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THE AQUEOUS CORROSION OF ZIRCALOY CLAD THORIUM

By
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Cambridge, Massachusetts

Technical Information Service Extension, Oak Ridge, Tenn.

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A. R. Kaufmann
Technical Director

ABSTRACT

Attempts were made to improve the ability of Zircaloy-clad thorium to survive exposure of the core to water entering through small defects in the cladding. The failure of defected specimens was attributed to inadequate core-cladding bonds, which were not improved by an interdiffusion heat treatment. The thorium core may also be so weak as to be the point of failure in bond tests and to crack under the stress induced by the volume expansion on corrosion. Carbon additions hardened the thorium and lowered the corrosion rates. Aging treatments did not increase the hardness, but did increase the corrosion rates.

The importance of the core-cladding bond is brought out by the successful protection of Zircaloy-clad uranium alloys against cladding defects. In this case, the interdiffusion heat treatment strengthens the bond sufficiently to permit compaction of oxide.

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I. INTRODUCTION

The use of cladding on uranium or thorium in water-cooled reactors does not completely avoid the danger of exposure of the reactive core metal to water. Lack of complete confidence in the cladding has led to reliance for corrosion resistance on high alloying of the core, culminating in the use of oxides of uranium or thorium. Guarantees of the soundness of the clad could obviate the need for alloying, and problems of reliable fabrication and testing methods to assure clad integrity have received considerable attention in this laboratory. In addition, an interdiffusion heat treatment was developed to protect Zircaloy-clad uranium against small defects in the clad.(1,2) The effectiveness of this heat treatment in providing protection is attributed not so much to improved corrosion resistance of uranium near the interface as a result of zirconium addition, but rather to the strengthening of the bond between the core and the clad. Material with this strengthened bond can resist the stress due to expansion of uranium on conversion to oxide. This oxide is confined and compacted to such an extent as to hamper further entry of water, thereby arresting corrosion of the uranium.

Although limited information was available on the corrosion of clad thorium or, for that matter, of bare thorium and its alloys, the application of the diffusion treatment to Zircaloy-clad seemed promising for several reasons. In boiling water, at least, thorium was known to corrode much more slowly than uranium. Additions of zirconium retard corrosion. Furthermore, since thorium's volume increase on conversion to oxide is less than uranium's, less stress would be exerted on the Zircaloy clad by corroding thorium.

However, diffusion treatment did not provide the hoped for protection of the thorium against defects in the Zircaloy. This failure is related to the inadequate bond strength before or after heat treatment. The results improved the understanding of the success of the treatment with Zircaloy-clad uranium, where the bond is strengthened by the treatment.

In the work described below, the effect of various heat treatments on the core-clad bond was first investigated qualitatively. The inadequacy of defected rods in corrosion by water at 500 or 650°F led to a more careful investigation of the bonds. These tests indicated that the thorium core could be an even greater source of weakness than the bond. Attempts were made to overcome this weakness by alloying with carbon and age hardening. The effect of these means of strengthening on corrosion resistance was investigated.

II. PREPARATION OF RODS

Zircaloy-clad thorium rods were prepared by coextrusion. The thorium core was either an Ames ingot (No. 1396) reduced from 3 to 1-1/2 inch diameter by a preliminary extrusion (No. 11697) in copper at 1350°F or a casting prepared especially to contain additional carbon. For the necessary castings, thorium was melted in a zirconia-washed graphite crucible with an addition of graphite powder and poured into a graphite mold. Although some difficulty was encountered in the attempted control of the carbon content, a set of castings was obtained with carbon content ranging from 0.14 to 0.64 $^{w}/o$. The Ames ingot contained 0.075 $^{w}/o$ carbon.

For extrusion, the thorium core was assembled with a Zircaloy-2 sleeve and a copper nose plug and cut-off in a copper can, which was then evacuated. The assembly was heated to 1400°F prior to extrusion. Reduction by 33x in extrusion from a 2-inch liner through a 0.350-inch die required about 170 tons, corresponding to extrusion constants in the neighborhood of 30,000 psi. Although extrusion constants were raised slightly by higher carbon contents of the thorium core, even the highest carbon content, 0.64 $^{w}/o$, introduced no problems in the extrusion. High carbon content did introduce a problem, however, in subsequent cold swaging. With carbon content up 0.33 $^{w}/o$, a reduction of 10-15% was successfully achieved. A carbon content of the thorium 0.49 $^{w}/o$ or higher made the core brittle enough to crack in the attempted swaging.

The ingots and clad rods used in this study are listed with their carbon contents in the first three columns of Table I. The cladding thickness was close to 0.030 inch.

