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THE EFFECT OF OXYGEN ON THE COMPATIBILITY  
OF TANTALUM AND POTASSIUM

R. L. Klueh

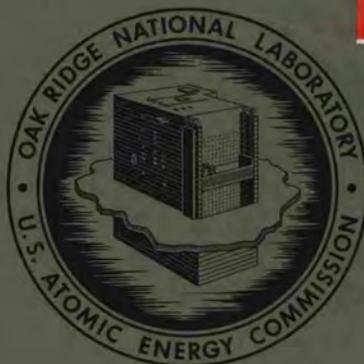
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R. L. Klueh

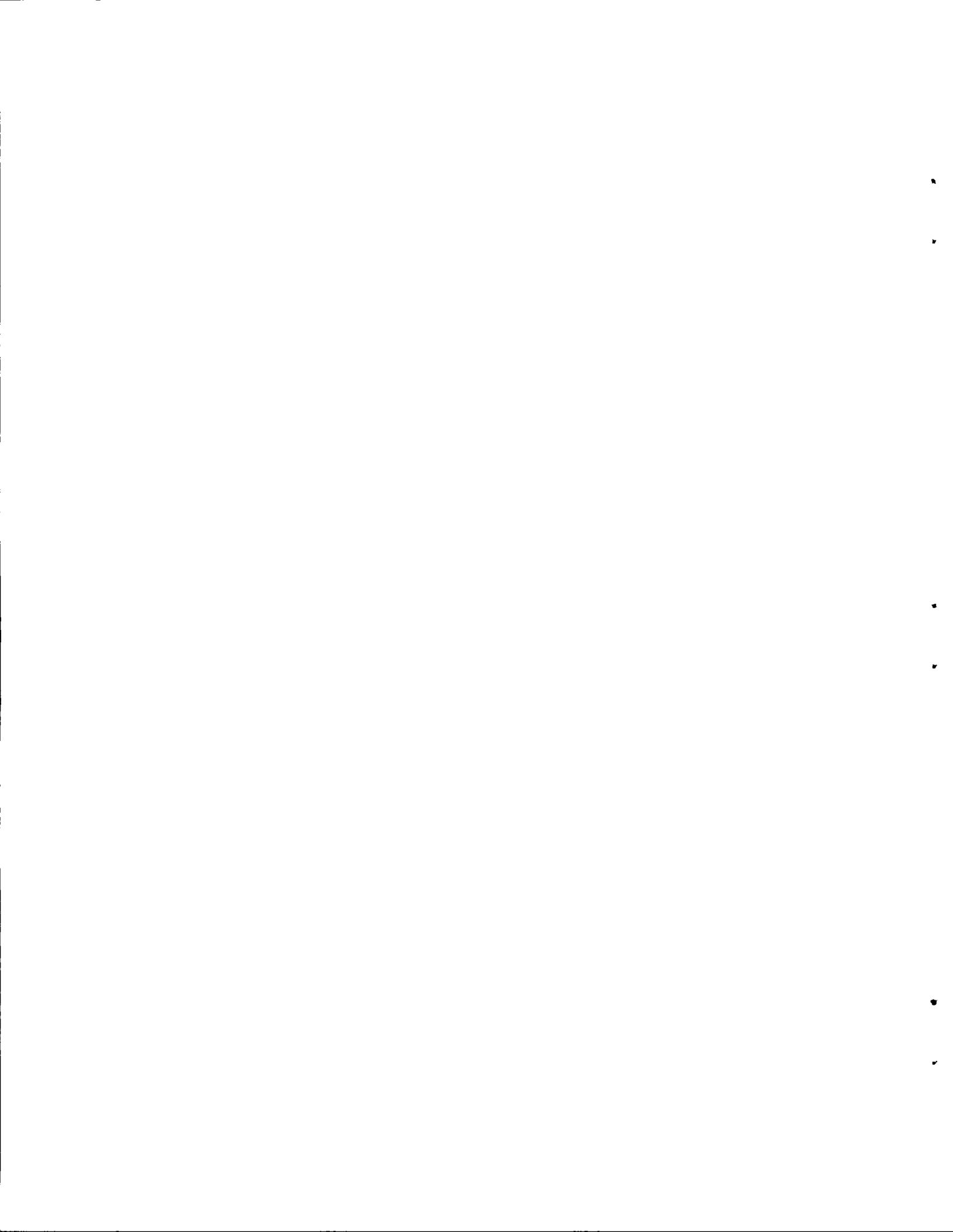
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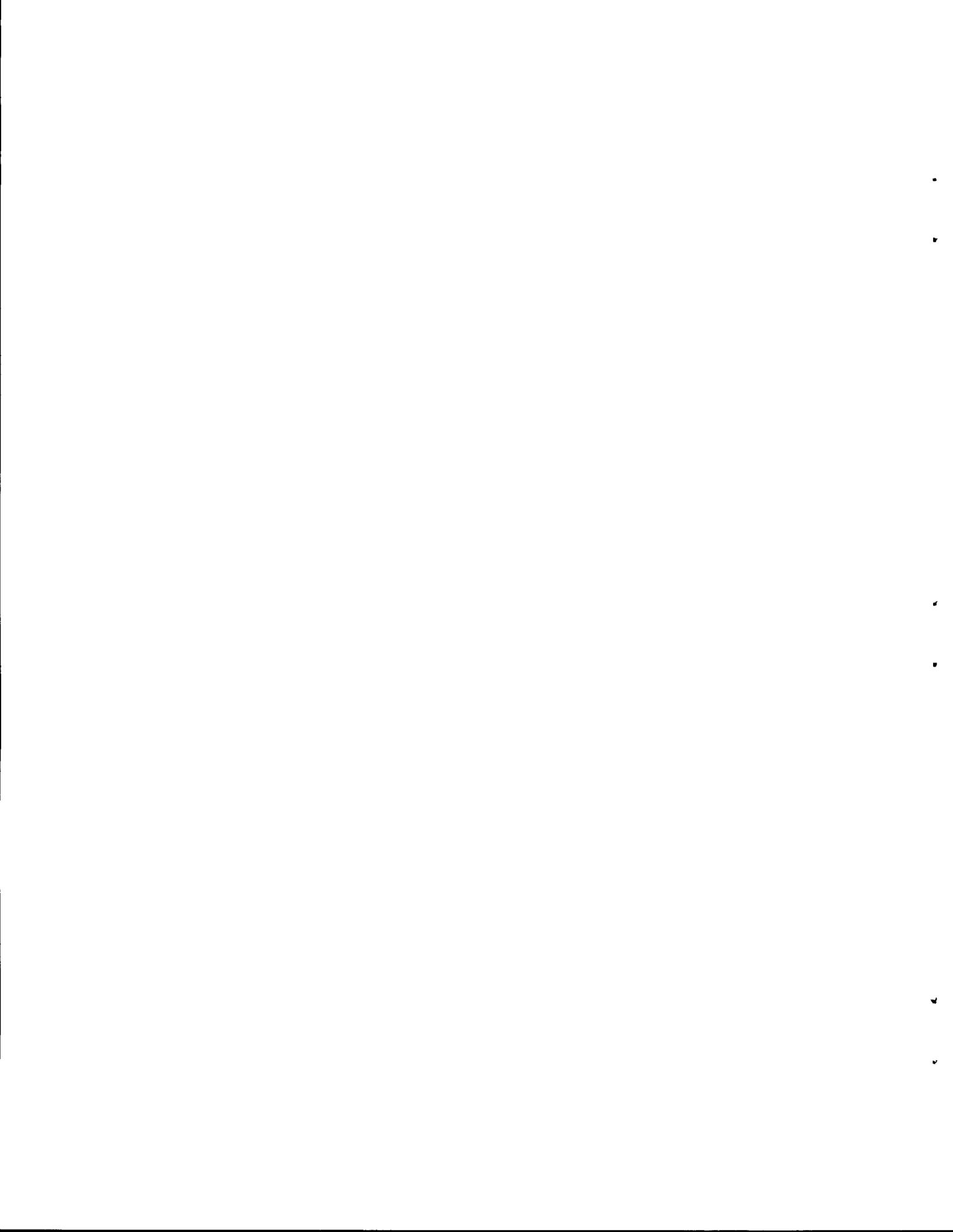


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# THE EFFECT OF OXYGEN ON THE COMPATIBILITY OF TANTALUM AND POTASSIUM

R. L. Klueh

## ABSTRACT

Static capsule tests were used to study the effect of oxygen in either phase on the compatibility of tantalum and potassium at 600, 800, and 1000°C. As the oxygen concentration of the potassium was increased, the amounts of tantalum in potassium after test also increased. The results indicate the formation of an unidentified ternary oxide phase (probably at the tantalum-potassium interface) that is either nonadherent or dissolved when the potassium is dissolved for chemical analysis. On the other hand, when the tantalum specimens contained oxygen above some threshold concentration that depends on test conditions, potassium penetrated the tantalum; both intergranular and transgranular attack occurred. The threshold levels for intergranular attack at 600, 800, and 1000°C were determined to be 500, 700, and 1000 ppm O, respectively. Again the explanation involves the formation of a ternary oxide phase.

