NASA TECHNICAL NOTE

NASA TN D-5875

C. 1

NASA TN D-5875

APPARENT SOLUBILITIES OF COMMERCIALLY PURE AND OXYGEN-DOPED TANTALUM AND NIOBIUM IN LIQUID POTASSIUM

by Stephan Stecura
Lewis Research Center
Cleveland, Ohio 44135

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JULY 1970

1. Report No. NASA TN D-5875	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle APPARENT SOLUBILITIES OF COMMERCIALLY PURE AND OXYGEN-DOPED TANTALUM AND NIOBIUM IN LIQUID POTASSIUM		5. Report Date July 1970 6. Performing Organization Code
7. Author(s) Stephan Stecura		8. Performing Organization Report No. E-5615
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		10. Work Unit No. 129-03 11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546		13. Type of Report and Period Covered Technical Note 14. Sponsoring Agency Code
15. Supplementary Notes		

16. Abstract

The apparent solubility of tantalum in potassium at 1055 and 1287 K is about 72 and 240 ppm by weight and that of niobium at 1055 and 1287 K is about 48 and 210 ppm by weight, respectively. The calculated heats of solution for tantalum and niobium solubilities in pure liquid potassium are 13.9±1.3 and 17.1±1.6 kcal/mole (58.2 and 71.5 kJ/mole), respectively. These apparent solubility data are believed to provide the upper limit for the true solubilities of tantalum and niobium between 1055 and 1287 K. Intentional doping of tantalum and niobium metals with oxygen increased the apparent solubilities of these two metals in liquid potassium. This effect of oxygen was related to K_3TaO_4 and K_3NbO_4 ternary oxides, respectively. These ternary oxides were recovered and identified. A hypothesis is proposed to explain these observations and those previously observed by others.

17. Key Words (*Suggested by Author(s)*) Apparent solubilities Effect of oxygen Tantalum Niobium Potassium	18. Distribution Statement Unclassified - unlimited		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 34	22. Price* $3.00

*For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151

APPARENT SOLUBILITIES OF COMMERCIALLY PURE AND OXYGEN-DOPED TANTALUM AND NIOBIUM IN LIQUID POTASSIUM

by Stephan Stecura
Lewis Research Center

SUMMARY

The apparent solubilities of commercially pure tantalum (Ta) and niobium (Nb) in liquid potassium containing less than 15 ppm by weight of oxygen were studied between 1055 and 1287 K. The apparent solubilities of these two metals in liquid potassium are represented by the relations

$$\left.\begin{aligned} \log \text{wt ppm Ta} &= 4.75\pm0.24 - \frac{3048\pm276}{T} \\ \log \text{wt ppm Nb} &= 5.23\pm0.30 - \frac{3739\pm343}{T} \end{aligned}\right\} \text{for 1055 to 1287 K}$$

where T is the absolute temperature. The calculated heats of solution for tantalum and niobium apparent solubilities in liquid potassium are 13.9±1.3 and 17.1±1.6 kilocalories per mole (58.2 and 71.5 kJ/mole), respectively. The apparent solubility values for commercially pure tantalum and niobium metals in liquid potassium are believed to have been influenced by oxygen. However, this oxygen influence is believed to be small. The apparent solubility values obtained herein provide an upper limit for the true solubilities of tantalum and niobium in liquid potassium. A method that is considered to be a more accurate one for obtaining the true solubility data for tantalum and niobium in liquid potassium is studying the kinetics of the solution as a function of oxygen concentration.

The effect of oxygen in tantalum and niobium metals on their apparent solubilities in liquid potassium was studied between 1063 and 1268 K. Tantalum and niobium concentrations in liquid potassium increase with an increase in their oxygen concentrations. The increased apparent solubilities of tantalum and niobium in potassium are related to the formation of K_3TaO_4 and K_3NbO_4 ternary oxides, respectively. These ternary oxides were recovered and identified. A hypothesis is proposed to explain these observations and those previously observed by others. It is proposed that oxygen in the refractory metal and in the liquid potassium diffuses toward the tantalum-potassium or niobium-potassium interface and forms tantalum or niobium oxides, which then react with potassium to form the K_3TaO_4 or K_3NbO_4 ternary oxide. The ternary oxide then dissolves in liquid potassium.

INTRODUCTION

One of the prime concerns in the development of advanced Rankine-type space power systems is the corrosion resistance of refractory metals or alloys to alkali metals at high temperatures. In such space power systems, potassium is of interest as a thermodynamic working fluid. Tantalum and niobium alloys are being considered as the container materials for potassium at high temperatures (ref. 1).

Solubility data are necessary to interpret corrosion data and to assist in predicting corrosion behavior. Although several studies on the resistance of refractory metals and alloys to corrosion by liquid potassium have been made (refs. 2 to 4), few quantitative solubility data are available. The limited data reported for tantalum and niobium (refs. 5 to 7) show a high degree of scatter, which can be attributed at least in part to the effects of interstitial impurities such as oxygen, nitrogen, and carbon. The effect of oxygen on the solubilities of refractory metals is especially critical (refs. 2, 5, and 8 to 10).

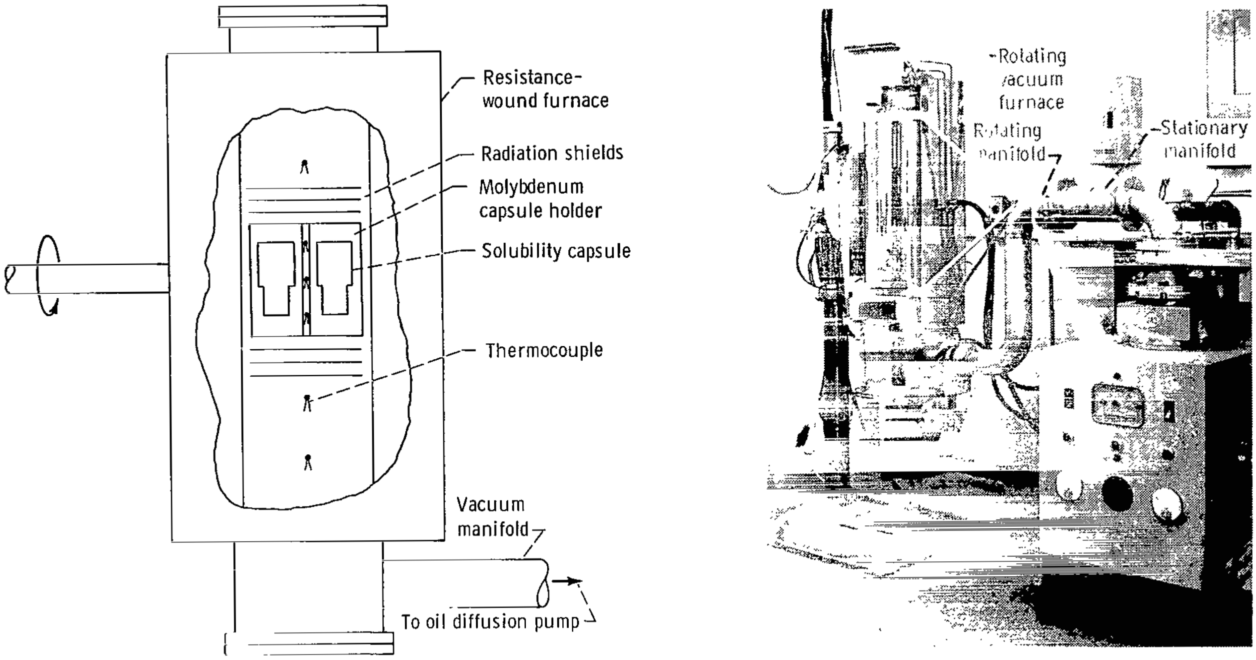
The purpose of this study was to obtain data for tantalum and niobium solubilities in liquid potassium. Data were also obtained for the effect of oxygen on these solubilities. The apparent solubilities and the effect of oxygen on the apparent solubilities of tantalum and niobium in liquid potassium were studied between 1055 and 1287 K by a rotatable-capsule method (refs. 9 and 11).

APPARATUS, MATERIALS, AND PROCEDURE

The data presented in this report were determined after allowing tantalum and niobium crucibles (which were the sources of both solutes and oxygen) to be in contact with high-purity potassium for 24 hours at the desired temperature. At the end of the 24-hour test time, the furnace was inverted and cooled to room temperature. Nickel capsules in which the crucibles and potassium had been sealed were opened, and the potassium containing the solute was removed for analysis.

Apparatus

Tantalum and niobium metals were studied between 1055 and 1287 K. The furnace used in obtaining the data was the same as that previously described by Stecura (ref. 9) and Swisher (ref. 11). A schematic diagram of the solubility furnace and a photograph of the equipment used in this study are shown in figure 1. This furnace can be inverted.



(a) Vacuum furnace.

(b) Overall view.

Figure 1. - Solubility apparatus.

The reason for rotating the furnace into the upside-down position is explained in the Procedure section.

Materials

The potassium used in this study contained less than 15 ppm by weight of oxygen. The total impurities in potassium were not greater than 0.01 weight percent (table I). Oxygen and nitrogen contents in potassium were determined by vacuum amalgamation and Kjeldahl methods, respectively. All other metallic impurities in potassium were determined by a mass spectrographic method.

Capsules (fig. 2(a)) used in this study served two purposes. They were containers for tantalum and niobium solute metals and potassium, and they were also the collectors for solute containing potassium at the end of a test run. Capsules were never used in this study as sources of solutes. These capsules were machined from polycrystalline nickel rod stock. The dimensions of such a capsule are given in figure 2(d).

