NASA TECHNICAL NOTE

NASA TN D-4310

c.1

NASA TN D-4310

TECHNIQUE FOR RECOVERY OF ALKALI-METAL REACTION PRODUCTS

by Randall F. Gahn
Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JANUARY 1968

TECHNIQUE FOR RECOVERY OF ALKALI-METAL REACTION PRODUCTS

By Randall F. Gahn

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 – CFSTI price $3.00

TECHNIQUE FOR RECOVERY OF ALKALI-METAL REACTION PRODUCTS

by Randall F. Gahn

Lewis Research Center

SUMMARY

Described herein is a procedure for the isolation and recovery of alkali-metal reaction products in an uncontaminated state. Separation of the reaction product from excess alkali metal is accomplished by vacuum distillation. All recovery operations are carried out in high-vacuum or inert gas atmospheres.

Two typical examples of the application and reproducibility of the procedure are presented: (1) the recovery of potassium tantalate (K_3TaO_4) from the potassium-tantalum-oxygen reaction, and (2) the recovery of potassium monoxide (K_2O) from the potassium-oxygen reaction. Reaction products are identified by both X-ray diffraction and chemical analysis.

INTRODUCTION

Central to the understanding of alkali-metal reactions, and in particular, the corrosion of materials by alkali metals, is the recovery and identification of reaction products. Basically, the problem of alkali-metal reaction-product recovery is twofold. First, the reaction product must be separated from excess alkali metal. Second, because alkali-metal reaction products generally react readily with water and/or carbon dioxide, the product must be protected from exposure to air prior to and during the separation and in subsequent handling.

Several attempts at alkali-metal reaction-product recovery have been reported (refs. 1 to 3). In these recovery attempts, it is likely that reaction-product contamination occurred. Generally, in the studies cited, excess alkali metal was removed by treatment with alcohol or ammonia. Additionally, in some instances the residues were exposed to air.

This report describes a procedure for the isolation and recovery of alkali-metal reaction products. The procedure was designed to minimize reaction-product contamination by carrying out all operations in high-vacuum or inert gas atmospheres. The separation of reaction products from excess alkali metal is accomplished by vacuum distillation to avoid the use of solvents or reactants. This procedure was applied to the recovery of products from the reactions of potassium and lithium with tantalum, niobium, vanadium, and oxygen. As an indication of the application and reproducibility of the procedure, two examples are detailed herein: (1) the isolation of the reaction product from the potassium-tantalum-oxygen system, (2) the isolation of the reaction product from the potassium-oxygen system.

EXPERIMENT

Apparatus

The product separation apparatus is shown in figure 1. The apparatus is fabricated of stainless steel except for the distillation chamber, which is made of glass.

All operations within the apparatus are carried out under a pressure of 7×10^{-6} torr (9.3×10^{-4} N/m^2) or less. Wilson seals are employed to permit manipulation in vacuum

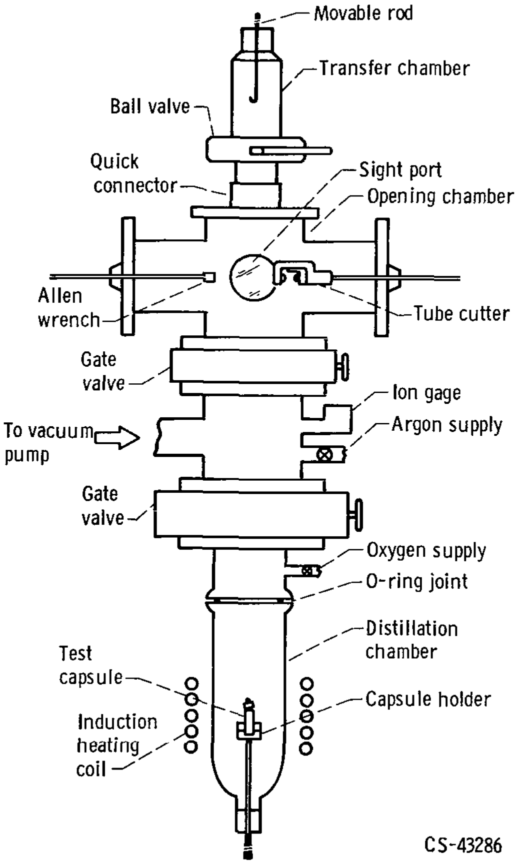

Figure 1. - Product separation apparatus.

of the handling devices (shown in fig. 1), which are the tube cutter, movable rod, Allen wrench, and capsule holder.