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## INTRODUCTION

The liquid alkali metals lithium, sodium, and potassium, because of their high volumetric heat capacities and high heat transport coefficients, are attractive as coolants for high-temperature nuclear reactors and as heat transfer and working fluids in the power generation systems that operate in conjunction with compact nuclear reactors. Design studies<sup>1</sup> for such a system have shown that potassium is the best choice for a single working fluid to cool the reactor and power the turbine. Since the operating temperatures of such a system are expected to approach 1000°C, the refractory metals tantalum and niobium and their alloys are being considered as structural and cladding materials.

Oxygen in a refractory metal-alkali metal system affects the compatibility in two ways, depending upon whether the oxygen is in the alkali metal or the refractory metal:

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<sup>1</sup>A. P. Fraas, "Boiling Potassium Reactor for Space," Nucleonics 22, 72 (1964).

1. When the oxygen concentration of the alkali metal is increased, the "apparent solubility" of the refractory metal (low in oxygen) in the alkali metal increases dramatically over the solubility in pure alkali metal<sup>2-4</sup> ("apparent solubility" is used to indicate that the exact nature of the refractory metal in the alkali metal is unknown).

2. When the oxygen concentration in tantalum or niobium exceeds some threshold level that depends upon the liquid alkali metal and temperature, the alkali metal rapidly penetrates the solid refractory metal<sup>2,5,6</sup> (both intergranular and transgranular penetrations are observed).

The first effect, oxygen-enhanced dissolution by alkali metals, has been explained by hypothesizing the formation of ternary oxides of the alkali metal and refractory metal.<sup>2,7</sup> Such oxides are viewed by some to be in the form of a separate condensed phase, but by others as a dissolved complex molecule. The existence of such an oxide phase at temperature has not been demonstrated, although indications are that it accompanies the penetration of oxygen-containing tantalum and niobium by alkali metals (second effect discussed above).<sup>5</sup> In studies on the niobium-potassium<sup>3</sup> and niobium-sodium<sup>4</sup> systems, we explained the effect of oxygen in the liquid alkali metal as due to interactions between solute species in the liquid solutions. By using thermodynamic interaction

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<sup>2</sup>A. P. Litman, The Effect of Oxygen on the Corrosion of Niobium by Liquid Potassium, ORNL-3751 (July 1965).

<sup>3</sup>R. L. Klueh, "The Effect of Oxygen on the Compatibility of Niobium with Potassium," Corrosion 25, 416-422 (1969).

<sup>4</sup>R. L. Klueh, "The Effect of Oxygen in Sodium on the Compatibility of Sodium with Niobium," pp. 171-176 in Proceedings of the International Conference on Sodium Technology and Large Fast Reactor Design, November 7-9, 1968, ANL-7520, Part 1.

<sup>5</sup>J. R. DiStefano, Corrosion of Refractory Metals by Lithium, ORNL-3551 (March 1964).

<sup>6</sup>R. L. Klueh, "Penetration of Refractory Metals by Alkali Metals," pp. 177-196 in Corrosion by Liquid Metals, ed. by J. E. Draley and J. R. Weeks, Plenum Press, New York, 1970.

<sup>7</sup>C. Tyzack, "The Behavior of Materials in Liquid Sodium," p. 239 in Inter-Disciplinary Symposium on Advances in Materials, The Institution of Chemical Engineers, London, 1964.

parameters<sup>8</sup> and comparing predicted and observed dissolution behavior, we found reasonable agreement, indicating that no third condensed phase was present in these systems.

The second effect, the penetration of oxygen-doped refractory metals by alkali metals, is the result of the formation of a ternary oxide on grain boundaries or preferred crystallographic planes within the solid.<sup>5,6</sup> We have proposed that penetration is caused by the formation of corrosion products that have a larger volume than the metal from which they form.<sup>6</sup> Pressure generated during the formation of the larger volume reaction products wedges open the material in front of the reaction products to form a crack. Liquid metal is then drawn to the crack tip by the low pressure of the cavity and by capillary action.

The only previous study of the tantalum-oxygen-potassium system was conducted by Hickam,<sup>9</sup> who studied the effect of potassium on oxygen-doped tantalum at 982°C. After test, he isolated  $K_3TaO_4$  and concluded that the formation of this compound could account for the effect of oxygen on the dissolution of tantalum in potassium. This conclusion does not take into account the complicating effect of the penetration that occurs when the oxygen-doped tantalum specimens are exposed to potassium (second effect discussed above). Moreover, to isolate the  $K_3TaO_4$ , Hickam<sup>9</sup> distilled the excess potassium from the tantalum specimens at 316°C (a procedure that could alter any corrosion product present at the test temperature<sup>10</sup>). For selected tests, he dissolved the potassium in alcohol and found that the atom ratio of tantalum to oxygen approached 1:4, which he also took to mean that  $K_3TaO_4$  was present at the test temperature. However, this ratio could be present in solution before the formation of the separate phase (i.e., oxygen could increase the solubility of tantalum by interactions between dissolved species).

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<sup>8</sup>C. Wagner, Thermodynamics of Alloys, Addison-Wesley, Cambridge, Mass., 1952.

<sup>9</sup>C. W. Hickam, Jr., "Corrosion Product of the Tantalum-Interstitial Oxygen-Potassium System at 1800°F (982°C)," J. Less-Common Metals 14, 315 (1968).

<sup>10</sup>C. B. Alcock, M. G. Barker, and G. P. Stavropoulos, "The Corrosion of Tantalum by  $Na_2O$ -Saturated Liquid Na," Corrosion Sci. 10, 105 (1970).

## EXPERIMENTAL PROCEDURE

The effect of oxygen on the compatibility of tantalum and potassium at 600, 800, and 1000°C was studied with the experimental system shown in Fig. 1. It consisted of a tantalum specimen in contact with potassium in a tantalum container, encapsulated, in turn, in stainless steel to protect the tantalum from the air during test. The capsules were loaded and welded in an argon-atmosphere chamber to prevent contamination of the potassium or tantalum.

To determine the effect of oxygen in potassium, we varied the oxygen concentration by adding  $K_2O$  to potassium that had been purified by exposure to zirconium foil at 800°C. To determine the effect of oxygen in tantalum, oxygen was added to the 99.9%-pure tantalum test

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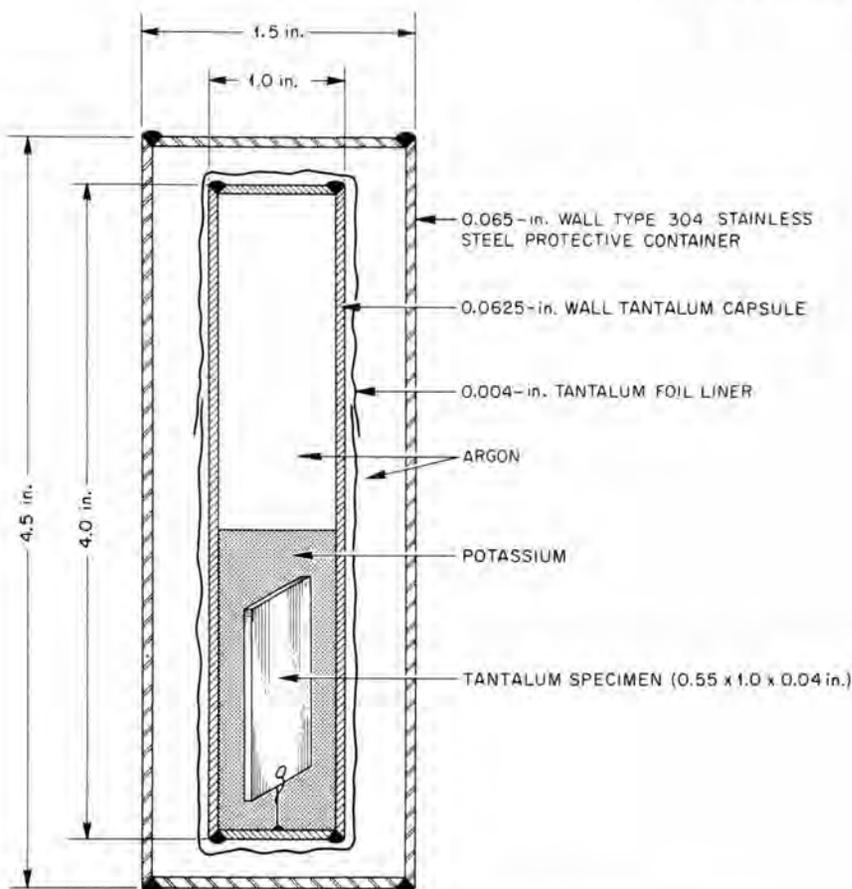


Fig. 1. Schematic Diagram of Test System.

specimens at 1000°C at an oxygen pressure of  $8 \times 10^{-5}$  torr in a vacuum system with a controlled oxygen leak. After oxidation the specimens were homogenized in vacuum at 1400°C for 4 hr; homogenization was verified by microhardness measurements. The oxygen concentration of the tantalum was determined by either vacuum-fusion or fast-neutron-activation analysis.