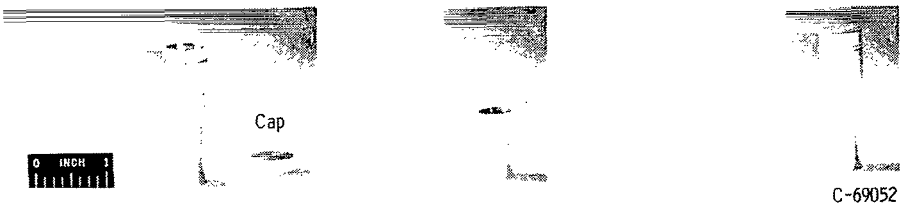
Hollow cylinders open at one end (fig. 2(b)) were the sources of solutes in all experiments. These cylinders are called crucibles throughout this study. Crucibles were

TABLE I. - IMPURITY CONTENT OF POTASSIUM, CRUCIBLE, AND CAPSULE METALS

Impurity	Potassium	Tantalum	Niobium	Nickel	Impurity	Potassium	Tantalum	Niobium	Nickel
	Concentration of impurity, ppm by weight					Concentration of impurity, ppm by weight			
Carbon[a]	(b)	5	7	111	Lead	(b)	1	1	<1
Oxygen[a]	15	12	64	13	Lithium	(b)	<1	<1	<1
Nitrogen[a]	2	22	41	18	Magnesium	1	<1	<1	<1
Hydrogen[a]	(b)	10	14	4	Manganese	(b)	<1	<1	2
Aluminum	3	<1	<1	5	Molybdenum	(b)	10	3	<1
Antimony	(b)	↓	↓	<2	Nickel	2	20	<1	High
Arsenic	↓	↓	↓	<1	Niobium	(b)	100	High	<1
Barium	↓	↓	↓	<4	Osmium	↓	<1	<1	<2
Beryllium	↓	↓	↓	<1	Palladium	↓	<1	<1	<1
Bismuth	↓	↓	↓	↓	Platinum	↓	10	<1	<2
Boron	0.5	↓	↓	↓	Potassium	High	<10	<10	<10
Bromine	(b)	↓	↓	↓	Rhodium	(b)	<1	<1	<1
Cadmium	↓	↓	↓	1	Rubidium	50	<1	↓	↓
Calcium	↓	↓	↓	2	Ruthenium	(b)	<1	↓	↓
Cesium	↓	↓	↓	<1	Silicon	0.5	5	↓	↓
Chlorine	↓	10	10	10	Silver	(b)	<1	↓	3
Chromium	0.5	5	<1	5	Sodium	↓	<1	↓	<1
Cobalt	(b)	<1	<1	5	Strontium	↓	<1	↓	<5
Copper	1	5	5	<1	Tantalum	↓	High	200	200
Fluorine	(b)	5	<1	10	Tellurium	↓	<1	<1	<5
Gallium	↓	<1	↓	<1	Thalium	↓	1	<1	<1
Germanium	↓	<1	↓	<2	Thorium	↓	50	1	<1
Gold	↓	20	↓	<1	Tin	↓	<1	1	<2
Hafnium	↓	<1	↓	<3	Titanium	↓	8	<1	8
Indium	↓	↓	↓	<1	Tungsten	↓	3	60	<1
Iodine	↓	↓	↓	<1	Vanadium	2	<1	<1	<1
Iridium	↓	↓	↓	<1	Zinc	(b)	3	2	6
Iron	2	20	2	10	Zirconium	(b)	<1	<1	<2

[a] Results obtained by chemical analyses. All other tantalum and niobium data obtained by optical spectrographic analyses. All other nickel and potassium data obtained by mass spectrographic analysis.

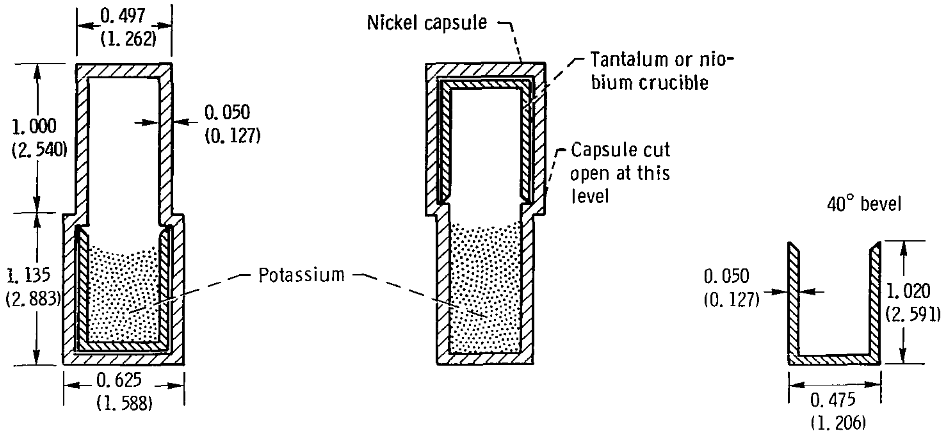
[b] Not detected.



(a) Nickel capsule.

(b) Tantalum or niobium crucible.

(c) Welded capsule.



(d) Position during test run.

(e) Position at end of test run.

(f) Crucible.

Figure 2. - Solubility capsule and crucible. (All dimensions are in inches (cm).)

machined from polycrystalline tantalum and niobium rod stock. The dimensions of such a crucible are given in figure 2(f).

The capsules and crucibles were first cleaned (see appendix A) and then analyzed for impurities. Analyses were done on two randomly selected capsules and/or crucibles of each appropriate metal. As indicated in table I, the maximum total impurity in the nickel, tantalum, or niobium used in this study was about 0.05 percent. Oxygen, nitrogen, carbon, and hydrogen contents in these metals were determined by inert-gas fusion, modified Kjeldahl (ref. 12), combustion, and hydrogen extraction methods, respectively. Metallic impurities were determined by either mass or optical spectrographic methods.

Oxygen-doped crucibles were used to study the effect of oxygen on the apparent solubilities of commercially pure tantalum and niobium metals in liquid potassium. Oxygen-doped tantalum crucibles used in this study contained about 800, 900, 1400, and 2000 ppm by weight of oxygen. Oxygen-doped niobium crucibles contained about 1200, 1400, 2600, and 4000 ppm by weight of oxygen. Both, tantalum and niobium crucibles were doped with oxygen as described by Barrett (ref. 13). No tantalum and niobium binary oxides were observed on the tantalum and niobium crucibles, all of which were annealed at 1589 K for 2 hours at a pressure of 10^{-8} torr before exposure to potassium.

Procedure

Apparent solubility studies. - The procedure used in determining the apparent solubilities of pure and oxygen-doped tantalum and niobium metals in liquid potassium was the same as that described in references 9 and 11. The nickel capsules were filled with about 1.2±0.08 grams of potassium in a vacuum chamber at a pressure of 5×10^{-6} torr. The crucibles were placed in the capsules, which were capped and electron beam welded at a pressure of about 5×10^{-6} torr. Then the capsules containing the tantalum or niobium crucibles and the potassium were placed into the furnace in the position shown in figure 2(d). In all experiments, capsules containing crucibles and potassium were heated at the desired temperatures at a pressure of 10^{-6} torr. Temperatures were measured with platinum - platinum-13-percent-rhodium thermocouples. Over a period of 96 hours, the maximum temperature variation along the capsule walls inside the molybdenum holder was ±4 at 1287 K. The estimated accuracy of the recorded capsule temperature was about ±8 at 1287 K.

At the end of a test run, the capsules were inverted by rotating the furnace to the upside-down position at the desired temperature. The rotation of the furnace to the upside-down position is necessary because the potassium containing tantalum or niobium in solution must be collected in a different metal container (e.g., the nickel capsule used in this study), as shown in figure 2(e). This permits the quantitative recovery of the tantalum or niobium that precipitates from potassium during cooling of the furnace to room temperature. After cooling to room temperature, the capsules were cut open at almost the middle, as indicated in figure 2(e). Solute-containing potassium was dissolved in butyl alcohol, and the inside walls of the smaller diameter sections of the nickel capsules were leached with hydrochloric acid to remove tantalum and niobium that precipitated from potassium on cooling to room temperature. The butyl alcohol and hydrochloric acid solutions were combined, and potassium was converted to potassium chloride in the manner described in reference 9. The concentrations of tantalum and niobium in the potassium chloride samples from the experiments using the undoped metals were determined by spectrophotometric analyses (ref. 14). The accuracies of these analyses are estimated to be ±8 percent. Concentrations of tantalum and niobium in potassium chloride samples from the experiments using oxygen-doped metals were determined by X-ray fluorescence analyses. The accuracies of X-ray fluorescence analyses are estimated to be ±10 percent.

Separation of ternary oxides from liquid potassium. - The ternary oxides of potassium-tantalum-oxygen and potassium-niobium-oxygen systems were recovered only in the experiments in which oxygen-doped tantalum and niobium metals were used. These ternary oxides were recovered in the product separation apparatus described by Gahn (ref. 15). From the experiments in which oxygen-doped crucibles were used, selected capsules were transferred to the product separation apparatus and cut open. Potassium heated to 598 K was evaporated from each of the capsules in 2 to 3 hours. Each capsule, now containing only the ternary oxide residue, was put into the transfer chamber of the product separation apparatus and transferred to an argon-filled glove box. In the glove box, some of the ternary oxide residue was put into X-ray capillary tubes for X-ray diffraction analysis. The rest of the ternary oxide residue was put into glass vials to be analyzed for potassium and tantalum or niobium contents.

RESULTS AND DISCUSSION

Apparent Solubilities of Commercially Pure Tantalum and Niobium

The apparent solubilities of commercially pure tantalum and niobium between 1055 and 1287 K were studied in liquid potassium. These apparent solubility data are presented in figures 3 and 4 and in table II. The data in these figures show high reproduci-

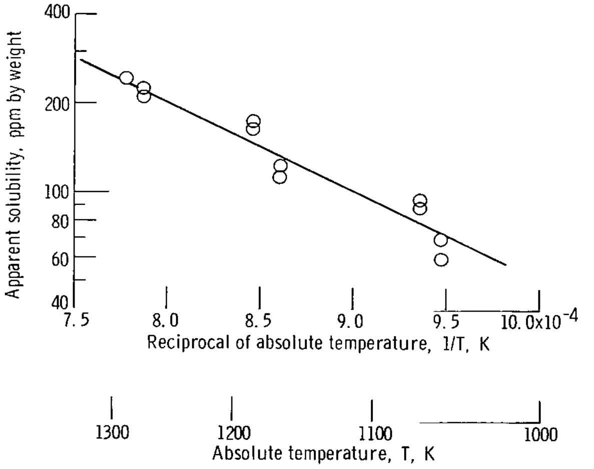


Figure 3. - Apparent solubility of commercially pure tantalum in potassium.

