NASA TECHNICAL NOTE

NASA TN D-3429

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by Coulson M. Scheuermann and Charles A. Barrett

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MAY 1966

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SUMMARY

The corrosion resistance of potential columbium and tantalum tubing alloys to refluxing potassium was tested at temperatures bracketing the maximum expected use temperatures of the advanced turboelectric space power systems, 1800° to 2400° F. Tests were conducted with reflux capsules made from rod stock machined to 1/2-inch diameter, $1\frac{3}{4}$-inch length, and 0.040-inch wall thickness. The capsule wall served as the test specimen. The initial oxygen content of the potassium was a maximum of 20 parts per million as determined by mercury amalgamation and vacuum distillation techniques. The oxygen content of the materials was generally 100 to 200 parts per million. The tests were performed in a vacuum of 10^{-7} to 10^{-8} torr for times up to 4000 hours. The → p7 materials studied were the columbium alloys B-33, SCb-291, Cb-1Zr, D-14, B-66, to p 8 FS-85, AS-55, D-43, C-129, and Cb-752; and the tantalum alloys Ta-10W, T-111, and T-222.

The gettered alloys (i.e., those containing the reactive elements zirconium or hafnium) were found to be more resistant to corrosive attack than the ungettered alloys under the test conditions. This behavior is attributed to the reaction of the gettering elements with dissolved oxygen in the alloy to form stable oxide precipitates within the alloy and thus prevent this amount of oxygen from entering into the corrosion reactions.

A mechanism is proposed, based on experimental results, that describes the oxygen accelerated corrosive attack of columbium and columbium alloys by potassium under refluxing conditions, involving the formation and solution of complex oxides. This mechanism may be expected to be applicable, in principle, to the other refractory metal - alkali metal systems as well. Cases of gettered and ungettered alloys are considered. The various reaction products, their roles in the corrosion process, and their disposition are discussed.

INTRODUCTION

Interplanetary space travel and longtime orbital and lunar-based manned space stations will require large quantities of electricity for propulsion, communications, and life support equipment. Advanced nuclear turboelectric generator systems in the megawatt range will probably be used to provide the electrical power for these operations.

A major uncertainty in the development of advanced space-power systems is containment materials for the thermodynamic working fluid. An operational system will require a containment material having adequate creep and corrosion resistance under the conditions of space operation at temperatures as high as 2400° F and for times in excess of 10 000 hours. At present, potassium is a favored choice for the working fluid, and columbium and tantalum alloys are candidates for the containment material.

The compatibility of columbium, tantalum, and their alloys with potassium above 1800° F has been the subject of increased study since 1960. The most recent comprehensive publications of research results in this area are references 1 and 2. From these reports, it can be seen that only four columbium- or tantalum-base alloys have been tested, all of them gettered (i.e., containing elements that have very strong tendencies to react with oxygen, such as zirconium and hafnium). These reports show that the gettered refractory-metal alloys tested are resistant to attack by the alkali metals.

This report presents the results of a corrosion capsule study to determine the resistance of 13 columbium- and tantalum-base tubing alloys (both gettered and ungettered) to refluxing potassium over the temperature range 1800° to 2400° F and for times up to 4000 hours. Also presented is a proposed corrosion mechanism for the corrosion of columbium and columbium alloys by refluxing potassium based on the results of the present investigation and the available literature.

The metallographic procedure used for the reflux capsule specimens is given in appendix D by Anne R. Kendra.

MATERIALS, APPARATUS, AND PROCEDURE

The corrosion resistance of the various potential tubing alloys to potassium was determined by means of reflux capsules (fig. 1), the capsule wall serving as the test specimen. In capsule tests such as these, liquid is vaporized from a pool at the bottom of the capsule and is condensed near the top of the capsule. The condensate then flows down the capsule wall and joins the bulk liquid, completing the circuit.

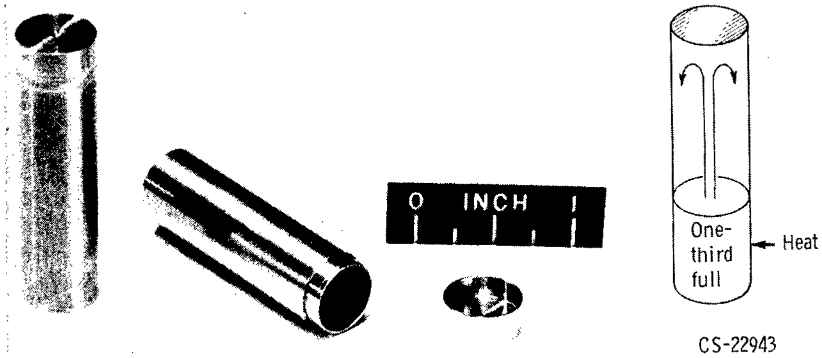


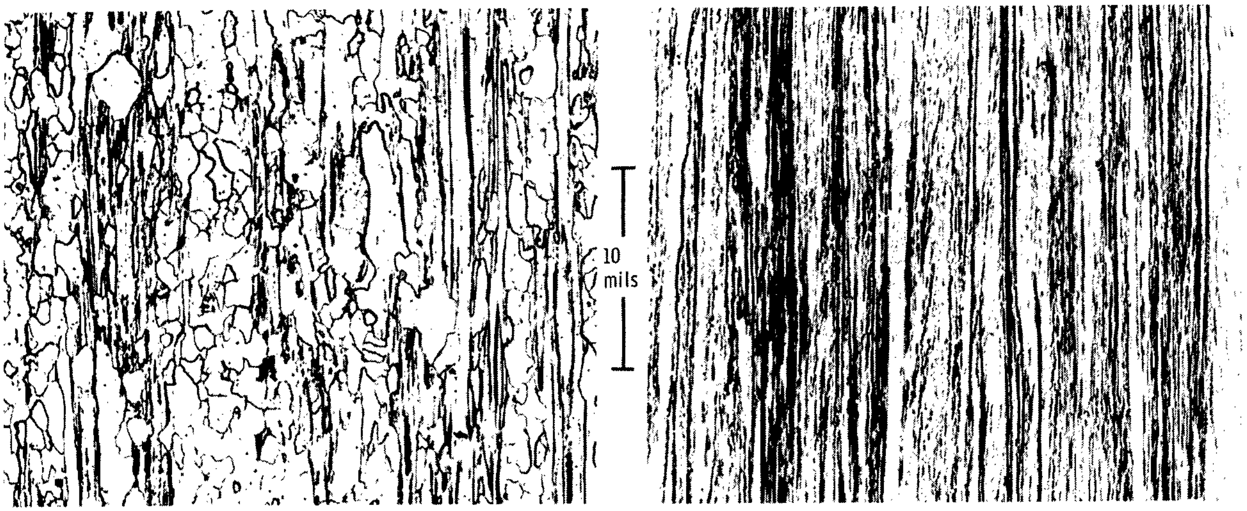
Figure 1. - Reflux capsule used in potassium corrosion study.

Materials

The alloys evaluated and their compositions are given in table I. The alloys were in the worked condition with the exceptions of AS-55, B-33 (heat XMM-8406), Cb-1Zr (heat 5122), and Ta-10W (heat 2356), which were recrystallized. The microstructures of these materials, as received, are shown in figure 2.

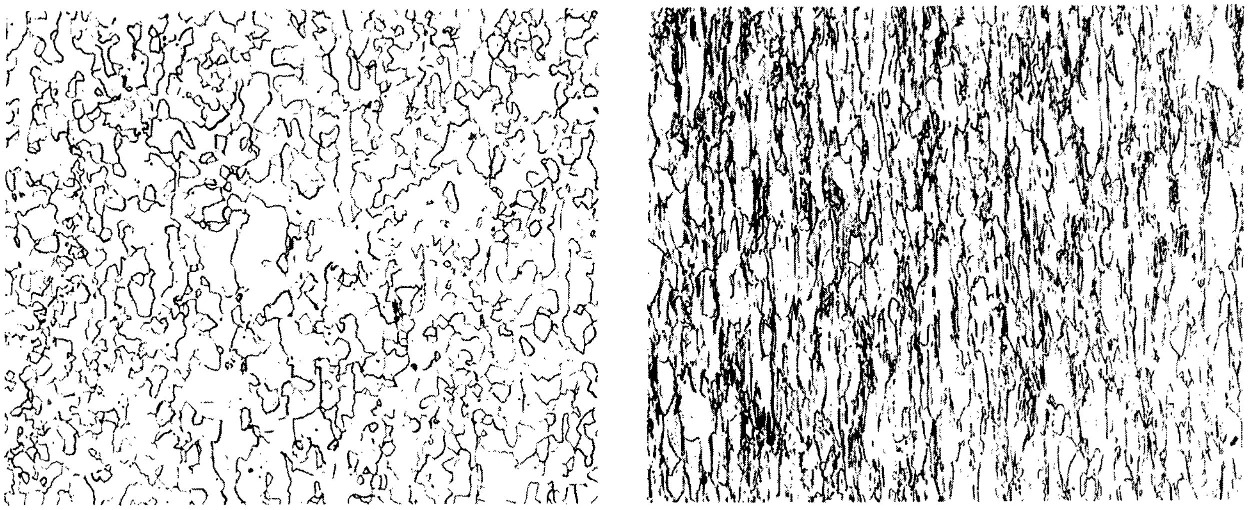
TABLE I. - CHEMICAL ANALYSES OF AS-RECEIVED ROD STOCK

Alloy	Heat	W	Zr	Hf	V	Mo	Y	Cb	Ta	C	O	N	H
		Weight percent								ppm			
B-33	XMM-8346	----	----	----	4.88	----	----	Bal.	-----	64	142	52	17
	XMM-8406	----	----	----	5.14	----	----		-----	63	113	57	18
	XMM-8641	----	----	----	4.24	----	----		-----	111	159	77	15
SCb-291	1996	8.37	----	----	----	----	----		9.69	14	101	119	30
Cb-1Zr	5118	----	0.91	----	----	----	----		-----	81	200	75	8
	5122	----	.98	----	----	----	----		-----	30	180	85	10
As-55	S-220	4.44	1.02	----	----	----	0.35		-----	722	260	130	23
	NAS-5515	4.66	.98	----	----	----	.30		-----	694	416	166	12
B-66	DX-526	----	.97	----	4.73	4.60	----		-----	62	176	62	12
D-43	X-110-322	9.4	1.0	----	----	----	----		-----	870	56	44	4
FS-85	85D-666	8.53	.80	----	----	----	----		26.95	58	148	41	10
Cb-752	5271	8.76	2.61	----	----	----	----		-----	60	458	123	18
D-14	14-385	----	4.78	----	----	----	----		-----	226	218	73	24
C-129	8-31340	9.75	----	9.81	----	----	----		-----	98	140	74	--
Ta-10W	2355	8.09	----	----	----	----	----	----	Bal.	41	48	9	15
	2356	9.70	----	----	----	----	----	----		33	37	37	4
T-111	DX-570	7.87	----	2.31	----	----	----	----		37	25	13	33
T-222	---------	8.45	----	2.31	----	----	----	----		141	48	18	4



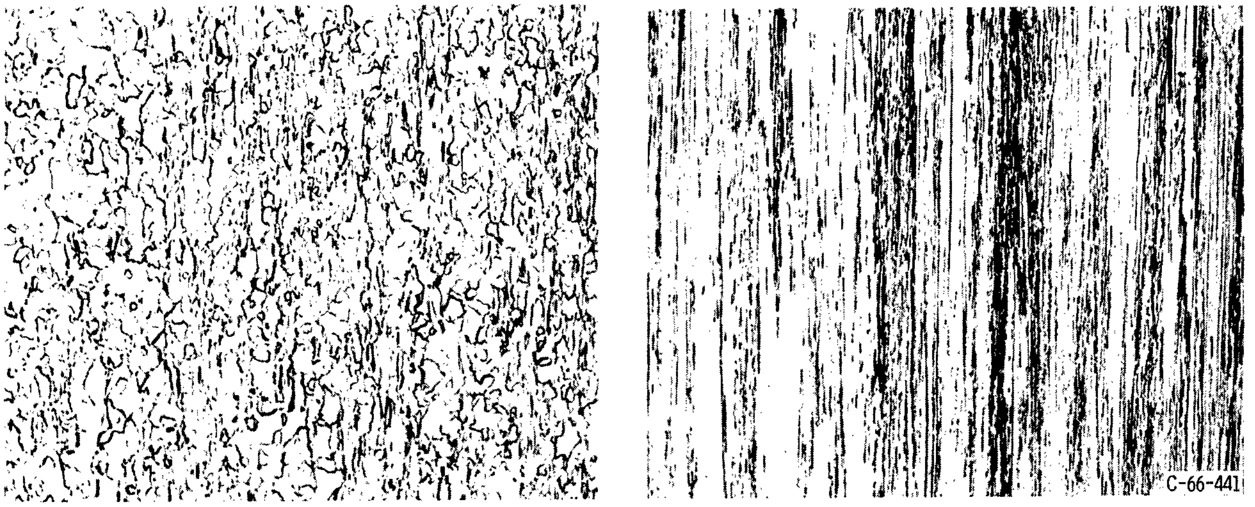
Heat XMM-8346

(b) SCb-291.



Heat XMM-8406

(c) B-66.

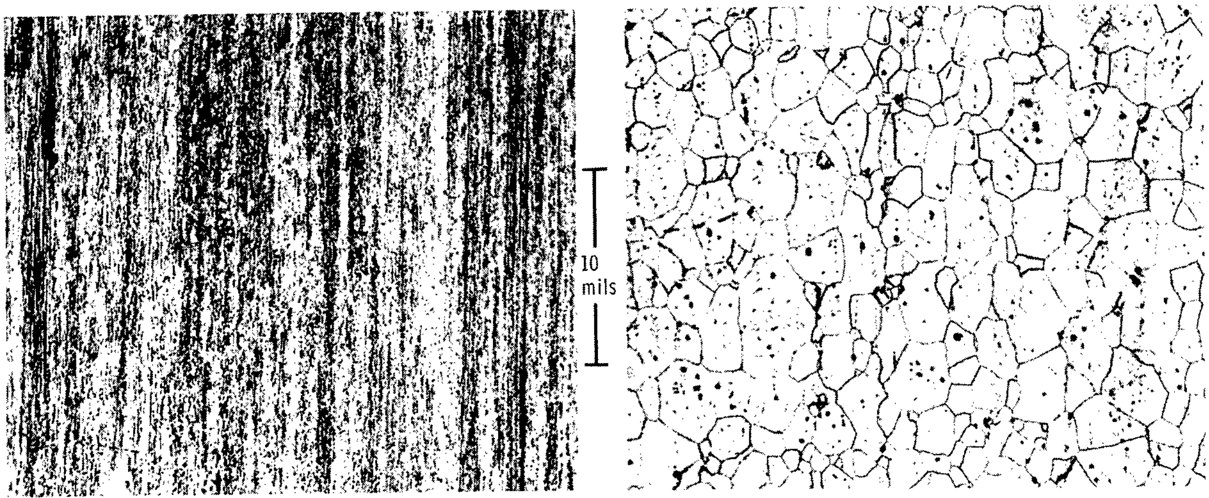


Heat XMM-8641

(a) B-33.