While heating to the test temperature, the specimens were in the vapor zone of the capsule, and when the system reached temperature, the capsule was inverted to expose the specimen to the liquid. When the test was completed, the capsule was inverted, quenched in liquid nitrogen, and opened in the argon chamber, and the potassium was removed by dissolving in chilled isopropyl alcohol. The potassium was recovered from the alcohol as potassium fluoride; the amount of tantalum present was determined by spectrographically analyzing the potassium fluoride. The extent of penetration of the oxygen-doped tantalum was determined metallographically.

#### EXPERIMENTAL RESULTS

Initially, these tests were designed for comparison with similar tests by Litman<sup>2</sup> on the niobium-oxygen-potassium system at 800 and 1000°C; the results of preliminary experiments at these temperatures are shown in Table 1. At the same time, because of LMFBR requirements using sodium at lower temperatures, we became interested in comparing the effect of oxygen in the alkali metals sodium, potassium, and lithium on tantalum and niobium at 600°C; Table 2 shows preliminary results for the tantalum-oxygen-potassium system at 600°C.

From these preliminary tests, we concluded that the effect of oxygen on the compatibility of tantalum and potassium was basically the same as its effect on the compatibility of niobium and potassium. Subsequent experiments were designed to study the two effects of oxygen discussed above.

Table 1. Effect of Oxygen on Compatibility of Tantalum and Potassium

Temperature (°C)	Time (hr)	Pretest Oxygen in Potassium (ppm) <sup>a</sup>	Oxygen in Tantalum (ppm) <sup>a</sup>		Weight Change (mg/cm <sup>2</sup> )	Post-test Tantalum in Potassium (ppm) <sup>a</sup>
			Before	After		
800	1	1,900	50	43	-0.0585	1,890
	3	2,000	50	29	-0.0594	2,990
	5	1,880	50	26	-0.0741	3,200
	100	2,000	50	19	-0.1520	2,640
	100	490	700 <sup>b</sup>	34	-1.950	2,480
	100	1,970	700 <sup>b</sup>	36	-1.880	3,120
	100	1,950	1,200 <sup>b</sup>	36	-3.240	7,570
	100	1,980	1,800 <sup>b</sup>	32	-6.650	6,850
1,000	0.5	2,020	50	39	-0.0460	3,860
	1	1,930	50	38	-0.0645	3,830
	2	2,020	50	50	-0.0745	4,620
	50	2,010	50	48	-0.202	14,120
	0.5	100	1,600 <sup>b</sup>	250	-5.91	3,680
	1	100	1,600 <sup>b</sup>	290	-5.86	4,980
	2	100	1,600 <sup>b</sup>	36	-6.06	5,110
	50	100	1,700 <sup>b</sup>	23	-6.28	6,830
	50	450	620	39	-1.92	9,640
	50	1,980	660	43	-1.86	15,070
	50	1,970	1,000 <sup>b</sup>	53	-3.23	7,780
	50	1,930	1,900 <sup>b</sup>	53	-6.50	20,600

<sup>a</sup>All concentrations are in parts per million by weight.

<sup>b</sup>Tantalum was penetrated by potassium.

Table 2. Effect of Oxygen on the Compatibility of Tantalum and Potassium Tested at 600°C for 500 hr

Pretest Oxygen in Potassium <sup>a</sup> (ppm)	Oxygen in Tantalum (ppm)		Weight Change (mg/cm <sup>2</sup> )	Post-test Tantalum in Potassium <sup>b</sup> (ppm)
	Before	After		
100	40	21	-0.031	2,200
600	40	23	-0.039	6,300
1,000	40	18	-0.088	4,200
1,400	40	24	-0.30	5,700
3,400	40	31	-0.92	12,000
20,400	40	48	-6.51	22,000
100	600	190	-0.57	3,000
100	1,300	1,300	+0.50	2,300

<sup>a</sup>Oxygen added as K<sub>2</sub>O to potassium containing 100 ppm O.

<sup>b</sup>Before test the potassium contained < 10 ppm Ta.

#### Effect of Oxygen in Potassium

The preliminary tests indicated that the tantalum-oxygen-potassium system was similar to the niobium-oxygen-potassium<sup>11,12</sup> and the niobium-oxygen-sodium<sup>13</sup> systems in that oxygen in potassium enhances the dissolution of the tantalum. Results of further tests designed to establish this effect are given in Table 3. The "apparent solubility" of tantalum increases with the concentration of oxygen in potassium.

<sup>11</sup>A. P. Litman, The Effect of Oxygen on the Corrosion of Niobium by Liquid Potassium, ORNL-3751 (July 1965).

<sup>12</sup>R. L. Klueh, "The Effect of Oxygen on the Compatibility of Niobium With Potassium," Corrosion 25, 416-422 (1969).

<sup>13</sup>R. L. Klueh, "The Effect of Oxygen in Sodium on the Compatibility of Sodium With Niobium," pp. 171-176 in Proceedings of the International Conference on Sodium Technology and Large Fast Reactor Design, November 7-9, 1968, ANL-7520, Part 1.

Table 3. The Effect of Oxygen in Potassium on the Dissolution of Tantalum<sup>a</sup>

Temperature (°C)	Time (hr)	Concentration in Potassium After Test, ppm	
		Oxygen <sup>b</sup>	Tantalum <sup>c</sup>
600	500	600	960
		1,100	1,100
		1,550	3,200
		2,650	3,600
		4,200	6,480
800	100	600	1,700
		1,100	3,550
		1,600	4,200
		2,650	5,670
		4,150	9,400
1,000	50	500	6,800
		1,050	8,600
		1,600	11,200
		2,600	11,900
		4,100	15,700

<sup>a</sup>No tantalum specimens were used in these tests.

<sup>b</sup>Calculated by mass balance.

<sup>c</sup>Determined by spectrographic analysis.

The specimens and capsules, especially those tested in potassium of higher oxygen content, had what appeared to be a superficial scale or discoloration of unknown origin. That is, the scale or discoloration may have been present at the test temperature, may have formed during cooling, or may be a result of the alcohol cleaning procedure. The dissolution of the potassium in isopropyl alcohol may have affected any scale that was present during test. The specimens and containers exposed to the high-oxygen potassium had a black "flaky" scale that partially spalled off during exposure to the alcohol. After alcohol exposure, the specimens were washed with distilled water from a

laboratory wash bottle, and the water was allowed to drain into the alcohol. The "flaky" scale dissolved in the water, and further, the water that was added to the alcohol caused the flaky material still remaining in the alcohol solution to dissolve. When the solutions stood overnight, however, they developed a yellowish precipitate, which dissolved in water and dissolved when the solution was heated. The amounts of this yellowish precipitate increased with the before-test oxygen concentration of the potassium and the test temperature. None of this was observed in the niobium tests.<sup>12</sup> We were unable to identify the precipitates and scales; in fact, only tantalum was detected on the specimen surfaces by x-ray diffraction.

In previous work on the niobium-oxygen-potassium<sup>12</sup> and niobium-oxygen-sodium<sup>13</sup> systems, we concluded that the final oxygen concentration of the niobium changed with the oxygen concentration of the liquid metal. From the phase rule it therefore follows that no third condensed phase existed at the test temperature. Oxygen concentrations for the tantalum specimens tested at 600°C, with and without the "scales," are given in Table 4. In this case, there is essentially no change (within experimental accuracy) in the oxygen concentration of the tantalum with increasing oxygen in potassium, indicating that a third condensed phase existed at the test temperature. Note that there is apparently little scale present (i.e., little difference between the oxygen concentration with and without the scale), an indication that the scale must be soluble in alcohol.

To further verify this conclusion, four tantalum capsules each were exposed to potassium with 100 ppm<sup>14</sup> O at 600, 800, and 1000°C. After test the potassium from two of the capsules for each temperature was poured into nickel containers and analyzed for oxygen by fast-neutron activation. Table 5 shows that the oxygen concentration of this potassium (with one exception) was much less than before the test, indicating that the oxygen had either diffused into the tantalum or remained with the potassium that adhered to the capsule wall when

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<sup>14</sup>All concentrations are in parts per million by weight.