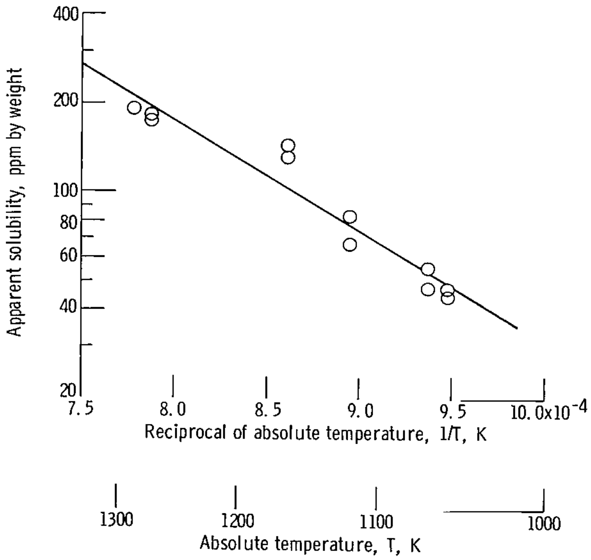


Figure 4. - Apparent solubility of commercially pure niobium in potassium.

TABLE II. - APPARENT SOLUBILITIES OF COMMERCIALLY PRODUCED TANTALUM AND NIOBIUM IN LIQUID POTASSIUM[a]

Temperature, K	Tantalum, ppm by weight	Niobium, ppm by weight
1287	240	191
1271	222	180
1271	211	174
1182	171	---
1182	167	---
1162	122	144
1162	112	130
1117	---	82
1117	---	66
1069	93	55
1069	88	47
1055	69	46
1055	59	44

[a] Data obtained by spectrophotometric analyses.

bility and are described by the relations

$$\left.\begin{aligned} \log \text{ wt ppm Ta} &= 4.75 \pm 0.24 - \frac{3048 \pm 276}{T} \\ \log \text{ wt ppm Nb} &= 5.23 \pm 0.30 - \frac{3739 \pm 343}{T} \end{aligned}\right\} \text{ for 1055 to 1287 K}$$

where T is the absolute temperature. These relations were derived by the least-squares method. The calculated heats of solution for these tantalum and niobium apparent solubilities in pure liquid potassium are 13.9±1.3 and 17.1±1.6 kilocalories per mole (58.2 and 71.5 kJ/mole), respectively.

Experimental solubility data cannot be accepted as true solubility data until it has been established that the experimental values were obtained at equilibrium conditions and that chemical reactions such as those involving interstitial elements did not influence the solution process. Otherwise, the experimental data can only be considered to be apparent solubility data and characteristic of the system used in obtaining the data. I believe that equilibrium conditions were probably established in the solubility study of undoped tantalum and niobium in liquid potassium reported herein. This contention is supported by the following: (1) I believe that the equilibrium conditions in liquid alkali-metal systems are established quite rapidly, probably in less than 4 hours (ref. 16). (2) In this study, tantalum and niobium metals remained in contact with liquid potassium for 24 hours at the desired temperatures. I believe that, even if some of the oxygen present in the tantalum and niobium metals did take part in the solution processes of these metals in liquid potassium, equilibrium conditions were established at the end of 24 hours. However, because of the slight amount of chemical reaction involving oxygen that might have occurred, I consider the tantalum and niobium solubility data presented in this study to be only apparent solubility data.

Data reported during the last 5 years have shown that the effect of oxygen on the solubilities of refractory metals in liquid potassium is very critical (refs. 2, 5, and 8 to 11). The effects of nitrogen and carbon on the solubilities of refractory metals in liquid potassium are believed to be negligible as compared with the effect of oxygen. In this study, the effect of oxygen on the solubilities of tantalum and niobium metals in liquid potassium was evaluated by (1) comparing the values of solubility and heat of solution for tantalum and niobium reported herein with those of other refractory metals, (2) studying the solubilities of tantalum and niobium metals in liquid potassium as a function of oxygen concentration in these metals, and (3) analyzing tantalum and niobium crucibles for oxygen content after exposure to potassium.

The apparent solubility values for tantalum and niobium in liquid potassium reported herein are very high as compared with those of molybdenum and vanadium (refs. 9 and 17). High apparent heats of solution for tantalum (13.9 kcal/mole or 58.2 kJ/mole) and niobium (17.1 kcal/mole or 71.5 kJ/mole) as compared with that of molybdenum (6.7 kcal/mole or 28.0 kJ/mole), suggest that chemical reactions may have occurred in the solution processes of tantalum and niobium in liquid potassium. This indication is further supported by the data presented herein in the following section, Effect of Oxygen. Therefore, I concluded that the tantalum and niobium apparent solubility values presented in figures 3 and 4 were influenced to some extent by the oxygen present in the systems.

It is not known by how much the oxygen increased the concentrations of tantalum and niobium in liquid potassium; however, I believe that the effect of oxygen was probably small. This may be inferred from the data in tables I and III because the oxygen concentrations in tantalum and niobium crucibles decreased only slightly after exposure to liquid potassium. Consequently, the true solubilities of tantalum and niobium in liquid potassium should be somewhat less than the apparent solubilities reported herein for these two metals in potassium between 1055 and 1287 K.

The solubility of tantalum in liquid potassium has previously been studied by McKisson et al. (ref. 6) and by Ginell and Teitel (ref. 7). When these data are compared with those reported in this study (fig. 5), it is apparent that the data presented herein are significantly lower than those presented in reference 6 and that they show better reproducibility than was observed in either of the previous studies. In refer-

TABLE III. - OXYGEN CONCENTRATIONS IN TANTALUM AND NIOBIUM CRUCIBLES AFTER EXPOSURE TO POTASSIUM FOR 24 HOURS[a]

Crucible number	Temperature,[b] K	Oxygen concentration in crucible, ppm by weight
Ta-51	1271	9
Ta-52	1271	10
Ta-60	1069	11
Nb-32	1271	57
Nb-35	1271	57
Nb-31	1162	55
Nb-36	1162	57

[a] Potassium not detected in tantalum and niobium crucibles.

[b] Temperature at which crucible was exposed to potassium.

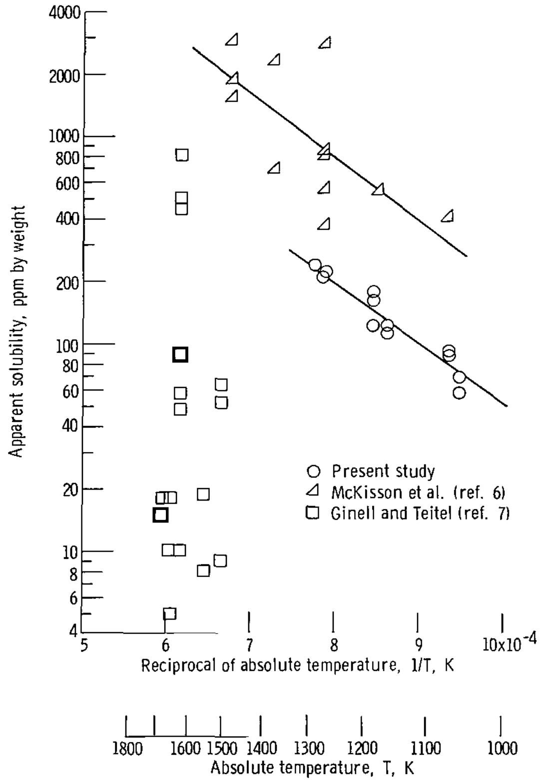


Figure 5. - Comparison of apparent solubility data for tantalum in potassium.

erence 6, the authors calculated the heat of solution for tantalum to be 13.2 kilocalories per mole (55.2 kJ/mole). Their value for the heat of solution is in good agreement with the calculated heat of solution (13.9 kcal/mole or 58.2 kJ/mole) reported in this study; however, I cannot offer a definite explanation for the higher apparent solubility values reported by them or for the very high degree of scatter in the data reported by Ginell and Teitel.

The solubility of niobium was previously studied by Cleary, Blecherman, and Corliss (ref. 5), McKisson et al. (ref. 6), and Ginell and Teitel (ref. 7). The comparison between the data reported in this study and those reported by the aforementioned authors is shown in figure 6. It is apparent that the data reported herein and those reported by Ginell and Teitel show good reproducibility. The data reported by the other authors have extensive scattering.

The solubility values for niobium reported by Ginell and Teitel are very low (fig. 6); however, the heat of solution for niobium in liquid potassium that I calculated from their data is about 54 kilocalories per mole (226 kJ/mole) and not 5.4 kilocalories per mole

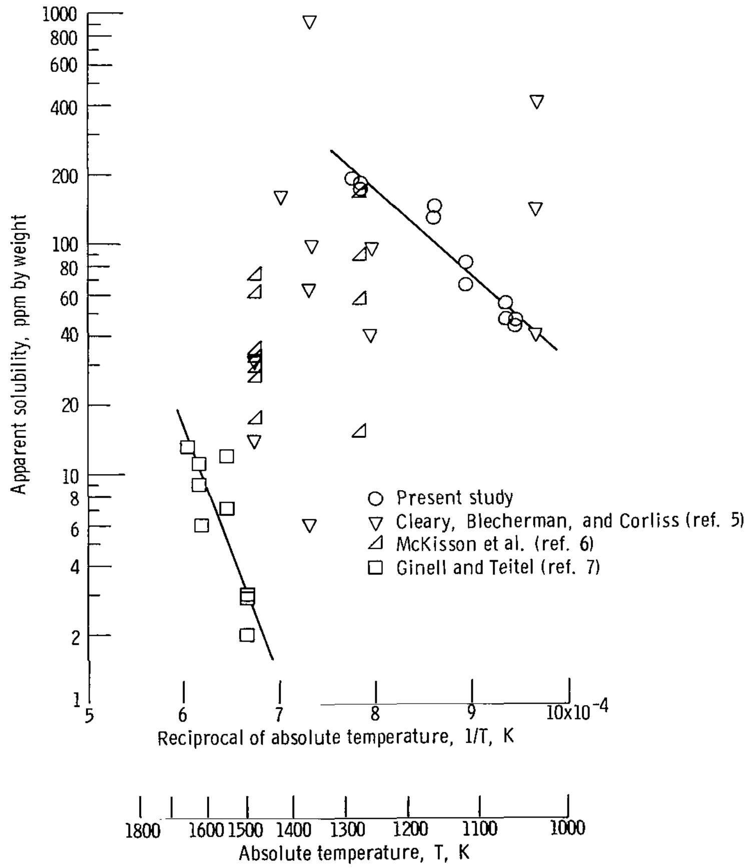


Figure 6. - Comparison of apparent solubility data for niobium in potassium.