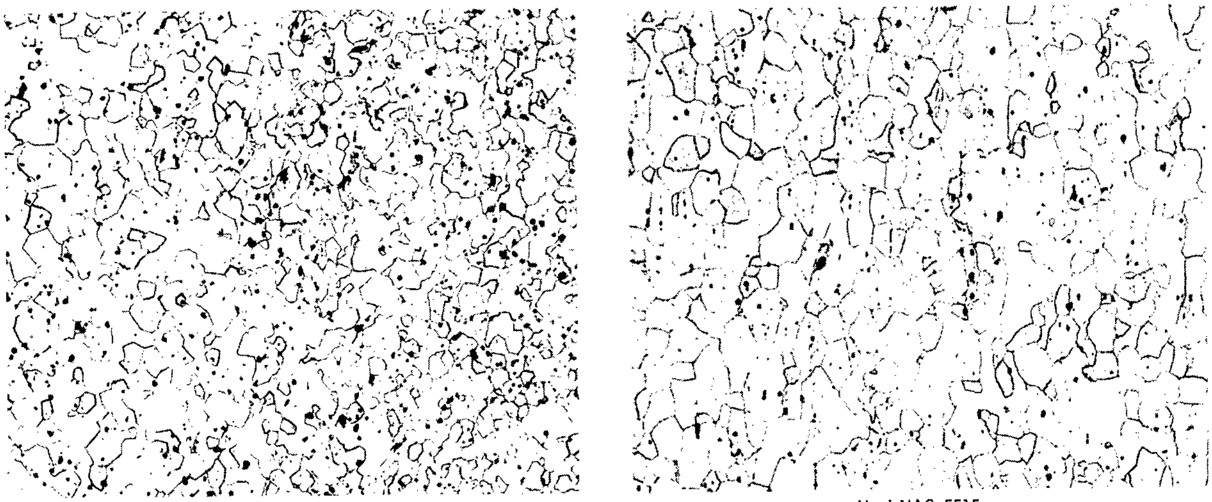
(d) D-43.

Figure 2. - Microstructures of as-received rod stock.



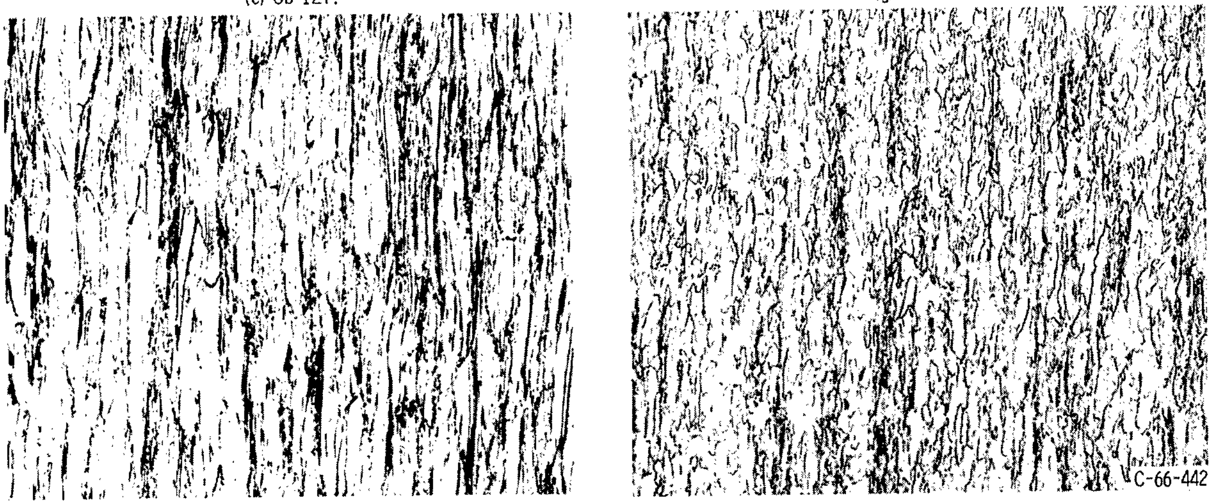
Heat 5118

Heat S-220



Heat 5122
(e) Cb-1Zr.

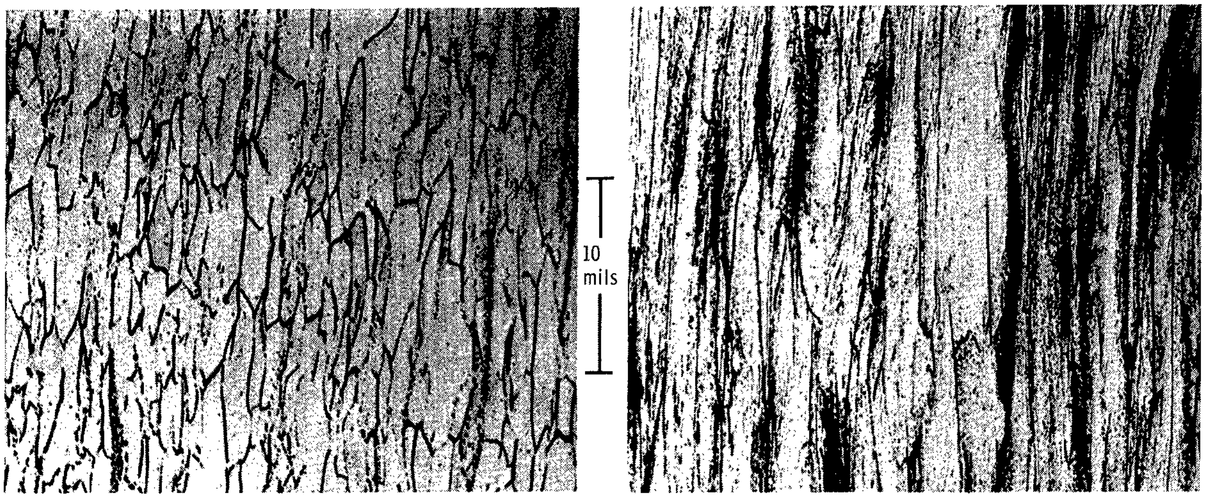
Heat NAS-5515
(g) AS-55.



(f) FS-85.

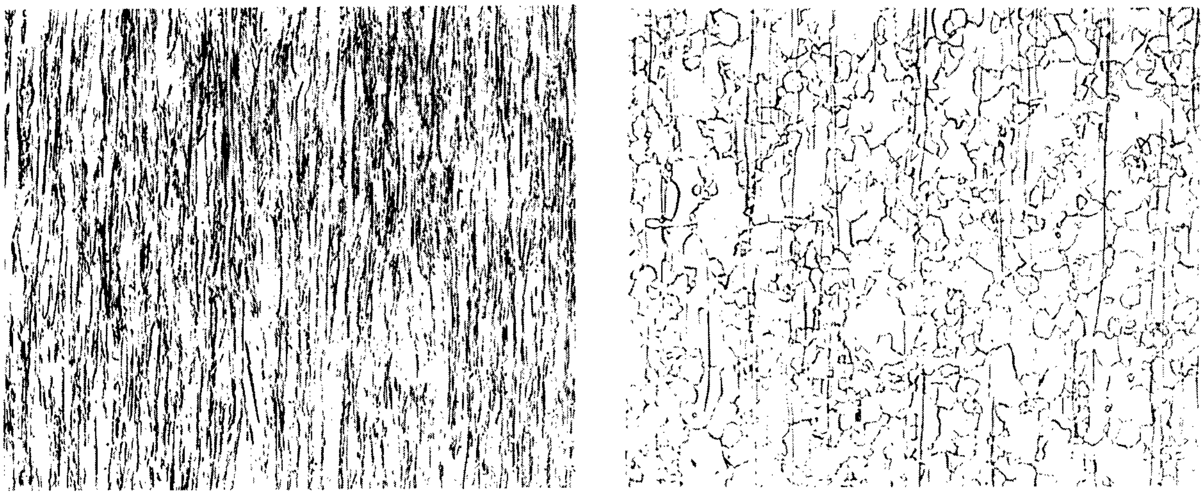
(h) Cb-752.

Figure 2. - Continued.



(i) D-14.

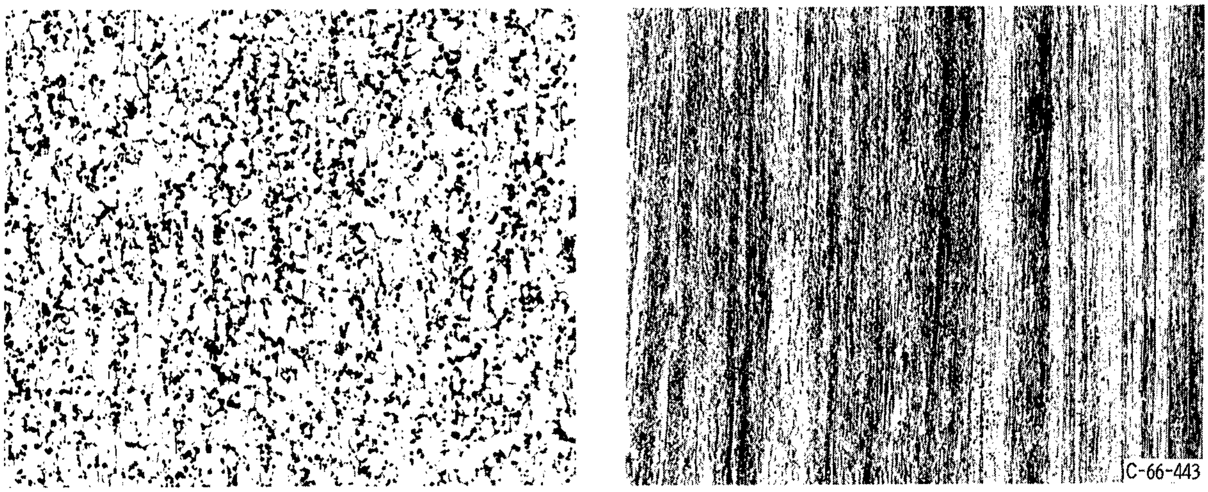
(j) C-129.



Heat 2355

Heat 2356

(k) Ta-10W.



(l) T-111.

(m) T-222.

Figure 2. - Concluded.

Capsule Preparation

As-received rod stock was trimmed to the approximate size, turned down in a lathe, and then precision drilled to form the capsule. The nominal dimensions of the finished capsules were $\frac{1}{2}$-inch outside diameter, $1\frac{3}{4}$-inch length, and 0.040-inch wall thickness.

After machining, the capsules were degreased and cleaned to ensure minimum surface contamination. The procedure used is given in appendix A.

The capsules were loaded with about $1\frac{1}{4}$ cubic centimeters of potassium, capped, and sealed by electron-beam welding in a special vacuum facility, at a pressure of about 10^{-5} torr. The procedure used is described in the Lewis motion picture (C-241, available on request) entitled Vacuum Handling of Air Sensitive Space Power System Materials. This procedure provided clean surfaces inside the capsules, allowed minimal contamination of the potassium during filling and welding, and minimized contamination from gases over the potassium in the capsule during the tests.

Capsule Testing

Prior to testing, platinum - platinum-13-percent-rhodium thermocouples were spot welded in an inert atmosphere to the top and bottom of each capsule. Eight capsules were then mounted in heaters to make up the test-bed assembly, and four tantalum heat shields were placed around each heater and capsule unit.

Testing was performed in high-vacuum chambers at pressures in the 10^{-7} to 10^{-8} torr range. The capsules were heated by tantalum heaters such as that shown in figure 3. Details of construction of these heaters are given in appendix B. Each heater was individually regulated to a set temperature by automatic control equipment. Test temperatures were recorded on multipoint strip-chart recorders. Initial startup conditions and their effects on oxygen contamination are discussed in appendix C. The nominal test

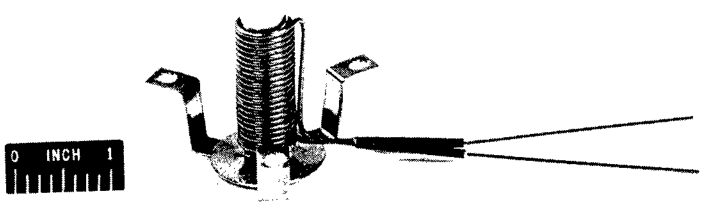


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Figure 3. - Coiled tantalum heater.

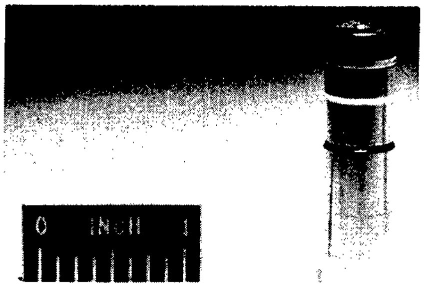

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Figure 4. - Typical capsule used to test effect of stress on corrosion.

temperatures, measured at the bottom of the capsules, were 1800°, 2200°, 2300°, and 2400° F. Nominal test times were 1000, 2000, and 4000 hours.

To explore the possibility of stress-induced corrosion, the hoop stress in the condensing region of the capsules was increased in test runs 4 and 5 by machining the wall to a thickness of approximately 0.020-inch over a 0.350-inch length along the top portion of the capsule (fig. 4).

Post-Test Processing

After removal from the test bed, the capsules were pierced by drilling under butyl alcohol. When the alcohol had completely reacted with the potassium within the capsules, the capsules were rinsed with distilled water and then cut lengthwise into two sections. One section of each capsule was mounted and examined metallographically. A description of the metallographic procedures is given in appendix D. X-ray and chemical analyses were made of selected capsule sections.

EXPERIMENTAL RESULTS

I, top 9 → 33

Test results are summarized in tables II and III. A summary of corrosion results is given in table II, and the results of vacuum-fusion analyses for oxygen from various regions of selected capsules are given in table III. A more complete description of test results for each alloy is given below.

