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Cleveland, Ohio

TECHNICAL PREPRINT prepared for Fourth Symposium on Refractory Metals sponsored by the Refractory Metals Committee of the Institute of Metals Division of AIME, French Lick, Indiana, October 3-5, 1965

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION · WASHINGTON, D.C. · 1965

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INTRODUCTION

A major uncertainty in the development of advanced space-power systems is that of materials for containment of the thermodynamic working fluid. An operational system will require a containment material having sufficient 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.

DiStefano and Hoffman (ref. 1) state that the most significant problem in refractory-metal - alkali-metal systems is the influence of the impurities, oxygen, nitrogen, and carbon, on corrosion. The effects of oxygen in these systems have been observed by several investigators (refs. 2 to 4), and the role of oxygen in terms of thermodynamic stabilities has been discussed (ref. 5).

A summary of the results of a corrosion capsule study to test the resistance of columbium- and tantalum-base tubing alloys to refluxing potassium over the temperature range 1800° to 2400° F and for times up to 4000 hours is presented herein. Also included is a proposed mechanism for the corrosion of columbium metal and alloys by refluxing potassium.

MATERIALS, APPARATUS, AND PROCEDURE

For a detailed description of materials, apparatus, and procedure used in this study, see reference 6. A brief description follows:

The materials tested and their nominal compositions are B-33 (Cb-4%V), SCb-291 (Cb-10%Ta-10%W), Cb-1%Zr, D-14 (Cb-5%Zr), AS-55 (Cb-5%W-1%Zr-0.2%Y-0.06%C), B-66 (Cb-5%Mo-5%V-1%Zr), D-43 (Cb-10%W-1%Zr-0.1%C), FS-85 (Cb-27%Ta-10%W-1%Zr), Cb-752 (Cb-10%W-2.5%Zr), C-129 (Cb-10%W-10%Hf), Ta-10%W, T-111 (Ta-8%W-2%Hf), and T-222 (Ta-9.6%W-2.4%Hf-0.01%C).

Capsules of these materials were machined from bar stock (fig. 1) in which the capsule walls served as the test specimen. The capsules, containing about $1\frac{1}{4}$ cc of potassium, were tested in high-vacuum chambers at pressures of 10^{-7} to 10^{-8} torr at temperatures of 1800°, 2200°, 2300°, or 2400° F for times up to 4000 hours. In tests of this type, liquid is vaporized from a pool at the bottom of the capsule and is condensed as a relatively pure liquid near the top of the capsule. The condensate flows down the capsule wall and joins the bulk liquid, which completes the circuit.

Metallographic examinations were made of all specimens. Vacuum fusion analyses for oxygen were made on selected specimens, and X-ray patterns were taken of some of the observed deposits and films for phase identification.

RESULTS

A summary of the corrosion test results is given in table I. Minimally, most alloys exhibited surface roughening, or etching, an example of which is shown in figure 2. In general, there was a marked difference between the results of the gettered alloys (those containing elements such as zirconium or hafnium which have very strong tendencies to react with oxygen) and ungettered alloys. The ungettered alloys were more severely attacked by potassium than were the gettered alloys, and exhibited solution and intergranular penetration (fig. 3). The alloy B-33 had up to 3.0 mils solution attack near the liquid-vapor interface after 1000 hours at 2200 F. The alloy SCb-291 under the same conditions showed about 2.0 mils of solution attack in the condensing section and extensive intergranular attack (up to 16 mils) throughout the liquid section. Capsules of Ta-10W at 2200° F failed by intergranular attack through the cap seal welds in 8 hours or less.

The gettered alloys, with the exception of Cb-1Zr, showed only relatively slight effects of potassium corrosion. The most notable common effect was a dark film or deposit ring at the liquid-vapor interface, an example of which is shown in figure 4. X-ray patterns taken of selected films found on the columbium alloys revealed the presence of ZrO_2 and columbium crystals. X-ray patterns from the films on the T-222 capsules showed the presence of $K_2Ta_4O_{11}$ with some WO_3; HfO_2 was not identified, but its presence could possibly have been masked by the lines of these other compounds. After 2000 hours at 1800° F, Cb-1Zr exhibited up to 7.0 mils of intergranular attack and grain removal at the liquid-vapor interface (fig. 5).