Table 4. Change in Oxygen Concentration of Tantalum After 500 hr at 600°C

Oxygen in Potassium <sup>a</sup> (ppm)	Oxygen <sup>b</sup> in Tantalum, <sup>c</sup> ppm	
	With Scale	Without Scale <sup>d</sup>
100	21	15
600	23	23
1,000	18	17
1,400	24	27
3,400	31	31
20,400	48	31

<sup>a</sup>Oxygen added as K<sub>2</sub>O to potassium containing 100 ppm O.

<sup>b</sup>Determined by vacuum-fusion analysis.

<sup>c</sup>Before test the tantalum contained 40 ppm O.

<sup>d</sup>Scale removed by acid cleaning.

the bulk of the liquid was poured out. Because of the short test times, (especially at 600 and 800°C), diffusion is unlikely (we also know that tantalum did not pick up oxygen in previous tests). The potassium that was analyzed for oxygen and the potassium that adhered to the walls were dissolved separately in isopropyl alcohol. The potassium from the other two capsules at each temperature was all dissolved directly from the tantalum capsule. All alcohol solutions were analyzed for tantalum and the results are summarized in Table 5.

From Table 5, it appears that the major portion of tantalum, as was the case for oxygen, remains in the thin layer of potassium that adheres to the capsule wall. Table 6 compares the total amounts of tantalum recovered from each capsule.

#### Effect of Oxygen in Tantalum

When the oxygen concentration of the tantalum exceeds a "threshold" level, the tantalum is penetrated by the potassium. Figure 2 shows a

Table 5. Results of Tests to Determine Location of Tantalum After Test<sup>a</sup>

Temperature (°C)	Time (hr)	Weight of Potassium, g		Oxygen in Bulk Potassium (ppm)	Tantalum in Potassium, ppm	
		Bulk <sup>b</sup>	Adhering to Capsule <sup>b</sup>		Bulk	Adhering to Capsule
600	50	5.68	c		430	
		5.33	0.15	< 10	64	9,700
		5.63	c		360	
		5.35	0.15	18	21	9,500
800	25	5.45	c		380	
		5.68	0.18	15	41	17,200
	.50	5.23	c		550	
		5.30	0.18	54	120	13,900
1,000	16	5.75	c		570	
		5.33	0.17	< 10	16	15,300
		5.38	c		510	
		5.90	0.22	< 10	8	11,400

<sup>a</sup>No tantalum specimens were used in these tests. Potassium contained 100 ppm O initially.

<sup>b</sup>Determined by flame photometry. The total potassium determined analytically was in excellent agreement with the potassium determined by weight when the capsules were loaded.

<sup>c</sup>Potassium was dissolved in alcohol directly from the capsule.

Table 6. Weight of Tantalum Recovered

Temperature (°C)	Weight of Tantalum Recovered, $\mu\text{g}$		
	Bulk	Adhering to Capsule	Total
600	2450		2450
	340	1450	1790
	2000		2000
	113	1420	1533
800	2050		2050
	230	3100	3300
	2900		2900
	620	2500	3120
1000	3300		3300
	87	2600	2687
	2730		2730
	47	2500	2547

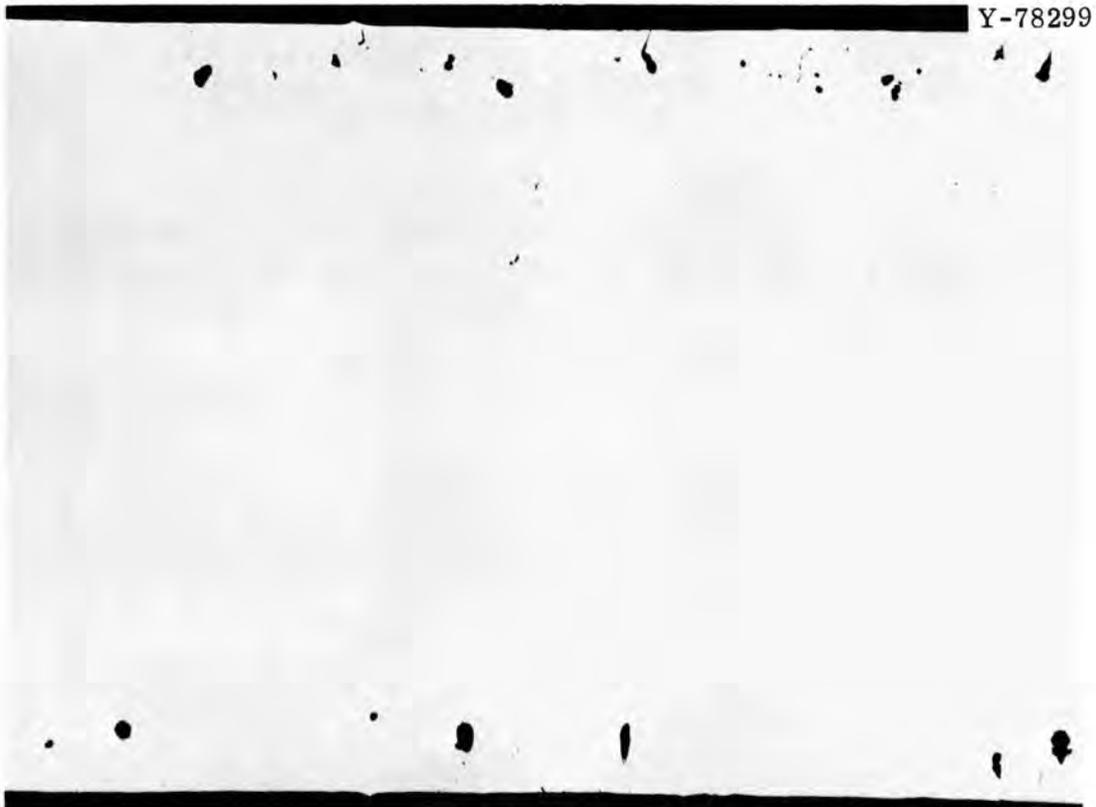


Fig. 2. Tantalum that Contained 600 ppm O and was Exposed to Potassium for 500 hr at 600°C. Unetched. 100X.

tantalum specimen that contained 600 ppm O and was exposed to potassium at 600°C. This specimen illustrates the type of attack that occurs just above the threshold concentration. The attack is completely intergranular (as revealed by etching) and terminates in a relatively large corrosion pocket or penetration "head." When the oxygen concentration is increased, the depth and number of grain boundaries attacked increase. Figure 3(a) shows a completely penetrated specimen that contained 1300 ppm O before exposure to potassium for 500 hr at 600°C.

When the oxygen concentration is high enough, transgranular attack also occurs (i.e., the threshold concentration for transgranular attack is greater than that for intergranular attack). Figure 3(b), which shows tantalum that contained 2000 ppm of O before exposure to potassium for 500 hr at 600°C, illustrates a specimen where transgranular attack has just begun.

Figure 4 shows tantalum specimens that initially contained approximately 700, 1200, and 2000 ppm O and were exposed to potassium for 100 hr at 800°C. Comparing these photomicrographs with Figs. 2 and 3, which show tantalum specimens doped to similar oxygen levels but exposed at 600°C, shows that an increase in temperature decreases the depth and amount of attack for a given oxygen concentration.

Figure 4(c) is especially interesting because of the unusual grain structure of the tantalum (i.e., the elongated grains parallel to the "flat" edge of the specimen). Compare the relatively deep penetration in the longitudinal direction with the shallower penetration in the transverse direction. Attack in the latter direction was confined to a band of small, equiaxed grains near the surface and was halted by grains elongated in the rolling direction. This confirms that only grain boundary attack occurred even though the tantalum contained as much oxygen as the specimen showing transgranular attack at 600°C.

