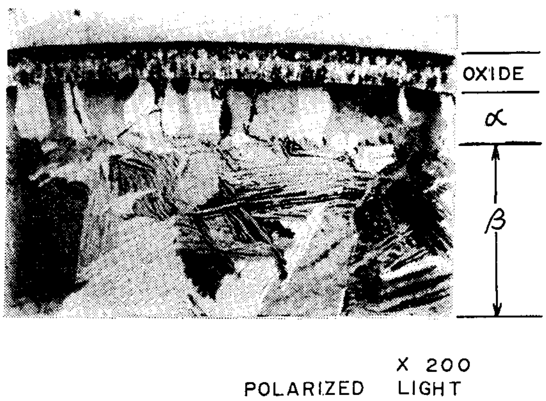

Fig. 4. Photomicrograph of Oxidized Zircaloy-4 Cladding.

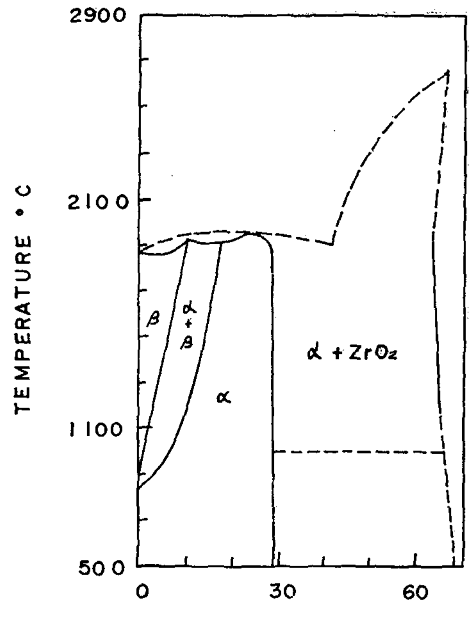

Fig. 5. A Phase Diagram of the Zirconium-Oxygen System

consisted of a layer of zirconium oxide, a layer of oxygen-rich α-zirconium, and a base section of zirconium of prior-β phase transformed to α-phase. The oxygen-rich α-zirconium, that is formed by oxygen diffusion, remained as a stable phase when the material was cooled from a test temperature.

The liimit of oxygen solubility in zirconium is only about 0.5%. When a highly oxygen saturated β-phase material is cooled slowly, zirconium oxide often precipitates along grain boundary[11] resulting in a extremely brittle structure. The amount of oxygen that can exist in various phases of the material (α, β and ZrO_2) at given temperature can be seen from the phase diagram for the zirconium-oxygen system in Fig. 5.

A relationship for the penetration of the oxygen-saturated α-zirconium phase into the Zircaloy tube matrix was applied to the results obtained. The relationship applied can be expressed as follows.

$$E=A\sqrt{Dt} \qquad (1)$$

where

E=Total width of the ZrO_2 layer and oxygen-saturated α-layer

A=parameter characteristic of the system (dimensionless)

D=diffusion coefficient (cm^2/sec)

t=time (sec)

The experimental data provide E and t, and the value of A was estimated by the plotting of E and $\sqrt{Dt}$.

Diffusion coefficient values were obtained by experimental temperature data presented by A. W. Lemmon.[12]

$$D=1.196\ \exp(-41000/RT) \qquad (2)$$

In this expression, R is 1.987cal/mole K and T is the sample temperature in K, the constant (41000) is the activation energy in calories per mole. The total thickness (E) of the ZrO_2/α-phase measured on our specimens was plotted against the square root of time as in Fig. 6.

The points form a set of two straight lines whose slopes are dependent on the test temperature.