Vacuum fusion analyses for oxygen were taken on sections of the walls of selected capsules and are shown in table II. In general, there was a significantly greater concentration of oxygen in the bottom sections of the capsules than in the top sections of the capsules after testing.

DISCUSSION

TEST RESULTS

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, AS-55, B-66, and FS-85; (2) Cb-1Zr; and (3) B-33, SCb-291, and Ta-10W. If reflux capsule test results 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. Based on the tests reported herein, the Cb-1Zr alloy (group 2) is probably of marginal corrosion resistance for power system applications. The ungettered alloys (group 3) are judged to be unsatisfactory because of the large amount of corrosive attack.

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. In this instance, the model must take into account the following general and specific experimental observations: (1) surface roughening, or etching, on both gettered and ungettered alloys, (2) higher oxygen concentrations in the bottom sections of the capsules than in the top sections, (3) localized attack near the liquid-vapor interface in the 2200° F, 1000-hour B-33 test, (4) solution and intergranular attack in the SCb-291 tests, (5) localized attack near the liquid-vapor interface in the Cb-1Zr tests, and (6) films containing ZrO_2 and columbium crystals in the region of the liquid-vapor interface in gettered alloy tests.

PROPOSED CORROSION MECHANISM

Since oxygen is believed to be the major influence on corrosion of the refractory metals and alloys with the alkali metals (refs. 1 to 4), any discussion of corrosion mechanism must consider the disposition and the form of association of oxygen in these systems. It is known, first, that a transfer of oxygen from columbium occurs, with potassium as the apparent transfer medium (refs 4 and 6), despite the fact that the direct transfer is not favored thermodynamically. Second, tests to determine the solubility of metals in the alkali metals (refs. 2 to 4) suggest that solution occurs by the formation of an oxygen-metal compound followed by solution of the compound, rather than by simple elemental solution of the metal. Third, in several experiments, potassium - refractory-metal complex oxides have been identified (refs. 2, 4, and 6).

In order to assess further the role of the complex oxides in the corrosion process, phase relations are needed. The only pertinent study, however, is that of the Cb_2O_5-K_2CO_3 system (ref. 7). Based on this study and on reference 8, an estimated Cb_2O_5-K_2O phase diagram was constructed and is shown in figure 6.

The following corrosion mechanism is presented for columbium and columbium alloys and 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 could be expected because of the different reactivity and stability of corrosion products.

The discussion of the corrosion mechanism is divided into two sections, (1) columbium and ungettered columbium alloys and (2) gettered columbium alloys. In each section two cases will be examined, Case I, in which only the oxygen initially present is available for reaction (i.e., 100 to 500 ppm in the alloys and < 20 ppm in the potassium), and Case II, in which an external source of oxygen is available (e.g., oxygen or water vapor in the test environment) (ref. 6). Case I is probably relevant only for short times in environments containing $> 10^{-8}$ torr partial pressure of oxygen. For long time tests (several thousands of hours) or with high environmental oxygen contamination levels, Case II is 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. (In all the following reactions the word "complex" will be used to denote a complex oxide of potassium and columbium.)

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

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. 6), 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 possibility, however, should not alter the basic corrosion pattern, only the composition of the complex oxide formed.

As indicated by figure 6, the complex oxides shown have appreciable solubility in liquid K_2O at the test temperatures. If the phase relations shown in figure 6 are assumed to be correct, the complex oxides can also be expected to have appreciable solubility in potassium, perhaps of the order of several weight percent:

$$\text{Complex} \longrightarrow [\text{Complex}]_K \qquad (2)$$

Oxygen initially present in solution in columbium or its alloy may permit a further reaction to form a complex oxide:

$$e\ K + f\ Cb + g[O]_{Cb} \longrightarrow h(\text{Complex}) \qquad (3)$$

$$e\,K + f[M]_{Cb} + g[O]_{Cb} \longrightarrow h(M\ \text{complex}) \qquad (4)$$

where M is an alloying element.