When tantalum with 700 ppm O was exposed to potassium at 1000°C, no penetration was detected; Fig. 5(a) shows the small amount of attack that a specimen with 1000 ppm O received, and Fig. 5(b) shows a specimen that contained 1700 ppm O; both were exposed to potassium for 50 hr at 1000°C. By examining the amount of attack for various oxygen concentrations, we determined that the threshold oxygen concentration for

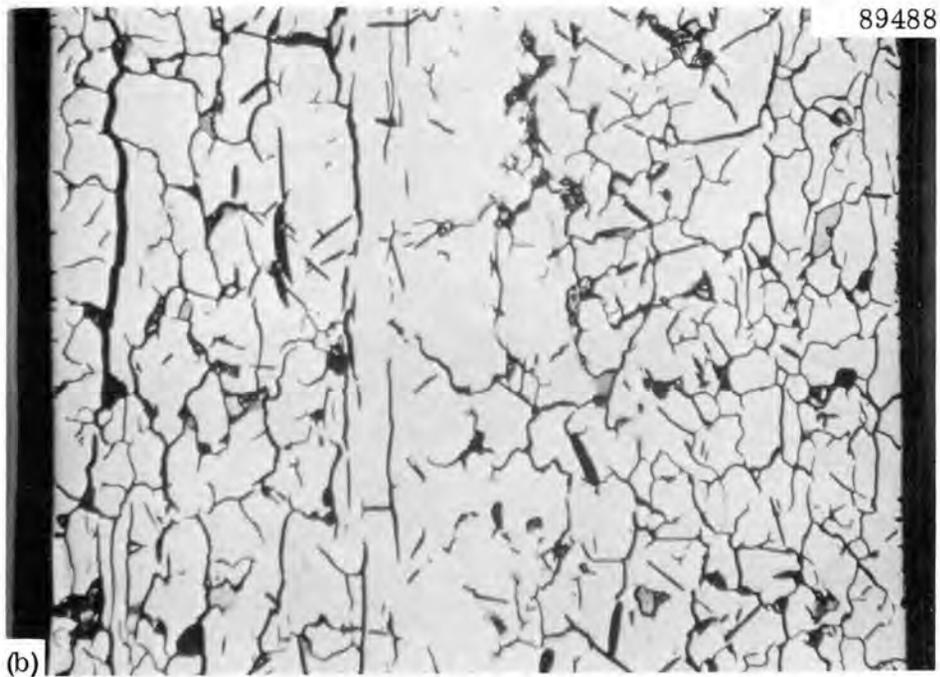
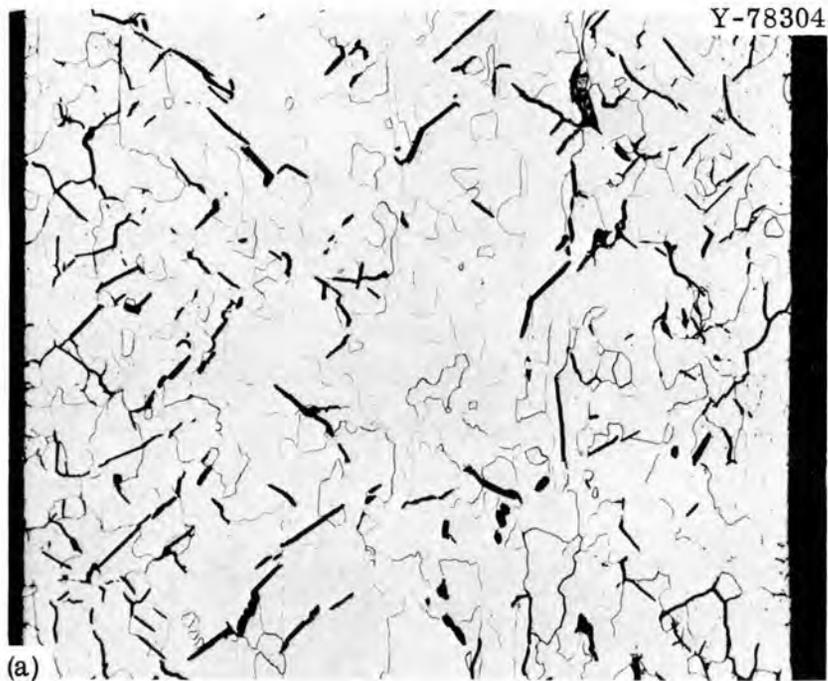


Fig. 3. Tantalum with Higher Oxygen Contents After Exposure to Potassium for 500 hr at 600°C. 100 $\times$ . Etched with H<sub>2</sub>O-HNO<sub>3</sub>-NH<sub>4</sub>HF. (a) 1300 ppm O. (b) 2000 ppm O. Note the start of transgranular attack at the specimen edge in (b).

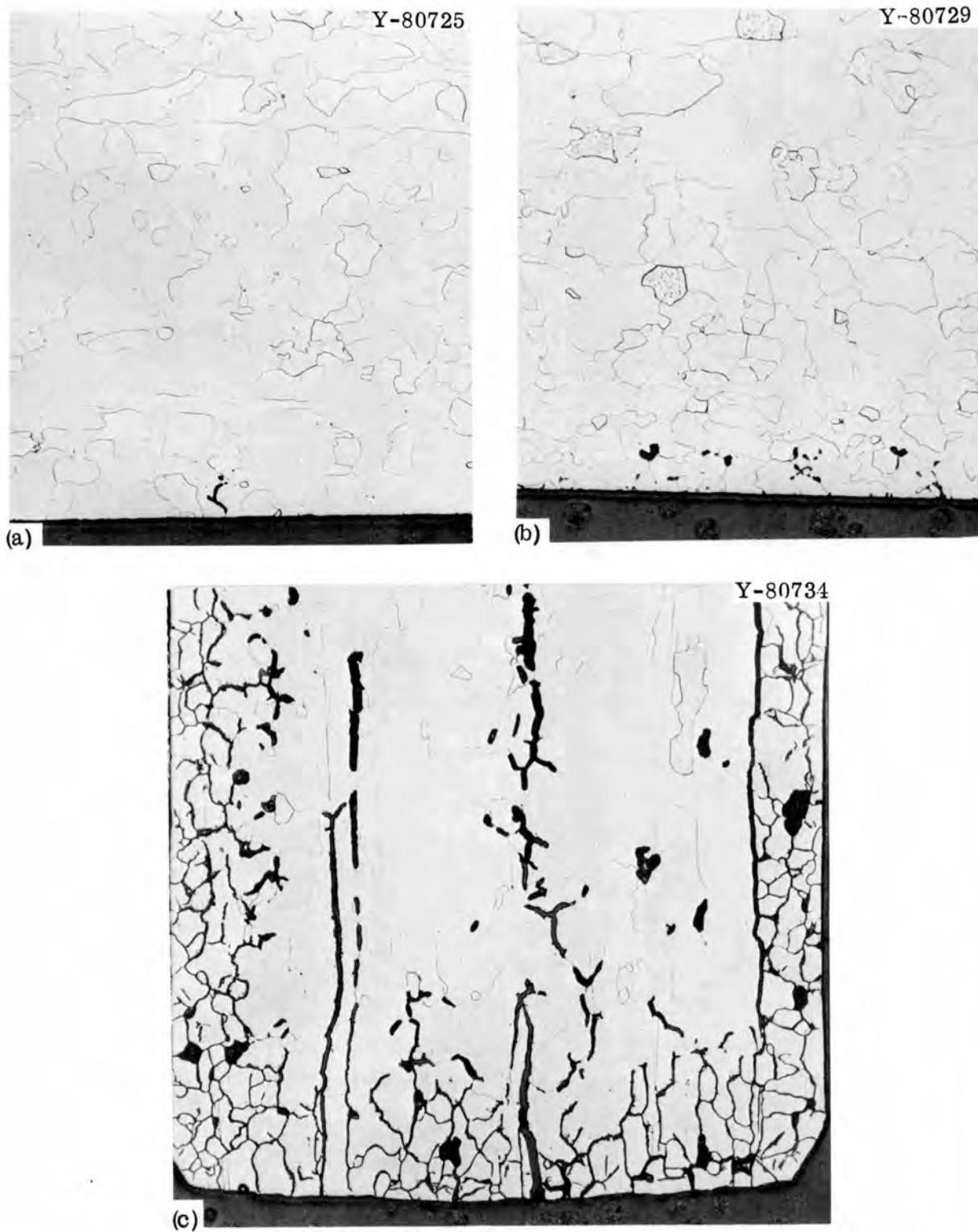


Fig. 4. Tantalum with Various Oxygen Contents After Exposure to Potassium for 100 hr at 800°C. 100X. Etchant:  $\text{H}_2\text{O}-\text{HNO}_3-\text{NH}_4\text{HF}$ .  
(a) 700 ppm O. (b) 1200 ppm O. (c) 2000 ppm O.