Fig. 7 shows a plot of E versus the square root of the product of the diffusion coefficient (D) and time (t) also, the equation was fitted

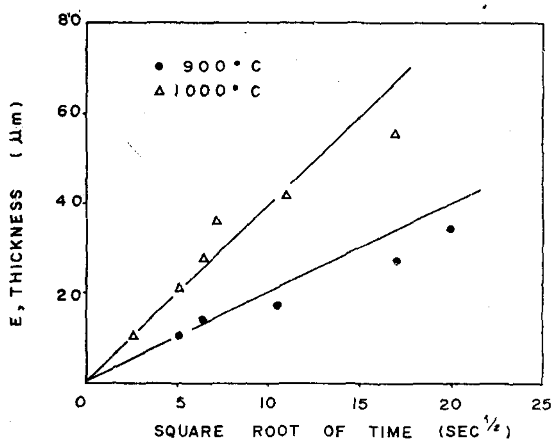

Fig. 6. Thickness(E) of the Combined ZrO_2/α Phase Layer Against the Square Root of Holding Time

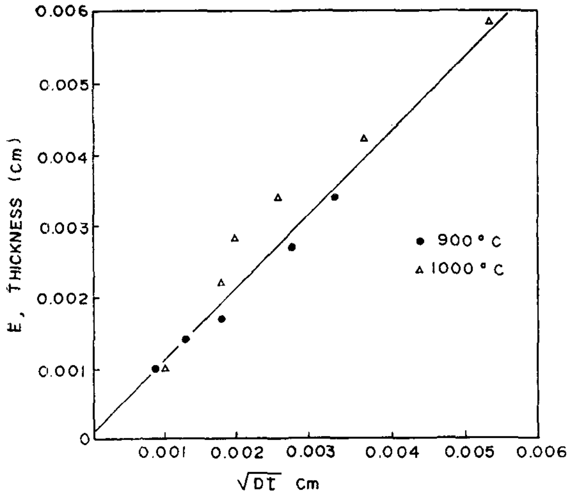

Fig. 7. Oxide Thickness(E) Plotted Against $\sqrt{Dt}$

by least square method.

A was determined from the slope as 1.1 and hence equation (3) was obtained

$$E=1.1\sqrt{Dt}+0.002 \quad (3)$$

III. 2 Embrittlement Behavior of Zircaloy-4 Cladding after Oxidatin in Steam.

The results of the uniaxial tensile test of Zircaloy-4 tube specimens oxidized at 900°, 1,000°C are shown in Fig. 8.

The ultimate tensile strength of the specimen xidized in steam for short duration increased slightly but after exposure of longer than one minute the strength decreased gradually. The

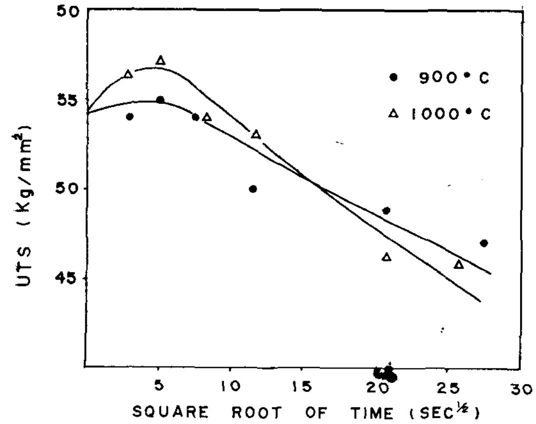

Fig. 8. Ultimate Tensile Strength Variations Plotted Against the Holding Time

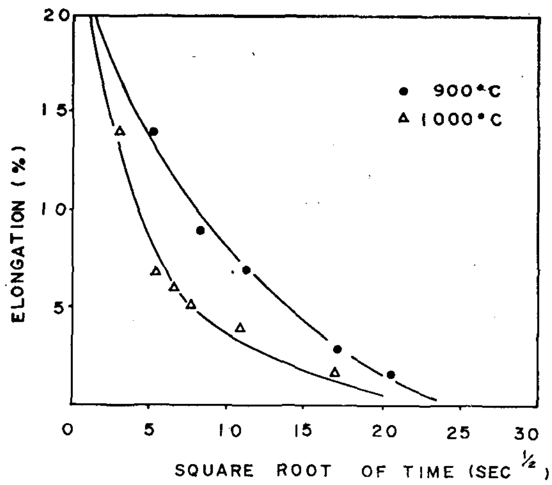

Fig. 9. Elongation Variations Plotted Against the Holding Time

slope of decrement for the ultimate tensile strength of Zircaloy-4 specimen oxidized at 1,000°C was greater than that of specimens oxidized at 900°C. Elongation vatiations of Zircaloy-4 specimens plotted againt holding time at high temperatures in steam are given in Fig. 9.

