

STRESS CORROSION CRACKING OF  
ZIRCONIUM IN NITRIC ACID

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ABSTRACT

The susceptibility of zirconium and its common alloys to stress corrosion cracking (SCC) in nitric acid was investigated by slow strain-rate and constant deflection techniques. Cracking occurred at 25°C over a wide range of acid concentrations and electrochemical potentials. The crack velocity increased slightly with increasing temperature. The failure mode was transgranular and the morphology was similar to SCC failures of zirconium alloys in other environments. The fracture was very orientation-dependent suggesting that it occurs on a single crystallographic plane in the material. The results of the study are not consistent with a hydrogen mechanism for cracking.

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## INTRODUCTION

Few materials have adequate general corrosion resistance for use in concentrated nitric acid at elevated temperatures. The stainless steels and some nickel-base alloys perform adequately at room temperature but are rapidly attacked when temperatures exceed 40 C (1,2,3). The heat affected zones of welds of unstabilized steels are particularly susceptible to localized attack in the as-welded condition (2). The aluminum alloys have better corrosion resistance than the stainless steels to concentrated nitric acid (greater than 95 percent) (2) but are also susceptible to attack of the heat affected zone in fuming nitric acid above 50 C (4) and are rapidly attacked by nitric acid at concentrations less than 95 percent HNO<sub>3</sub> (5).

Tantalum (6), platinum (1), and Duriron<sup>(R)</sup> (6), have excellent corrosion resistance in concentrated nitric acid and in red fuming nitric acid both at 25 C and at elevated temperatures. However, all three materials are difficult to fabricate and tantalum and platinum are expensive, whereas Duriron<sup>(R)</sup> is a cast material and is only available in restricted geometries. Glass lined vessels are occasionally used in fuming nitric acid at elevated temperatures (7) but are difficult to fabricate and maintain.

Titanium has excellent general corrosion resistance in concentrated nitric acid but is susceptible to stress corrosion cracking (SCC) and pyrophoricity in anhydrous HNO<sub>3</sub> containing NO<sub>2</sub> (8,9). Gilbert and Funk (8) found that commercial grade titanium was susceptible to both

forms of attack at ambient temperature in  $\text{HNO}_3$  containing less than 1 percent  $\text{H}_2\text{O}$  and greater than 10 percent  $\text{NO}_2$ . Zirconium and its alloys have very low corrosion rates in concentrated nitric acid and in red fuming nitric acid (10), are relatively easy to fabricate, and are inexpensive compared to tantalum and platinum. However, the chemical similarities between zirconium and titanium suggest that zirconium may also exhibit SCC in red fuming nitric acid although none has been reported in the literature. Indeed, zirconium alloys are susceptible to SCC in many of the environments in which failures of titanium alloys have also been observed. Cracking of both titanium (11) and zirconium (12,13) has been reported in methanolic solutions containing halogens, in halogen acids and in halide salts. Accordingly, the following study was conducted to evaluate the SCC susceptibility of zirconium alloys in concentrated  $\text{HNO}_3$  and in red fuming nitric acid.

### EXPERIMENTAL PROCEDURE

#### Materials

Stress corrosion testing was conducted on commercial grade zirconium, Zircaloy-2 and Zircaloy-4. Rod stock was used for a major portion of the studies but limited testing was also conducted on sheet stock of Zircaloy-4. Chemical analyses of these materials are given in Table 1.

### Acid Preparation

Nitric acid containing a range of  $H_2O$  contents was used in this study.  $HNO_3$  containing greater than 30 percent  $H_2O$  was prepared by dilution of reagent grade 70 percent  $HNO_3$ .  $HNO_3$  containing 10-30 percent  $H_2O$  was prepared by dilution of reagent grade 90 percent  $HNO_3$ .  $HNO_3$  containing less than 10 percent  $H_2O$  was prepared by distilling a mixture of 500 g  $KNO_3$  and 1000 ml of 100 percent  $H_2SO_4$ . The 100 percent  $H_2SO_4$  was prepared by adding 285 ml of oleum (containing 30 percent excess  $SO_3$ ) to 715 ml of 97 percent  $H_2SO_4$ . The distillation was performed at 38 C under reduced pressure ( $\sim 20$  mm Hg). The anhydrous  $HNO_3$  (containing less than 0.1 percent  $H_2O$ ) so produced was sparged with  $NO_2$  at a rate of 90 ml/minute at 25 C to generate red fuming  $HNO_3$ . Solutions containing a range of  $NO_2$  contents were produced by varying the sparging time from 0.5 hours to 3 hours. These samples were analyzed by wet chemical techniques and a sparging time- $NO_2$  content curve was generated. From this curve, the sparging time to produce the desired  $NO_2$  content was determined. Following  $NO_2$  addition, the acids were analyzed for water content by near infrared absorption using techniques developed by White and Barrett (14). Generally, the water content of the acids increased to 0.3 - 0.4 weight percent during  $NO_2$  sparging.