B-33 (Cb-4V)

The capsules of recrystallized B-33 (heat XMM-8406) tested at 1800° F were run for 2000 hours. No gross attack was found; however, a slight surface etching, or grain

Whole Table

TABLE II. - SUMMARY OF CORROSION TEST RESULTS

Temperature, ^{o}F	Time, hr	Alloy	Run	Corrosive attack			Comments
				Type	Depth, mils	Location	
1800	110	Ta-10W Ta	6	Intergranular	12	Weld	----------------------------
	1000	SCb-291 Cb	6	Intergranular	1.5	Weld	----------------------------
	2000	B-33 Cb	1	None	----	-----------------	----------------------------
	2000	Cb-1Zr Cb	1	Intergranular	7.0	Liquid-vapor interface	----------------------------
				Intergranular	.8	Liquid section	General attack
	4000	T-222 Ta	7	None	----	-----------------	----------------------------
2200	8	Ta-10W	6	Intergranular	16	Weld	----------------------------
	123	Cb-1Zr	1	Solution	----	Condensing section	General attack
				Intergranular	4.5	Liquid-vapor interface	1.5-mil deposit
	1000	SCb-291	6	Solution	2.0	Condensing section	General attack
				Intergranular	16	Liquid section	General attack
	1000	B-33	4	Solution	1.0	Condensing section	----------------------------
				Solution	3.0	Liquid-vapor interface	Highly localized
	2000	D-43 Cb	3	None	----	-----------------	Film at liquid-vapor interface
	4000	Cb-752 Cb	2	↓	----	-----------------	Columbium and zirconium dioxide film at liquid-vapor interface
	↓	D-14 Cb	2		----	-----------------	Columbium and zirconium dioxide film at liquid-vapor interface
		AS-55 Cb	2		----	-----------------	Heavy etching, about 0.2 mil
		B-66 Cb	2	Solution	.2	Condensing section	Columbium and zirconium dioxide film at liquid-vapor interface
		C-129 Cb	2	None	----	-----------------	Film at liquid-vapor interface
		T-111 Ta	2		----	-----------------	Film at liquid-vapor interface
		FS-85 Cb	7	↓	----	-----------------	Columbium or tantalum film at liquid-vapor interface
		T-222	7		----	-----------------	$K_2Ta_4O_{11}$ film at liquid-vapor interface
2300	380	B-33	5	Intergranular	1.0	High stress area in condensing section	Very slight solution attack at liquid-vapor interface
	2000	D-43	3	None	----	-----------------	Amber film over entire inner surface
	2000	FS-85	3	None	----	-----------------	Film at liquid-vapor interface
	2000	T-111	3	None	----	-----------------	Film at liquid-vapor interface
2400	2000	FS-85	3	None	----	-----------------	Film at liquid-vapor interface
	2000	T-111	3	None	----	-----------------	Film at liquid-vapor interface
	4000	T-222	7	None	----	-----------------	$K_2Ta_4O_{11}$ film at liquid-vapor interface

to p 33

TABLE III. - VACUUM-FUSION ANALYSES FOR OXYGEN

Alloy	Run	Temperature, °F	Time, hr	Oxygen content, ppm			
				Pretest	Post-test		
				(a)	Top (b)	Center (c)	Bottom (d)
B-33	8	1800	2000	159	206	291	323
B-33	8	1800	2000	159	214	217	212
B-33	8	2200	2000	159	318	306	836
SCb-291	6	2200	1000	101	149	---	175
Ta-10W	6	2200	8	37	[e]55	---	34
Cb-1Zr	8	1800	2000	200	242	262	437
Cb-1Zr	8	1800	2000	200	241	235	252
Cb-1Zr	8	2200	115	200	254	767	753
Cb-1Zr	8	↓	115	200	245	284	610
D-14	2		4000	218	174	---	3050
AS-55	2		4000	260	276	---	426
B-66	2		4000	176	124	---	1100
D-43	3		2000	56	187	---	295
FS-85	2		4000	148	168	---	247
Cb-752	2		4000	458	181	---	1160
C-129	2		4000	140	180	---	1150
T-111	3	2300	2000	25	48	---	74
T-222	7	2400	4000	48	57	---	1780

[a] Sample taken from the original rod stock.

[b] Sample taken from the top third area of the capsule wall.

[c] Sample taken from the central third area of the capsule wall.

[d] Sample taken from the bottom third area of the capsule wall.

[e] Sample taken from the weld area.

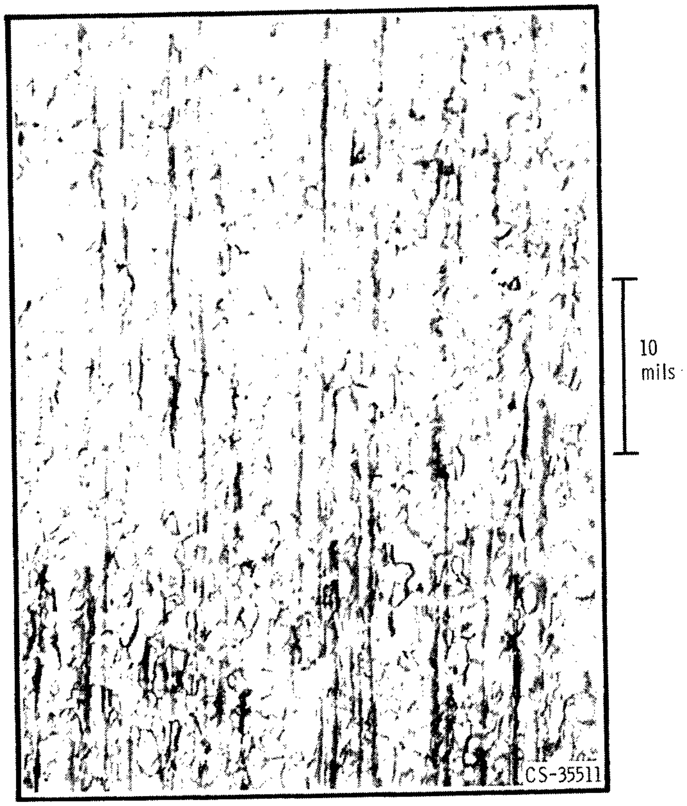


Figure 5. - Microstructure of replica of inside surface of B-33 capsule (heat XMM-8406) tested at 1800° F for 2000 hours with refluxing potassium.

delineation, by the potassium was found (fig. 5), and some general grain growth was observed. The capsule tested at 2200° F for 2000 hours (fig. 6) had much heavier grain delineation and an attack of approximately 1.0 mil at the liquid-vapor interface. In addition, there was up to 1.5 mils of intergranular attack at a corner in the condensing section. Very large grains were found throughout the condensing section and were also present along the inside edge of the capsule at the very bottom of the liquid zone. A test with a capsule from heat XMM-8346 (partially wrought) at 2200° F for 1000 hours yielded similar results, except that the solution attack at the liquid-vapor interface was approximately 3.0 mils deep (fig. 7).

There did not appear to be any effect of stress on the corrosion of B-33 at 2200° F after 1000 hours. At 2300° F the thin-walled capsule, bearing an initial stress of 3380 pounds per square inch, failed by creep rupture after 380 hours. Failure occurred after a creep strain of 45 percent. A comparison of this capsule with the regular-walled control capsule tested for the same time and at the same temperature is shown in figure 8. The capsule with the original 0.040-inch wall had an initial stress of approximately 1880 pounds per square inch. After the test, the capsule showed the usual grain delineation and a slight attack at the liquid-vapor interface. The grains were extremely large in the condensing section of the capsule and decreased somewhat in size in the liquid section.

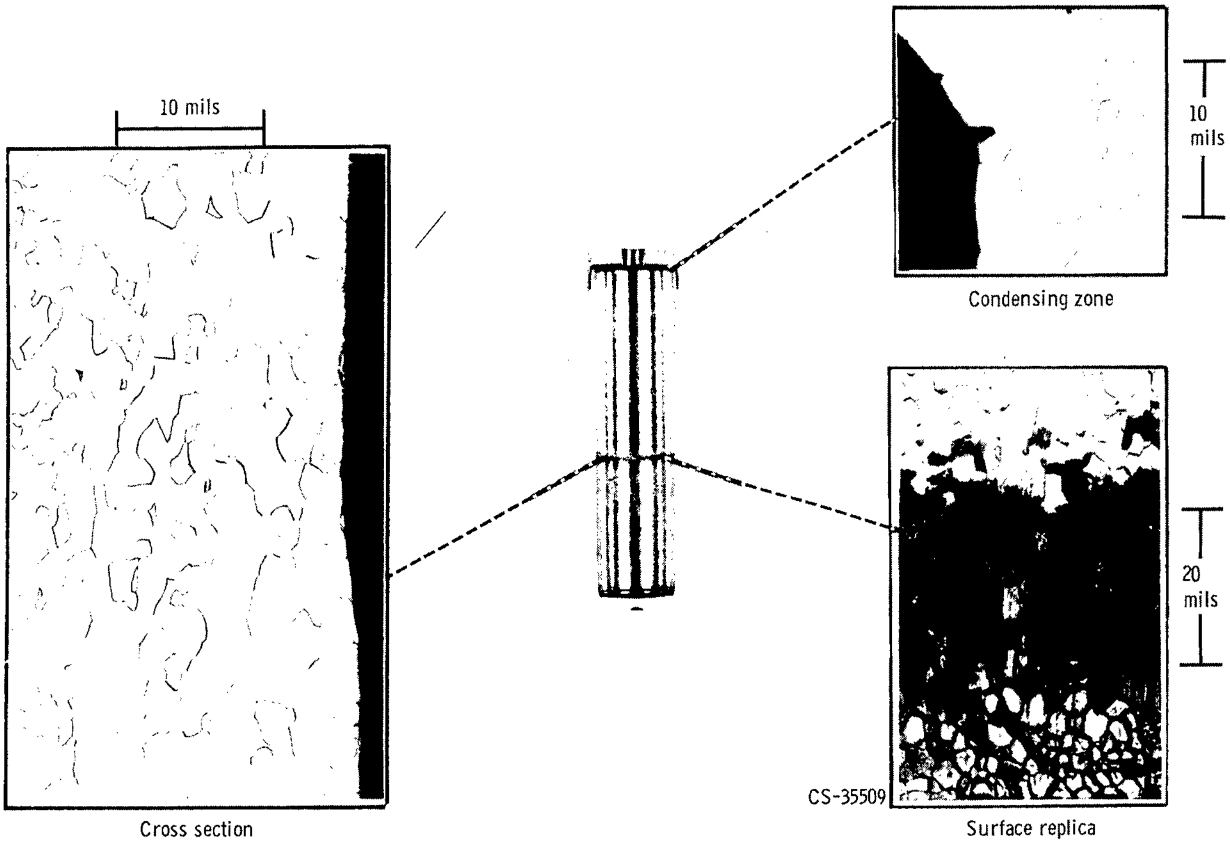


Figure 6. - Microstructure of B-33 capsule (heat XMM-8406) tested at 2200° F for 2000 hours with refluxing potassium.

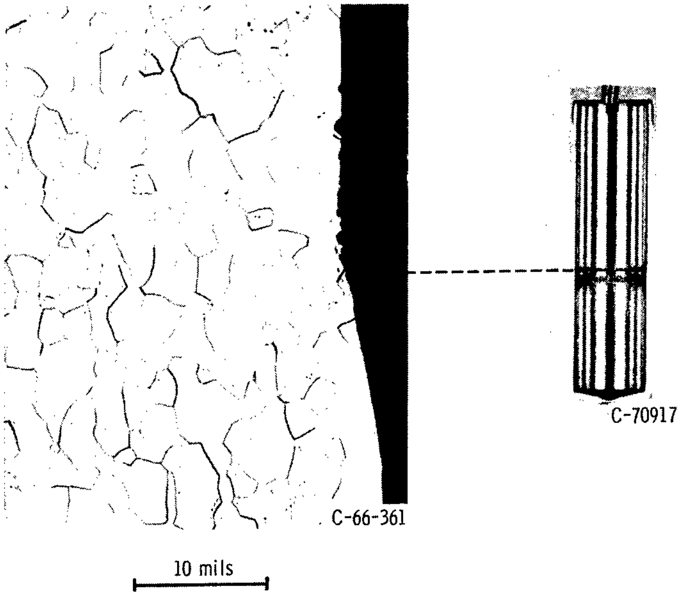
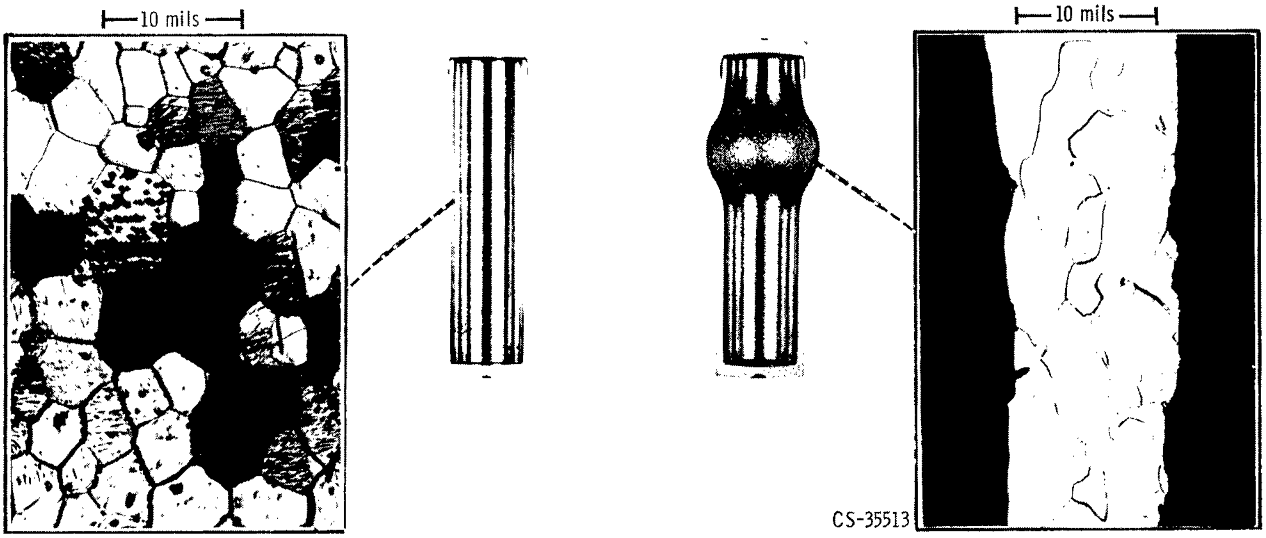


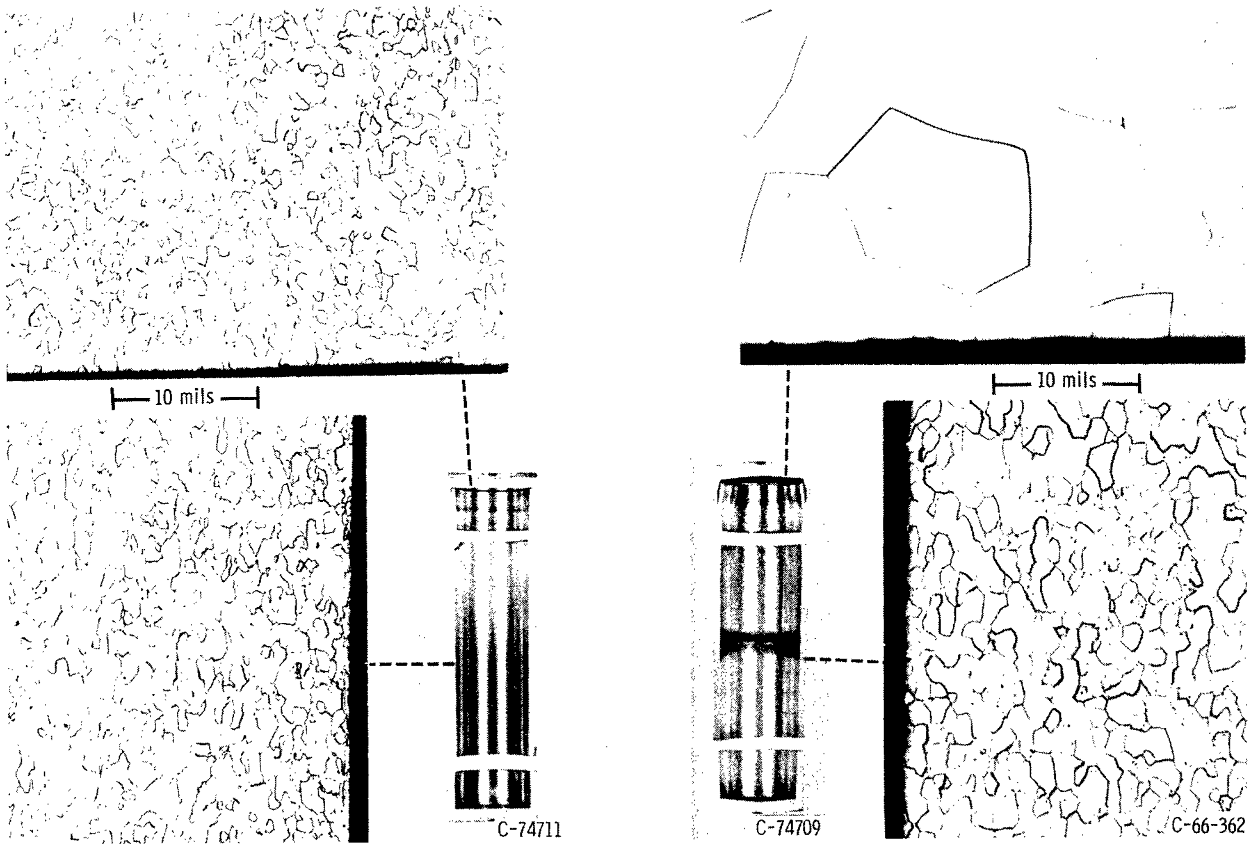
Figure 7. - Microstructure of B-33 capsule (heat XMM-8346) tested at 2200° F for 1000 hours with refluxing potassium.