Procedure

Potassium-tantalum-oxygen reaction-product recovery. - A sealed tantalum capsule, 1.27 centimeters in diameter by 4.45 centimeters long, containing potassium (~20 ppm oxygen) and a tantalum wire specimen that was doped with a known amount of oxygen (in the range of 2000 to 4000 ppm) is heated at 1255° K for 100 hours in a vacuum furnace (ref. 4). Following the reaction, a metal wire loop is spot welded to the top of the capsule, and the capsule is secured by means of a set screw in the capsule holder of the product separation apparatus. The apparatus is evacuated, and the capsule is outgassed by heating between 423° and 473° K for 1/2 hour. The capsule is raised to the opening chamber and positioned in the jaws of the tube cutter. By rotating the holder 150° in each direction, an opening is made in the capsule without completely severing the lid. The intact lid acts as a potassium vapor deflector during the potassium distillation process. The capsule is lowered into the distillation chamber and heated from 3 to 5 hours, to a maximum temperature of 598° K (ref. 5). The vaporized potassium condenses on the inside walls of the air-cooled distillation chamber. Following distillation, the capsule is raised to the opening chamber, loosened in the holder, and lifted into the transfer chamber by the use of the hooked, movable rod. The transfer chamber, under vacuum, is transferred to an argon glove box, where the reaction product is removed from the capsule and prepared for the desired analysis.

Potassium-oxygen reaction-product recovery. - In the initial stage of this procedure, the product separation apparatus is modified by replacing the transfer chamber with a potassium extruder chamber (ref. 6). A metal crucible, 1.27 centimeters in diameter by 4.45 centimeters long, is placed in the capsule holder. The apparatus is evacuated, and the crucible is outgassed. Next, the crucible is raised into the extruder chamber, filled with about 1 gram of potassium by extrusion, and lowered into the distillation chamber. The potassium in the crucible is heated to 398° K, and the distillation chamber is valved off from the rest of the apparatus. A known amount of oxygen is admitted and allowed to react with the molten potassium. After the uptake of oxygen, the distillation chamber is opened to the vacuum system, and the potassium is distilled by heating to 598° K. Next, the extruder chamber is replaced with the transfer chamber. The crucible is raised to the opening chamber, loosened in the holder, and lifted into the transfer chamber. The transfer chamber is taken to the argon glove box for the product recovery.

RESULTS

A total of 70 alkali-metal reaction-product separations were made by the described procedure. Reaction products from the potassium-tantalum-oxygen, potassium-niobium-oxygen, lithium-tantalum-oxygen, lithium-niobium-oxygen, lithium-vanadium-oxygen, and potassium-oxygen systems were quantitatively isolated and identified by X-ray diffraction and chemical analysis. Two typical results are given as examples.

Potassium-Tantalum-Oxygen Reaction-Product Recovery

The product recovered from the potassium-tantalum-oxygen reaction was potassium tantalate, K_3TaO_4, a crystalline, hygroscopic solid. The contents of five test capsules were chemically analyzed for potassium and tantalum, and the results are given in table I. The average ratio of potassium to tantalum was calculated to be 0.655±0.031 (table I). The theoretical ratio of potassium to tantalum for the compound K_3TaO_4 is 0.648.

TABLE I. - POTASSIUM-TANTALUM-OXYGEN

REACTION-PRODUCT CHEMICAL ANALYSIS

[Theoretical ratio of potassium to tantalum for K_3TaO_4, 0.648.]