In case of the specimen oxidized at 1,000°C for one minute, the elongation of the specimen was less than 5%. The elongation, however, decreased rapidly with increasing exposure time.

The hoop strength and circumferential elong-

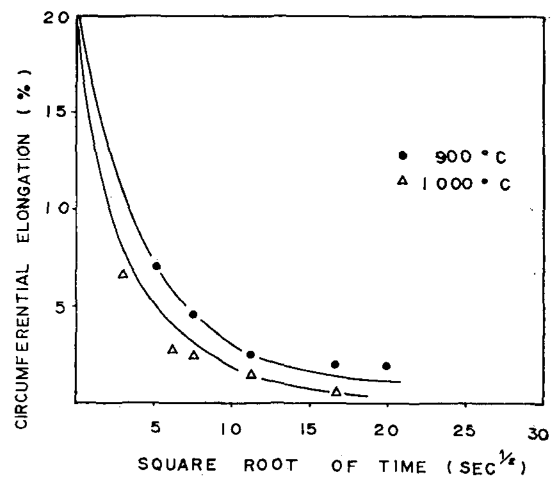

Fig. 10. Circumferential Elongation Rate Variations Plotted Against the Holding Time

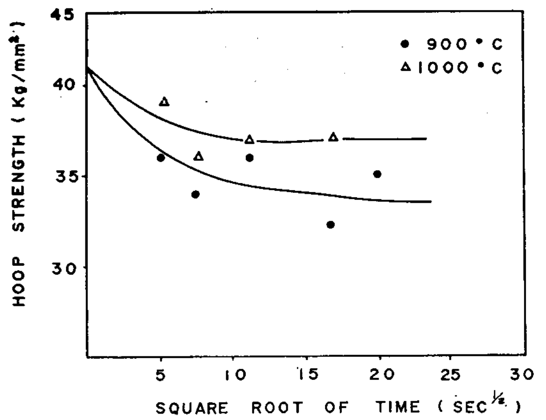

Fig. 11. Hoop Strength Variations Plotted Against the Holding Time

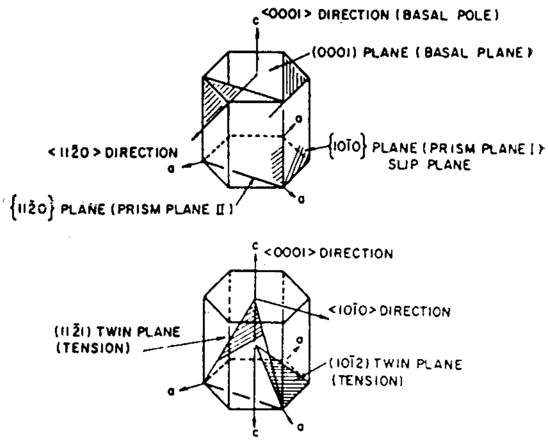

Fig. 12. Slip and Twinning Planes in Alpha-Zirconium.

ation data were obtained by the ring expansion tests. As shown in Fig. 10, the value of circumferential elongation decreased rapidly as a function of holding time at 900°C and 1,000°C in steam.

This phenomena show the similarity to the result of tensile test which appear to be a good indication of embrittlement behavior of oxidized Zircaloy-4 cladding. Fig. 11 shows dependence of the hoop strength of oxidized Zircaloy-4 specimens on holding time at 900°C and 1,000°C in steam.

During short time exposure in steam the hoop strength decreased a little initially and then did not change much with further exposure.

III. 3 Texture Effect.

Zircaloy has the hexagonal close-packed crystal structure below 830°C, and zirconium alloys exhibit anisotropic mechanical properties in different directions. This is because only few deformation systems operate in the hexagonal crystal structure of α-zirconium.[13,14] These systems, illustrated in Fig. 12 are slip on the $\{10\bar{1}0\}$ prism plane in the $\langle 11\bar{2}0\rangle$ direction, and twinning under tension on the $\{10\bar{1}2\}$ and $\{11\bar{2}1\}$ plane in the [0001] basal pole direction.