### Stress Corrosion Testing

Most of the stress corrosion testing was conducted using the slow strain-rate technique (15). Cylindrical specimens 4.8 mm in diameter x 179 mm in length were cut from the rod stock and reduced gauge sections 2.5 mm

in diameter x 12.5 mm in length were machined in each specimen. The gauge section of each specimen was abraded with Number 600 SiC and cleaned in acetone and in distilled water. The specimens were tested in air tight Teflon<sup>(R)</sup> cells and were strained to failure at  $2.5 \times 10^{-6}$ /s. The electrochemical potential was controlled for some tests using a potentiostat. In these tests the counter electrode, constructed of platinum, was positioned around the specimen to assure uniform distribution of current. The reference electrode, a saturated calomel electrode (SCE), was connected to the cell by means of a bridge and Luggin probe, the tip of which was located within 1 to 2 mm of the specimen. The temperature of the cell was maintained by electrical resistance tape connected to a proportional temperature controller. The temperature sensor was sheathed in Teflon<sup>(R)</sup> and immersed in the test solution.

Following failure the specimens were examined with a low-power optical microscope. If cracking was found, the specimens were metallographically sectioned along the axis and the maximum depth of secondary cracking was measured. A cracking velocity was calculated by dividing the maximum depth of secondary cracking by the time to failure. The fracture surfaces of selected specimens were also examined with a scanning electron microscope (SEM).

Limited stress-corrosion testing was conducted on U-bend specimens of Zircaloy-4. Specimens 25 mm x 50 mm x 0.83 mm were sheared from the sheet stock with the long axis both parallel and perpendicular to the rolling direction of the sheet, formed into U-bends and strained elastically with Type 304 stainless steel bolts according to specification ASTM G30. The specimens were electrically isolated from the stainless steel bolts

with Teflon<sup>(R)</sup> spacers. Specimens were cleaned in acetone and in distilled water and exposed to the test environment in air-tight Teflon<sup>(R)</sup> cells.

### Potentiodynamic Polarization

Potentiodynamic polarization curves were obtained for Zircaloy-4 in aerated and deaerated 90 percent HNO<sub>3</sub> at 25 C using a potentiostat and a potential sweep generator. Cylindrical specimens 4.8 mm in diameter by 25 mm in length were cut from the rod stock abraded with Number 600 SiC and mounted with specimen holders having Teflon<sup>(R)</sup> compression gaskets. The test solution was either aerated or deaerated by sparging with air or N<sub>2</sub> at a rate of 40 ml/min for 30 minutes. The electrode potential was then scanned either positive or negative from the free corrosion potential at a rate of 6V/h, and the current flow and the potential of the test electrode were recorded.

### RESULTS

During slow strain-rate testing Zircaloy-4 developed cracks under freely corroding conditions in 90 percent HNO<sub>3</sub> at 25 C. Examination of the fracture surfaces with an optical microscope showed that the color varied with distance from the center of the specimen. The regions near the free surface displayed a black tarnished appearance and this gradually changed to a metallic appearance, characteristic of the unexposed metal, at the center. The gauge length of the specimens was also covered with a black tarnish film.

SEM examination of the fracture surfaces showed that failure occurred transgranularly as cleavage-like flat facets which were separated by steps that frequently formed river patterns. Thin whiskers of metal were present on the fracture surfaces indicating that undercutting of adjacent facets had occurred. Secondary cracks were also present on the fracture surfaces. Typical SEM photographs are given in Figures 1a and 1b. Specimens were metallographically examined and cracking was frequently found to follow the axes of the tensile specimens, as shown in Figure 2.

Slow strain-rate tests were conducted on commercial grade zirconium and on Zircaloy-2 in 90 percent  $\text{HNO}_3$  to compare cracking susceptibility with Zircaloy-4. All three alloys exhibited approximately equal susceptibility to SCC under freely corroding conditions at 25 C.

The influence of acid concentration on cracking velocity at 25 C is shown in Figure 3 from which it can be seen that the maximum crack velocity occurred in 90 percent  $\text{HNO}_3$ . It should be noted, however, that even in 60 percent acid, the lowest concentration tested, cracking occurred. Slow strain-rate tests also were conducted on Zircaloy-4 and on commercial grade zirconium in red fuming nitric acid to evaluate the influence of  $\text{NO}_2$  on cracking. Results presented in Table 2 show that the presence of  $\text{NO}_2$  did not significantly affect cracking. Note that the latter test condition causes SCC of titanium (8,9).