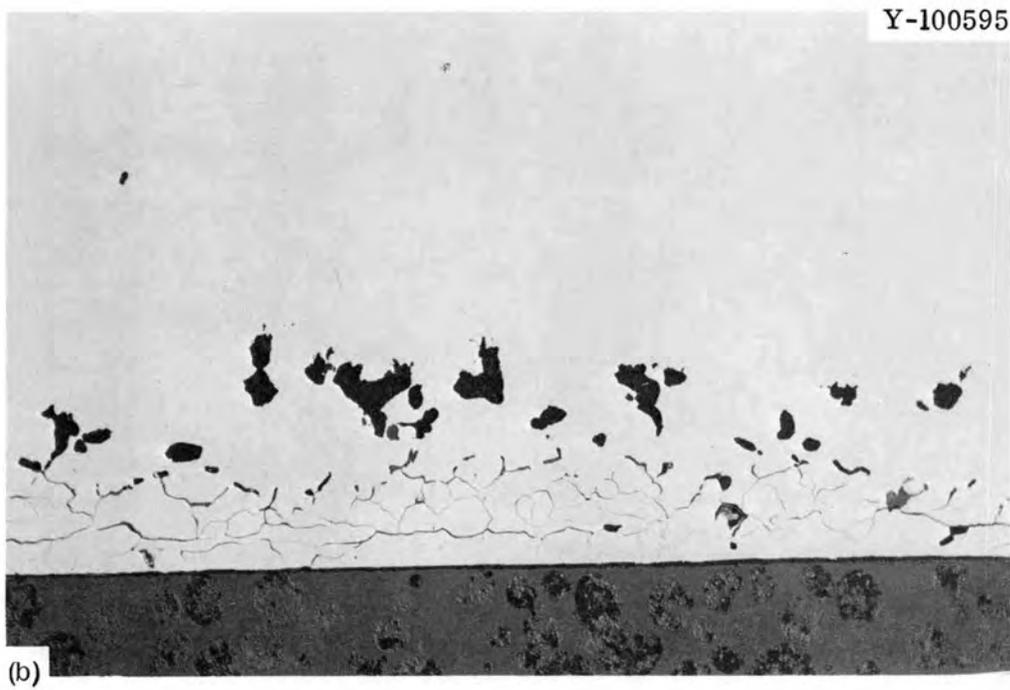
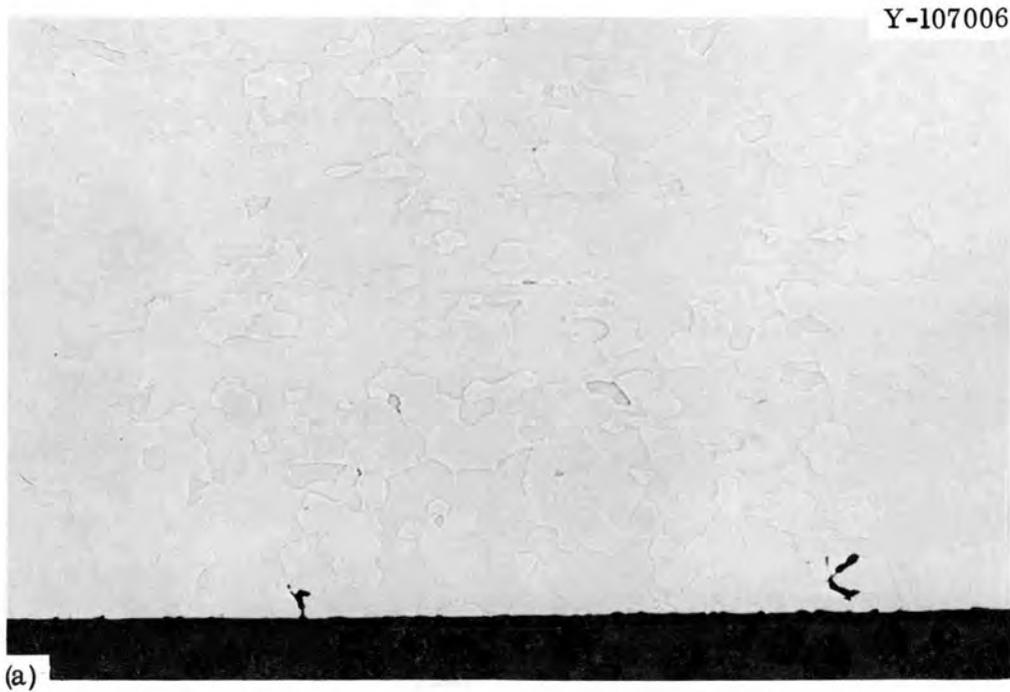


Fig. 5. Oxygen-Doped Tantalum Exposed to Potassium for 50 hr at 1000°C. 100×. (a) Initially 1000 ppm O; etched with H<sub>2</sub>O-HNO<sub>3</sub>-NH<sub>4</sub>HF. (b) Initially 1700 ppm O; unetched.

potassium penetration of tantalum increases with increasing temperature. These levels for intergranular attack are approximately 500, 700, and 1000 ppm O at 600, 800, and 1000°C, respectively. Transgranular attack has a higher threshold at each temperature.

We previously pointed out that penetration is extremely rapid.<sup>15,16</sup> Figure 6 compares tantalum specimens that contained 1600 ppm O and were exposed to potassium for 0.5 and 2 hr at 1000°C. After 2 hr there was no additional penetration. Specimens with similar oxygen concentrations showed no further attack, even after 50 hr.

We feel that attack of oxygen-doped tantalum proceeds by the formation of a ternary oxide<sup>16</sup> (i.e., an oxide that contains potassium and tantalum). However, all attempts to quantitatively identify the corrosion product were unsuccessful. Penetrated tantalum exposed to potassium for prolonged periods lost oxygen (Tables 1 and 2, pp. 6 and 7). The oxygen concentrations at 800 and 1000°C decreased to a level near that found in undoped tantalum exposed at the same temperatures for comparable times. Since only intergranular penetration occurred in most of these tests, only a very small fraction of the total oxygen is tied up in a corrosion product, and apparently the corrosion product dissolves in the potassium as the system approaches equilibrium. Dissolution of the corrosion product on prolonged exposure to potassium, as well as corrosion product lost during exposure to alcohol and during metallographic preparation, could explain the apparent absence of such products in the after-test microstructures.

## DISCUSSION

### Effect of Oxygen in Potassium

When these experiments were begun, we expected to find the effect of oxygen in potassium (for a similar range of oxygen concentrations) on tantalum-potassium compatibility similar to its effect on the

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<sup>15</sup>J. R. DiStefano, Corrosion of Refractory Metals by Lithium, ORNL-3551 (March 1964).

<sup>16</sup>R. L. Klueh, "Penetration of Refractory Metals by Alkali Metals," pp. 177-196 in Corrosion by Liquid Metals, ed. by J. E. Draley and J. R. Weeks, Plenum Press, New York, 1970.

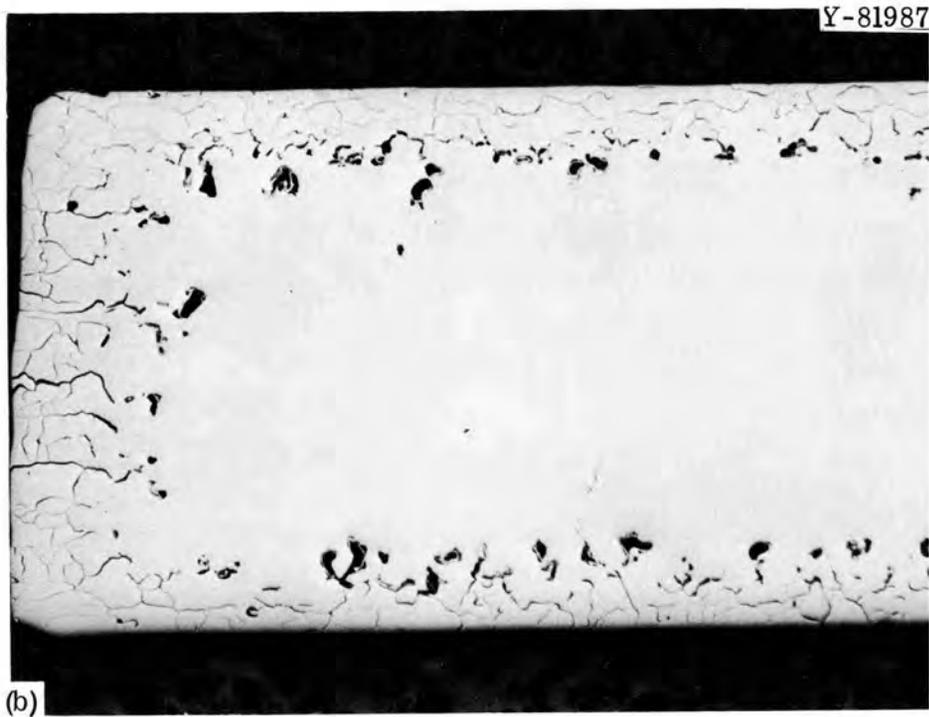
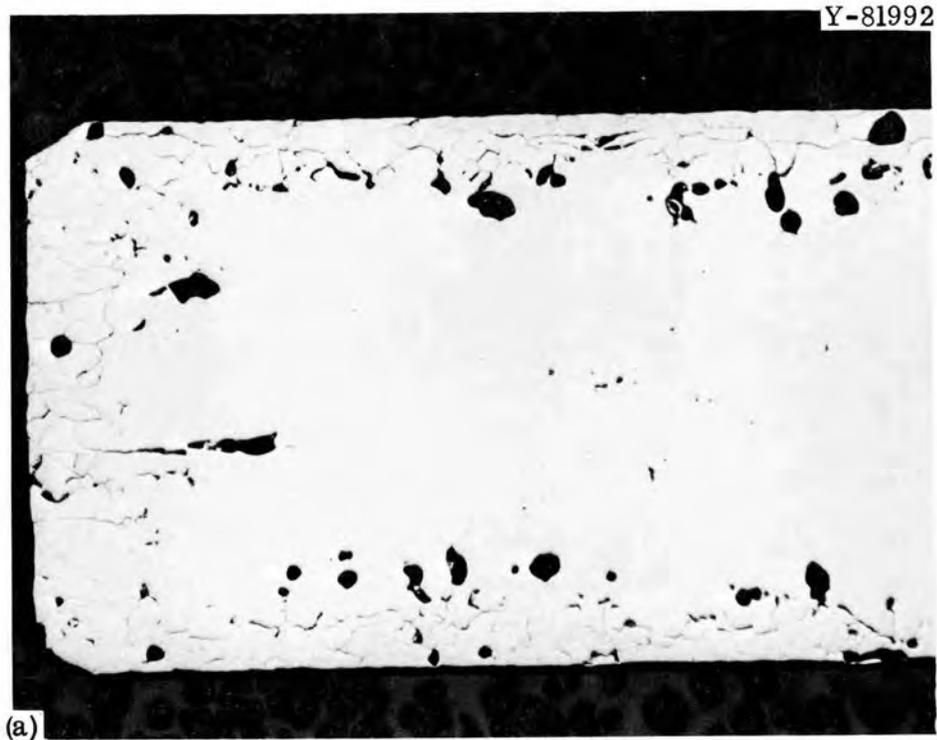