Surface replica

Cross section of thin wall

Figure 8. - Effect of stress on corrosion. B-33 capsules (heat XMM-8346) both tested at 2300° F for 380 hours with refluxing potassium.



1800° F for 2000 hr

2200° F for 2000 hr

Figure 9. - Microstructures of B-33 capsules (heat XMM-8641) after testing with refluxing potassium.

The thin-walled portion of the first capsule showed up to 1.0 mil of intergranular attack; otherwise, there appeared to be no significant difference between the two capsules.

Heat XMM-8461 (partially wrought) was tested for 2000 hours at 1800° and 2200° F. No gross corrosion effects were noted in these tests; however, at 2200° F a dark area was observed at the liquid-vapor interface (fig. 9). Vacuum fusion analyses of the capsule walls (table III) indicated that the bottom of the capsule had a higher oxygen content than the top. This effect became more accentuated with increasing temperature.

SCb-291 (Cb-10Ta-10W)

After 1000 hours at 1800° F, SCb-291 exhibited up to 1.5 mils of intergranular attack at the weld. Visually there appeared to be some slight attack at the liquid-vapor interface; however, it was not observed metallographically. The microstructure of this capsule revealed considerable grain growth over that of the as-received material, but still showed only partial recrystallization.

At 2200° F after 1000 hours, this alloy showed extensive intergranular attack (up to 16 mils) throughout the liquid section and some solution attack in the condensing section (fig. 10). Deposits were evident, and X-ray patterns indicated that the lower band of deposits shown in figure 10 were large crystals of columbium, while the upper band, which was not observable metallographically, was composed of very small columbium crystals and large tungsten crystals. The microstructure was completely recrystallized. Sections of this capsule were analyzed for oxygen (table III). The analysis showed a slightly higher concentration in the bottom section than in the top section.

Ta-10W

All Ta-10W capsules tested failed by corrosive attack in less than the planned test time of 1000 hours. The capsule tested at 1800° F failed at 110 hours by intergranular penetration through a thin 10-mil section of the weld (fig. 11). There was also up to 1.0 mil of intergranular attack in the recrystallized area surrounding the weld. The worked structure seemed to be unaffected. At 2200° F, failure occurred at 8 hours with the same type of attack. Again, the worked structure was unaffected. Results of vacuum-fusion analyses of the weld and a section in the liquid zone of the capsule are given in table III. The bottom section had essentially the same concentration as that of the pretest sample, while the section from the weld area had a slightly higher concentration.

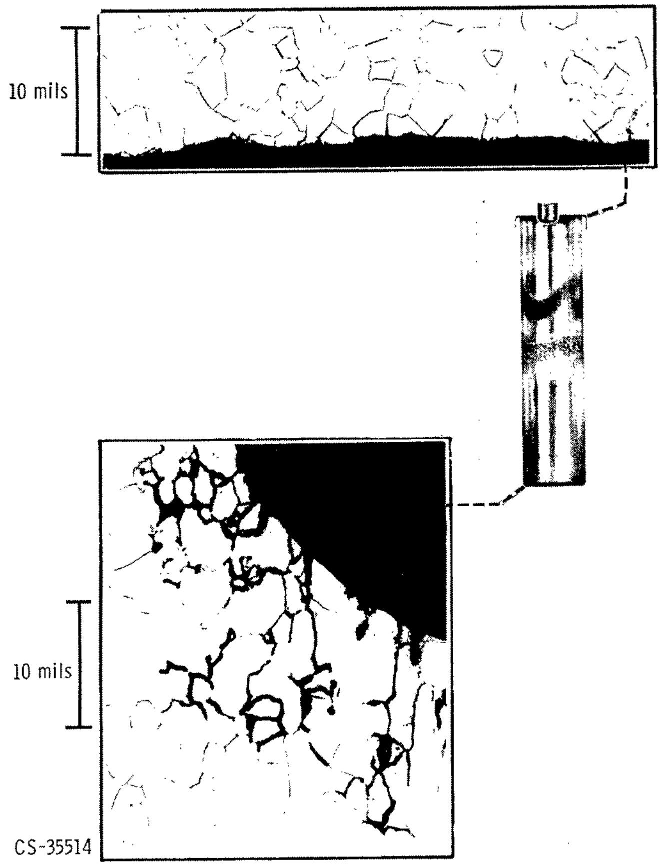
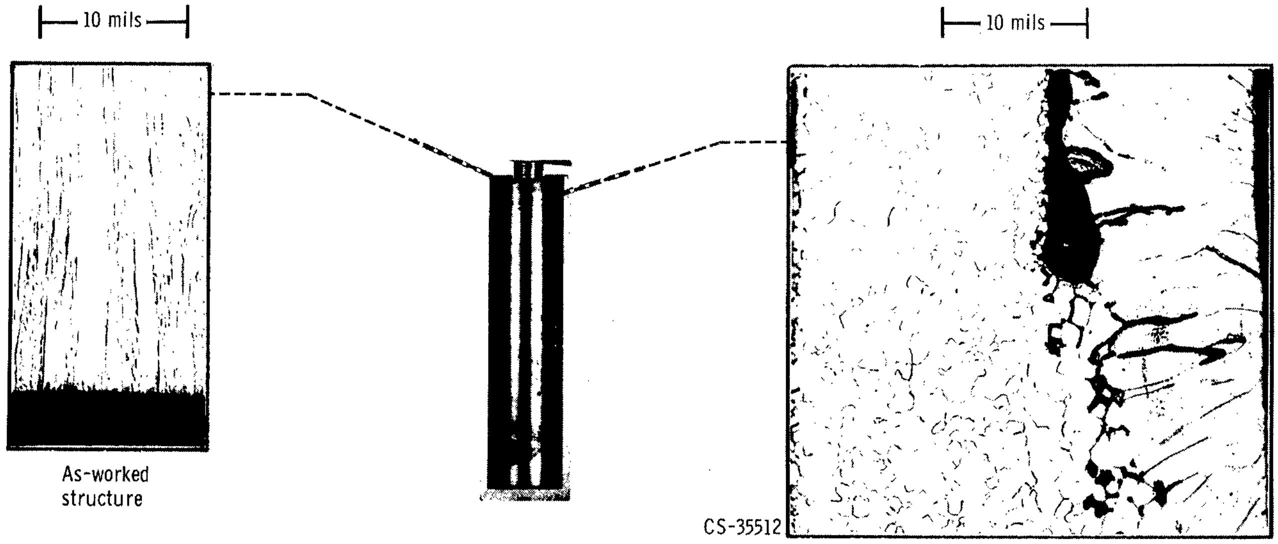


Figure 10. - Microstructures of SCb-291 capsule tested at 2200° F for 1000 hours with refluxing potassium.

Cb-1Zr

Recrystallized Cb-1Zr (heat 5122) was tested at 1800° F for as long as 2000 hours and at 2200° F for times up to 123 hours (fig. 12). At 1800° F for 2000 hours, there was 7.0 mils of intergranular attack and grain removal at the liquid-vapor interface and 0.8 mil of intergranular attack at the bottom of the capsule. There appeared to be a slight amount of general grain growth during the test and a pronounced grain growth throughout the condensing section down to the liquid-vapor interface, extending to a maximum depth of 6.0 mils. At 2200° F the capsules failed by creep rupture after 54 and 123 hours. The capsule that failed at 123 hours showed 4.5 mils of intergranular attack at the liquid-vapor interface, 1.5 mils of deposit buildup just below the interface, up to 1.5 mils of intergranular attack in the liquid section, and general solution attack at the top of the condensing section. The microstructure exhibited very large grains throughout the capsule. There also appeared to be a fine network of precipitates throughout many of the grains.

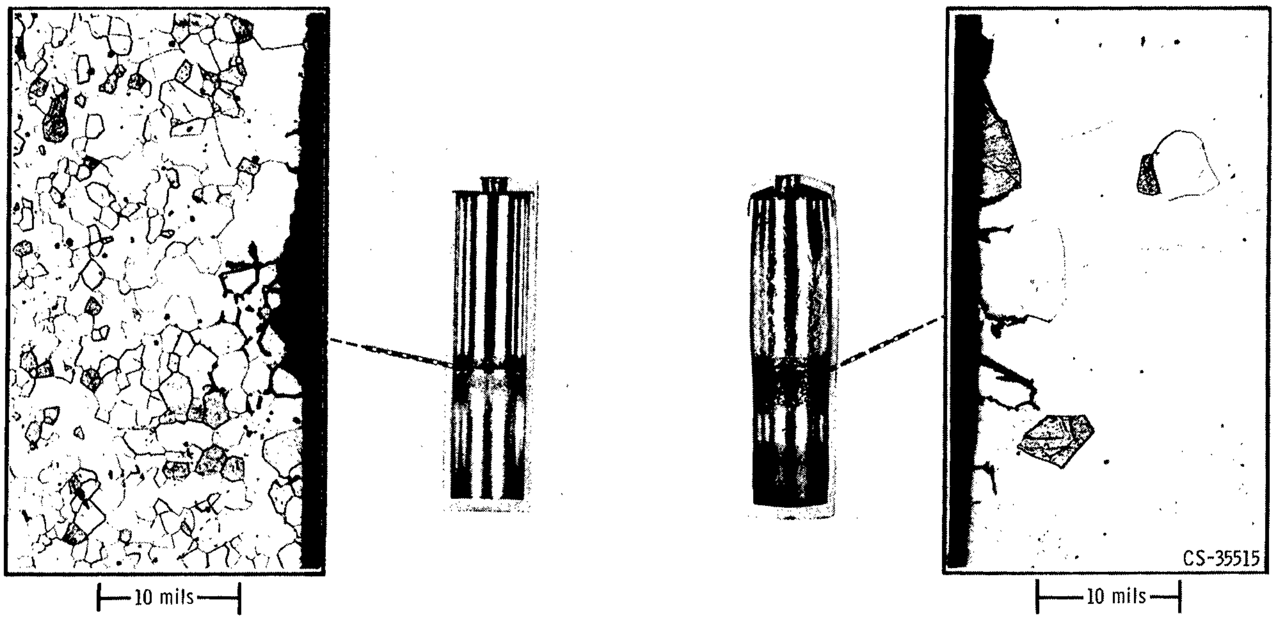
Capsules of Cb-1Zr (heat 5118) were tested at 1800° F for 2000 hours and at 2200° F



As-worked structure

Weld area

Figure 11. - Microstructure of as-worked Ta-10W capsule (heat 2355) after testing for 110 hours at 1800° F with refluxing potassium.

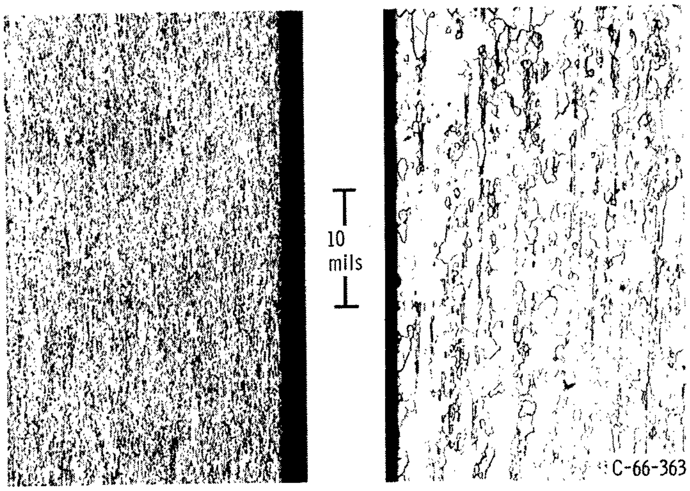


1800° F for 2000 hr

2200° F for 123 hr

Figure 12. - Microstructures of capsules of Cb-1Zr (heat 5122) after testing with refluxing potassium.

Liquid-vapor interface



1800° F for 2000 hr

2200° F for 115 hr

Figure 13. - Microstructures of Cb-1Zr capsules (heat 5118) after testing with refluxing potassium.

up to 115 hours (fig. 13) in the as-received, cold-worked condition. Unlike the results from heat 5122, no intergranular or solution attack was found. Results of vacuum-fusion analyses for oxygen (table III) were found to be similar to the results obtained for B-33, showing greater oxygen contents at the bottom than at the top of each capsule and an increase of oxygen content with temperature.

D-14 (Cb-5Zr)

Capsules of D-14 were tested at 2200° F for 2000 and 4000 hours (fig. 14). A slightly irregular surface at the very top of these capsules indicates the possibility of some general solution attack there. The extreme bottom of the capsules appeared to have localized pitting. There also were a heavy grain delineation and a dark film deposit at the liquid-vapor interface. An X-ray pattern of the film from the 4000-hour capsule indicated it was made up of crystals of columbium and zirconium dioxide. Results of vacuum-fusion analyses for oxygen on this capsule showed a very large increase in oxygen content for the bottom section, while the concentration in the top section actually decreased slightly.

Both capsules were recrystallized. Stringers of precipitates, presumably zirconium dioxide, extend parallel to the axis of the original rod stock; in addition, there was a limited amount of random precipitation. Precipitate-depleted zones were observed along the inner edge of the wall at the condensing sections of these capsules, extending to depths of 1.5 and 2.0 mils at 2000 and 4000 hours, respectively.