(22.6 kJ/mole) as reported by these authors. This very high value for the heat of solution for niobium in liquid potassium would indicate a definite chemical reaction, probably involving oxygen. In addition, I cannot explain why Ginell and Teitel could not obtain the same reproducibility in the tantalum solubility data as they did in the niobium solubility data. I observed a strong similarity in the data for tantalum and niobium in liquid potassium. On the basis of the generally similar chemical behavior of these group V elements, I believe that the behavior observed in this study is more consistent.

Recently, the solubilities in potassium of tantalum from three tantalum alloys and of niobium from two niobium alloys were studied between 1473 and 1890 K by Eichelberger, McKisson, and Johnson (ref. 10). They calculated that the presence of a gettering element, such as zirconium, hafnium, or titanium, in the refractory metal substantially reduces the apparent solubility of refractory metal. The effect was attributed to the strong affinity of the gettering element for oxygen.

Effect of Oxygen

The apparent solubilities of oxygen-doped tantalum and niobium metals between 1063 and 1268 K were studied in liquid potassium containing less than 15 ppm by weight of oxygen. These data are presented in figures 7 and 8 and in tables IV and V. The straight lines in figures 7 and 8 were drawn only to show the relative increases in tantalum and niobium concentrations with an increase in oxygen concentration. No other deduction can be made from these data because equilibrium conditions were not established at the end of 24 hours at the desired temperatures. This is apparent from the data presented in

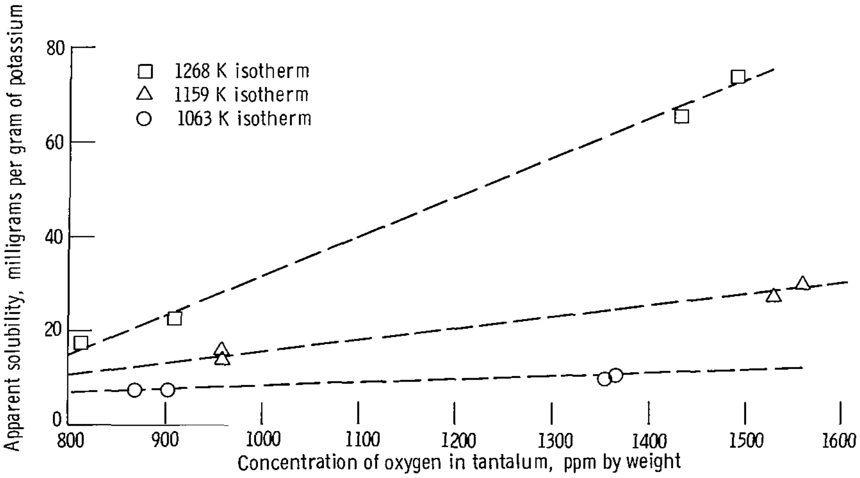


Figure 7. - Apparent solubility of oxygen-doped tantalum in liquid potassium.

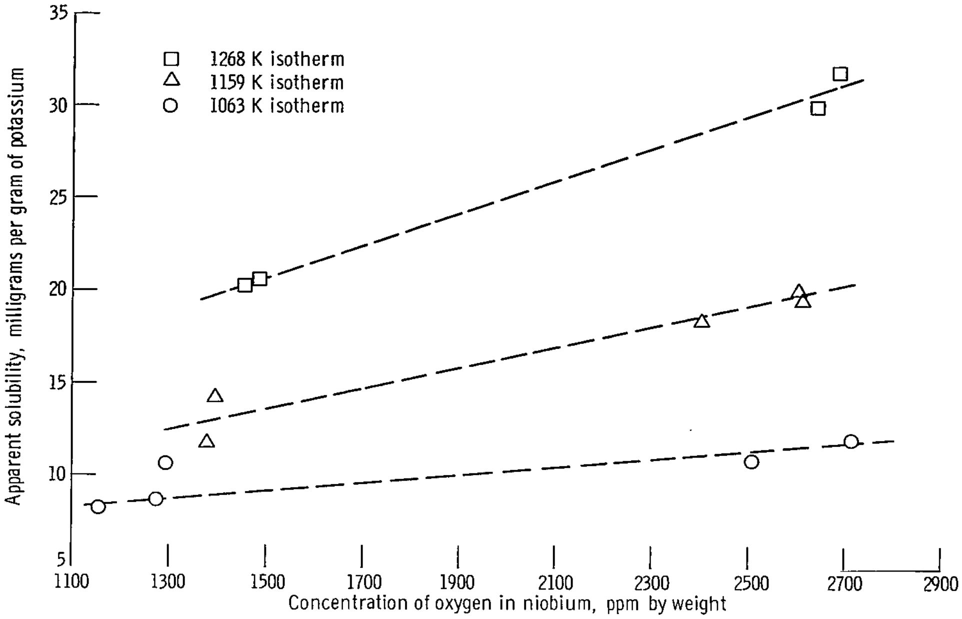


Figure 8. - Apparent solubility of oxygen-doped niobium in liquid potassium.

TABLE IV. - APPARENT SOLUBILITY OF OXYGEN-DOPED TANTALUM IN LIQUID POTASSIUM[a, b]

Temperature, K	Oxygen concentration in crucible, ppm by weight	Weight of crucible, g	Tantalum per gram of potassium, mg
1268	1490	20.8157	74.0
1268	1430	20.5912	65.6
1159	1560	21.1379	30.8
1159	1530	20.7127	27.6
1063	1370	20.6559	10.8
1063	1360	20.9799	10.3
1268	830	20.6495	17.2
1268	920	20.5665	22.6
1159	960	20.4573	13.7
1159	960	20.1572	15.0
1063	900	20.6404	7.6
1063	870	20.2965	7.6

[a] Data obtained by X-ray fluorescense analysis.

[b] Results from oxygen analysis on selected crucibles showed that the oxygen concentration in tantalum crucibles after exposure to potassium decreased very significantly (e.g., for runs at 1268 K, the oxygen concentration was less than 50 ppm by weight).

TABLE V. - APPARENT SOLUBILITY OF OXYGEN-DOPED NIOBIUM IN LIQUID POTASSIUM[a, b]

Temperature, K	Oxygen concentration in crucible, ppm by weight	Weight of crucible, g	Niobium per gram of potassium, mg
1268	2650	10.0662	30.0
1268	2690	10.2040	32.0
1159	2620	9.9992	19.6
1159	2600	9.9247	20.0
1159	2400	10.5911	18.4
1063	2510	10.0057	10.8
1063	2710	10.0495	12.1
1268	1460	9.8866	20.3
1268	1490	10.5967	20.6
1159	1400	10.1105	14.2
1159	1380	9.9981	11.8
1063	1270	10.3104	8.7
1063	1290	10.6234	10.8
1063	1160	10.8259	8.2

[a] Data obtained by X-ray fluorescence analysis.

[b] Results from oxygen analysis on selected crucibles showed that oxygen concentration in niobium crucibles after exposure to potassium decreased very significantly (e.g., for runs at 1268 K, the oxygen concentration was less than 100 ppm by weight).

figure 9, which shows that tantalum and niobium concentrations in liquid potassium were increasing with exposure time, even at the end of 90 hours.

The increases in the concentrations of tantalum and niobium in liquid potassium must be assumed to be due to the diffusion of oxygen from the tantalum and niobium metals. X-ray diffraction patterns were obtained for the tantalum and niobium samples scraped from the inside and outside crucible surfaces that have not been in direct contact with the bulk potassium. The exact locations on the crucibles from which these tantalum and niobium samples were scraped off are shown in figure 10. The recovery of samples from the inside and outside crucible surfaces is described in appendix B. The tantalum samples were recovered from the surfaces of tantalum crucibles that had been doped to oxygen levels between 790 and 2170 ppm by weight and exposed to potassium at temperatures from 1063 to 1328 K for 13 to 96 hours. The niobium samples were recovered from the surfaces of niobium crucibles that had been doped to oxygen levels between 1300 and 4280 ppm by weight and exposed to potassium at temperatures from 1063 to 1328 K for 24 hours. The X-ray diffraction patterns obtained for these tantalum and niobium sam-

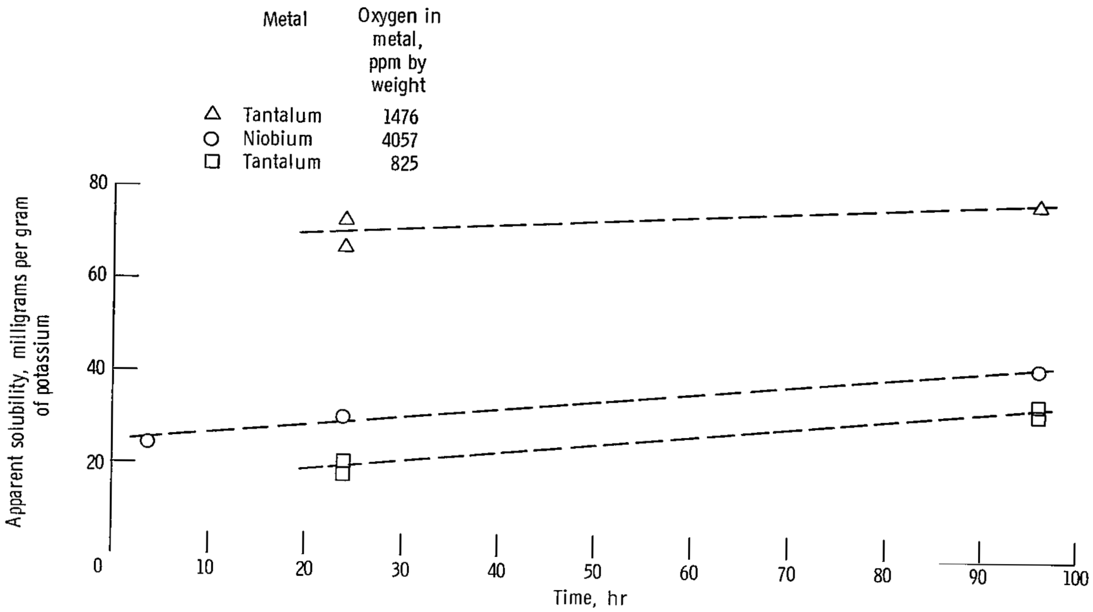


Figure 9. - Apparent solubilities of oxygen-doped tantalum and niobium in potassium with time at 1268 K.