III. DIFFUSION HEAT TREATMENT

The diffusion heat treatment was approached as a possible method of strengthening the core-cladding bond and thereby improving the corrosion resistance of the composite. Heat treated samples were examined metallographically, but no chemical analyses were performed to establish the extent of interdiffusion. The attempted heat treatments were evaluated primarily on the basis of their effect on bond strength.

Short rods were wrapped in tantalum foil and heated in sealed evacuated Vycor tubes for periods of 1, 4, and 24 hours at 750, 800, 850, 885, and 1000°C. They were cooled in the furnace, in air or by water quenching.

A. Metallography

Metallographic examination of heat treated samples showed a narrow, granular layer of fairly constant thickness near the thorium (Figs. 2, 3). The granular appearance was attributed to zirconium precipitated from solid solution during cooling. On the Zircaloy side, a band was seen which widened as time and temperature increased. At times, this wide band seemed to consist of at least two concentric bands (Figs. 2a, 3a), especially in water quenched samples (Figs. 2b, 3b). Microhardness traverses of these bands indicated, however, that a single band was present, with the amount and nature of precipitate changing gradually between its two edges. Thus, in the sample shown in Fig. 3a, the indentations in filar units from the Zircaloy to the thorium were 350, 347, 356, 324, 315, 320, 308, and 311. The jump from the 350 range to the 320 range did not correspond to the apparent disappearance of the acicular phase. This diffusion layer was always harder than either the Zircaloy or thorium.

Relatively little attention was paid to specimens heat treated at 1000°C, because it was found early that the bonds were notoriously poor.

Their most striking metallographic feature was the Zircaloy's Widmanstätten structure, extending in some cases to the outer edge of the cladding. No attempt was made to help resolve the question of a two-phase beta region in the thorium-zirconium system above 900°C.(3,4)

As extruded, the composite showed only slight evidence of interdiffusion. The metallographic appearance (Fig. 1) resembled that found elsewhere.(5)

B. Bond Tests

A convenient qualitative method of testing the bonds of coextruded rods is the chisel test. A rod section about half an inch long is cut through the axis until the remaining thickness of core approximates the clad thickness. The two halves of this short rod are pried apart. The adherence of the core to the clad during this bending is an indication of the quality of the bond. Good bonds cause a break in which core and clad are not distinguished. A poor bond leads to peeling of the clad.

Bond tests performed on the first rods, with a thorium core low in carbon, showed what seemed to be good bonds obtained by coextrusion, and perhaps even improved by swaging. Except perhaps for some heat treatments at 850°C, the diffusion treatments weakened the bond. Corrosion tests demonstrated rapid failure of defected samples as extruded, as swaged, and after several 850°C heat treatments. These tests led to re-examination of the bonds by the stud test, in an attempt to obtain a measure of the strength of bonds resulting from different treatments. In this test, a Zircaloy stud is welded to the cladding. A tensile test is then performed to determine the stress necessary to break the bond. This test showed low strengths for the composite, of the order of 20,000 psi. Even more important, examination of the tip of the stud showed that the break was occurring in the thorium, at least for as-extruded or as-swaged material (Fig. 4a). Heat treatment shifted the point of weakness to the diffusion layer (Fig. 4b). Similar, but less conclusive results were found on closer examination of a sample from the chisel test (Fig. 5). Adherence of thorium to the stud was also shown by x-ray and spectrographic analysis. This evidence of weakness in the thorium led to a shift in emphasis from attempts to strengthen the bond by diffusion treatment to attempts to strengthen the thorium core by carbon addition and age hardening.

IV. EFFECT OF CARBON ADDITION AND AGING

A. Mechanical Properties

Evidence of weakness in the thorium core led to attempts to strengthen it. Work by others(6,7) had shown that carbon is outstanding in strengthening thorium. The applicability of age hardening is indicated by the decrease in carbon's solubility with decreasing temperature, and has been demonstrated elsewhere(7).

On the basis of this earlier work, an aging treatment for 10 hours at 350°C was chosen to follow solution annealing for 2 hours at 850°C. Hardness data are included in Table I for extruded and swaged samples subjected to this treatment. These data show the hardening effect of carbon on cast or extruded material, which are quite similar. No further hardening is seen, however, as a result of aging, even when the carbon content is high. Any hardening achieved by swaging is apparently lost in the solution anneal before aging.

Some strengthening of the core was found in stud tests of clad rods with high carbon contents. In these tests, failure still occurred in the thorium core, as was found in metallographic specimens similar to those shown in Fig. 4. In the chisel test, however, the clad peeled readily, showing that the composite was still inadequate. The solution anneal and aging treatment had questionable effect on bonds.