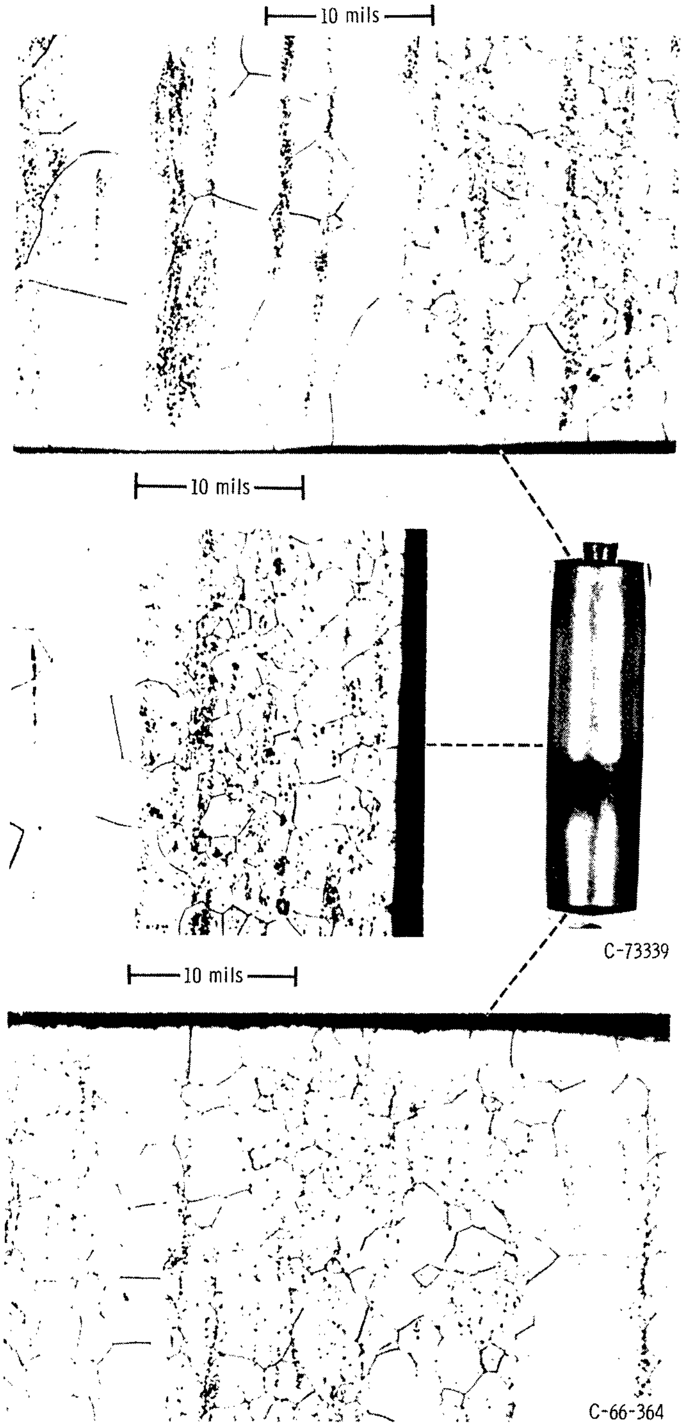
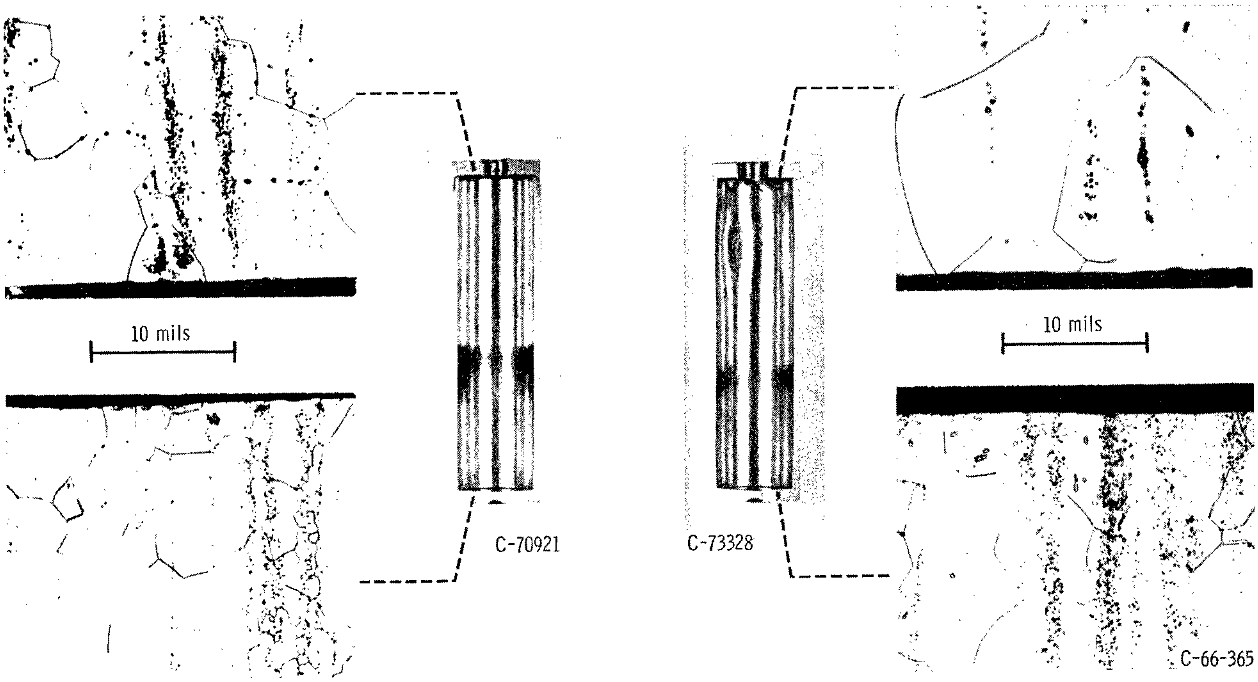


Figure 14. - Microstructures of D-14 capsule tested at 2200° F for 4000 hours with refluxing potassium.

AS-55 (Cb-5W-1Zr-0.2Y-0.06C)

A capsule of AS-55 (heat NAS-5515) was tested at 2200° F. The test was terminated at 1022 hours by a weld failure. No gross effects of corrosion were observed. There was a slight surface grain delineation, which was common to most of the materials tested. The capsule structure showed no noticeable change in grain size or precipitate distribution during the test, with the exception of an additional fine precipitate throughout the bottom portion of the capsule.

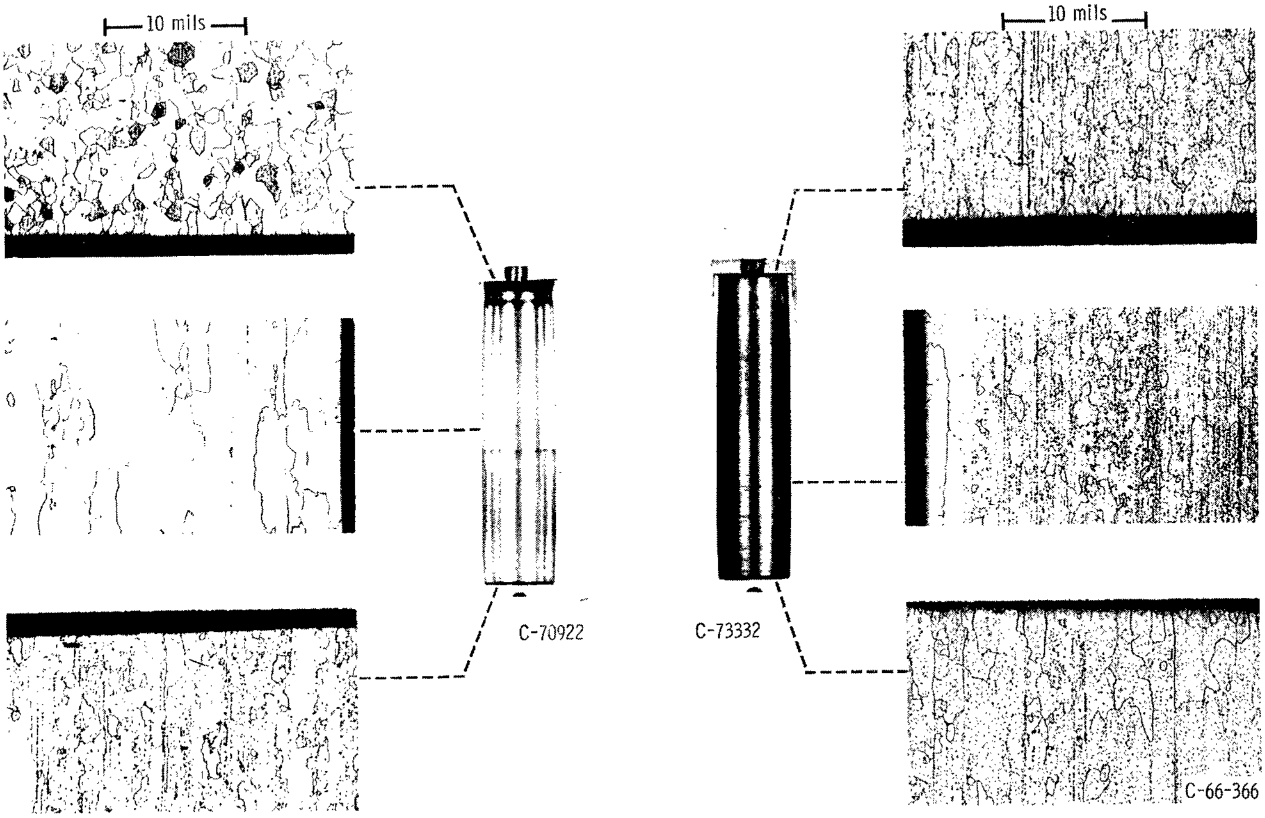
Heat S-220 was tested at 2200° F for 4000 hours. Again, there were no gross corrosion effects; however, the inside surface was dulled because of etching by the potassium to a maximum depth of about 0.2 mil near the liquid-vapor interface. There was no noticeable change in grain size. Coarse precipitates seemed to be located principally along grain boundaries with some scattered through the inside of the grains; whereas, fine precipitates were found throughout and appeared to increase from the top to the bottom of the capsule. The density of fine precipitates seemed less near the grain boundaries than at the center of the grains. The results of a vacuum fusion analysis for oxygen showed an increase in oxygen concentration in the bottom section of this capsule.



2000 hr

4000 hr

Figure 15. - Microstructures of B-66 capsules after testing at 2200° F with refluxing potassium.



2200° F

2300° F

Figure 16. - Microstructures of D-43 capsules after testing for 2000 hours with refluxing potassium.

B-66 (Cb-5Mo-5V-1Zr)

Capsules of B-66 were tested at 2200° F for 2000 and 4000 hours. A dark film was found inside both capsules in the region of the liquid-vapor interface. Both capsules had slight amounts of grain delineation. An X-ray pattern of the film from the 4000-hour capsule revealed that it consisted of zirconium dioxide and columbium crystals. Metallography revealed no definite signs of gross corrosion in the capsule tested for 2000 hours, but a slightly irregular surface indicated solution attack to a maximum depth of about 0. 2 mil in the condensing section of the capsule tested for 4000 hours. No gross precipitation was found in the as-received material (fig. 2(c)). In both of the test capsules, however, there were large amounts of a second phase appearing as precipitates strung out in bands parallel to the axis of the original rod stock (fig. 15). In general, precipitates were more numerous and smaller in the bottom of the capsules than in the top, these differences becoming greater with time. The precipitates were larger in the capsule tested for 4000 hours than in the capsule tested for 2000 hours. In addition, the capsule tested for 4000 hours showed a large grain growth in the condensing section throughout the wall thickness. The results of vacuum-fusion analyses on this capsule showed a great increase in oxygen concentration in the bottom section and a slight decrease in oxygen concentration in the top section.

D-43 (Cb-10W-1Zr-0.1C)

At 2200° F for 2000 hours, D-43 did not show corrosion effects except for a dark film at the liquid-vapor interface. Metallographic results showed small recrystallized grains in the very top of the capsule, the remainder of the capsule being only partially recrystallized with very fine precipitates throughout (fig. 16). The results of vacuum fusion analyses for oxygen in this capsule showed a greater increase in oxygen content in the bottom section than in the top section.

A capsule tested at 2300° F for 2000 hours showed no attack, but had an amber film over the entire inner surface. The alloy was partially recrystallized and had a fairly uniform distribution of precipitates that were coarser than those in the capsule tested at 2200° F. In addition, there was a decrease in the amount of precipitation through the inner 5 mils of the walls near the liquid-vapor interface (fig. 16).

No effect of stress on corrosion was observed at 2200° F or at 2300° F for 1000 hours in tests similar to those used on B-33. At 2200° F the thin-walled capsule had an initial stress level of 2920 pounds per square inch. This capsule underwent a creep strain of 15 percent. The control capsule had an initial stress level of 1530 pounds per square inch and underwent a creep strain of 3. 5 percent. In the 2300° F test, the thin-walled section of the capsule had an initial hoop stress of 3900 pounds per square inch and experienced a creep strain of 37 percent. The control capsule had an initial hoop stress of 2020 pounds per square inch and experienced a creep strain of 6.9 percent.

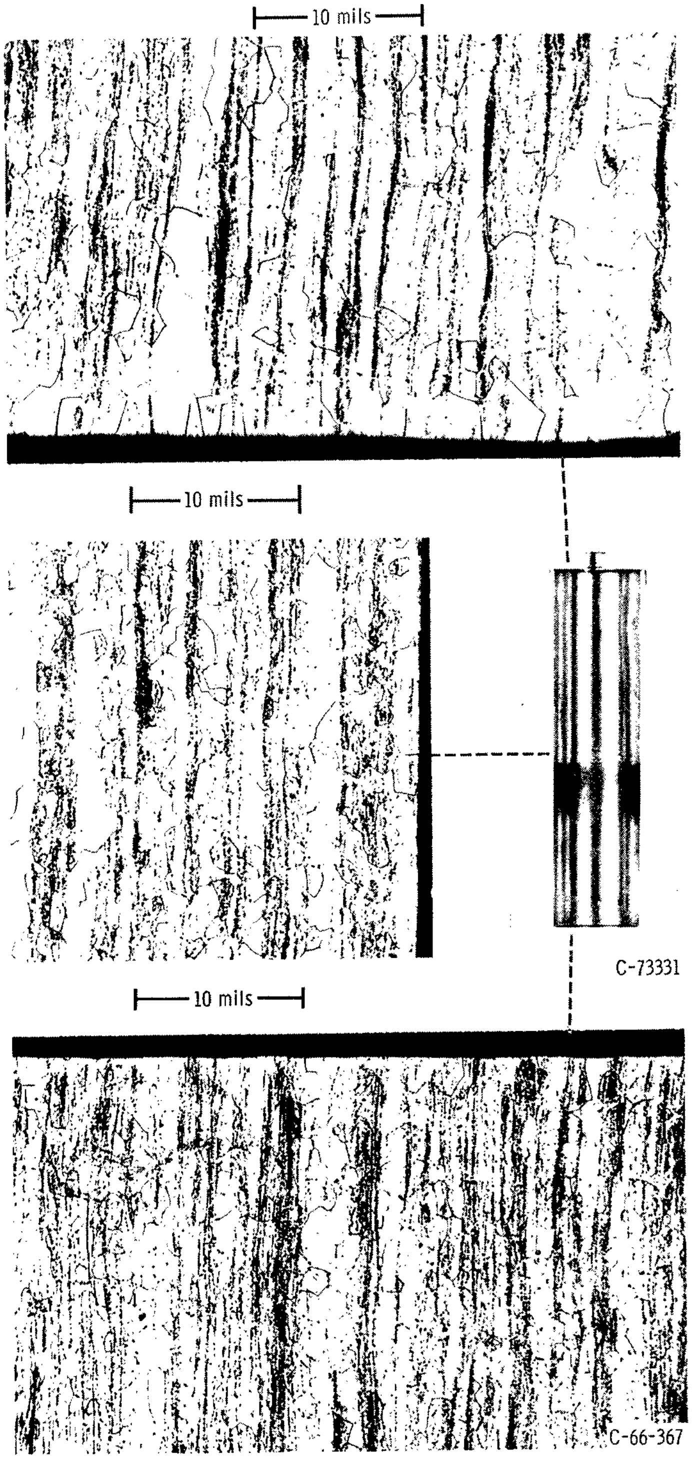


Figure 17. - Microstructures of FS-85 capsule tested at 2200° F for 4000 hours with refluxing potassium.