The flow stress for slip is lower than that for twinning and this results in higher strength when a majority of grains are oriented with their "c" axis parallel to the stress axis rather than with their "a" axis.[15,16]

According to the tension test reported by R.A. Holt, the Zircaloy tubes that have a majority of grains oriented with their "c" axis parallel to the stress axis have about 40% higher yield strength than the Zircaloy tubes having grains oriented with the "a" axis parallel to the stress axis.

During fabrication a preferred orientation or crystallographic texture is developed in the grains of α-zirconium alloys that depends on the manufacturing process.[17] Crystallographic textures can be represented in several ways; one method is the inverse pole figure technique that measures the intensities of all the crystallographic planes in a given direction. The texture may then be compared on the basis of several idealized orientations of the basal poles as shown in Fig. 13.

Zircaloy tubes manufactured by different pro-

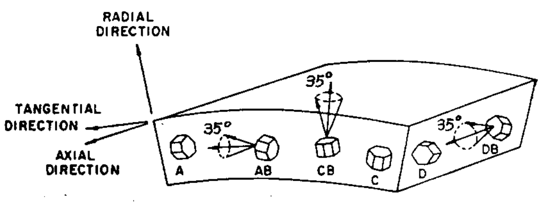

Fig. 13. The Idealized Orientations.

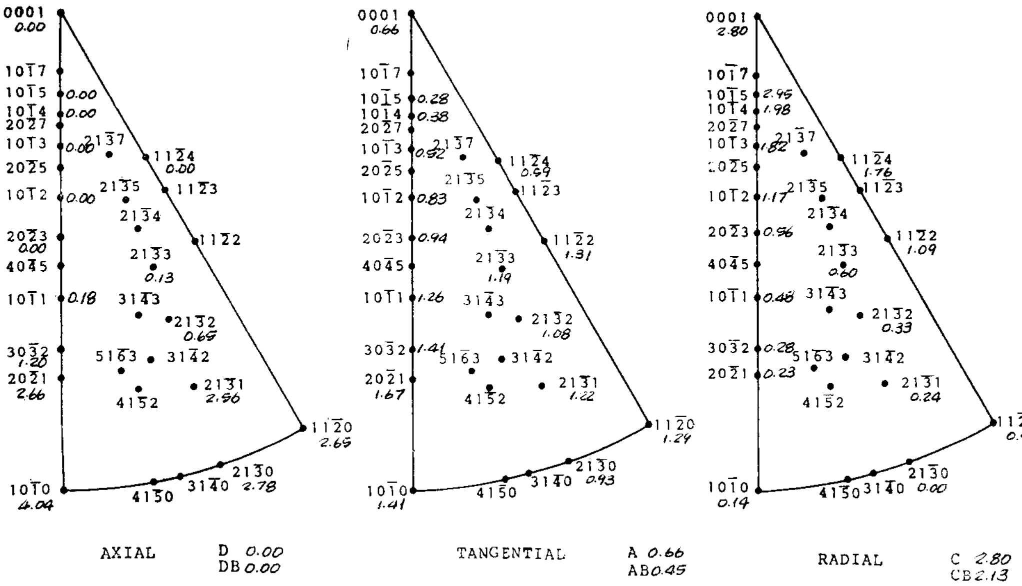

Fig. 14-a. Tnverse Pole Figures of As Received Zircaloy-4 Cladding.