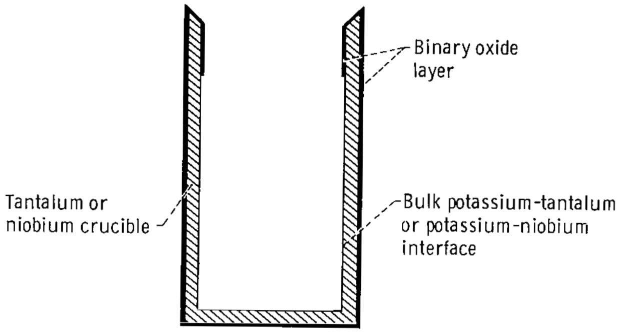


Figure 10. - Cross section of crucible showing location of binary oxides.

ples were indexed according to the crystallographic data for various tantalum and niobium oxides reported in references 18 to 23.

The samples from the tantalum crucibles contained Ta_6O, Ta_4O, Ta_2O, TaO, TaO_2, and Ta_2O_5 oxides. No samples could be recovered from the crucible surfaces that had been in direct contact with the bulk potassium. Visual observation showed that the surface which was in direct contact with bulk potassium was shinier than other surfaces and that no dark film was present.

The samples from the niobium crucibles contained Nb_6O, Nb_4O, Nb_2O, NbO, NbO_2, and Nb_2O_5 oxides. In some niobium samples, $NbO_{(1.64 \text{ to } 1.68)}$ oxide was also found.

Again, an attempt was made but no niobium oxides were recovered from the crucible surfaces that had been in direct contact with the bulk potassium. Visual observation showed that no dark film was present on these surfaces and that these surfaces were shinier than other surfaces that were not in direct contact with bulk potassium. However, it should be apparent that it is likely that the crucibles inside the capsules could have been completely covered by a very thin film of liquid potassium. It can be inferred from these observations that, whenever tantalum or niobium metal is in contact with potassium, oxygen diffuses toward the interface and forms binary oxides. These binary oxides then probably react with potassium to form ternary oxides that dissolve in bulk potassium.

I believe that tantalum and niobium oxides were not detected at the tantalum - bulk potassium and niobium - bulk potassium interfaces because all or some of these oxides reacted with potassium and formed tantalum and niobium ternary oxides, respectively. These ternary oxides then dissolved in liquid potassium. Indeed, such ternary oxides were recovered from liquid potassium. Tantalum ternary oxides were recovered from the experiments in which crucibles containing 840, 1440, and 1930 ppm by weight of oxygen were exposed to liquid potassium at desired temperatures for 24 hours. Niobium ternary oxides were recovered from the experiments in which niobium crucibles containing 2870, 3810, and 4180 ppm by weight of oxygen were exposed to liquid potassium at desired temperatures for 24 hours. The composition of tantalum and niobium ternary oxides was established by chemical analyses, and the results of these analyses are shown in tables VI and VII. The probable compositions of these two ternary oxides are K_3TaO_4

TABLE VI. - ANALYSIS OF POTASSIUM-TANTALUM-OXYGEN TERNARY OXIDE

Sample	Potassium, wt. %	Tantalum, wt. %	Oxygen, wt. %	Weight of ternary oxide, mg	Oxygen in crucible, ppm by weight
Ta-1	31.2	50.2	[a]18.6	[b]70.50	840
Ta-2	31.4	49.1	19.5	103.61	1440
Ta-3	30.6	48.6	21.1	47.44	1930
Ta-4	33.1	51.3	15.6	29.03	1930
Ta-4	31.8	51.8	16.5	21.64	1930
Average	31.6	50.2	18.3	------	----
Theoretical for K_3TaO_4	32.4	50.0	17.7	------	----

[a] Weight of oxygen was determined by weight difference (i.e., weight of ternary oxide minus combined weights of potassium and tantalum determined by wet chemical analyses).

[b] Amount of potassium-tantalum-oxygen ternary oxide analyzed.

TABLE VII. - ANALYSIS OF POTASSIUM-NIOBIUM-OXYGEN TERNARY OXIDE

Sample	Potassium, wt. %	Niobium, wt. %	Oxygen, wt. %	Weight of ternary oxide, mg	Oxygen in crucible, ppm by weight
Nb-1	41.1	36.1	[a]22.8	[b]63.30	2860
Nb-2	41.2	35.5	23.2	66.70	3810
Nb-3	40.3	34.9	24.7	59.52	4170
Nb-3	42.1	34.5	23.3	48.66	4170
Nb-4	41.8	34.6	23.6	68.86	4190
Nb-4	42.8	36.6	20.6	8.93	4190
Average	41.6	35.4	23.0	------	----
Theoretical for K_3NbO_4	42.8	33.9	23.3	------	----

[a] Weight of oxygen was determined by weight difference (i.e., weight of ternary oxide minus combined weights of potassium and niobium determined by wet chemical analyses).

[b] Amount of potassium-niobium-oxygen ternary oxide analyzed.

and K_3NbO_4. In addition, the X-ray diffraction patterns obtained for these two ternary oxides were completely indexed. The indexed X-ray diffraction data (see appendix C) indicate that each tantalum or niobium ternary oxide recovered from liquid potassium consisted of a single compound and not a set of compounds whose total compositions would amount to a 3:1 ratio of potassium to tantalum or niobium.

Proposed Solubility Method

Because oxygen affects the solubilities of tantalum and niobium in liquid potassium, the true solubilities of these metals in liquid potassium cannot be determined by experimental methods such as those described in references 5, 6, and 9. These methods depend on the process of simple solution of solute in solvent. This is not what happens when tantalum and niobium dissolve in liquid potassium in the presence of oxygen. True solubilities for these two metals can only be determined by the process of simple solution of solute in solvent when the effect of oxygen as well as the effects of nitrogen and carbon on the solubilities are reduced to the point where they become truly negligible. I believe that the reduction of the effect of oxygen to such a level would be very difficult if not impossible.

Therefore, I believe that one method by which the true solubilities of tantalum and niobium in liquid potassium can probably be determined is that of studying the rates of solutions of these metals as functions of oxygen concentrations. The data obtained from

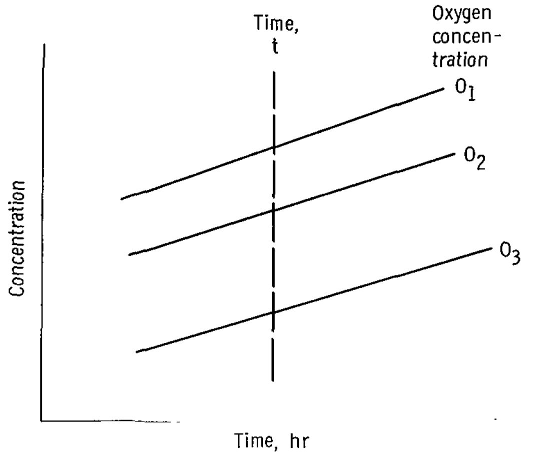


Figure 11. - Apparent solubility of oxygen-doped metal in liquid-alkali metal at temperature T_1.

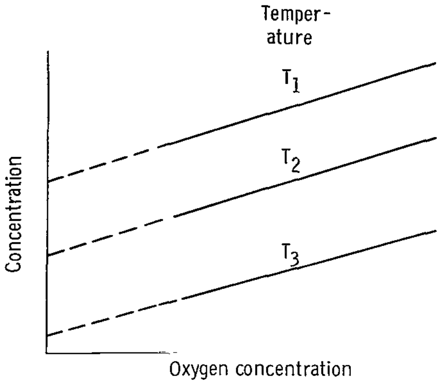


Figure 12. - Apparent solubility of oxygen-doped metal in liquid-alkali metal at time t.

such a study should probably be similar to those in figure 11. At least three sets of such data should be obtained. For example, tantalum containing oxygen concentrations O_1, O_2, and O_3 should be studied at temperatures T_1, T_2, and T_3 for various times. Therefore, three sets of curves similar to those in figure 11 would be obtained. Then, by drawing a line through each set of data at time t (fig. 11), one will obtain isotherms at temperatures T_1, T_2, and T_3 at oxygen concentrations O_1, O_2, and O_3. By plotting these intercept values of t on the graph of tantalum or niobium concentration against oxygen concentration, one can expect to obtain data similar to those in figure 12. When the resulting isotherms in figure 12 are extrapolated to zero oxygen concentration, values can probably be obtained that are either the true solubility values or closer to the true solubility values for tantalum or niobium in pure liquid potassium than can be expected from the more conventional methods that have been used so far (refs. 5 to 7 and 9).

Proposed Corrosion Processes

The observations made in this and previous studies have led me to propose a sequence of processes that I believe explain the sometimes varied and seemingly contradictory results found in the reports on potassium corrosion and solubility studies. This hypothesis is based on the following observations:

(1) This study as well as others (refs. 2, 5, 8, and 24) have shown that tantalum and niobium concentrations in liquid potassium increase when the oxygen contents of the tantalum and niobium are increased. In such cases, the oxygen concentration in the

tantalum and niobium metals has been reduced.

(2) In a like manner, when oxygen concentration in the potassium is increased, concentrations of tantalum and niobium in liquid potassium increase (refs. 2 and 24).

(3) Tantalum and niobium ternary oxides have been recovered from the liquid potassium (this study and ref. 8).

(4) Tantalum and niobium binary oxides have been recovered from the metal surfaces after exposure to potassium at high temperatures (this study and ref. 2).

The observations stated in points 1, 2, and 3 suggest, as has been previously proposed, that tantalum (or niobium), potassium, and oxygen somehow react at the metal-liquid interface to form a ternary oxide that dissolves in the potassium. The only thermodynamic requirement for such a reaction is that the free energy of formation for the ternary oxide be more negative than either of the binary oxides.

However, the presence of a binary oxide on the surface of tantalum or niobium after exposure to potassium injects an apparent thermodynamic anomaly that must be explained. It is apparent from points 1, 2, and 3 that oxygen must diffuse both within the solid metal and within the liquid potassium toward the solid-liquid interface. The proposed lower free energy of formation for the ternary oxide can explain this increase in the concentration of tantalum or niobium in liquid potassium, but it cannot explain the presence of tantalum or niobium binary oxides. Furthermore, on the basis of free energies of formation for tantalum, niobium, and potassium oxides and/or the free energy of oxygen solution in these metals (refs. 2, 25, and 26), oxygen should not diffuse out of tantalum or niobium toward the interface.