FS-85 (Cb-28Ta-10W-1Zr)

Capsules of FS-85 were tested at 2200° F for times up to 4000 hours, at 2300° F for times up to 2000 hours, and at 2400° F for 2000 hours. None of these tests showed any corrosion other than a fairly heavy film at the liquid-vapor interface. All of the capsules had recrystallized during testing. There appeared to be a precipitate-depleted zone along the inside edge of the capsules, predominantly in the condensing sections. The affected depths were up to 4 mils at 2200° F for 4000 hours, up to 7 mils at 2300° F for 2000 hours, and up to 6 mils at 2400° F for 2000 hours. The precipitates were strung out in bands parallel to the axis of the original rod stock. (For an example, see fig. 17.)

Tests for the effect of stress on corrosion at 2200° and 2300° F for 1000 hours were negative. The stress levels, 3060 pounds per square inch at 2200° F and 3910 pounds per square inch at 2300° F, induced only a moderate amount of creep strain, 0.9 and 2.7 percent, respectively.

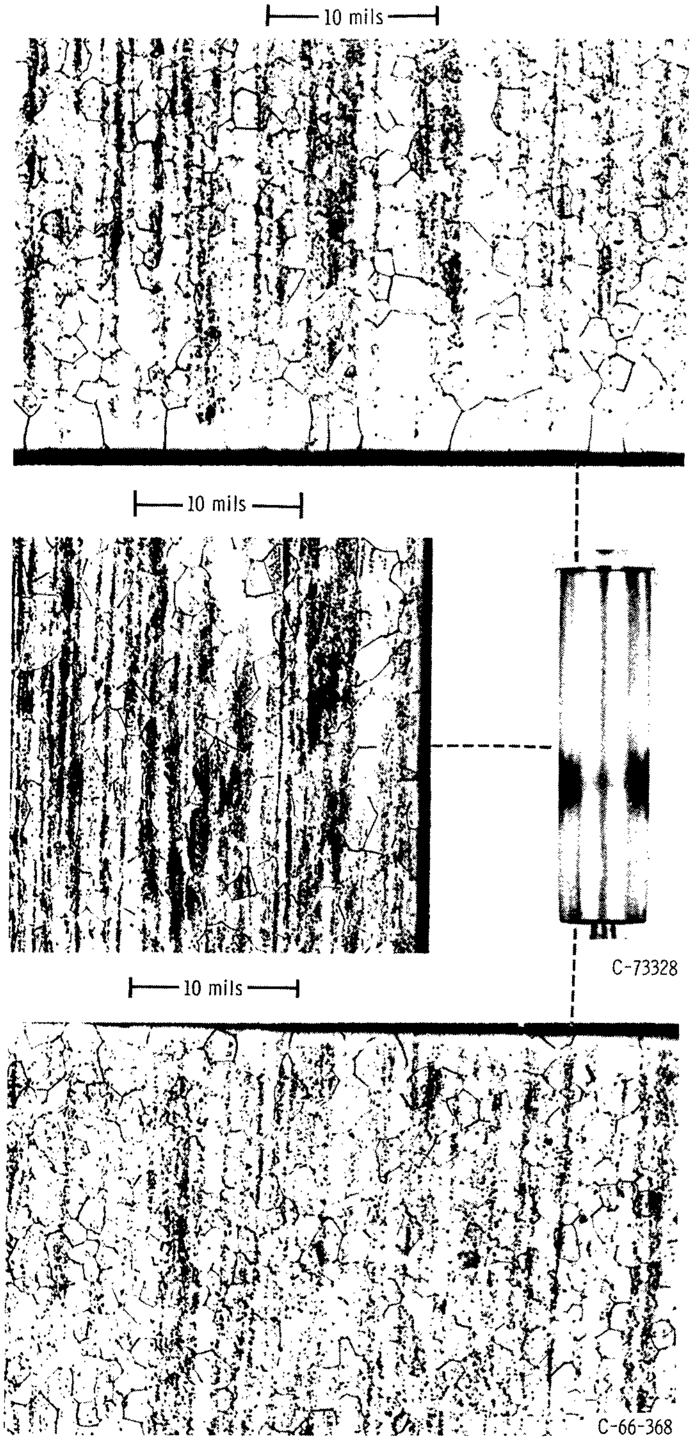


Figure 18. - Microstructures of Cb-752 capsule tested at 2200° F for 4000 hours with refluxing potassium.

An X-ray pattern of the film on a capsule tested at 2200° F for 4000 hours revealed only the presence of particles of either tantalum or columbium. The results of vacuum-fusion analyses showed an increase in oxygen concentration in the bottom section of this capsule.

Cb-752 (Cb-10W-2.5Zr)

Tests performed on Cb-752 at 2200° F for 2000 and 4000 hours resulted in no gross corrosion (fig. 18). As with most of the other gettered alloys of columbium, a heavy film developed at the liquid-vapor interface. The X-ray patterns of the film on the capsule that was tested for 4000 hours revealed the presence of two very small-grained columbium phases with slightly different lattice parameters and zirconium dioxide with about half the intensity of the columbium.

The capsules were completely recrystallized with precipitates strung out parallel to the axis of the original rod stock. The precipitates are larger and more numerous at 4000 hours. There is a noticeable reduction in the amount of precipitation near the inner edge of the capsule, predominantly in the condensing section, becoming more definite with increasing time. At 4000 hours the affected depth reached 8.0 mils.

The capsule tested for 4000 hours

was analyzed for oxygen (table III) and showed a large increase in oxygen concentration in the bottom section and a definite decrease in oxygen concentration in the top section.

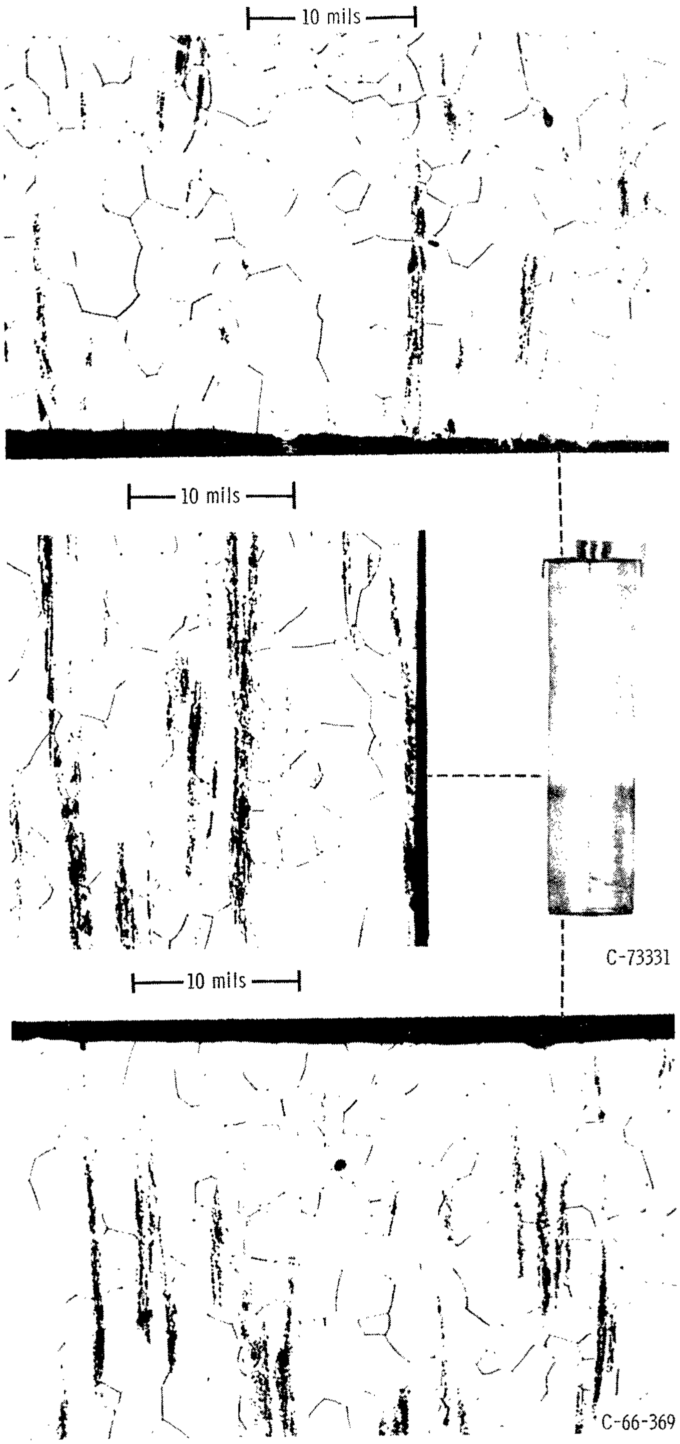


Figure 19. - Microstructures of C-129 capsule tested at 2200° F for 4000 hours with refluxing potassium.

C-129 (Cb-10W-10Hf)

The C-129 alloy, tested at 2200° F for 2000 and 4000 hours, indicated no gross corrosive attack. There were, however, grain delineation and a dark film at the liquid-vapor interface in both capsules (fig. 19).

The capsules had completely recrystallized and precipitates were strung out as in the as-received rod stock. There appeared to be a precipitate-depleted area extending to a depth of about 2.0 mils at the very top of the capsule tested for 4000 hours.

The results of vacuum-fusion analyses for the capsule tested for 4000 hours showed a great increase of oxygen in the bottom section and a slight increase of oxygen in the top section.

T-111 (Ta-8W-2Hf)

Potassium had very little effect on T-111. Figure 20 shows a capsule tested at 2300° F for 2000 hours. This capsule was typical of those tested. The only effect seemed to be the formation of a faint film at the

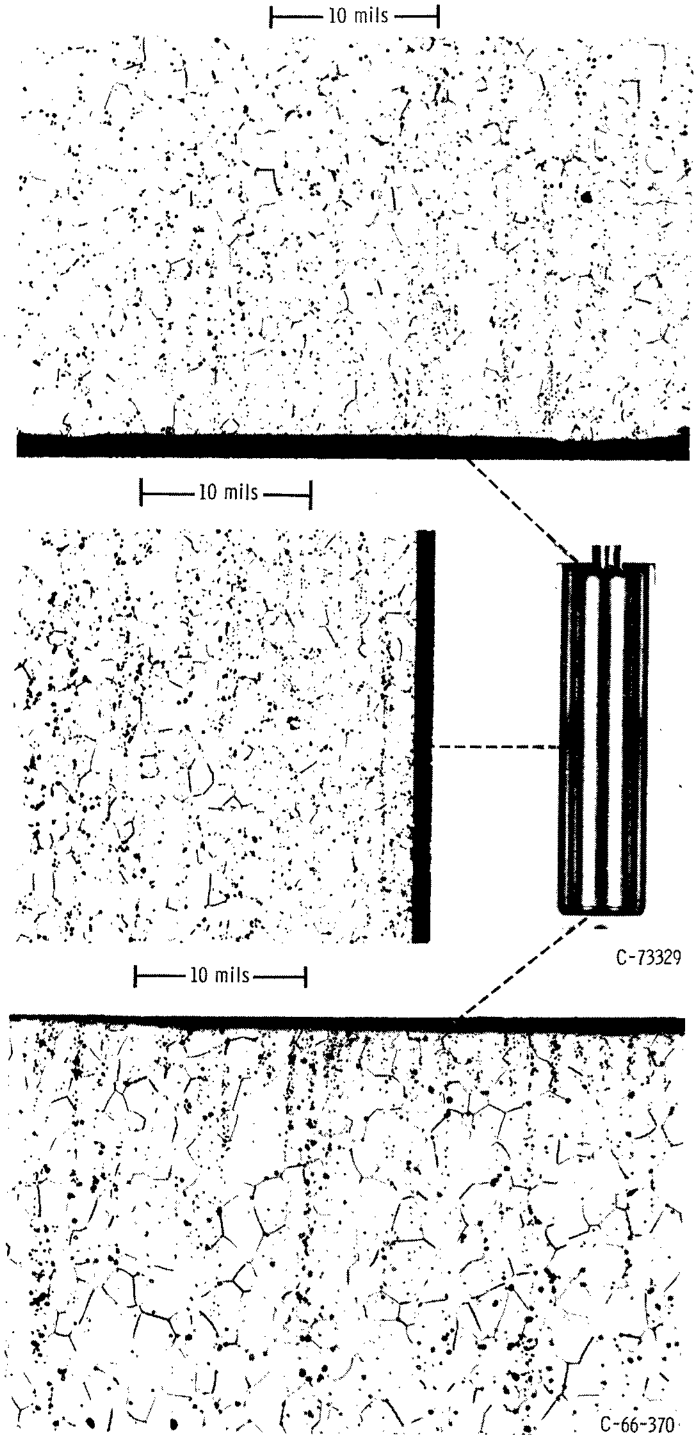


Figure 20. - Microstructures of T-111 capsule tested at 2300° F for 2000 hours with refluxing potassium.

liquid-vapor interface. Results of analyses on this capsule for oxygen are given in table III and show slight increases in oxygen in both top and bottom sections.

The tests for the effect of stress on corrosion were abortive because the stress levels imposed were not great enough to produce measurable creep.

T-222 (Ta-9.6W-2.4Hf-0.01C)

With the exception of the capsules tested at 2400° F, very little effect of potassium was observed on T-222. At 2400° F, films were found at the liquid-vapor interfaces that reflected light, such as might be observed from crystal faces. Metallography, however, did not reveal any deposits. In areas where there were large amounts of precipitation within the alloy, there were fewer precipitates along the grain boundaries than within the grains. There appeared to be fewer precipitates along the inside edge of the capsules tested at 2400° F than in the bulk alloy, and also a slight roughening along this edge (fig. 21).