B. Corrosion of Thorium Alloys

Consideration of alloying with carbon and age hardening as means of strengthening the thorium core required establishment of the effect of these factors on the corrosion rate of the thorium. It was realized that any adverse effect of the carbon or heat treatment on corrosion could offset whatever strengthening might be achieved, but either factor offered the possibility of improving the corrosion resistance. Data were therefore obtained on the aqueous corrosion of a set of samples with various carbon contents and metallurgical histories. Attention was devoted primarily to sections of coextruded rods where the cladding surrounds the exposed areas, which thus remain fixed. Sections of some castings were also tested, but the rapid attack reduces the exposed area quickly and leads to calculation of misleadingly low rates on the basis of the original area. Even with the clad sections, considerable scatter is observed in the rates. To some extent, this scatter is related to the method of calculating the rates. The calculation allows only for the time at the test temperature and does not take into account the time of heating and cooling, when significant corrosion must occur. This additional time is particularly important relative to the short periods at temperature in a test: one to five hours at 500°F, one hour at 650°F. In spite of these limitations, trends can be deduced from consideration of the representative data in Table II. Rate data at 650°F are generally based on one hour tests, since the high rates limited tests for longer periods. The 500°F data are based on accumulated test periods of one to about ten hours Where the apparent rate changed markedly with the total test time, the different rates are given with the corresponding accumulated test times.

Several trends may be seen in the 500°F data. The rate of weight loss is increased slightly by swaging. A more marked rate increase is caused by age hardening, especially at higher carbon contents. As noted above, data on cast material are hardly comparable with those on sections of rods, but here too, the adverse effect of aging is noted. Carbon additions decrease the corrosion rate, as has been noted previously at low temperature(8).

The 650°F data have too much scatter to permit the deduction of any trends. These data do not rule out the possibility that the trends noted at 500°F may still apply, being masked by the high rates.

All samples tested for about 200 hours in boiling water corroded at approximately the same rates, ranging from very slight weight gains to losses of about 10 $mg/cm^2/mo$. These rates agree with those reported in the literature. The reported loss of 62.1 mg/cm^2 in 88 hours at water at 315°C (600°F)(9) is out of line with all other available data and is apparently superseded by a later report from the same laboratory(10).

Because of the possible role of thorium-zirconium alloys at the interface of clad specimens, preliminary data were obtained on the corrosion of sections of arc-melted alloy buttons containing 25, 50, and 75 w/o thorium. Accumulated test times were 40 hours and about 8 hours at 500°F and 650°F respectively. These buttons were tested as melted, and corrosion brought out segregation in them The rates are worth nothing nevertheless, since they are consistent with other data on the improvement by zirconium(11, 12) and tend to rule out the possibility that an alloy of inferior corrosion resistance is responsible for corrosion at the interface.

Corrosion Rates of Arc-Melted Th-Zr Alloys in High Temperature Water

Weight Loss, $g/cm^2/mo$

Zr, w/o	500°F	650°F
25	5.5	70
50	2.5	40
75	0.80	8

V. CORROSION TESTS OF INTENTIONALLY DEFECTED RODS

It was noted at the outset of this report that the primary goal of this program was the development of Zircaloy-cald thorium capable of surviving exposure of the core to high temperature water through small defects in the cladding. Samples modified by an interdiffusion heat treatment and other means were tried at various stages to determine whether any improvement had been achieved in the behavior of intentionally defected specimens. The defects had a diameter of 7 mils and penetrated to the core. The first tests were in 650°F water. For later tests, 500°F water was used. It was hoped that the much lower corrosion rate of the bare alloy in 500°F (Table II) would favor survival of defected rods at this temperature.

No significant increase in the life of a defected specimen was found as a result of any of the three attempted modifications: interdiffusion heat treatment, carbon addition, and aging. In fact, not even lowering the test temperature increased the specimen's life significantly. In general, bulging of the Zircaloy cladding was clearly seen after several hours in test. This bulging progresses until after about 24 hours or less, the cladding ruptures, exposing more core and leading to complete attack on the core accompanied by full length rupture of the cladding. The progressive failure seems to be slower and less violent than when the core is uranium. Stages in the growth of a "mole" around the defect can be observed. Thus, some alleviation of the catastrophic failure is introduced by the slower corrosion of thorium and the lower volume increase on conversion to oxide. It is clear, however, that at the present stage, the corrosion behavior of Zircaloy-clad thorium rods leaves a great deal to be desired.