The potential dependence of SCC susceptibility of Zircaloy-4 was studied in 90 percent  $\text{HNO}_3$  to determine whether the material could be anodically or cathodically protected from cracking. Prior to controlled potential testing, polarization curves were obtained in 90 percent  $\text{HNO}_3$



at 25 C. Aeration or deaeration did not affect the polarization behavior. The resulting curve for deaerated  $\text{HNO}_3$  (Figure 4) shows that the free corrosion potential was approximately 1.08V (SCE) and that corrosion increased rapidly on anodic polarization. Results of the SCC tests, given in Figure 5, show that crack velocity was a maximum near the free corrosion potential and gradually decreased upon cathodic polarization whereas it sharply decreased upon anodic polarization. However, rapid general corrosion occurred at the anodic potentials.

The temperature dependence of the crack velocity in Zircaloy-4 is shown in Figure 6. The data indicates a slight increase with increasing temperature but the data are too scattered to determine an activation energy for crack growth.

U-bends of Zircaloy-4 were exposed to 90 percent  $\text{HNO}_3$  under freely corroding conditions at 25 C. Specimens that were oriented with the plane of maximum stress parallel to the rolling direction failed within 3 weeks whereas specimens oriented with the plane of maximum stress perpendicular to the rolling direction did not fail in 2 months but cracking was evident along the rolling direction, as shown in Figure 7. The failed specimens were examined with a low-power optical microscope and the fracture surfaces were covered with a black tarnish. Specimen edges were also tarnished whereas the free surfaces were unattacked. The fracture surfaces were examined with a SEM and the features were generally obliterated by the thick tarnish but in areas where surface detail was evident the morphology was similar to that found in specimens tested by the slow strain-rate method.

DISCUSSION

Zirconium has very good resistance to most mineral acids and to strong alkali solutions. It has been pointed out by Shrier (16) that because of this unique property zirconium is an excellent material for sections of chemical plants demanding alternate contact with strong acids and alkalis. In light of the results reported here, however, the above statement needs to be modified. Our results clearly indicate that zirconium and its common alloys are susceptible to stress corrosion cracking in nitric acid solutions. We did not define all the conditions under which cracking will occur, but certainly at concentrations of 60 weight percent or greater cracking of stressed zirconium is highly likely even at room temperature. Perhaps at lower acid concentrations cracking would not occur, but safe conditions for use of zirconium equipment in nitric acid will have to be determined experimentally.

The morphology of the transgranular failure was cleavage-like and similar to that observed in zirconium in other environments (17). The fact that fracture was very orientation-dependent suggests that it occurs on a single crystallographic-plane in the material. In zirconium and zirconium-tin alloys the rolling direction is  $[10\bar{1}0]$  (lies in basal plane) and the basal plane is inclined  $\sim 40$  degrees with respect to the rolling plane (18,19). Thus, fracture most likely occurs on the basal plane or on one of the family of planes whose zone axis is  $[10\bar{1}0]$ ; namely,  $\{\bar{1}2\bar{1}4\}$ ,  $\{\bar{1}2\bar{1}2\}$ ,  $\{\bar{1}2\bar{1}1\}$ , or  $\{\bar{1}2\bar{1}0\}$ . The hydride habit plane in zirconium is reported to be  $\{10\bar{1}0\}$  (20,21) and thus it is difficult to reconcile

the SCC with a hydride-fracture model. Results of the electrochemical studies also are not consistent with a hydrogen model that would necessitate hydrogen entry into the metal through hydrogen reduction. The electrochemical potential range in which cracking was observed, 0.7 - 1.1V (SCE), is considerably more noble than the hydrogen reversible potential in this environment and thus hydrogen formation during corrosion and subsequent absorption by zirconium is highly unlikely.

#### ACKNOWLEDGEMENTS

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TABLE 1. CHEMICAL ANALYSES OF  
ZIRCONIUM USED IN STUDY

Alloy	Form	Composition, Weight Percent					
		C	Cr	Fe	Hf	Ni	Sn
Zircaloy-4	0.83 mm (0.0325 inch) sheet	0.0120	0.100	0.225	<0.005	<0.0035	1.46
Zircaloy-4	4.75 mm (3/16 inch) diameter rod	0.0095	0.120	0.210	0.008	<0.0035	1.54
Zircaloy-2	4.75 mm (3/16 inch) diameter rod	0.011	0.100	0.160	<0.005	0.050	1.49
Commercial Grade Zirconium	4.75 mm (3/16 inch) diameter rod	0.013	0.045	0.045	0.010	--	--

TABLE 2. SCC VELOCITIES OF ZIRCALOY-4 AND COMMERCIAL GRADE ZIRCONIUM IN VARIOUS ENVIRONMENTS AT 25 C UNDER FREELY CORRODING CONDITIONS; STRAIN RATE  $2.5 \times 10^{-6}$ /SEC