I propose that the real driving force is provided, not by the low free energies of formation for the ternary oxides, but by the lowering of the free energies of formation for the tantalum and niobium binary oxides at the interface. This lowering of free energies at the interface is due to a surface interaction energy at the tantalum- or niobium-potassium interface. Therefore, the binary oxides are formed first, and then they react with potassium to form ternary oxides at the interface. Ternary oxides then dissolve in liquid potassium.

Therefore, it is proposed that the corrosion (or apparent solubility) of tantalum or niobium in potassium in the presence of oxygen can probably be described by this sequence of events. Immediately on exposure of tantalum or niobium to potassium, the interaction at the interface between tantalum (or niobium) and potassium lowers the free energy of formation of the tantalum oxides (or niobium oxides), thus setting up oxygen activity gradients within the tantalum (or niobium) and potassium. These activity gradients are the driving force for oxygen diffusion toward the interface. On arrival at the interface, the oxygen combines with tantalum or niobium to form a tantalum or niobium binary oxide. These binary oxides then probably react with potassium, and possibly with additional oxygen arriving at the interface, to form the ternary oxides. The ternary oxide then dissolves in liquid potassium, thereby preventing its accumulation at the interface. In locations where there is no bulk liquid potassium, a buildup of tantalum or niobium oxides could be expected, which should result in a layered sequence of oxides typical of a metal-oxygen diffusion couple. Effective removal of these oxides could not be accomplished since there was no bulk potassium with which they could react. Indeed, as pointed out in this study in the section Effect of Oxygen, tantalum and niobium oxides of various stoichiometries have been recovered.

The basic requirement for this sequence to occur would be a lowering of the free energies of formation of tantalum or niobium oxides at the tantalum- or niobium-potassium interface due to an interaction of tantalum or niobium with potassium. Unfortunately, this interaction energy at the tantalum- or niobium-potassium interface cannot be calculated because no surface tension data are known to be available for these two systems. Such an interaction could satisfactorily account for the diffusion of oxygen out of potassium and tantalum or niobium toward the interface. The recovery of tantalum and niobium oxides from the crucible surfaces and also the recovery of tantalum and niobium ternary oxides from potassium tend to suggest that elemental or ionic oxygen in these metals was probably not transferred directly to the potassium. Oxygen probably is transferred to potassium as a part of a compound that is formed at the interface and then is dissolved in potassium.

CONCLUDING REMARKS

The apparent solubilities and the effect of oxygen on the apparent solubilities of tantalum (Ta) and niobium (Nb) were studied between 1055 and 1287 K in liquid potassium. The potassium used in all the experiments performed in this study contained less than 15 ppm by weight of oxygen.

The true solubilities of tantalum and niobium in liquid potassium cannot be determined by experimental methods that depend on the process of simple solution of solute in solvent. Therefore, I was only able to obtain the apparent solubility values for tantalum and niobium in liquid potassium. However, I believe that the oxygen effect on the apparent solubility values reported herein was small. Therefore, the true solubility values for tantalum and niobium in liquid potassium should be somewhat lower than those reported in this study. The apparent solubilities of tantalum and niobium between 1055 and 1287 K can be represented by the relations: $\log \text{wt ppm Ta} = (4.75 \pm 0.24) - (3048 \pm 276)/T$ and $\log \text{wt ppm Nb} = (5.23 \pm 0.30) - (3739 \pm 343)/T$, respectively. The apparent heats of solution for tantalum and niobium in liquid potassium are 13.9±1.3 and 17.1±1.6 kilocalories per mole (58.2 and 71.5 kJ/mole), respectively.

Tantalum and niobium concentrations in liquid potassium increase with the increase of oxygen concentrations in these two metals. From the available data, I have inferred the following sequence of events to explain the observations reported herein and those previously reported by others: (a) the diffusion of oxygen out of tantalum and niobium metals and potassium toward the tantalum- and niobium-potassium interfaces, (b) the formation of tantalum and niobium binary oxides at the interface, (c) the reaction of these binary oxides with potassium to form ternary oxides, and (d) the dissolution of these ternary oxides in liquid potassium.

Tantalum and niobium binary oxides were recovered from the metal surfaces that were not in contact with bulk liquid potassium. Tantalum and niobium ternary oxides were recovered from liquid potassium and identified by chemical analyses to be K_3TaO_4 and K_3NbO_4, respectively. X-ray diffraction patterns for both of these ternary oxides were completely indexed.

I believe that a more accurate method of obtaining the true solubility data for tantalum and niobium in liquid potassium is that of studying the kinetics of the solution as a function of oxygen concentration.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 21, 1970,
129-03.

APPENDIX A

PREPARATION OF CRUCIBLES AND CAPSULES

The tantalum and niobium crucibles and nickel capsules were ultrasonically cleaned in a fluorinated hydrocarbon and then ultrasonically cleaned in a detergent. Subsequent cleaning procedures for crucibles or capsules of each metal were different and are described in the following sections.

Tantalum

Tantalum crucibles, after being rinsed with distilled water, were etched for 2 to 5 seconds at room temperature. The etchant solution was 55 parts concentrated sulfuric acid, 25 parts of 70-percent-by-weight nitric acid, and 20 parts of 49-percent-by-weight hydrofluoric acid. Finally, the crucibles were rinsed several times with distilled water and dried under vacuum.

Niobium

Niobium crucibles, after being rinsed with distilled water, were placed into 49-percent-by-weight hydrofluoric acid for 2 to 5 minutes at room temperature until the metal started to wet. The crucibles were then etched for 1 to 2 minutes at room temperature. The etchant solution was 20 parts of 49-percent-by-weight hydrofluoric acid, 20 parts of 70-percent-by-weight nitric acid, and 60 parts distilled water. Finally, the crucibles were rinsed several times with distilled water and dried under vacuum.

Nickel

Nickel capsules, after being rinsed several times with distilled water, were etched at 363 K for 1/2 to 1 minute. The etchant solution was 30 parts of 70-percent-by-weight nitric acid, 10 parts of concentrated orthophosphoric acid, 10 parts of concentrated sulfuric acid, and 50 parts of glacial acetic acid. The capsules were rinsed several times with distilled water and dried under vacuum.

APPENDIX B

RECOVERY OF OXIDE FILM SAMPLES FROM SURFACES OF OXYGEN-DOPED CRUCIBLES AFTER TESTING

Samples for X-ray diffraction analyses were recovered from outside and inside surfaces of tantalum and niobium crucibles. These surfaces had not been in contact with bulk liquid potassium during testing. When the capsules were opened, the crucibles were removed and placed in absolute ethyl alcohol for about 5 minutes. Only crucibles that contained little or no potassium, as confirmed by the presence of little or no reaction with absolute ethyl alcohol, were used for oxide film recovery.

The crucibles were then transferred to glass vials containing distilled water and were left there for 30 to 40 minutes to dissolve any potassium tantalate or potassium niobate that might have been present on the walls of the crucibles. The crucibles were rinsed several times with distilled water and again put into vials containing absolute ethyl alcohol. After about a 30-minute soaking, the crucibles were rinsed several times with absolute ethyl alcohol and then several times with acetone.

The outer and inner walls of the crucibles were scraped with a spatula. The resulting samples were put into X-ray capillary tubes, and X-ray diffraction patterns were obtained using Cu K_{α} radiation.

APPENDIX C

CRYSTALLOGRAPHIC MODIFICATIONS OF K_3TaO_4 AND K_3NbO_4

Tantalum and niobium ternary oxides were prepared by exposing oxygen-doped tantalum and niobium metals to potassium at desired temperatures for 24 hours. The ternary oxides were separated from excess potassium at 598 K in a product separation apparatus described by Gahn (ref. 15). The composition of these ternary oxides was determined by chemical analyses, and the data are presented in tables VI and VII. The recovered tantalum and niobium ternary oxides were K_3TaO_4 and K_3NbO_4, respectively. The same ternary oxide for tantalum was recovered from potassium by Hickam (ref. 8). Hickam also obtained an X-ray diffraction pattern but did not index it. This pattern is in very good agreement with the X-ray diffraction data obtained in this study (table VIII). Tantalum ternary oxide (K_3TaO_4) was previously also prepared by Reisman et al. (ref. 27) in a differential thermogravimetric apparatus. Their partial and un-indexed X-ray diffraction data for K_3TaO_4 are in very good agreement with the data obtained in this study (table VIII). Niobium ternary oxide (K_3NbO_4) was previously prepared by Guerchais in a thermogravimetric apparatus (ref. 28). These partial and un-indexed X-ray diffraction data are also in very good agreement with the data obtained in this study (table IX).

Although all these workers reported tantalum or niobium ternary oxides, they did not index their X-ray diffraction patterns in order to establish that their X-ray data were obtained for pure compounds. It is possible that two or more ternary oxides or even potassium oxide and tantalum or niobium oxides could be present in such a ratio that the results of chemical analyses would tend to confirm a 3:1 ratio of potassium to tantalum or potassium to niobium found in K_3TaO_4 or K_3NbO_4. It is because of this uncertainty that I have decided to index the X-ray diffraction data obtained in this study.

The X-ray diffraction data obtained in this study for tantalum and niobium ternary oxides were indexed by the Hesse-Lipson procedure and also by Ito's methods (ref. 29). The indexed X-ray diffraction data are presented in tables X and XI. All experimental d-spacing values for K_3TaO_4 and K_3NbO_4 were indexed. Both of these ternary oxides belong to the orthorhombic system. The lattice parameter values for K_3TaO_4 are a, 14.19±0.05 Å; b, 17.04±0.06 Å; and c, 12.41±0.04 Å. The lattice parameter values for K_3NbO_4 are a, 12.05±0.04 Å; b, 14.34±0.05 Å; and c, 10.50±0.03 Å.

On the basis of the complete indexing of X-ray diffraction data, the ternary oxides for tantalum and niobium recovered in this study can be considered to be single compounds that probably contain minor amounts of impurities that were not detected. It can further safely be assumed that the X-ray diffraction data reported in references 8, 26, and 27 were also single compounds with minor amounts of impurities.