Examination of sections of corroded specimens helps explain the present inadequacy of the clad thorium. The previously noted weakness of the thorium core permits cracking of the core (Fig. 6b) and increasing exposure of surface to the water. In addition, the core-cladding bond is poor enough to permit corrosion at the interface (Fig. 6a). Evidence for such bond-line corrosion was seen in short clad rods which were tested with bare flat ends exposed. Often the core of these samples because most deeply recessed near the clad, indicating preferential attack at the interface. It is unlikely that the presence of zirconium in the thorium closest to the cladding seriously impairs this thorium's corrosion resistance. The more plausible explanation of the preferential attack is poor bonding, permitting penetration of water.

These results show that improvement of the corrosion resistance of defected rods depends on strengthening of the thorium and improvement of the bond. Alloying of the thorium is not likely to contribute very much to its strength,(7) but its possible improvement of the bond warrants investigation. More attention has to be paid to the reduction ratio and temperature of coextrusion. In this investigation, these conditions were kept fixed, in the mistaken belief that the resulting bond was adequate.

Alloying may be considered as a means of improving the core's corrosion resistance. It should be noted that the success of the diffusion treatment in the case of Zircaloy-clad uranium depends on the presence of about 2 $^w/o$ or more of zirconium in the core. Similar alloying might demonstrate a marked effect in Zircaloy-clad throium. In light of the unsuccessful tests of clad thorium in 500°F water, however, some skepticism is in order regarding the potential benefit of alloying of the thorium to lower its corrosion rate. At 500°F the corrosion rate of thorium is about 50 times lower than at 650°F (Table II). In contrast, the addition of 2 $^w/o$ zirconium lowers the corrosion rate of uranium by a factor of about 5. Thus, whereas thorium's corrosion rate at 500°F hardly exceeds 100 $gm/cm^2/mo$ (Table II), the U-2 $^w/o$ Zr alloy loses about 500 and 3000 $gm/cm^2/mo$ at 500°F and 650°F respectively. These figures indicate the relative unimportance of the core's corrosion rate compared to the bond strength. With clad uranium alloy, the bond can be made strong enough to resist the stress due to expansion of uranium on conversion to oxide, which is confined and compacted to such an extent as to hamper further entry of water. Thus, the corrosion rate need hardly be of concern any more, once this point is reached. It may be achieved because of uranium dioxide having properties lending themselves to the compaction mechanism.

VI. SUMMARY AND RECOMMENDATIONS

It has not been possible to obtain Zircaloy-clad thorium capable of surviving exposure of the core to high temperature water through 7-mil defects in the cladding. The inadequate bond of the coextruded rod is not improved by an interdiffusion heat treatment. Water can attack the thorium core not only at the base of the defect but also along the core-cladding interface. The expansion due to the increase in the thorium's volume on conversion to oxide causes bulging and, before long, cracking of the Zircaloy cladding, which is unable to confine and compact the oxide. In contrast to this situation, the bond of Zircaloy-clad uranium alloys can be made strong enough to avoid attack at the interface and to permit compaction of the oxide formed at the base of small defects. Prime attention has to be paid to strengthening the bond of Zircaloy-clad thorium; the adequacy of the fabrication technique cannot be taken for granted.

Strengthening of the thorium core is also desirable to avoid cracking as a result of the stresses induced by the volume expansion on corrosion. In addition, a stronger core would permit clearer evaluation of the bond strength. Carbon additions were found to harden the thorium and to lower the corrosion rates. Aging treatments did not increase the hardness, but did increase the corrosion rates.

Alloying additions to the core should be investigated as means of improving the life of clad thorium. The improvement may result from a lowered corrosion rate of the core or from improvement of the bond. Uranium-throrium core alloys are of particular practical interest. An alloying element such as uranium may help improve the bond and also provide more favorable conditions for compaction of the oxide.

The corrosion rate of thorium is strongly dependent on temperature. Since coolant temperatures have not been specified for possible applications of Zircaloy-clad thorium, tests at temperatures below 500°F are warranted to establish whether there is a practical temperature below which unmodified Zircaloy-clad thorium is capable of surviving small defects in the cladding.

VII. TABLES AND FIGURES

Table I

Hardness of Th-C Alloys Following Various Metallurgical Treatments

Rockwell-Superficial, 15 kg Brale Tip

Ingot	Coextruded Rod	C, $^{w}/_{o}$	As Cast	As Extruded	As Extruded and Aged*	As Swaged**	As Swaged and Aged*
Virgin Thorium		0.011	21				
11697		0.075		43			
(from Ames 1396)	11741			38	36		
	12314			36	40		
	15012			37	38	44	38
	15243						
ThX31	15014	0.14	51	53	55	57	52
ThX45	15013	0.33		64	65	66	65
ThX36	14567	0.49		70	68		
ThX46		0.53	72				
ThX37	14569	0.57	76	68	69		
ThX42	14568	0.64	70	68	68		

*2 hr at 850°C; 10 hr at 350°C.
**Approximately 15% cold reduction.