Material	Environment	Cracking Velocity, mm/sec
Zircaloy-4	21.2M (90%) HNO <sub>3</sub>	$2.9 \times 10^{-6}$
Zircaloy-4	HNO <sub>3</sub> containing 5% H <sub>2</sub> O + 5% NO <sub>2</sub>	$1.6 \times 10^{-6}$
Zircaloy-4	HNO <sub>3</sub> containing 3% H <sub>2</sub> O + 20% NO <sub>2</sub>	$1.6 \times 10^{-6}$
Zirconium	HNO <sub>3</sub> containing 0.65% H <sub>2</sub> O + 30% NO <sub>2</sub>	$3.5 \times 10^{-6}$
Zirconium	HNO <sub>3</sub> containing 0.4% H <sub>2</sub> O + 30% NO <sub>2</sub>	$1.9 \times 10^{-6}$



350X

a



650X

b

FIGURE 1. SCANNING ELECTRON MICROSCOPE PHOTOGRAPHS OF THE FRACTURE SURFACE OF A ZIRCALOY-4 SPECIMEN TESTED IN 90 PERCENT  $\text{HNO}_3$  AT 25 C UNDER FREELY CORRODING CONDITIONS; STRAIN RATE  $2.5 \times 10^{-6}$ /sec



500X

8J819

FIGURE 2. PHOTOMICROGRAPH OF A METALLOGRAPHIC SECTION THROUGH SECONDARY CRACKS FOUND ON THE GAUGE LENGTH OF A ZIRCALOY-4 SPECIMEN TESTED IN 90 PERCENT  $\text{HNO}_3$  AT 25 C UNDER FREELY CORRODING CONDITIONS; STRAIN RATE  $2.5 \times 10^{-6}$  /sec