Reactions (1) to (4), when only limited amounts of oxygen are available, should result in a rough, or etched, appearance on the inside surface of the capsules, such as that generally observed in both the gettered and ungettered alloy corrosion capsules.

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 (3) and (4). Under the proper conditions of time and temperature, this should give rise to wall recession, as was observed for SCb-291. In addition, since impurities are known to concentrate at grain boundaries, pronounced intergranular attack should be expected, as was also observed in SCb-291 capsules.

The continuing formation of the complex oxides and their dissolution in the potassium, when an external source of oxygen is available, will lead to an increase in the concentration of complex oxide in the liquid pool and thereby reduce the driving force for the formation and solution of the complex oxide in this 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. A buildup of oxygen concentration in the bottom half of the capsule wall would therefore be expected, as was generally observed in these tests (table II).

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 would contribute to complex oxide formation and solution on the surface above the liquid pool. Attack of the B-33 capsule tested for 1000 hours at 2200° F was in agreement with this surmise.

Gettered Columbium Alloys

Those elements considered as getters, in the alloys studied, 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. Effective getters of oxygen are unlikely to form complex oxides with potassium (ref. 5) but will probably be dissolved directly. If zirconium is considered as representative of these elements, the reaction can be written

$$[\mathrm{Zr}]_{\mathrm{Cb}} \longrightarrow [\mathrm{Zr}]_{\mathrm{K}} \qquad (5)$$

<u>Case I</u>. - Zirconium can influence the corrosion process by reacting with oxygen in the bulk alloy to form the stable ZrO_2:

$$[\mathrm{Zr}]_{\mathrm{Cb}} + 2[\mathrm{O}]_{\mathrm{Cb}} \longrightarrow \mathrm{ZrO_2} \qquad (6)$$

Oxygen is thus effectively prevented from entering into reactions (2) to (4). Studies (ref. 9) have shown that reaction (6) is time, temperature, and concentration dependent. The reaction will proceed only when a certain minimum concentration of oxygen is present, 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 reaction

(3) or (4) before reaction (6) can proceed to any appreciable extent.

Oxidation of zirconium may also occur in the liquid potassium pool. Here, dissolved zirconium from reaction (5) is brought into contact with dissolved complex oxide arising from reactions (1) to (4). The following general reaction may be written:

$$k[\mathrm{Zr}]_K + m[\mathrm{Complex}]_K \longrightarrow k\ \mathrm{ZrO_2} + (\text{Reduction products}) \qquad (7)$$

The nature of the reduction products formed in reaction (7) will depend on the extent of the reduction of the complex. At various stages in the reduction the products could conceivably include (1) a complex oxide at a lower oxidation state, (2) potassium, (3) columbium oxides, or (4) columbium. The generally observed film deposits in test capsules near the liquid-vapor interface containing both ZrO_2 and columbium crystals are consonant with the products expected from reaction (7).

Case II. - In the case of oxygen entering the capsule from the test environment, continuing amounts of complex oxide formation at the condensate region (reaction (3)) and ZrO_2 precipitation within the bulk alloy (reaction 6)) can be expected. Also, as with the ungettered alloys, an increase in oxygen concentration at the bottom of the capsule should take place. This oxygen enrichment was observed in all the materials tested (table II). If the amount of oxygen in the bottom of the capsule exceeds the amount that the available getter can consume by reaction (6), diffusion of oxygen toward the top of the capsule should markedly increase. This increase should result in increased attack near the liquid-vapor interface, as previously described for the case of the ungettered alloy, B-33. Attack of this type was observed with Cb-1Zr but not with D-14 (Cb-5%Zr), even though the test conditions for D-14 were more stringent than for Cb-1Zr; this result is expected in light of the much greater zirconium content of D-14.

SUMMARY

The compatibility of 13 columbium- and tantalum-base alloys with refluxing potassium was determined in a series of capsule tests at 1800° to 2400° F and for times up to 4000 hours. The following conclusions were drawn:

(1) The ungettered refractory metal alloys are more rapidly and drasticly attacked by refluxing potassium then are the gettered alloys.