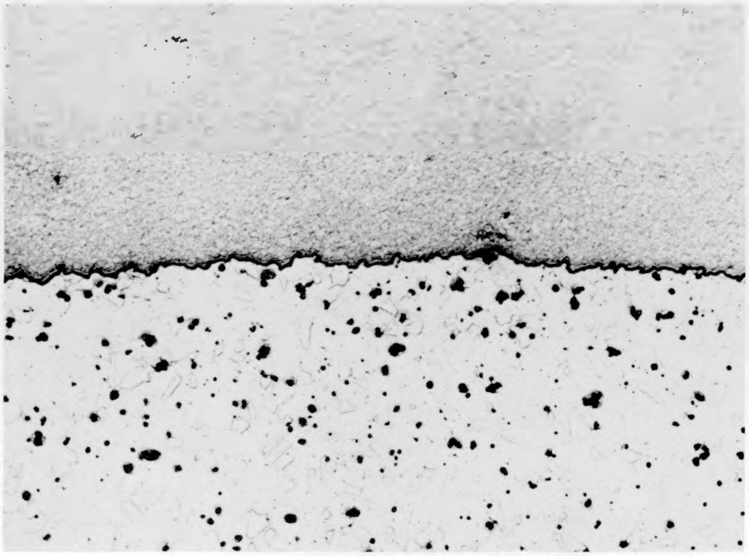
Table II

Corrosion Rates of Th-C Alloys in High Temperature Water

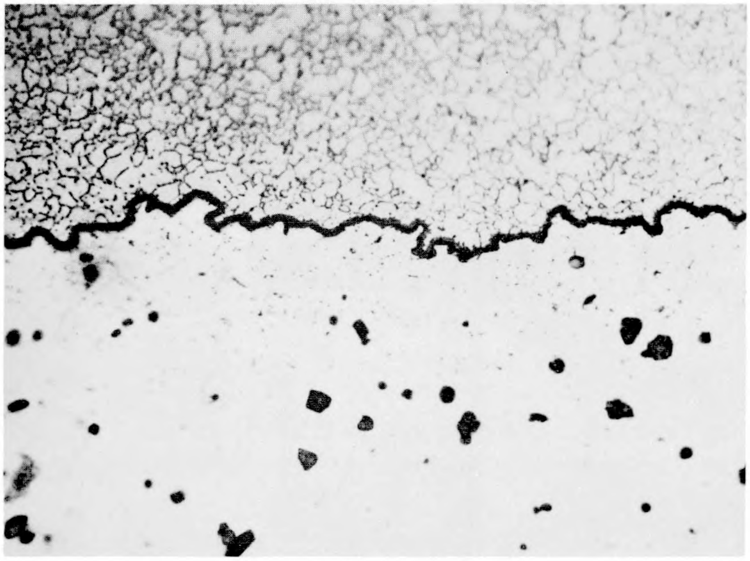
Weight Loss, gm/cm^2/mo

	C, $^w/_o$	As Cast	Cast and Age Hardened	As Extruded	As Extruded and Age Hardened	As Swaged	As Swaged Age Hardened
500° Water	0.07			80	150	100	500
	0.14	40	100	80	300		
	0.33			50	75	45	50
	0.49			10	50	25	
	0.53	(2)	(1)				
	0.57	*	*	20	74(2 hr) 230(7 hr)		
	0.64	1(4 hr) 20(15 hr)	6(2 hr) 80(7 hr)	20	40(2 hr) 80(7 hr)		
650° Water	0.07			2500	2500	2500	
	0.14	*	*	2900	8000	*	
	0.33			5400	3000	4000	
	0.49			3300	5400	*	
	0.53	*	*				
	0.57	1000	*	3400	7200		
	0.64			3200	6900		

* Failed rapidly; no quantitative data obtained.