TABLE VIII. - COMPARISON OF X-RAY DIFFRACTION PATTERNS FOR TANTALUM TERNARY OXIDE (K_3TaO_4)

Present study	Hickam (ref. 8)	Reisman et al. (ref. 27)
Interplanar distance, d, Å		
9.35	-----	----
8.50	-----	----
7.10	7.3	----
6.32	6.5	6.36
6.21	-----	6.10
5.82	6.0	5.96
5.27	5.4	5.32
5.02	5.1	5.03
4.68	-----	4.61
4.27	4.27	4.27
4.18	4.15	4.13
4.09	-----	----
4.02	-----	4.02
3.966	-----	3.92
3.872	-----	----
3.686	3.72	3.73
3.594	-----	----
3.545	3.53	3.54
3.510	-----	----
3.336	3.37	----
3.270	3.20	----
3.140	-----	3.18
3.025	3.06	3.06
2.981	2.99	2.99
2.891	2.87	2.88
2.842	2.79	2.81
2.765	2.74	----
2.673	-----	----
2.631	-----	----
2.627	-----	----
2.550	2.56	2.56
2.494	2.48	----
2.399	2.40	2.40
2.366	-----	----
2.300	2.27	----
2.207	2.22	----
2.167	2.17	----
2.152	-----	----
2.111	2.12	----
2.032	2.07	----
2.006	2.01	----
1.981	1.992	----
1.947	1.951	----
1.919	1.920	----
-----	1.897	----
[a]1.881	[b]1.883	1.88

[a] Plus many additional lines below 1.881 Å.

[b] Plus 70 additional lines below 1.883 Å.

TABLE IX. - COMPARISON OF X-RAY DIFFRACTION PATTERNS FOR NIOBIUM TERNARY OXIDE (K_3NbO_4)

Present study	Guerchais (ref. 28)	Present study	Guerchais (ref. 28)
Interplanar distance, d, Å		Interplanar distance, d, Å	
7.88	----	2.019	----
7.16	----	1.998	----
6.02	----	1.977	1.98
4.91	4.98	1.950	----
4.45	4.31	1.924	----
3.95	4.04	1.908	----
3.863	----	1.874	----
3.521	----	1.826	----
3.264	----	1.802	----
3.118	----	1.783	----
3.009	3.04	1.763	1.76
2.957	----	1.740	----
2.829	2.84	1.701	----
2.773	----	1.636	1.66
2.660	----	1.572	----
2.631	----	1.547	----
2.612	2.60	1.531	1.52
2.556	----	1.507	----
2.520	----	1.487	----
2.450	----	1.476	----
2.409	----	1.459	----
2.346	2.34	1.450	----
2.331	----	1.432	1.44
2.304	----	1.411	----
2.283	----	1.394	----
2.228	----	1.387	----
2.177	2.16	1.377	----
2.132	----	[a]1.343	1.36
2.083	----		

[a] Plus many additional lines below 1.343 Å.

TABLE X. - X-RAY DIFFRACTION PATTERN FOR POTASSIUM TANTALATE (K_3TaO_4)[a]

hkl	d-Spacing, Å	Intensity	Lattice parameter, Å			hkl	d-Spacing, Å	Intensity	Lattice parameter, Å		
			a	b	c				a	b	c
101	9.35	10	14.2	-----	12.4	422	2.891	8	14.17	17.02	12.39
020	8.50	3	-----	17.0	-----	204	2.842	8	14.19	17.04	12.41
200	7.10	3	14.2	-----	-----	501	2.765	1	14.18	-----	12.40
121	6.32	2	14.3	17.1	12.4	134	2.673	3	14.18	17.03	12.40
002	6.21	2	----	-----	12.4	521	2.631	1	14.18	17.04	12.41
211	5.82	2	14.2	17.1	12.4	053	2.627	2	-----	17.02	12.39
130	5.27	4	14.2	17.0	-----	512	2.550	4	14.17	17.02	12.39
022	5.02	6	-----	17.0	12.4	442	2.494	1	14.18	17.03	12.39
202	4.68	2	14.2	-----	12.4	170	2.399	7	14.19	17.04	-----
040	4.27	2	-----	17.1	-----	600	2.366	<1	14.20	-----	-----
231	4.18	1	14.2	17.1	12.4	244	2.366	<1	14.20	17.05	12.42
222	4.09	↓	14.2	17.0	12.4	611	2.300	3	14.18	17.03	12.40
013	4.02		-----	17.0	12.4	602	2.207	2	14.17	-----	12.39
103	3.966		14.17	-----	12.39	235	2.167	1	14.20	17.05	12.42
141	3.872		14.17	17.02	12.40	631	2.152	<1	14.20	17.06	12.42
330	3.686	6	14.19	17.05	-----	453	2.111	<1	14.18	17.03	12.40
123	3.594	1	14.17	17.02	12.39	116	2.032	2	14.19	17.04	12.41
400	3.545	1	14.18	-----	-----	055	2.006	1	-----	17.04	12.41
042	3.510	1	-----	17.03	12.40	561	1.981	<1	14.19	17.04	12.41
411	3.336	2	14.16	17.00	12.38	721	1.947	1	14.18	17.03	12.39
420	3.270	1	14.17	17.02	-----	651	1.919	<1	14.19	17.04	12.41
332	3.140	1	14.21	17.06	12.42	604	1.881	1	14.19	-----	12.41
233	3.025	7	14.19	17.04	12.41	624	1.838	2	14.20	17.06	12.42
114	2.981	5	14.17	17.03	12.40	703	1.818	1	14.18	-----	12.39

[a] Lattice parameters calculated by plotting a, b, and c values against $\cos^2\theta$ and extrapolating to 90° are a, 14.19±0.05 Å; b, 17.04±0.06 Å; c, 12.41±0.04 Å. X-ray diffraction pattern was obtained by using Cu K_α radiation and nickel filter.

TABLE X. - Concluded. X-RAY DIFFRACTION PATTERN FOR POTASSIUM TANTALATE (K_3TaO_4)[a]

hkl	d-Spacing, Å	Intensity	Lattice parameter, Å			hkl	d-Spacing, Å	Intensity	Lattice parameter, Å		
			a	b	c				a	b	c
563	1.807	2	14.20	17.06	12.42	815	1.437	<1	14.19	17.05	12.41
406	1.788	2	14.20	-----	12.42	10, 0, 0	1.419	↓	14.19	-----	-----
800	1.775	2	14.20	-----	-----	408	1.419	↓	14.17	-----	12.39
455	1.745	4	14.17	17.03	12.40	158	1.406	↓	14.20	17.05	12.42
662	1.745	4	14.19	17.05	12.41	765	1.374	↓	14.19	17.04	12.41
811	1.745	4	14.17	17.03	12.40	019	1.374	↓	-----	17.05	12.41
820	1.734	1	14.17	17.02	-----	068	1.361	↓	-----	17.05	12.40
802	1.705	<1	14.19	-----	12.41	925	1.314	2	14.18	17.04	12.41
714	1.691	2	14.21	17.07	12.43	747	1.272	1	14.18	17.04	12.40
037	1.691	2	-----	17.03	12.40	464	1.272	1	14.20	17.05	12.42
066	1.670	<1	-----	17.03	12.40	288	1.235	<1	14.19	17.04	12.41
822	1.670	<1	14.17	17.02	12.40	10, 4, 4	1.235	<1	14.19	17.04	12.41
734	1.625	1	14.18	17.03	12.40	079	1.198	2	-----	17.02	12.39
813	1.625	↓	14.20	17.06	12.43	369	1.198	2	14.17	17.02	12.39
842	1.583	↓	14.19	17.04	12.40	709	1.141	1	14.20	-----	12.42
851	1.561	↓	14.19	17.04	12.41	729	1.130	1	14.18	17.03	12.40
028	1.524	2	-----	17.02	12.40	877	1.115	<1	14.20	17.05	12.41
208	1.514	2	14.18	-----	12.40	938	1.085	1	14.18	17.03	12.40
824	1.514	2	14.18	17.03	12.40	839	1.068	1	14.18	17.03	12.39
086	1.485	<1	-----	17.05	12.42	859	1.037	<1	14.18	17.04	12.40
646	1.461	1	14.17	17.02	12.40	949	1.008	<1	14.19	17.04	12.41

[a] Lattice parameters calculated by plotting a, b, and c values against $\cos^2\theta$ and extrapolating to 90° are a, 14.19±0.05 Å; b, 17.04±0.06 Å; c, 12.41±0.04 Å. X-ray diffraction pattern was obtained by using Cu K_α radiation and nickel filter.

TABLE XI. - X-RAY DIFFRACTION PATTERN FOR POTASSIUM NIOBATE (K_3NbO_4)[a]

hkl	d-Spacing, Å	Intensity	Lattice parameter, Å			hkl	d-Spacing, Å	Intensity	Lattice parameter, Å		
			a	b	c				a	b	c
101	7.88	10	12.0	-----	10.5	440	2.304	2	12.04	14.33	-----
020	7.16	5	-----	14.3	-----	224	2.283	3	12.05	14.34	10.51
200	6.02	2	12.0	-----	-----	521	2.228	7	12.03	14.32	10.49
211	4.91	6	12.0	14.3	10.5	062	2.177	2	-----	14.35	10.51
130	4.45	2	12.1	14.4	-----	352	2.132	1	12.04	14.34	10.50
202	3.95	1	12.0	-----	10.5	253	2.083	3	12.05	14.35	10.51
310	3.863	4	12.04	14.33	-----	170	2.019	1	12.05	14.34	-----
231	3.521	2	12.03	14.31	12.49	244	1.998	1	12.05	14.33	10.50
141	3.264	6	12.04	14.33	10.50	334	1.998	1	12.05	14.34	10.51
312	3.118	6	12.06	14.36	10.52	404	1.977	4	12.03	-----	10.50
400	3.009	10	12.04	-----	-----	611	1.950	2	12.03	14.31	10.49
042	2.957	10	-----	14.32	10.49	035	1.924	1	-----	14.34	10.51
033	2.829	5	-----	14.36	10.52	424	1.908	2	12.05	14.35	10.50
420	2.773	3	12.03	14.31	-----	602	1.874	│	12.04	-----	10.50
242	2.660	2	12.06	14.35	10.52	631	1.826	│	12.07	14.36	10.52
004	2.631	4	-----	-----	10.52	325	1.802	↓	12.05	14.34	10.50
402	2.612	3	12.04	-----	10.50	453	1.783	6	12.02	14.31	10.49
233	2.556	1	12.04	14.33	10.50	514	1.763	1	12.06	14.35	10.51
114	2.520	<1	12.02	14.30	10.48	552	1.740	1	12.04	14.34	10.50
424	2.450	2	12.02	14.31	10.49	026	1.701	3	-----	14.34	10.51
204	2.409	3	12.05	-----	10.51	701	1.701	3	12.07	-----	10.52
501	2.346	3	12.03	-----	10.50	226	1.636	2	12.04	14.33	10.50
350	2.331	3	12.03	14.32	-----	046	1.572	3	-----	14.32	10.49

[a] Lattice parameters calculated by plotting a, b, and c values against $\cos^2\theta$ and extrapolating to 90° are a, 12.05±0.04 Å; b, 14.34±0.05 Å; c, 10.50±0.03 Å. X-ray diffraction pattern was obtained by using Cu K_α radiation and nickel filter.