(2) The corrosion resistance of the test alloys grouped in order of decreasing corrosion resistance to refluxing potassium is (1) T-111, T-222, C-129, D-14, Cb-752, D-43, AS-55, B-66, and FS-85; (2) Cb-1Zr; and (3) B-33, SCb-291, and Ta-10W. The corrosion resistance of the alloys in the first group appears to be sufficient for consideration of their use as containment materials in advanced space-power systems. The second group is probably of marginal corrosion resistance. The thrid group is judged to be unsatisfactory for containment of refluxing potassium.

A mechanism for the corrosion of columbium and columbium alloys by refluxing potassium has been proposed, consonant with the experimental results. The mechanism, involving a proposed potassium-columbium complex oxide intermediate, is described for both gettered and ungettered alloys (1) for the case in which only small amounts of oxygen are present initially and (2) for the case in which large amounts of oxygen are available because of environmental contamination.

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TABLE I. - SUMMARY OF REFLUX CAPSULE TEST RESULTS (REF. 6)

Temperature, °F	Time, hr	Alloy	Corrosive attack			Other comments
			Type	Depth, mils	Location	
1800	110	Ta-10W	Intergranular	12	Weld	-------------------------
↓	1000	SCb-291	Intergranular	1.5	Weld	-------------------------
↓	2000	B-33	None	----	-----------------	-------------------------
↓	2000	Cb-1Zr	Intergranular	7.0	Liquid-vapor interface	-------------------------
↓			Intergranular	.8	Liquid section	General attack
↓	4000	T-222	None	----	-----------------	-------------------------
2200	8	Ta-10W	Intergranular	16	Weld	-------------------------
↓	123	Cb-1Zr	Solution Intergranular	---- 4.5	Condensing section Liquid-vapor interface	General attack 1.5 mils deposit
↓	1000	SCb-291	Solution Intergranular	2.0 16	Condensing section Liquid section	General attack General attack
↓	1000	B-33	Solution Solution	1.0 3.0	Condensing section Liquid-vapor interface	------------------------- -------------------------
↓	2000	D-43	None	----	-----------------	Film at liquid-vapor interface
↓	4000	Cb-752	↓	----	-----------------	Cb and ZrO_2 film at liquid-vapor interface
↓	↓	D-14	↓	----	-----------------	Cb and ZrO_2 film at liquid-vapor interface
↓	↓	AS-55	None	----	-----------------	Heavy etching, about 0.2 mils
↓	↓	B-66	Solution	0.2	Condensing section	Cb and ZrO_2 film at liquid-vapor interface
↓	↓	C-129	None	----	-----------------	Film at liquid-vapor interface
↓	↓	T-111	↓	----	-----------------	Film at liquid-vapor interface
↓	↓	FS-85	↓	----	-----------------	Cb or Ta film at liquid-vapor interface
↓	↓	T-222	↓	----	-----------------	$K_2Ta_4O_{11}$ film at liquid-vapor interface
2300	380	B-33	Intergranular	1.0	High stress area in condensing section	Very slight solution attack at liquid-vapor interface
↓	2000	D-43	None	----	-----------------	Amber film over entire inner surface
↓	↓	FS-85	↓	----	-----------------	Film at liquid-vapor interface
↓	↓	T-111	↓	----	-----------------	↓
2400	↓	FS-85	↓	----	-----------------	↓
↓	↓	T-111	↓	----	-----------------	↓
↓	4000	T-222	↓	----	-----------------	$K_2Ta_4O_{11}$ film at liquid-vapor interface

TABLE II. - SUMMARY OF REFLUX CAPSULE VACUUM FUSION ANALYSES FOR OXYGEN (REF. 6)

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

[a] Sample taken from original rod stock.
[b] Sample taken from top third area of capsule wall.
[c] Sample taken from central third area of capsule wall.
[d] Sample taken from bottom third area of capsule wall.
[e] Sample taken from weld area.