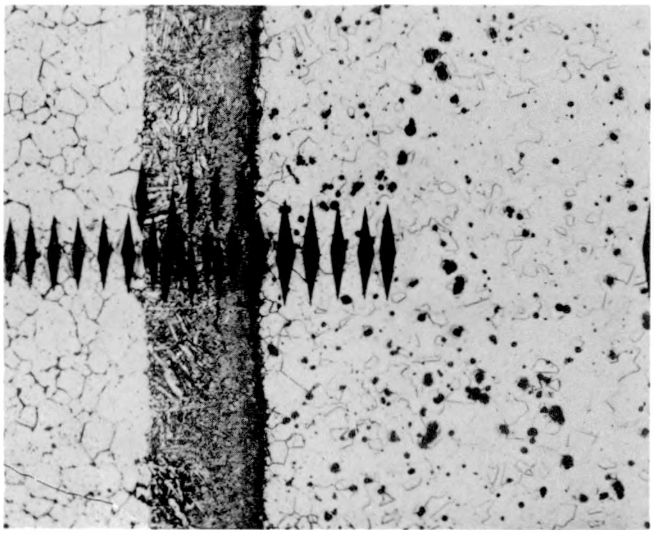


150X Bt. Lt. (a) A-868-1a



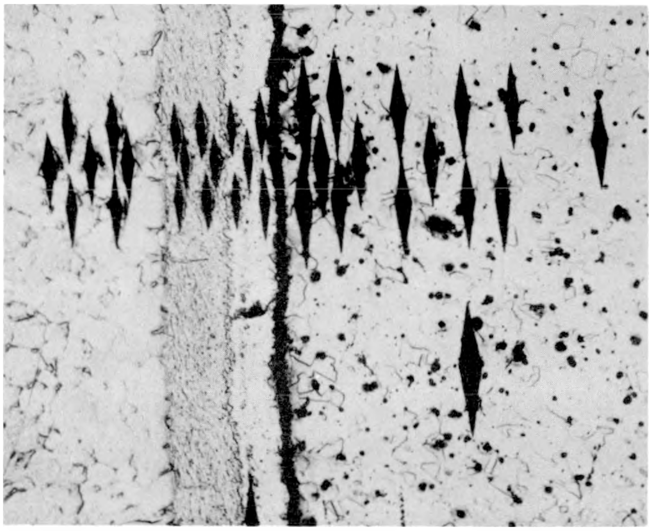
500X Bt. Lt (b) A-868-1b

Fig. 1 - Zircaloy-2-clad thorium. Extrusion 11741, as coextruded. Zircaloy on top. Electropolished in aceto-perchloric bath.



150X Bt. Lt. A-884-6b

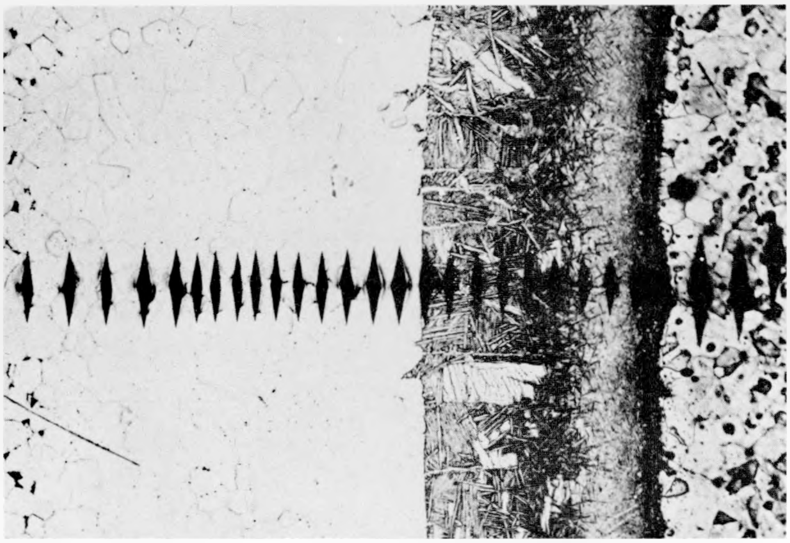
(a) Air cooled



150X Bt. Lt. A-884-7b

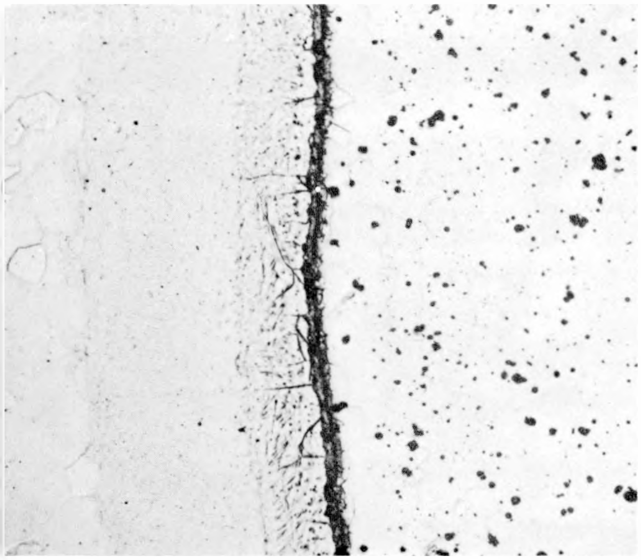
(b) Water quenched

Fig. 2 - Zircaloy-2-clad thorium. Extrusion 11741. Heat treated 4 hours at 850°C. Zircaloy on left. Electropolished.