Fig. 6. Tantalum that Contained 1600 ppm O and was Exposed to Potassium for (a) 0.5 hr and (b) 2 hr at 1000°C. 75x. Unetched.

niobium-potassium<sup>17</sup> and niobium-sodium<sup>18</sup> compatibility. For the latter systems, the results could be explained in terms of the effect of oxygen on the solubility of niobium in the alkali metals. The effect was characterized by using thermodynamic interaction parameters<sup>19</sup> to express empirically the activity coefficient of niobium or oxygen in the alkali metal. For the niobium systems, we also found that the equilibrium distribution coefficient for the partitioning of oxygen between niobium and the alkali metal was a function of the oxygen concentration of the alkali metal.

The same explanation will not apply to the tantalum-oxygen-potassium system since all indications are that a third condensed phase is present at the test temperature. Under these conditions, the phase rule dictates that there is no distribution coefficient; that is, the oxygen concentration of the tantalum and potassium is fixed. The nature of this third phase is not known since it was not identified; however, it must be a ternary oxide. Potassium oxides are unstable in the presence of tantalum, and if the phase was tantalum oxide, the final oxygen concentration of the tantalum would be much larger (i.e., the equilibrium oxygen solubility at 600°C is more than 500 ppm and increases with temperature<sup>20</sup>). As discussed previously,<sup>16</sup> we believe that the alkali metal penetration of refractory metals is the result of ternary oxide formation within the refractory metal. There is no reason, therefore, why ternary oxide formation at the tantalum-potassium interface should not also be possible.

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<sup>17</sup>R. L. Klueh, "The Effect of Oxygen on the Compatibility of Niobium with Potassium," Corrosion 25, 416-422 (1969).

<sup>18</sup>R. L. Klueh, "The Effect of Oxygen in Sodium on the Compatibility of Sodium with Niobium," pp. 171-176 in Proceedings of the International Conference on Sodium Technology and Large Fast Reactor Design, November 7-9, 1968, ANL-7520, Part 1.

<sup>19</sup>C. Wagner, Thermodynamics of Alloys, Addison-Wesley, Cambridge, Mass., 1952.

<sup>20</sup>E. Gebhardt and H. D. Seghezzi, "Investigations in the System Niobium-Oxygen II. Solution of Oxygen in Niobium and Precipitation of Oxides from Supersaturated Solid Solutions," Z. Metallk. 54, 623 (1963).

In actual fact, the apparent difference between tantalum and niobium may be more a difference of degree than behavior. Implicit in the interaction parameter treatment of the niobium-oxygen interactions in potassium and sodium is the assumption that the effect of oxygen on the activity coefficient of niobium is due to atomic (or molecular) interactions within the solution. Although these interactions are expressed as  $\epsilon_0^{(\text{Nb})}$  (i.e., the interaction parameter for oxygen and niobium), indicating, at first glance, interactions between the niobium and oxygen atoms in the solution, the treatment is entirely phenomenological and nothing about specific atomistic or molecular interactions is to be implied. The interactions are undoubtedly highly complex and involve interactions between all species. If it is assumed that, as postulated for the tantalum-oxygen-potassium system, the first phase that precipitates when oxygen is added to the liquid metal is a ternary oxide, then the niobium-oxygen-potassium and niobium-oxygen-sodium systems are saturated at higher oxygen concentrations than the tantalum-oxygen-potassium system and also these concentrations are higher than the oxygen concentrations tested.<sup>17,18</sup> In other words, the ternary oxide for the tantalum-oxygen-potassium system has essentially no solubility in the liquid and precipitates almost immediately when oxygen is added to the liquid.

A difference between the behavior of tantalum and niobium in alkali metals has been verified for the case of alkali metal penetration.<sup>16</sup> The threshold oxygen concentration (on a weight percent basis) for niobium penetration is about twice that required for tantalum penetration. Obviously, the present data indicate more than a factor of 2 difference between tantalum and niobium; however, it should be kept in mind that the oxygen is in two different media. For penetration the oxygen is in the refractory metal, whereas for dissolution the oxygen is in the alkali metal.

Although we concluded that a third phase was present at the test temperature, the phase was not identified. It is probably the  $\text{K}_3\text{TaO}_4$  found by Hickam.<sup>21</sup> This conclusion is enhanced by the recent work of

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<sup>21</sup>C. W. Hickam, Jr., "Corrosion Product of the Tantalum-Interstitial Oxygen-Potassium System at 1800°F (982°C)," J. Less-Common Metals 14, 315 (1968).

Alcock et al.,<sup>22</sup> who studied the oxidation of tantalum in oxygen-saturated sodium and found oxidation to proceed by the formation of a  $\text{Na}_3\text{TaO}_4$  scale on the surface. Also, Addison et al.<sup>23</sup> found that when oxides of niobium were reacted with excess potassium, niobium metal and  $\text{K}_3\text{NbO}_4$  resulted. Similarly, when  $\text{K}_2\text{O}$  and niobium were reacted, potassium, niobium, and  $\text{K}_3\text{NbO}_4$  resulted. Both results indicate that the first oxide to form was  $\text{K}_3\text{NbO}_4$ . Note that the oxygen concentration of these latter experiments was much greater than that used in the niobium corrosion tests<sup>17,18</sup> (e.g., Addison et al.<sup>23</sup> used a  $\text{K}_2\text{O}:\text{Nb}$  ratio of 2.5, giving a  $\text{K}:\text{Nb}:\text{O}$  ratio of 4:2:1), and these results do not contradict the conclusions of those tests.

One unexplained observation is the apparent change in the tantalum concentration in potassium with temperature at constant oxygen concentration, shown in Table 3, p. 8. For the special tests of Table 5, p. 11, when the potassium contained 100 ppm O, there was very little change in the tantalum concentration with temperature. At higher oxygen concentrations, however, we observed higher tantalum concentrations in potassium after test, the higher the temperature. This may be because the high-temperature scales were more loosely adherent or more easily dissolved in alcohol, or it may represent a change in the nature or solubility of the ternary oxide with temperature.

#### Effect of Oxygen in Tantalum

The effect of temperature on potassium penetration of tantalum must be discussed in terms of two effects: the threshold oxygen concentration and the diffusion of oxygen from the tantalum to the potassium. When the oxygen-doped tantalum is exposed to potassium, penetration and oxygen diffusion from the tantalum to the potassium occur simultaneously.

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<sup>22</sup>C. B. Alcock, M. G. Barker, and G. P. Stavropoulos, "The Corrosion of Tantalum by  $\text{Na}_2\text{O}$ -Saturated Liquid Na," Corrosion Sci. 10, 105 (1970).

<sup>23</sup>C. C. Addison, M. G. Barker, and R. M. Lentonbon, "Reactions of the Oxides of Niobium with Liquid Potassium," J. Chem. Soc. A 1970, 1465.