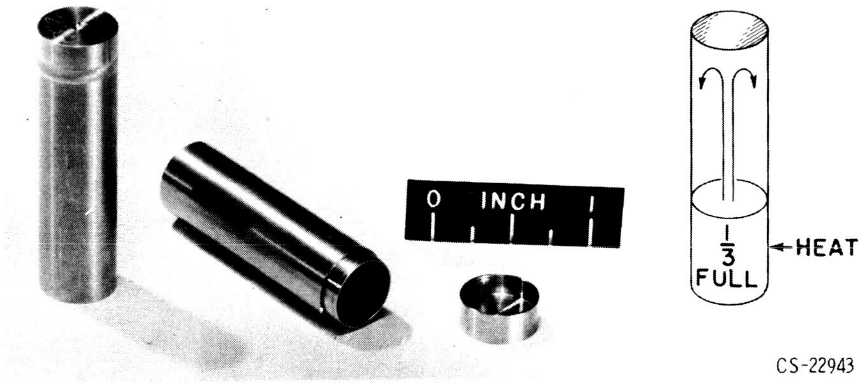

Figure 1. - Reflux capsule used in potassium corrosion study.

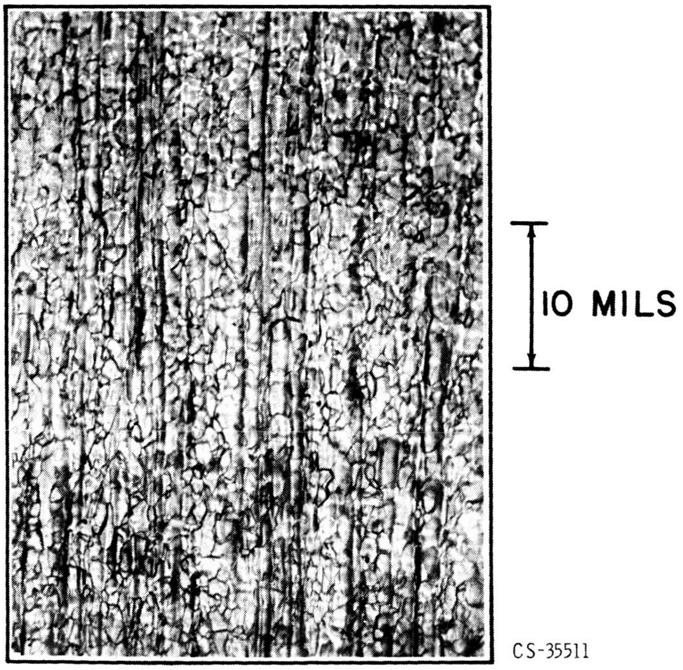

Figure 2. - Replica of inner surface at condensing section of B-33 capsule, tested at 1800° F for 2000 hours.

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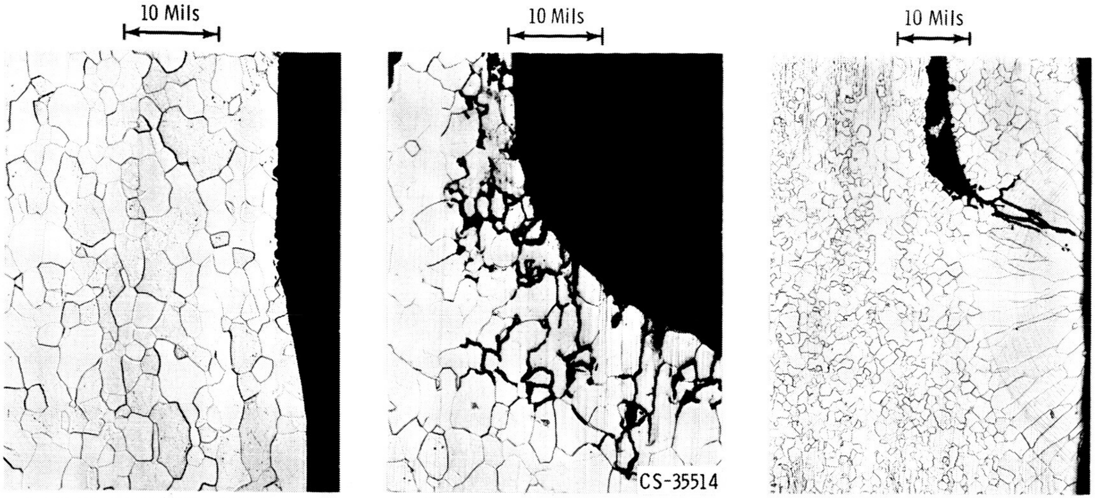

(a) B-33 at 2200° F for 1000 hours. Liquid-vapor interface.