The X-ray powder patterns from the films on the capsules tested for 4000 hours at 2200° and 2400° F both showed the films to be mainly $K_2Ta_4O_{11}$ with some tungsten oxide. No hafnium dioxide was identified; however, if it were present, it could possibly have been masked by the

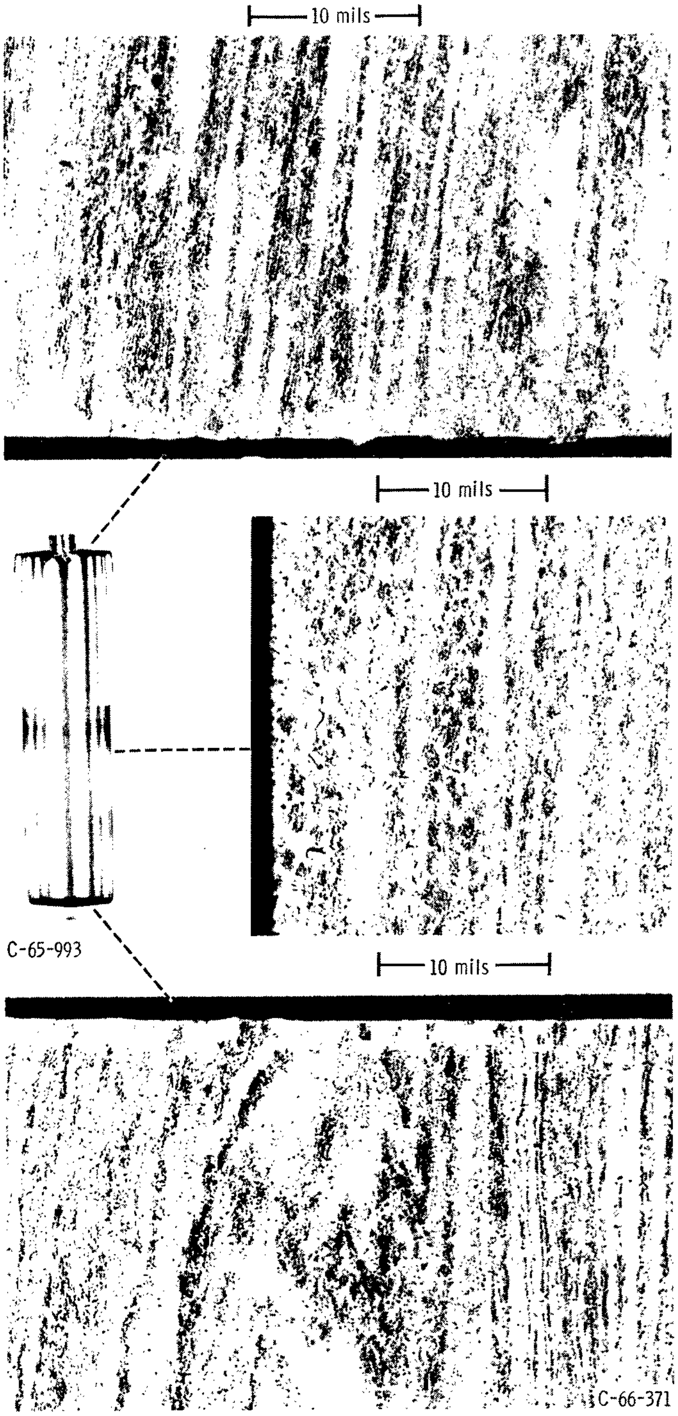


Figure 21. - Microstructures of T-222 capsule tested at 2400° F for 4000 hours with refluxing potassium.

lines of the other compounds.

Vacuum-fusion analyses of the capsule tested at 2400° F for 4000 hours are given in table III. These show a very large increase in oxygen concentration in the bottom section of the capsule and a slight increase in oxygen concentration in the top section.

DISCUSSION

The most noticeable trend observed in this study was that the ungettered alloys were less resistant to corrosion by refluxing potassium than were the gettered alloys. All of the ungettered alloys showed considerable attack, either solution or intergranular, while the gettered alloys exhibited only slight corrosion effects. The gettered alloy, Cb-1Zr, however, did show a moderate amount of corrosion. A possible explanation of the behavior of these alloys will be presented in the discussion of corrosion mechanism (p. 28).

For purposes of comparison, each alloy can be placed in one of three groups. The groups, in order of decreasing corrosion resistance, are as follows: (1) T-111, T-222, C-129, D-14, Cb-752, D-43, B-66, AS-55, and FS-85; (2) Cb-1Zr; and (3) B-33, SCb-291, and Ta-10W. If results of reflux capsule tests are assumed to correspond to the corrosion in full-scale space-power systems, the corrosion resistance to refluxing potassium of all nine alloys in the first group appears to be sufficient for consideration of their use as space-power system containment materials. The Cb-1Zr alloy (group 2) may be of marginal corrosion resistance because of the doubts raised by the different results from the two heats of material tested, probably due to the effects of grain size and oxygen contamination. The ungettered alloys (group 3) are judged to be unsatisfactory because of the large amount of corrosive attack.

In addition to solution and intergranular attack, two corrosion-related effects were noted. First, more grain growth was found in the top section of most of the capsules tested than in the bottom section, even though the temperature of the capsule was lower at the top than at the bottom. Since grain growth is promoted by a reduction of impurities or alloy content of a metal, the concomitantly observed variation of oxygen throughout the capsule (i. e. , a lower oxygen concentration in the top section than in the bottom section) probably accounts for the variation in grain growth.

Second, it was noted that second-phase precipitation was less at the top than at the bottom sections of the capsules for most of the gettered alloys, and in many cases there was also a precipitate-depleted zone along the inner edge of the capsule top section. The top-to-bottom variation in precipitate density is probably related to the previously mentioned oxygen variation throughout the capsule. The inner-edge precipitate depletion is most likely the result of the removal of gettering element, either hafnium or zirconium, from these locations by solution in the potassium.

As an aid in predicting corrosion results, or extrapolating from known data, it would be helpful to have a model of the potassium - refractory metal corrosion process. Although the present state of knowledge precludes the formulation of a corrosion mechanism in complete detail, the information obtained in this study together with information from other sources does permit the outlining of a provisional mechanism.

Since oxygen is believed to be the major influence on corrosion of metals and alloys with the alkali metals (refs. 3 to 11), a corrosion mechanism must necessarily consider the disposition and the form of association of oxygen in these systems. Previous corrosion investigations and solubility studies have resulted in several pertinent observations. First, it is known that a transfer of oxygen from columbium occurs with potassium as the apparent transfer medium (refs. 8 and 12) despite the fact that the direct transfer is not favored thermodynamically. Second, tests to determine the solubility of metals in the alkali metals (refs. 5 to 7) suggest that solution occurs by the formation of an oxygen-metal compound followed by solution of the compound, rather than simple elemental solution of the metal. Third, in several instances the presence of potassium - refractory metal complex oxides have been confirmed (refs. 7 and 9).

In order to assess the role of the complex oxide in the corrosion process, phase relations are needed. The only available pertinent study, however, is that of the

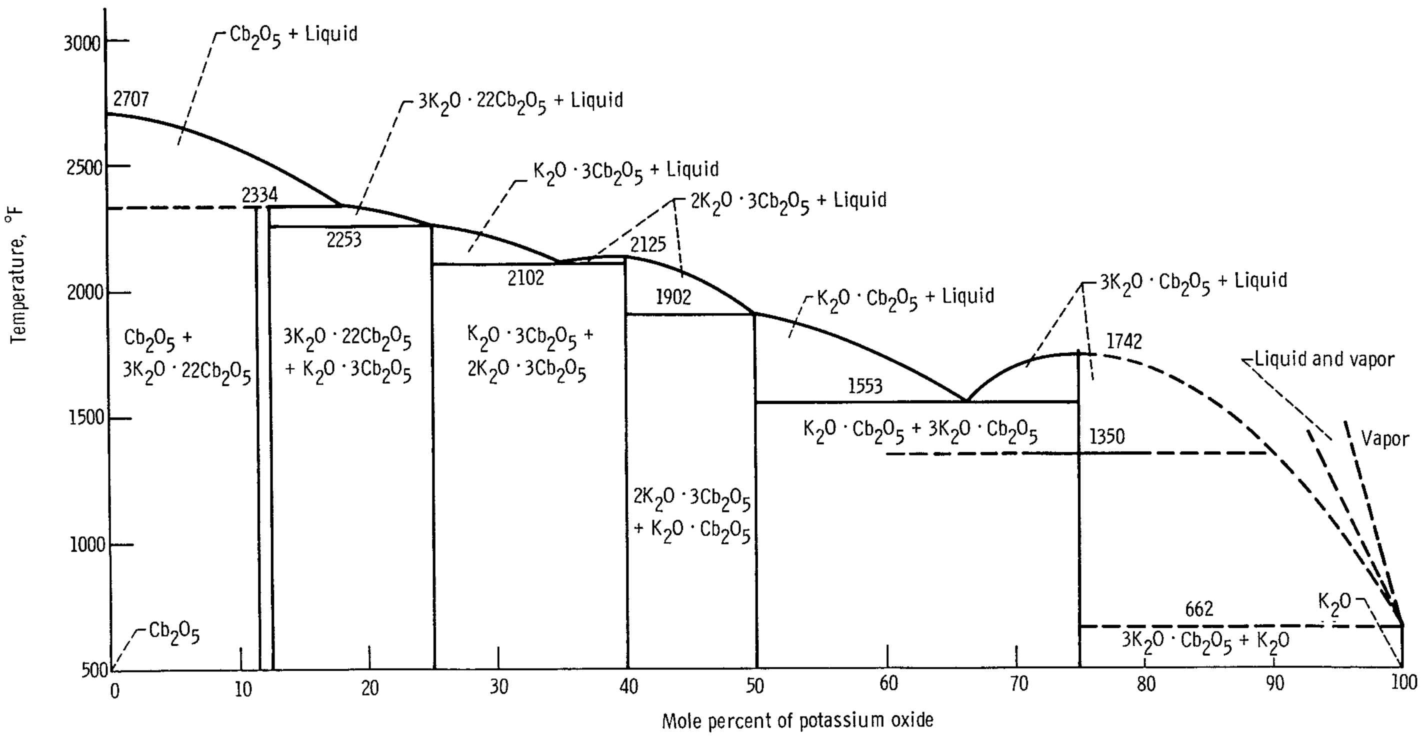


Figure 22. - Estimated Cb$_2$O$_5$-K$_2$O phase diagram based on references 13 and 14.

columbium oxide-potassium carbonate (Cb_2O_5-K_2CO_3) system (ref. 13). For purposes of elucidating the proposed corrosion mechanism, an estimated columbium oxide-potassium oxide (Cb_2O_5-K_2O) phase diagram was constructed, based on references 13 and 14 (fig. 22).

The provisional corrosion mechanism that follows is presented for columbium and columbium alloys with potassium. It is assumed, however, that a similar series of processes would describe the corrosion of the other refractory metals and alloys by potassium as well as by other alkali metals, though undoubtedly some differences can be expected because of different reactivity and stability of corrosion products. The mechanism has as its main feature, the formation of a columbium - potassium complex oxide. The formation of this complex, its dissolution into the liquid potassium, and its reaction with other alloying elements are covered in the following discussion.

The discussion of the corrosion mechanism is divided into two sections: Columbium and Ungettered Columbium Alloys, and Gettered Columbium Alloys. In each section two cases will be examined: case I, in which only the oxygen initially present is available for reaction (100 to 500 ppm in the alloys and less than 20 ppm in the potassium) and case II, in which an external source of oxygen is available (oxygen or water vapor in the test environment). Case I is probably relevant only for short times in environments containing a partial pressure of oxygen greater than 10^{-8} torr. For long test times (several thousand hours) or with high environmental oxygen contamination levels, case II is believed to be significant.

Columbium and Ungettered Columbium Alloys

Case I. - Upon test startup, adsorbed oxygen and residual oxide films on capsule inner surfaces can react with the potassium and columbium to form a complex oxide:

$$a\,K + b\,Cb_pO_q \longrightarrow c(\text{complex}) + d\,Cb \qquad (1)$$

(In these reactions the word "complex" is used to denote a complex oxide of potassium and columbium, except where otherwise noted.)

Since the low oxygen ends of the refractory metal - alkali metal - oxygen ternary systems have not been investigated, it is not certain that the complex oxides shown for the binary system, Cb_2O_5-K_2O (fig. 22), are actually those phases in equilibrium with the liquid at the test temperatures. It is possible that the phases in equilibrium with the liquid are compounds formed with columbium at a lower oxidation state. This, however, should not alter the basic corrosion pattern, only the composition of the complex oxide formed. It is also likely that these unknown complex oxides would have melting points near or below the testing temperatures and, therefore, have high solubilities in the original liquid phase.

As indicated in figure 22, the complex oxides shown have appreciable solubility in liquid potassium oxide (K_2O) at the test temperatures. If it is assumed that the phase relations shown in figure 22 are correct, the complex oxides can also be expected to have appreciable solubility in potassium, perhaps of the order of several weight percent.

In addition to the absorbed oxygen and residual oxide films on the capsule surface, oxygen initially present in the columbium or its alloy may permit a further reaction to form the complex oxide:

$$\mathrm{e\,K + f\,Cb + g\,[O]_{Cb} \longrightarrow h\,(complex)} \tag{2}$$

$$\mathrm{e\,k + f\,[M]_{Cb} + g\,[O]_{Cb} \longrightarrow h\,(M\ complex)} \tag{3}$$

where M is an alloying element.

The occurrence of reactions (1) to (3) when only limited amounts of oxygen are available may be expected to lead to a rough or grain-etched appearance on the inside surfaces of the capsules, as a result of the dissolution of the small amount of available complex oxide. Figure 5 (p. 11) gives an example of this roughening. The preferential removal of material from the grain boundaries may be attributed to the expected greater concentration of oxygen in the grain boundary areas. This would lead to more complex oxide formation in the grain boundary areas than in the bulk grains and therefore more removal of columbium from those areas.

Case II. - When a source of oxygen is present in the guise of oxygen in the test environment, diffusion through the capsule wall would provide a continuing supply of oxygen for reactions (2) and (3). Under the proper conditions of time and temperature, this would give rise to wall recession through the continuing production of the complex oxide at the columbium-potassium interface and its removal by dissolution into the potassium. Since impurities are known to concentrate at grain boundaries, pronounced intergranular attack could be expected also. These effects were observed in SCb-291 (fig. 10).

The continuing formation of the complex oxides and their dissolution in the potassium when an external source of oxygen is available would lead to an increase in the concentration of the complex oxide in the liquid pool and thereby reduce the driving force for solution of the complex oxide and reduce the rate of formation of the complex oxide in the lower section of the capsule. The continuous presence of pure potassium at the condensing section, on the other hand, would sustain a high removal rate of oxygen in that location through complex oxide formation and solution. Therefore, a buildup of oxygen concentration in the bottom half of the capsule wall would be expected, as was generally observed in these tests (table III).

The oxygen gradient resulting from the enhanced oxygen concentration in the lower portion of the capsule should promote the diffusion of oxygen through the wall toward the upper part of the capsule. If the potassium flowing down the inside surface is not saturated with the complex oxide, the oxygen diffusing upward through the wall could contribute to complex-oxide formation and solution of the capsule surface above the liquid pool. The attack observed at the liquid-vapor interface region on the B-33 capsules in figures 6 to 8 was in agreement with this surmise.

Gettered Columbium Alloys

For the alloys studied, those elements considered as getters are yttrium in AS-55; hafnium in C-129, T-111, and T-222; and zirconium in Cb-1Zr, D-14, AS-55, B-66, D-43, FS-85, and Cb-752.

In general, effective getters of oxygen are not likely to form complex oxides with potassium (ref. 9) but will probably be dissolved directly. Considering zirconium as representative of these elements, this reaction can be written:

$$[\mathrm{Zr}]_{\mathrm{Cb}} \longrightarrow [\mathrm{Zr}]_{\mathrm{K}} \qquad (4)$$

Case I. - Zirconium can influence the corrosion process by reacting with oxygen in the bulk alloy to form stable zirconium dioxide.

$$[\mathrm{Zr}]_{\mathrm{Cb}} + 2[\mathrm{O}]_{\mathrm{Cb}} \longrightarrow \mathrm{ZrO_2} \qquad (5)$$

Thus, the oxygen would be effectively prevented from entering into reactions (2) and (3). Studies (ref. 15) have shown, however, that reaction (5) is time, temperature, and concentration dependent. The reaction will proceed only when a certain minimum concentration of oxygen is exceeded, the exact concentration being dependent upon temperature and zirconium content. Because of this, it is possible that when minimal oxygen concentrations are present, oxygen can be consumed by reactions (2) and (3) before reaction (5) can proceed to any appreciable extent, since times for diffusion of oxygen through the capsule wall are very short at the temperatures of this study.