150X Bt. Lt.   A-884-2b

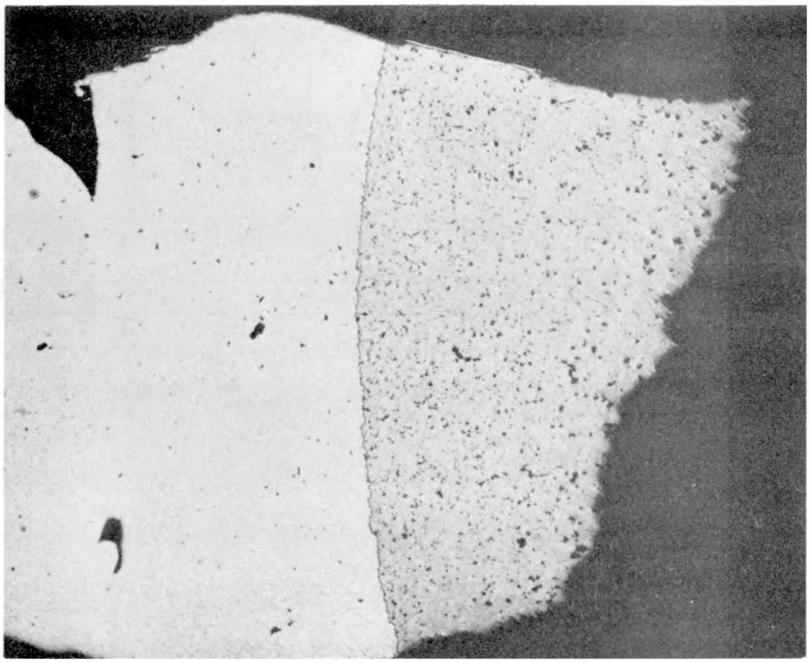
(a) Air cooled



150X Bt. Lt.   A-884-3c

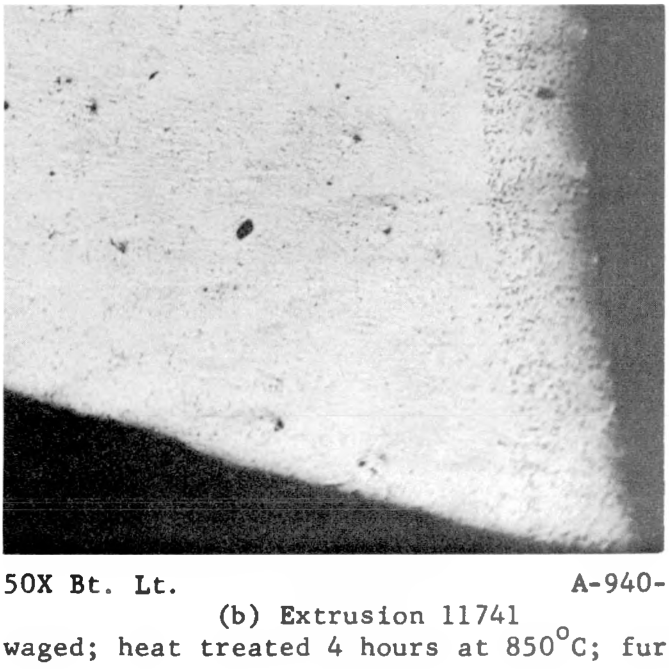
(b) Water quenched

Fig. 3 - Zircaloy-2-clad thorium. Extrusion 11741. Heat treated 24 hours at 850°C. Zircaloy on left. Electropolished.