The estimated threshold oxygen concentrations given above assume that penetration begins immediately when the specimen is exposed to the liquid metal. This is probably a good assumption since penetration proceeds rapidly and is very quickly completed.<sup>24,25</sup> The fact that penetration of the tantalum that contained 1600 ppm O ceased after 0.5 hr at 1000°C can also be explained by the two oxygen-competitive processes. Diffusion calculations show that the oxygen concentration at a depth of 0.015 in. [approximate penetration depth after 0.5 hr, see Fig. 6(a)] is below 1000 ppm (threshold oxygen concentration). Hence, the oxygen concentration is below the threshold, and penetration should - and does - halt.

We previously proposed a wedging mechanism to explain the alkali metal attack of refractory metals.<sup>25</sup> Wedging is caused by the formation of a ternary oxide that has a larger volume than the metal from which it forms. The pressure generated by the reaction product would wedge open the material in front of it to form a crack. Liquid metal is drawn to the crack tip by the low pressure of the cavity and by capillary action.

In the present experiments, we found further evidence that the corrosion product that forms has a larger volume than the tantalum it replaces. After exposure to potassium for 50 hr at 1000°C, the surface of the tantalum specimen that contained 2000 ppm O appeared rough, as seen in Fig. 7(a). At higher magnification, however, the roughness was identified as surface protuberances, as shown in Fig. 7(b). When the specimens were sectioned, we found that the position of the subsurface corrosion "heads" matched the locations of the protuberances, as seen in Fig. 8. In other words, the corrosion "heads" distorted the external surface of the specimens when the stresses generated by the larger volume material could not be restrained by the surrounding material.

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<sup>24</sup>J. R. DiStefano, Corrosion of Refractory Metals by Lithium, ORNL-3551 (March 1964).

<sup>25</sup>R. L. Klueh, "Penetration of Refractory Metals by Alkali Metals," pp. 177-196 in Corrosion by Liquid Metals, ed. by J. E. Draley and J. R. Weeks, Plenum Press, New York, 1970.

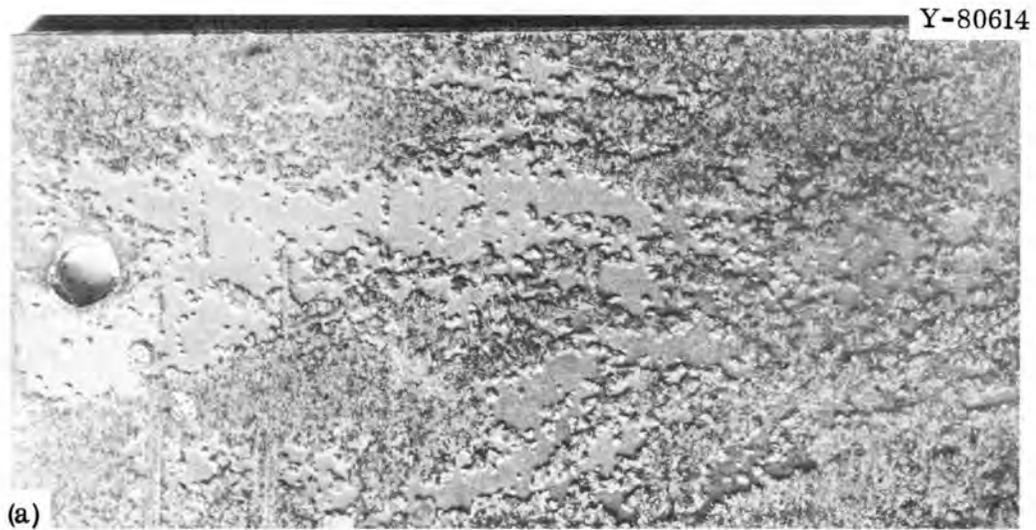


Fig. 7. External Surface of Tantalum Specimen with 2000 ppm O Exposed to Potassium for 50 hr at 1000°C. (a) View of entire specimen at about 5 $\times$ . (b) View at 25 $\times$  showing that the roughness is the result of surface protuberances.

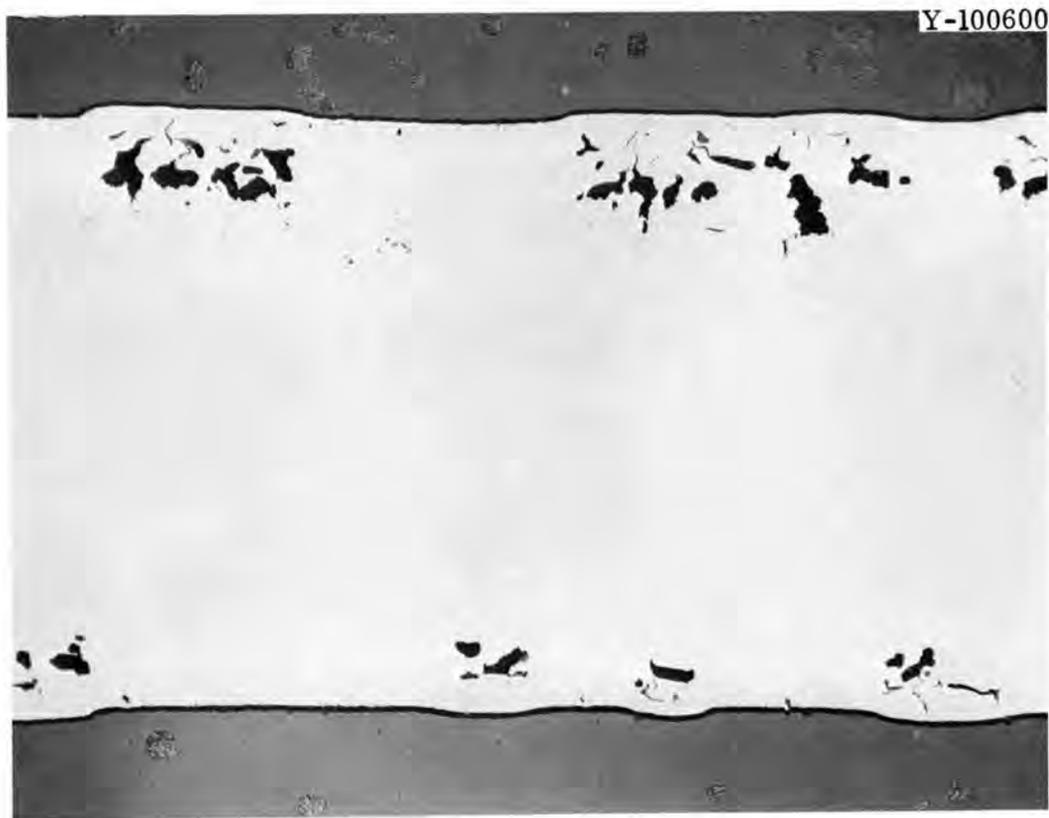


Fig. 8. Cross Section of Specimen in Fig. 7, Which Shows How the Protuberances Were Formed. 75X. Unetched.

Surface protuberances, when observed, are always in conjunction with attack that shows the large "heads" at the end of the penetration, although not all attack involving "heads" causes protuberances. The distance of the corrosion "heads" from the external surface probably determines whether protuberances form.

We previously explained that corrosion "heads" found on the ends of penetrations may result when liquid transfer to the reaction front (penetration front) controls the penetration rate.<sup>25</sup> These heads are found only at higher test temperatures ( $> 600^{\circ}\text{C}$ ), where oxygen diffusion becomes important. When penetration slows or stops because enough liquid cannot be supplied, oxygen can diffuse from the immediate surroundings to the reaction front and react locally with the available liquid (i.e., oxygen diffuses to the reaction front at a rate greater than or equal to the rate at which liquid arrives at the reaction front). Reaction ceases when the oxygen of the specimen is depleted.

## SUMMARY AND CONCLUSIONS

Oxygen affects the compatibility between tantalum and potassium in two ways, depending upon whether oxygen is in the potassium or tantalum. Increasing the oxygen concentration of the tantalum results in increased dissolution of the tantalum by the potassium. Oxygen redistribution indicates that the enhanced dissolution is the result of the formation at temperature of a third condensed phase, a ternary oxide, which either flakes off during exposure to potassium or dissolves in alcohol when the potassium is dissolved (i.e., it is expected that the oxide would form at the tantalum-potassium interface). There is some evidence that the scale dissolves in the alcohol. The behavior of oxygen in potassium on tantalum is different than its effect on niobium (over the same oxygen concentration range), where no third phase is believed to form.

When the oxygen concentration of the tantalum exceeds a threshold concentration, the potassium penetrates the tantalum. Both intergranular attack and transgranular attack occur; the threshold concentrations for intergranular penetration were found to be 500, 700, and 1000 ppm O at 600, 800, and 1000°C, respectively. Penetration occurs by the formation of a ternary oxide, and we postulated that the penetration mechanism involves wedging due to the formation of a corrosion product that has a larger volume than tantalum. Evidence of stresses generated by the larger volume corrosion products was found.

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