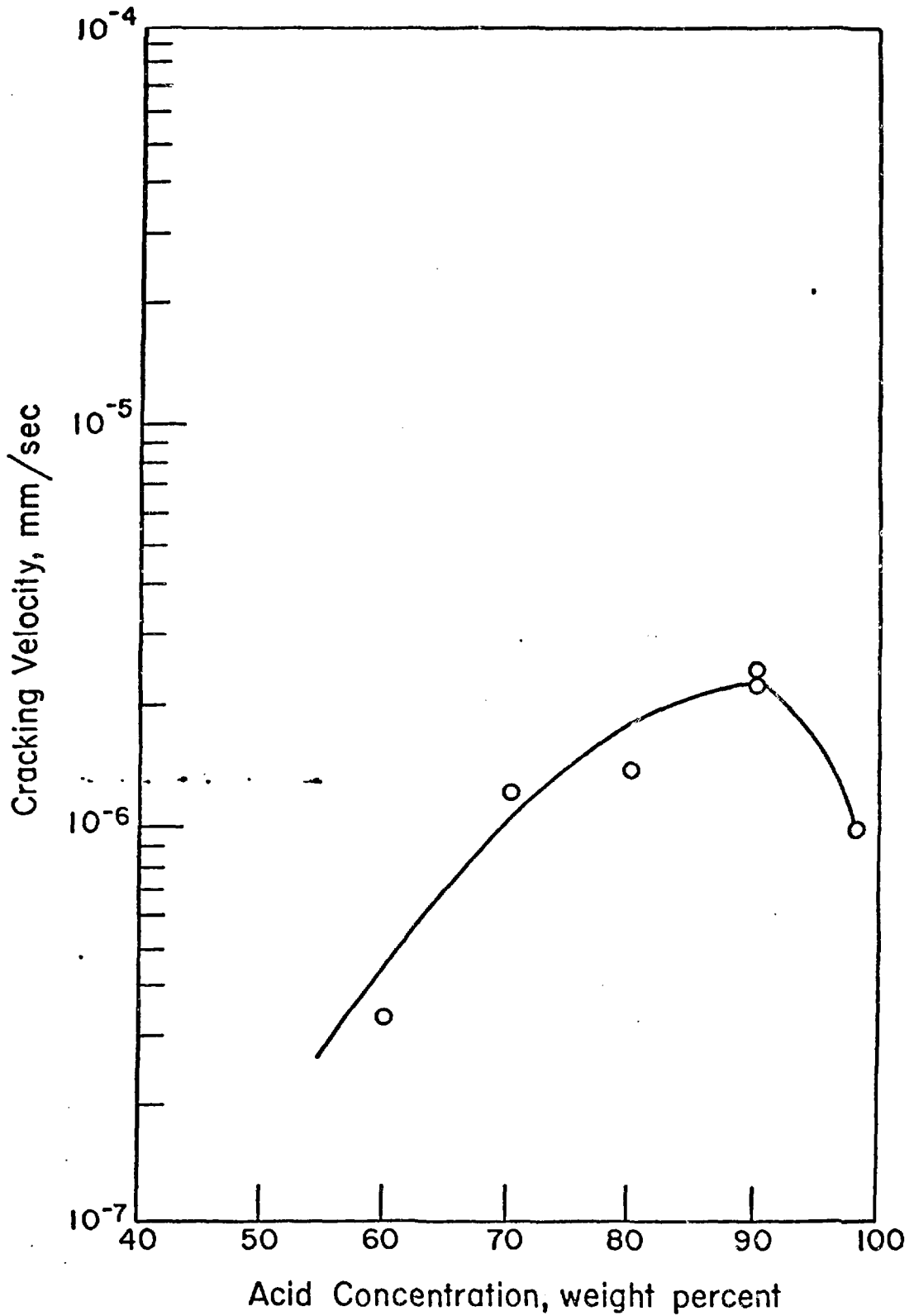


FIGURE 3. THE EFFECT OF  $\text{HNO}_3$  CONCENTRATION ON CRACK VELOCITY IN ZIRCALOY-4 TESTED AT 25 C UNDER FREELY CORRODING CONDITIONS; STRAIN RATE  $2.5 \times 10^{-6}$  /sec