(b) SCb-291 at 2200° F for 1000 hours. Liquid section.

(c) Ta-10W at 2200° F for 8 hours. Cap seal weld.

Figure 3. - Examples of oxygen-accelerated attack observed in ungettered alloys.

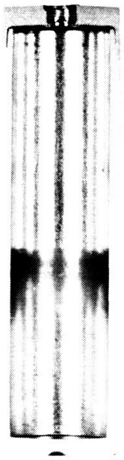

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Figure 4. - Capsule of B-66 tested at 2200° F for 2000 hours.

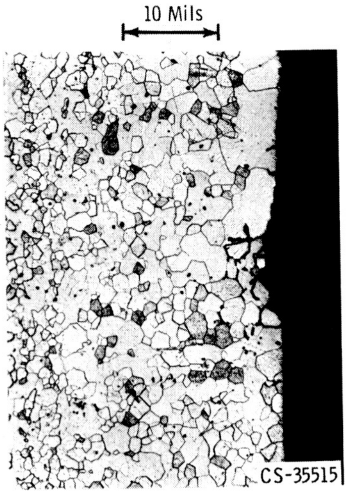

Figure 5. - Oxygen-accelerated attack near liquid-vapor interface of a Cb-1Zr capsule tested at 1800° F for 2000 hours.

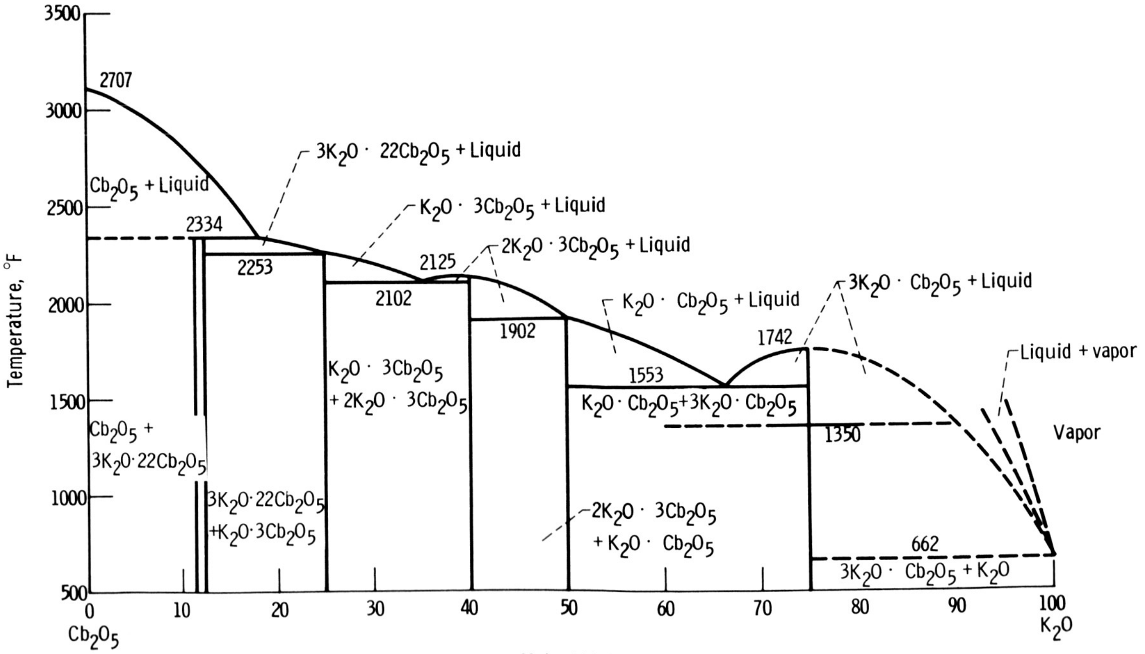

Figure 6. - Estimated Cb_2O_5-K_2O phase diagram based on references 7 and 8.

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