Oxidation of zirconium may also occur in the liquid potassium pool. Here, dissolved zirconium would be in contact with dissolved complex oxide arising from reactions (1) to (3). The general reaction may be written as follows:

$$k\,[\mathrm{Zr}]_{\mathrm{K}} + m\,[\mathrm{complex}]_{\mathrm{K}} \longrightarrow k\,\mathrm{ZrO_2} + (\text{reduction products}) \qquad (6)$$

The nature of the reduction products formed in reaction (6) will depend on the extent of the reduction of the complex. At various stages in the reduction the products could conceivably include the following: a complex oxide at a lower oxidation state, potassium, columbium oxides, or columbium. The nature of the observed film deposits in test capsules near the liquid-vapor interface containing both zirconium dioxide and columbium crystals are consonant with the products expected from reaction (6).

Case II. - In the case of oxygen entering the capsule from the test environment, continuing complex-oxide formation at the condensate region (reaction (2)) and zirconium dioxide precipitation within the bulk alloy (reaction (5)) can be expected. Also, as with the ungettered alloys, an increase in oxygen concentration at the bottom of the capsule should take place. Consistent with the latter expectation, oxygen enrichment was observed in all the materials tested (table III). If at some time the amount of oxygen in the bottom of the capsule exceeds the amount that the available getter can consume by reaction (5), diffusion of oxygen toward the top of the capsule should markedly increase and thereby lead to increased attack near the liquid-vapor interface, as previously proposed in the case of the ungettered alloy, B-33. Such attack was observed with Cb-1Zr. With D-14 (Cb-5Zr) liquid-vapor interface attack was not found, even though the test conditions for D-14 were more severe than for Cb-1Zr; this, however, is not unexpected in view of the much greater zirconium content of D-14 and hence greater total oxygen gettering potential.

In contrast to the results found for the gettered columbium alloys, the tantalum alloy, T-222, tested at 2200° and 2400° F, showed a complex-oxide deposit. Assuming the proposed mechanism and its tantalum analog are correct, complementary explanations for complex-oxide deposition can be considered. First, if the solubility of hafnium in potassium is much less than that of zirconium, the amount of hafnium transported to the pool would be small and hence the total amount of dissolved complex oxide reduced by the hafnium would be small. Second, if the free energy of formation of the tantalum complex oxide is more negative than that of hafnium dioxide, the complex oxide should not be reduced by the hafnium, even if it were present in the pool in large amounts. In either instance, when the accumulation of the complex oxide in the potassium pool exceeded the solubility limit, deposition of the complex oxide would result.

Surface Energy Effects

In addition to the chemical attack by complex-oxide formation at impurity-rich grain boundaries, enhanced solution effects due to the surface energy phenomenon must be considered as a possible mode of concurrent corrosion attack. Unfortunately, a lack of pertinent information precludes a quantitative evaluation of the importance of surface energy effects on the corrosion observed in this study. It is known, however, that intergranular penetration by a liquid metal will occur (ref. 16) when the solid-solid (γ_{SS}) and solid-liquid ($\gamma_{s\ell}$) surface tensions are favorable. When $|\vec{\gamma}_{ss}| > 2\,|\vec{\gamma}_{s\ell}|$, the groove angle established at the grain boundaries becomes zero and a separation of the grains is accomplished by the transport of solid metal through solution and redeposition to some other solid surface. Based on the fact that oxygen lowers the surface tension of liquid alkali metals and thereby decreases $\gamma_{s\ell}$, enhanced intergranular attack by alkali metals at the liquid-solid interface is expected in the presence of sufficient oxygen.

Effects of Grain Impurity and Grain Size

In the discussion of the corrosion mechanism, it was assumed that the entire metallic structure of the starting material was chemically uniform, or in other words had all its impurities in solution; however, this is not always the case. In practice, fabrication procedures such as welding and heat treatment of worked structures will more than likely result in a continuous network of impurities along grain boundaries.

When the corrosion of materials is greatly affected by impurities, such as apparently occurs in alkali-metal corrosion of refractory metals, the segregation of impurities at the grain boundaries can be serious. In general, as-worked structures would probably give the best resistance to intergranular attack because any impurity that might have been in the original grain boundaries would have been made discontinuous by the cold working process. Conversely, as-welded structures should be most susceptible to intergranular attack because of the natural segregation of impurities in the grain boundaries during the solidification process. The test results for the Ta-10W capsules can serve as an example of the effect of impurity distribution on corrosion. As was noted in the section EXPERIMENTAL RESULTS, the worked Ta-10W structure showed no attack, while critical intergranular attack was observed in the weld area (fig. 11). This grain impurity effect may also, at least in part, explain the observation of attack in the recrystallized Cb-1Zr (heat 5122) and the absence of it in the cold-worked Cb-1Zr (heat 5118).

Additionally, when grain size is extremely large, penetration along the relatively short grain boundary paths can result in rapid structural failure (again note Ta-10W). Small grain size will minimize this effect by presenting a more tortuous penetration path, thereby lengthening the time required for complete penetration and failure of the structure. In general, alloys with relatively high recrystallization temperatures, and consequently a relatively low potential for grain growth, should be less affected by intergranular attack than alloys with relatively low recrystallization temperatures.

CONCLUSIONS

The investigation of the compatibility of columbium and tantalum tubing alloys with refluxing potassium yielded the following conclusions:

1. The test alloys, grouped in order of decreasing resistance to corrosion by refluxing potassium, are as follows: (1) T-111 (Ta-8W-2Hf), T-222 (Ta-9.6W-2.4HF-0.01C), C-129 (Cb-10W-10Hf), D-14 (Cb-5Zr), Cb-752 (Cb-10W-2.5Zr), D-43 (Cb-10W-1Zr-0.1C), AS-55 (Cb-5W-1Zr-0.2Y-0.06C), B-66 (Cb-5Mo-5V-1Zr), and FS-85 (Cb-28Ta-10W-1Zr); (2) Cb-1Zr; and (3) B-33 (Cb-4V), SCb-291 (Cb-10Ta-10W), and Ta-10W. The corrosion resistance of the alloys in the first group appears to be good, since they all showed less than 0.5 mil attack under the test conditions of a minimum of 2000 hours at 2200° F or higher. The second group (Cb-1Zr) may have marginal corrosion resistance. However, an unequivocal judgement cannot be made on the basis of the reported tests, since the two different heats of material gave conflicting results, possibly due to differences in grain size and oxygen contamination. The alloys in the third group are judged to be unsatisfactory for containment of boiling potassium because of the heavy attack generally observed.

2. It has been shown that the gettered refractory-metal alloys (those containing the reactive elements zirconium or hafnium) are more resistant to corrosion by refluxing potassium than are the ungettered alloys.

3. A mechanism for the corrosion of columbium and columbium alloys by refluxing potassium has been proposed consonant with experimental results. The mechanism, involving a proposed potassium-columbium complex oxide intermediate, is described for both gettered and ungettered alloys when only small amounts of oxygen are present initially and when large amounts of oxygen are available because of environmental contamination.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 25, 1966.

APPENDIX A

CLEANING PROCEDURE

The capsules used in this study were degreased with trichloroethylene to remove all oils and greases. Chips and foreign matter were removed by ultrasonic cleaning in a detergent bath. Residual stains and oxides were removed with an acid etch of the following composition by volume: 55 parts sulfuric acid, 25 parts nitric acid, and 20 parts hydrofluoric acid. The capsules were dipped into this solution for no longer than 15 seconds, rinsed with distilled water, and dried in a desiccator. The dry capsules were stored in clean polyethylene bags until used.

APPENDIX B

HEATER CONSTRUCTION DETAILS

The coiled tantalum heaters used in this study were made as follows:

(1) Two-inch lengths of high-purity swageable aluminum oxide tubing, 0.057-inch outside diameter with a 0.024-inch inside diameter, were strung onto a 6-foot-long 0.020-inch-diameter tantalum wire.

(2) The insulated tantalum wire was sheathed in a 0.080-inch-diameter, 0.008-inch-wall tantalum tube. This assembly was then compacted by swaging to a 0.060-inch diameter.

(3) Enough of the tubing and alumina insulation were removed from one end of the swaged tubing from step 2 to bare about one inch of wire.

(4) A piece of the 0.080-inch-diameter tantalum tube mentioned in step 2 was then swaged to 0.060-inch diameter and cut into 2-inch lengths. These were then swaged to 0.040 inch, except about the last 1/2 inch. The 0.060-inch-diameter end was then swaged onto the bared wire in the assembly from step 3, leaving approximately 3/8 inch of bare wire showing.

(5) Pieces of high-purity swageable alumina, 7/8-inch length, 0.088-inch diameter with a 0.045-inch inside diameter, were slipped onto the exposed-wire end of the assembly from step 4, butting against the tube, and covering the 3/8-inch length of bare wire and 1/2 inch of the 0.040-inch-diameter-end piece. A $1\frac{1}{8}$-inch piece of $\frac{1}{8}$-inch-diameter tantalum tube with a 0.020-inch wall was slipped over the piece of alumina and allowed to hang over the heater tube about 1/4 inch. The end was then swaged to 0.100 inch.

(6) The termination end of the assembly from step 5 then had the 0.100-inch swaged tubing peeled back to the alumina to prevent arcing between the wire and the tube.

(7) The swaged tantalum heater was then wound on a 1/2-inch-diameter mandrel into the configuration shown in figure 3 (p. 7) to receive the lower third of the capsule during the test. The other end is then completed by the procedure outlined in the preceding steps 3 to 6.

APPENDIX C

OXYGEN CONTAMINATION EFFECTS OF TEST STARTUP CONDITIONS

When the series of tests reported in this report was started, a startup procedure was instituted that was thought to be sufficient to assure ample control over oxygen contamination of test capsules. This procedure is outlined as follows:

(1) The test bed was installed and the chamber sealed.

(2) The chamber was evacuated by means of a mechanical pump and a liquid nitrogen baffled diffusion pump.

(3) The chamber was then baked out.

(a) When the pressure fell below 10^{-5} torr, heat was applied to the chamber walls and the capsules.

(b) The chamber walls were heated to 350° F and the capsules to 500° to 600° F range.

(c) The system was allowed to bake out overnight.

(4) The capsules were then heated to test temperature.

(a) The heat to the chamber walls was turned off.

(b) Heat was applied to the capsules as rapidly as possible, maintaining a pressure of less than 8×10^{-6} torr.

(c) When necessary, cooling water was started through the coils on the chamber to keep the chamber walls cool.

(d) When the capsules reached approximately 1000° F, the sputter-ion pump was turned on. From this point on, until test temperature was reached, the diffusion pump was used only as an auxiliary pump to be utilized whenever the pressure exceeded 5×10^{-6} torr.

(e) When test temperature was reached, the diffusion pump was turned off.

The test results (table III), however, suggest that this procedure was not stringent enough to avoid excessive oxygen pickup by the capsules.

The following equation, derived from the kinetic theory of gases, was then used to estimate the oxygen contamination during the transient test startup:

$$\dot{w} = 0.058SP(M/T)^{1/2} \tag{C1}$$

where

$\dot{w}$ oxygen pickup rate, $g/(cm^2)(sec)$

S sticking probability

P	partial pressure of active species, torr
M	molecular weight of the active species
T	absolute temperature, $^{\circ}K$

The temperature T was taken as the capsule temperature, 1477° K (2200° F). The sticking probability S was taken as 0.1 in all cases. Water vapor was assumed to be the active gaseous species and its partial pressure inside the heat shields was assumed to be an order of magnitude greater than the chamber pressure.

Using equation (C1), the oxygen content of the capsules at 2200° F in parts per million then becomes

$$O_2 = 3.2\times10^{-2} At/W \tag{C2}$$

where:

A	capsule surface area, cm^2
t	time, sec
W	initial capsule weight, g

Since the surface area of the capsules used in this study was approximately 21 square centimeters and the weights of the lower density columbium alloy capsules were about 18 grams, from equation (C2) it was estimated that as much as 810 parts per million of oxygen could be picked up during the first 6 hours at or near 2200° F. This value is very close to the vacuum-fusion analyses for the post-test samples taken from the bottom portion of B-33 and Cb-1Zr capsules tested at 2200° F. (The bottom portions are used for comparison because removal of oxygen by reaction with potassium was expected to be a minimum here (see case II of the section Columbium and Ungettered Columbium Alloys), which made the observation of oxygen contamination effects more likely at this location.) Therefore, the contamination of the capsules during the initial test startup conditions could account for a large portion of the observed increase in oxygen concentration.

Assuming the applicability of equations (C1) and (C2) to the test situation, capsule geometry strongly influences the amount of oxygen contamination that is picked up, and thereby the nature and extent of corrosion. By reducing the alloy surface-to-volume ratio, contamination is reduced proportionately. For example, with a reflux capsule with a 1-inch outside diameter, an 11-inch length, and an 0.080-inch wall thickness, such as that used in the reflux capsule program described in reference 17, the oxygen pickup for the startup conditions previously described is calculated to be 410 parts per million, approximately half of the amount calculated for the capsules used in this report. The effect of capsule geometry on oxygen pickup may account for some of the discrepancies in alkali metal - refractory metal corrosion results reported between investigators employing test specimens of different sizes and shapes.

APPENDIX D

METALLOGRAPHIC PROCEDURE

by Anne R. Kendra

The two basic metallographic problems in this study were the maintainance of square specimen edges during polishing and the development of appropriate etching techniques.

The metallographic specimens were entire halves of capsules sectioned longitudinally, having neither the size nor shape desirable for good metallographic results. The specimen areas of prime interest were along the inside edges of the capsule; thus, the shape was such that the natural shrinkage of mounting material caused the mount to pull away from the edges. The mounting technique described below was used to minimize this problem.

Each half of the sectioned capsules to be mounted were cleaned with ethanol. The sections were filled with a mixture of bakelite and epoxy resin and were allowed to harden overnight at room temperature. The filled sections were placed face down on copper plates. Two-inch diameter open-end copper cylindrical holders were placed around each section, filled with epoxy resin, and left to harden overnight at room temperature.

The specimens were removed from the holders, rough ground under cold water on 120-, 400-, and 600-grit silicon carbide papers, and placed in groups of eight in a vibratory polisher on Japanese silk with a slurry of 5-percent hydrogen peroxide solution and 0.1-micron alumina for approximately 4 hours. Finally, the specimens were polished for about 1 hour in a vibratory polisher on billiard cloth with a plain 0.1-micron alumina-water slurry.

After the final polishing procedure, the specimens were placed in water in an ultrasonic cleaner to remove all traces of abrasive. They were then etched with a modified solution of nitric acid, hydrofluoric acid, hydrogen peroxide, and acetic acid, the quantities of each being determined by the specific alloy to be etched and its prior treatment.

Since the specimens varied drastically in hardness and structure, each specimen and each area on the specimen had to be etched separately with the appropriate etchant composition and concentration. Because of this, only the ingredients for the etchant solution, not their quantities, are given in this metallographic procedure.

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