TABLE XI. - Concluded. X-RAY DIFFRACTION PATTERN FOR POTASSIUM NIOBATE (K_3NbO_4)[a]

hkl	d-Spacing, Å	Intensity	Lattice parameter, Å			hkl	d-Spacing, Å	Intensity	Lattice parameter, Å		
			a	b	c				a	b	c
732	1.547	1	12.05	14.34	10.51	930	1.287	1	12.03	14.32	-----
703	1.547	↓	12.07	-----	10.53	754	1.287	↓	12.05	14.35	10.51
741	1.531	↓	12.02	14.30	10.48	772	1.278	↓	12.04	14.33	10.50
800	1.507	↓	12.06	-----	-----	466	1.278	↓	12.04	14.33	10.50
554	1.507	↓	12.02	14.31	10.49	376	1.262	2	12.04	14.33	10.50
723	1.507	↓	12.02	14.31	10.48	228	1.262	2	12.04	14.33	10.50
653	1.487	↓	12.03	14.32	10.49	853	1.244	1	12.03	14.32	10.49
455	1.476	2	12.04	12.33	10.50	048	1.234	2	-----	14.34	10.51
820	1.476	2	12.07	14.36	-----	338	1.207	1	12.04	14.33	10.50
750	1.476	2	12.05	14.34	-----	952	1.183	↓	12.05	14.35	10.51
644	1.459	1	12.06	14.35	10.52	774	1.177	↓	12.04	14.33	10.50
127	1.459	1	12.05	14.34	10.51	019	1.165	↓	-----	14.36	10.52
545	1.450	1	12.06	14.37	10.52	961	1.160	↓	12.04	14.33	10.50
037	1.432	<1	-----	14.35	10.51	219	1.142	<1	12.04	14.33	10.50
831	1.423	<1	12.04	14.35	10.51	806	1.142	<1	12.05	-----	10.51
066	1.411	2	-----	14.33	10.50	855	1.124	2	12.03	14.32	10.49
724	1.411	2	12.05	14.34	10.51	963	1.108	1	12.05	14.35	10.51
466	1.394	1	12.04	14.33	10.50	954	1.101	1	12.04	14.34	10.50
635	1.387	↓	12.03	14.32	10.49	972	1.095	1	12.04	14.33	10.50
840	1.387	↓	12.04	14.33	-----	846	1.087	<1	12.04	14.34	10.50
734	1.377	↓	12.04	14.33	10.50	747	1.079	↓	12.04	14.34	10.50
813	1.377	↓	12.05	14.34	10.51	916	1.062	↓	12.06	14.36	10.52
842	1.343	<1	12.05	14.34	10.51	776	1.052	↓	12.04	14.32	10.50
851	1.322	1	12.04	14.34	10.50	718	1.041	↓	12.04	14.33	10.50
664	1.322	1	12.01	14.29	10.47	837	1.037	1	12.03	14.32	10.49
804	1.306	2	12.04	-----	10.50	738	1.020	1	12.04	14.34	10.50
118	1.300	2	12.04	12.34	10.50						

[a] Lattice parameters calculated by plotting a, b, and c values against $\cos^2\theta$ and extrapolating to 90° are a, 12.05±0.04 Å; b, 14.34±0.05 Å; c, 10.50±0.03 Å. X-ray diffraction pattern was obtained by using Cu K_α radiation and nickel filter.

REFERENCES

1. Anon.: Space Power Systems Advanced Technology Conference. NASA SP-131, 1966.
2. Litman, Arnold, P.: The Effect of Oxygen on the Corrosion of Niobium by Liquid Potassium. Rep. ORNL-3751, Oak Ridge National Lab., July 1965.
3. Scheuermann, Coulson M.; and Barrett, Charles A.: Compatibility of Columbium and Tantalum Tubing Alloys with Refluxing Potassium. NASA TN D-3429, 1966.
4. Jansen, D. H.; and Hoffman, E. E.: Niobium-1%Zirconium, Natural-Circulation, Boiling-Potassium Corrosion Loop Test. Rep. ORNL-3603, Oak Ridge National Lab., May 1964.
5. Cleary, R. E.; Blecherman, S. S.; and Corliss, J. E.: Solubility of Refractory Metals in Lithium and Potassium. Rep. TIM-850, Pratt & Whitney Aircraft, Nov. 1965.
6. McKisson, R. L. et al.: Solubility Studies of Ultra Pure Transition Elements in Ultra Pure Alkali Metals. NASA CR-610, 1966.
7. Ginell, W. S.; and Teitel, R. J.: Determination of the Solubility of Transition Metals in Molten Potassium. Rep. SM-48883, Douglas Aircraft Co., Dec. 1965.
8. Hickam, C. William, Jr.: Corrosion Product of the Tantalum-Interstitial Oxygen-Potassium System at 1800° F (1255° K). NASA TN D-4213, 1967.
9. Stecura, Stephan: Solubilities of Vanadium, Titanium, and Zirconium in Liquid Potassium. NASA TN D-5093, 1969.
10. Eichelberger, R. L.; McKisson, R. L.; and Johnson, B. G.: Solubility of Refractory Metals and Alloys in Potassium and in Lithium. NASA CR-1371, 1969.
11. Swisher, James H.: Solubility of Iron, Nickel, and Cobalt in Liquid Potassium and Effect of Oxygen Gettering Agents on Iron Solubility. NASA TN D-2734, 1965.
12. Kallmann, Silve; Hobart, Everett W.; Oberthin, Hans K.; and Brienza, Walter C., Jr.: Determination of Traces of Nitrogen in Refractory Metals and Alloys by Hydrofluoric Acid - Phosphoric Acid - Potassium Dichromate Decomposition and Indophenol Photometry. Anal. Chem., vol. 40, no. 2, Feb. 1968, pp. 332-335.
13. Barrett, Charles A.: Controlled Oxygen Additions to Refractory Metals. NASA TM X-1799, 1969.
14. Kolthoff, I. M.; and Elving, Philip J., eds.: Treatise on Analytical Chemistry. Part II, Vol. 6. Interscience Publ., 1964.

15. Gahn, Randall F.: Technique for Recovery of Alkali-Metal Reaction Products. NASA TN D-4310, 1968.

16. Kovacina, T. A.; and Miller, R. R.: The Solubility of Nickel in Sodium by a Tracer Technique. Nucl. Sci. Eng., vol. 10, no. 2, June 1961, pp. 163-166.

17. Stecura, Stephan: Solubilities of Molybdenum and Tungsten in Liquid Potassium. NASA TN D-5504, 1969.

18. Lehovec, K.: Lattice Structure of β-Ta_2O_5. J. Less-Common Metals, vol. 7, no. 6, Dec. 1964, pp. 397-410.

19. Brauer, G.; Müller, Horst; und Kühner, G.: Oxide der Tieftemperaturoxydation von Niob und Tantal. J. Less-Common Metals, vol. 4, no. 6, Dec. 1962, pp. 533-546.

20. Norman, N.: Metallic Oxide Phases of Niobium and Tantalum. I. X-ray Investigations. J. Less-Common Metals, vol. 4, no. 1, Feb. 1962, pp. 52-61.

21. Lapitskii, A. V.; Simanov, Y. P.; and Artamonova, E. P.: The Formation of Lower Oxides of Niobium and Tantalum in Some Reactions of Reduction and Oxidation. Russ. J. Inorg. Chem., vol. 2, no. 1, 1957, pp. 122-141.

22. Klechkovskaya, V. V.; Troitskaya, N. V.; and Pinsker, Z. G.: Electron Diffraction Study of One of the Cubic Oxides of Niobium. Soviet Phys. Crystall., vol. 10, no. 1, July-Aug. 1965, pp. 28-35.

23. Steeb, Siegfried; and Renner, Jörg: Ermittlung der Struktur von Niobsuboxid (Nb_4O) mit Elektronenbeugung. Z. Metallkde, vol. 56, no. 8, 1965, pp. 531-534.

24. Patriarca, P.; and Harms, W. O., Comps.: Fuels and Materials Development Program, Quarterly Progress Report for Period Ending June 30, 1968. Rep. ORNL-4330, Oak Ridge National Lab., Nov. 1968, pp. 142-146.

25. Wicks, C. E.; and Block, F. E.: Thermodynamic Properties of 65 Elements - Their Oxides, Halides, Carbides, and Nitrides. Bulletin 605, Bureau of Mines, Department of Interior, 1963.

26. Glassner, Alvin: The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500° K. Rep. ANL-5650, Argonne National Lab., 1957.

27. Reisman, Arnold; Holtzberg, Frederic; Berkenblit, Melvin; and Berry, Margaret: Reactions of the Group VB Pentoxides with Alkali Oxides and Carbonates. III. Thermal and X-ray Phase Diagrams of the System K_2O or K_2CO_3 with Ta_2O_5. J. Am. Chem. Soc., vol. 78, no. 18, Sept. 20, 1956, pp. 4514-4520.

28. Guerchais, Jacques E.: Reactions Entre L'oxyde de Niobium et le Carbonate de Potassium par Voie Seche; Hydrolyse des Produits Obtenus (III). Societe Chimique de France, Bulletin 1962, pp. 103-107.

29. Azároff, Leonid V.; and Buerger, Martin J.: The Powder Method in X-ray Crystallography. McGraw-Hill Book Co., Inc., 1958.

NASA-Langley, 1970 —— 17 E-5615

> *"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."*
>
> —NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Notes, and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546