Capsule	Weight of metal found, mg		Ratio of potassium to tantalum
	Tantalum[a]	Potassium[b]	
1	6.62	4.00	0.604
2	7.97	5.50	.690
[c]3	[d]6.15	4.25	.691
	[d]1.02	.675	.662
[c]4	4.70	3.06	.651
	4.30	2.80	.651
5	4.73	3.00	.634
Average	-----	-----	0.655±0.031

[a] Tantalum determined spectrophotometrically with pyrogallol.

[b] Potassium determined by flame photometry.

[c] Reaction product divided into two samples.

[d] Average value of duplicate analysis on sample.

TABLE II. - POTASSIUM-OXYGEN REACTION-PRODUCT X-RAY DIFFRACTION ANALYSIS

hkl	Reference 8[a]		This work	
	Interplanar distance, d, Å(10^{-8} cm)	Intensity[b]	Interplanar distance, d, Å(10^{-8} cm)	Intensity[b]
111	3.74	w	3.72	m-
200	3.23	s	3.18	vs
220	2.29	vs	2.27	vs
311	1.953	w	1.943	vw
222	1.866	m	1.850	s
400	1.613	m	1.604	m-
331	1.480	vw		
420	1.443	m+	1.434	m
422	1.316	s	1.309	s
511	1.241	vw		
440	1.140	m	1.136	w
531	1.091	vw		
600	1.074	m	1.069	w
620	1.019	m+	1.016	w
533	.9850	vvw		
622	.9717	m-	.9683	vw
444	.9298	w	.9274	vw
551	.9036	vvw		
640	.8939	w-	.8908	vw
642	.8614	m+	.8581	w
820			.7780	m-

[a] K_2O prepared by reduction of mercuric oxide with potassium. X-ray camera used had 1/2 the radius of camera used in present work. For purposes of comparison, scale of intensity values used in ref. 8 was converted to conform with scale in present work.

[b] Intensity code: s, strong; m, medium; w, weak; v, very.

Identification of the product was further confirmed by a comparison of its X-ray diffraction pattern with that for K_3TaO_4 cited in reference 7. The pertinent patterns are tabulated and discussed in reference 4.

Potassium-Oxygen Reaction-Product Recovery

Two potassium-oxygen reaction tests were made. In the first test, X-ray diffraction analysis indicated that the reaction product was potassium monoxide, K_2O, by a comparison of its X-ray diffraction pattern with the reported pattern for K_2O (ref. 8). These data are compared in table II. In the second test, the reaction product was transferred to a weighing bottle in the argon glove box. After weighing, the reaction product was dissolved in water, titrated with standard acid, and analyzed for potassium by flame photometry. The chemical analysis results that follow indicate the product to be K_2O.

Actual weight, mg	
K-O reaction product	3.19
K found by flame photometry	2.58
K found by titration	2.47
Theoretical weight, mg	
K, if product is K_2O	2.65

DISCUSSION

The results of the product-recovery tests serve to validate the techniques employed. The chemical and physical analyses indicate that the hygroscopic compounds K_3TaO_4 and K_2O were recovered in an uncontaminated condition. The reproducibility of the chemical analysis results for the potassium-tantalum-oxygen reaction product show that (1) the method used to open the capsule does not contaminate the product, and (2) potassium separation from the product was complete.

A potential limitation of the separation method should be noted. The source of this limitation involves the time and temperature required for the distillation of the alkali metal and the changes in concentration that occur during distillation. Conceivably, certain reaction products that are initially formed under a given set of conditions might subsequently suffer alteration under the conditions of distillation.

In the case of the potassium-oxygen reaction, there is a good probability that reaction-product alteration occurred during distillation. It was shown that potassium peroxide, K_2O_2, and potassium superoxide, KO_2, are produced during the low-temperature and low-pressure oxidation of potassium (ref. 9). Heating of these oxides in the presence of excess potassium (as occurs during distillation) would lead to their conversion to the more stable monoxide, K_2O (the product recovered in the tests reported herein).