50X Bt. Lt. A-940-4

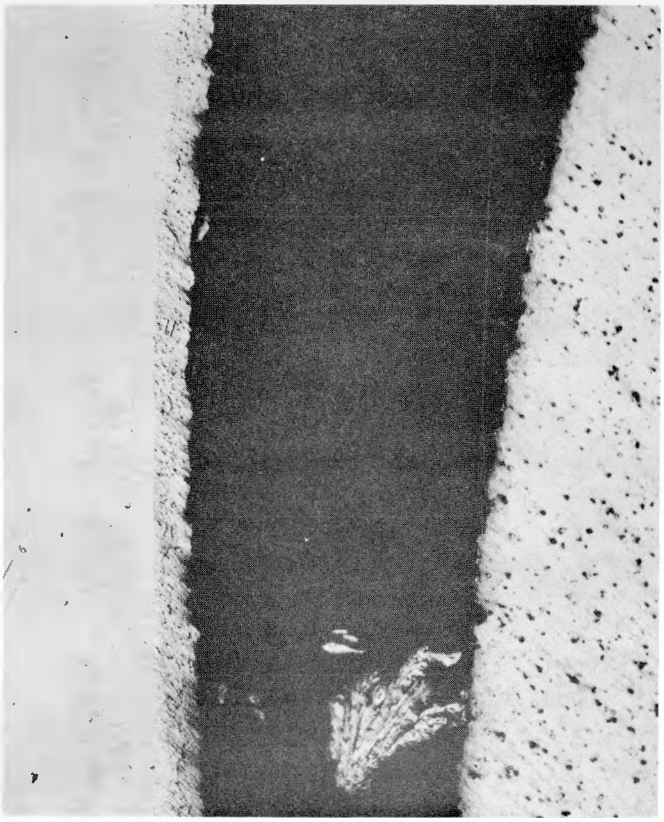
(a) Extrusion 12314
as swaged



150X Bt. Lt. A-940-1

(b) Extrusion 11741
swaged; heat treated 4 hours at 850°C; furnace cooled

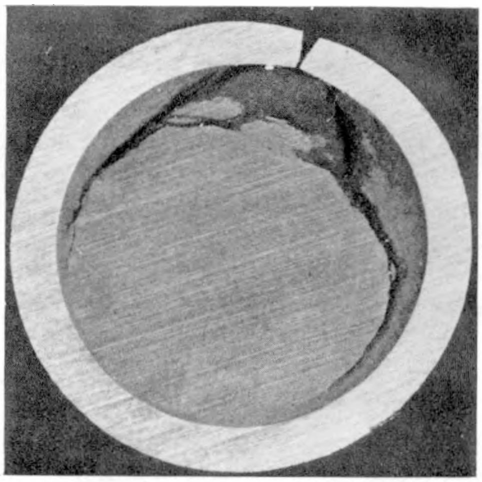
<u>Fig. 4</u> - Tip of broken stud after tensile test of stud welded to Zircaloy cladding. Zircaloy on left. Mechanically polished.



100X Bt. Lt.

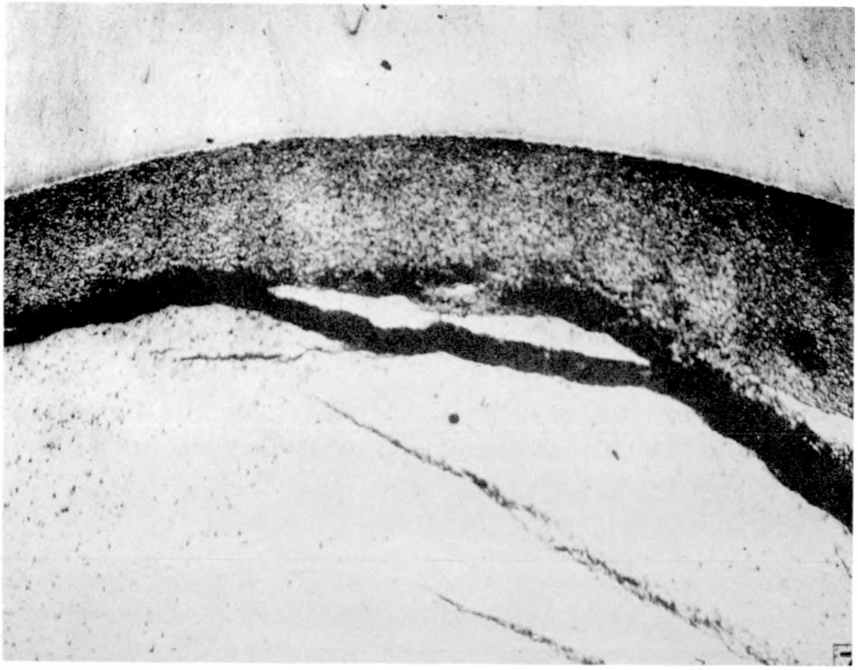
A-915-19

Fig. 5 - Sample from qualitative bond test. Extrusion 12314. Heat treated 4 hours at 800°C; air cooled. Zircaloy on left. Mechanically polished.



About 8X Bt. Lt.   RF4923

(a)



50X Bt. Lt.   A-1075-b

(b)

Fig. 6 - Defected specimen (14569-11) sectioned and polished to defect after 16 hours in 500°F water. Mechanically polished.

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