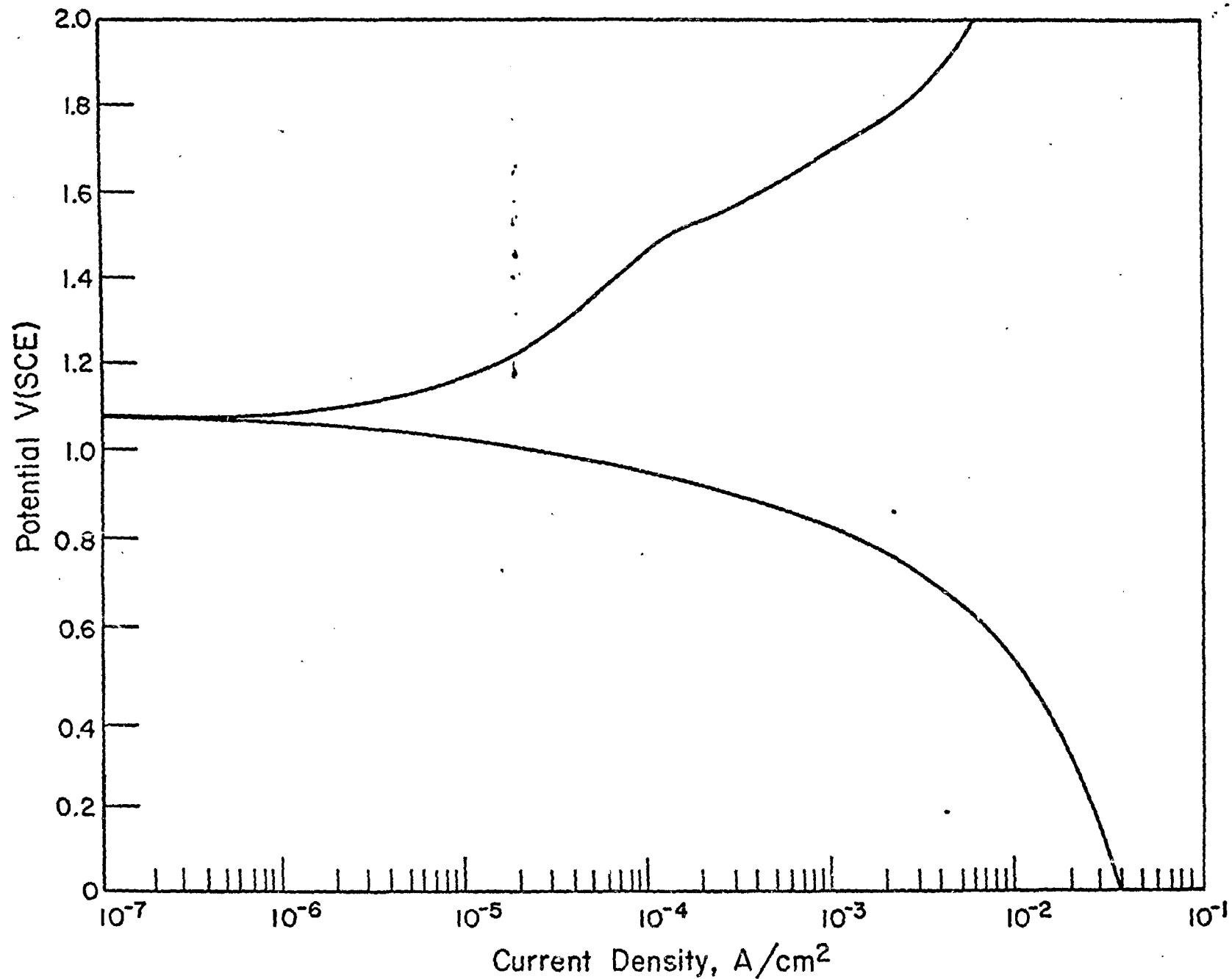


FIGURE 4. POTENTIODYNAMIC POLARIZATION CURVE FOR ZIRCALOY-4  
IN 90 PERCENT HNO<sub>3</sub> AT 25 C

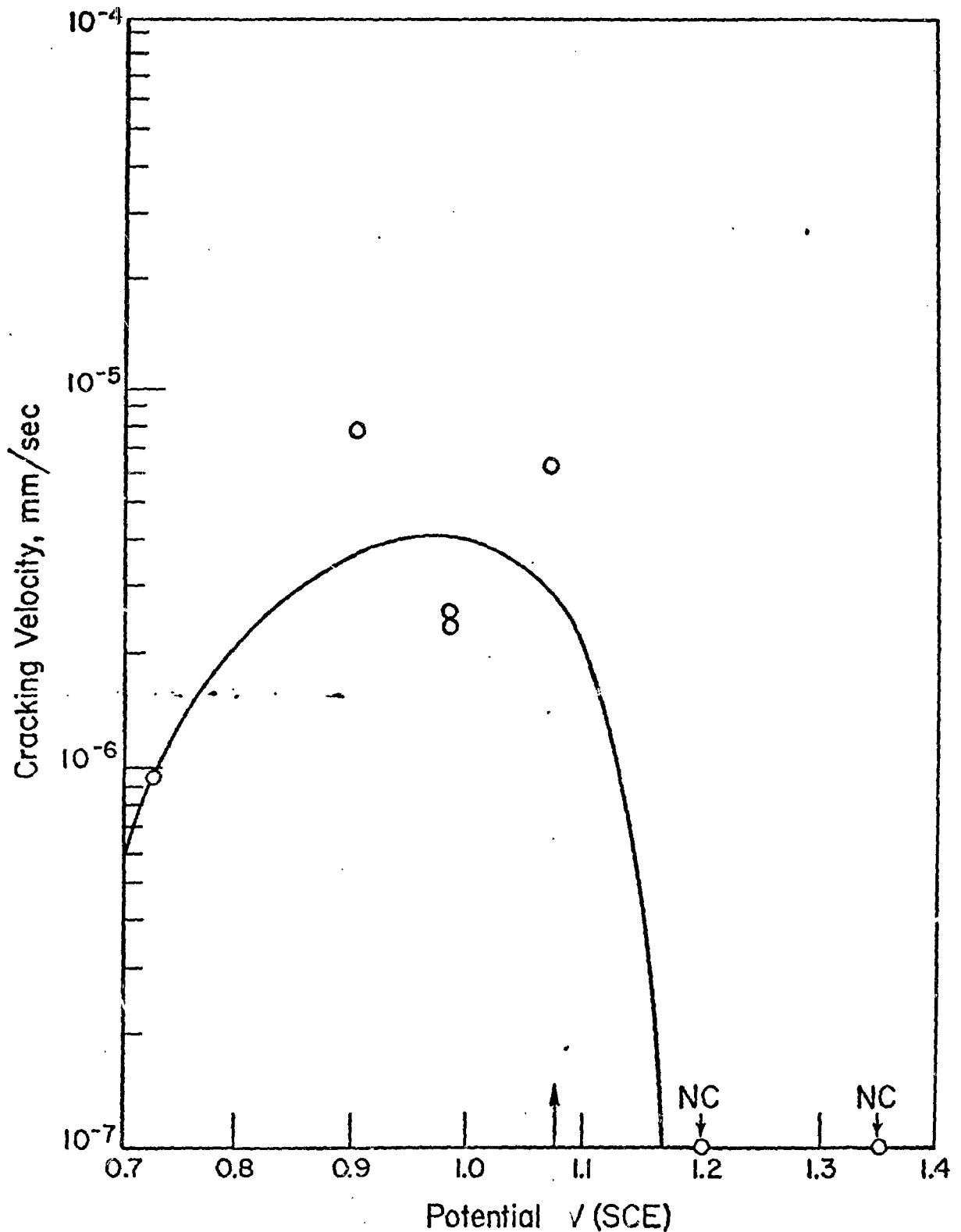


FIGURE 5. THE EFFECT OF POTENTIAL ON THE CRACK VELOCITY IN ZIRCALOY-4 TESTED IN 90 PERCENT  $\text{HNO}_3$  AT 25 C; STRAIN RATE  $2.5 \times 10^{-6}/\text{sec}$