In the case of the potassium-tantalum-oxygen reaction, however, an alteration of the reaction product during distillation is not expected because the distillation temperature is much lower than the reaction temperature. Support for the contention that no alteration of the reaction product had occurred was obtained in a separate test. In this test, following the high-temperature potassium-tantalum-oxygen reaction, the contents of the test capsule were dissolved in alcohol. A tantalum analysis was made on the alcohol solution. Analysis of the tantalum wire by X-ray diffraction indicated the complete depletion of oxygen; that is, the lattice parameter of the tantalum wire following the high-temperature reaction was the same as the lattice parameter of the wire before oxygen doping. If it is assumed that all of the depleted oxygen is in the reaction product, the ratio of tantalum to oxygen calculated was 1:4. This ratio is in agreement with the tantalum-oxygen ratio for K_3TaO_4.

SUMMARY OF RESULTS

Described herein was a procedure for the isolation and recovery of alkali-metal reaction products. Products of the potassium-tantalum-oxygen, potassium-niobium-oxygen, lithium-tantalum-oxygen, lithium-niobium-oxygen, lithium-vanadium-oxygen, and potassium-oxygen systems were recovered and identified by X-ray diffraction and chemical analysis.

Typical examples of product recovery were presented in detail for the hygroscopic compounds: potassium tantalate from the potassium-tantalum-oxygen reaction, and potassium monoxide from the potassium-oxygen reaction. These reaction products were completely separated from excess potassium and were recovered in an uncontaminated condition. The result of an independent test indicates that there was no alteration of the product of the potassium-tantalum-oxygen reaction as a result of the time, temperature, and concentration conditions imposed during distillation. It is suspected, however, that the initially formed product of the potassium-oxygen reaction is altered during subsequent distillation. This latter case suggests a potential limitation of the recovery procedure.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, October 5, 1967,
129-03-03-01-22.

REFERENCES

1. Litman, Arnold P.: The Effect of Oxygen on the Corrosion of Niobium by Liquid Potassium. Rep. No. ORNL-3751, Oak Ridge National Lab., July 1965.
2. Tyzack, C.: The Behavior of Materials In Liquid Sodium. Advances in Materials. Inter-Disciplinary Symposium, Third and Fourth Sessions. Inst. Chem. Engrs., Apr. 7, 1964, pp. 151-158.
3. Cleary, R. E.; Blecherman, S. S.; and Corliss, J. E.: Solubility of Refractory Metals in Lithium and Potassium. Rep. No. TIM-850, Pratt and Whitney Aircraft, Oct. 27, 1965.
4. Hickam, C. William, Jr.: Corrosion Product of the Tantalum - Interstitial Oxygen - Potassium System at 1800° F (1255° K). NASA TN D-4213, 1967.
5. Gahn, Randall F.; and Rosenblum, Louis: Accuracy of Three Methods for Determination of Oxygen in Potassium at Concentrations Less Than 20 Parts Per Million. NASA TN D-3239, 1966.
6. Dupraw, William A.; Graab, Judson W.; and Gahn, Randall F.: Determination of Oxygen in Potassium. Anal. Chem. vol. 36, no. 2, Feb. 1964, pp. 430-431.
7. 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.
8. Zintl, E.; Harder, A.; and Dauth, B.: Lattice Structure of the Oxides, Sulphides, Selenides and Tellurides of Lithium, Sodium and Potassium. Z. Elektrochem., vol. 40, no. 8, Aug. 1934, pp. 588-593.
9. Kraus, Charles A.; and Parmenter, Ellis F.: Further Studies of the Oxides of Potassium. J. Am. Chem. Soc., vol. 56, no. 11, Nov. 1934, pp. 2384-2388.

NASA-Langley, 1968 —— 17 E-4148

"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