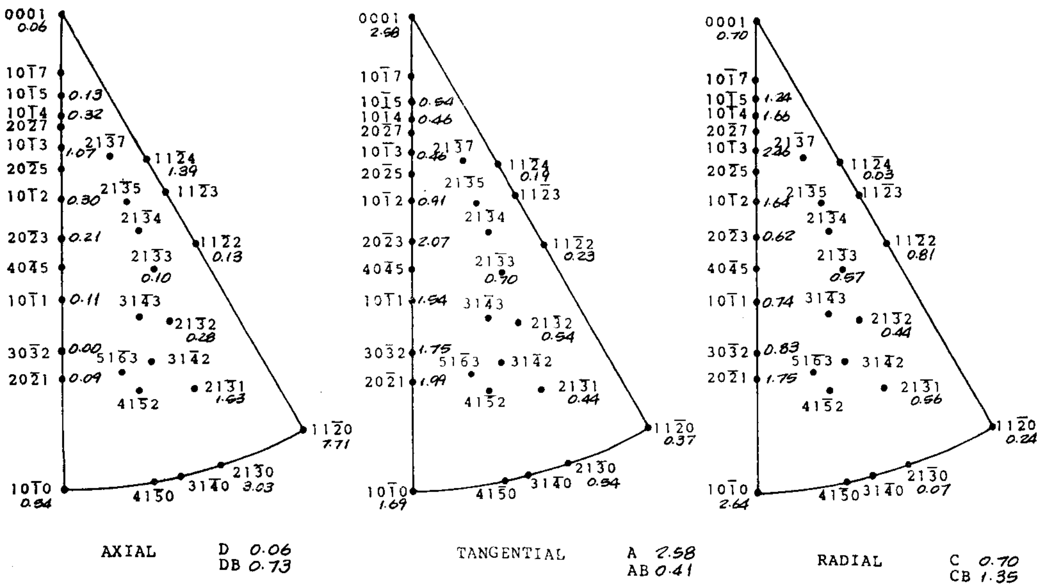

Fig. 14-b. Inverse Pole Figures of 1000°C Heat Treated Zircaloy-4 Cladding.

cessing methods can have different properties of grains in different orientations and thus have different mechanical properties. For fuel cladding the C and CB orientations are desired and are most popular orientations. Fig. 14-a shows the inverse pole figure measured from the as received fuel cladding for the CANDU MW600 type reactor.

As shown in the figure, the texture coefficient for C and CB orientations was 2. 80 and 2. 13 each. Also, for the A and AB orientations the texture coefficient was determined as 0. 66 and

0.45 each.

When the Zircaloy cladding is heated at 1,000 °C during 30 seconds in vacuum, the orientation of grains are changed to that shown in Fig. 14-b. The texture coefficient of A orientation increased but the texture coefficient of C and CB decreased. Also, the texture coefficient of D and DB slighty increased.

In longitudinal tensile tests and ring expansion tests for as received tubes, the grains are oriented for deformation by slip. For the cladding that were heated at 1,000°C the grain orientations of A was increased. It means that the deformation will be by slip in tensile test but in case of the ring expasion tests, the stress is applied as tangential direction and so deformation will happen by twinning, for the A grains.

Because of the above mentioned reasons the hoop stress of heat treated but not oxidzed part of Zircaloy cladding will be higher than the as received cladding. Also, the circumferential elongation will be decreased as shown in Fig. 10.

Fig. 11. shows that the hoop strength of oxidized specimens that did not decrease appreaciably depend on the exposure time and it can be explained by the increase of A grain orientation.

IV. Conclusion

The following conclusions were drawn from the oxidation and embrittlement test of the Zircaloy fuel cladding

(1) The thickness of the oxide and oxygen-saturated α-phase layer of Zircaloy cladding that resulted from exposure to high temperature and steam environment can be expressed as a function of temperature and time

$E=1.1\sqrt{Dt}+0.002.$

(2) The diameter of Zircaloy tubes increased by 1.5% maximum as a result of an exposure to steam at 900°C and 1,000°C.

(3) The tensile strengh of Zircaloy tube specimens exposed to high temperature steam for a short duration slightly increased compared with that of the as received tubes but prolonged exposure time the tensile strength decreased rapidly.

(4) The hoop strengh of Zircaloy tube specimens oxidized did not decrease appreciably with increasing exposure time at high temperature. This result may be accounted for the effect of the crystallographic texture change of Zircaloy clading tubes.

(5) Axial and circumferential elongation decreased rapidly with increased exposure time and oxidation temperature. This phenomena appears to indicate significant embrittlement behavior of Zircaloy cladding exposed to high temperature steam.

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