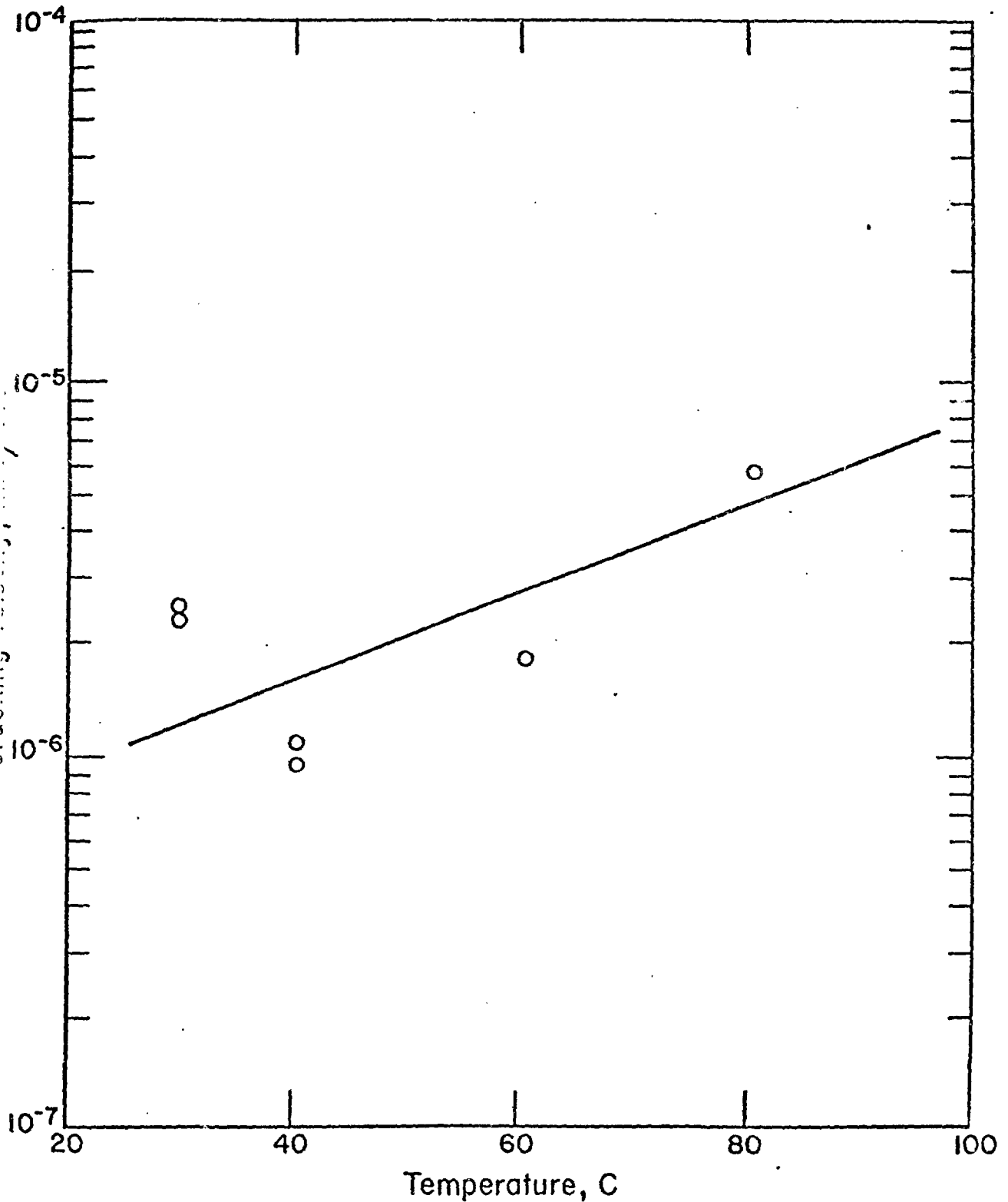
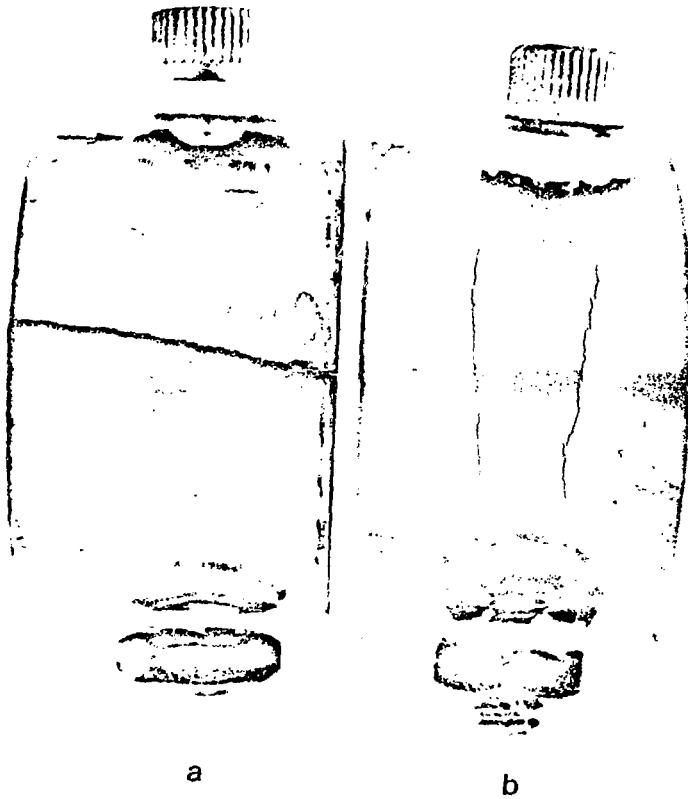


FIGURE 6. THE EFFECT OF TEMPERATURE ON THE CRACK VELOCITY IN ZIRCALLOY-4 TESTED IN 90 PERCENT  $\text{HNO}_3$  UNDER FREELY CORRODING CONDITIONS; STRAIN RATE  $2.5 \times 10^{-6}/\text{sec}$



2X

FIGURE 7. LOW-POWER OPTICAL MICROGRAPH OF U-BEND SPECIMENS OF ZIRCALOY-4 TESTED IN 90 PERCENT  $\text{HNO}_3$  at 25 C UNDER FREELY CORRODING CONDITIONS WITH THE PLANE OF MAXIMUM STRESS PARALLEL (a) AND PERPENDICULAR (b) TO THE ROLLING DIRECTION

## REFERENCES

- (1) Corrosion Data Survey, Fifth Edition, Hamner, N. E., Ed., NACE, 1974, p 130.
- (2) Sands, G. A., Industrial and Engineering Chemistry, Volume 40, Number 10, October, 1948, p 1937.
- (3) Willging, J. F., Hirth, J. P., Beck, F. H., and Fontana, M. G., Corrosion Volume 11, Number 2, February, 1955, p 71t.
- (4) Horst, R. L., Corrosion, Volume 12, Number 10, October, 1956, p 77.
- (5) Fontana, M. G., Industrial and Engineering Chemistry, Volume 45, February, 1953, p 93 a.
- (6) Kaplan, H. and Andrus, S., Industrial and Engineering Chemistry, Volume 40, Number 10, October, 1948, p 1947.
- (7) Private Communication, Dr. J. Valencourt, Hercules Incorporated, January, 1979.
- (8) Gilbert, L. L., and Funk, C. W., Metals Progress, Volume 70, Number 11, 1956, p 93.
- (9) Rittenhouse, J. B., "The Corrosion and Ignition of Titanium in Fuming Nitric Acid", External Publication Number 338, Jet propulsion Laboratory, California Institute of Technology, May, 1956.
- (10) Corrosion Data Survey, Fifth Edition, Hamner N. E., Ed., NACE, 1974, p 131.
- (11) Proceedings of Seminars on Accelerated Crack Propagation of Titanium in Methanol, Halogenated Hydrocarbons and Other Solutions; March, 1967, DMIC Memo 228.
- (12) Mori, K., Takamura, A., and Shimose, T., Corrosion, Volume 22, Number 2, 1966, p 29.
- (13) Cox, B., Corrosion Volume 28, Number 6, 1972, p 207.
- (14) White, L., and Barrett, W. J., Analytical Chemistry, Volume 28, Number 10, 1956, p 1538.
- (15) Parkins, R. N., Stress Corrosion Cracking - The Slow Strain Rate Technique, ASTM, STP, 665, Ugiansky, G. M., and Payer, J. H., Eds., 1979, p 5.
- (16) Corrosion, Volume 1 Second Edition, Shrier, L. L., Ed., Newnes-Buttersworth, London 1976, p 5:53.
- (17) Cox, B., Corrosion, Volume 30, Number 6, 1974, p 191.

REFERENCES  
(Continued)

- (18) Lustman, B. and McGeary, R. K., Transactions American Institute of Mining and Metallurgical Engineers, Volume 197, 1953, p 284.
- (19) McGeary, R. K. "Rate of Annealing of Cold-Rolled Zirconium-Tin Alloys," Report WAPD-7-44, August, 1953.
- (20) Bailey, J. E., Acta-Met., Volume 11, 1963, p 267.
- (21) Warren, M. R. and Beavers, C. J., Journal of Nuclear Materials, Volume 26, 1968, p 273.