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HIGH PURITY URANIUM COMPOUNDS

Final Report

by

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Final Report

HIGH PURITY URANIUM COMPOUNDS

I Introduction

High purity uranium compounds were needed for precision calorimetric investigations being conducted by the Chemical Engineering Division of the Argonne National Laboratory. Because these compounds could not be commercially obtained in the necessary purity and stoichiometry, they have to be specially prepared and analyzed; this program was initiated for that purpose. The purity and stoichiometry were to be established by chemical analysis and X-ray diffraction. The objectives of the project were to explore methods of preparation, and to prepare 500-gram samples of compounds from the following: UAl_3, UAl_4, UBe_{13}, UB_2, UB_4, UB_{12}, UC, U_2C_3, UC_2, UN, UN_2, US, US_2, USi, USi_2, USi_3, USe_2, and UTe. Actually, fourteen of these were prepared, plus UAl_2. Small samples of USe and USe_2 were prepared, and numerous attempts were made to prepare USi.

II Summary

During the course of this project, equipment and techniques were developed for preparing a number of uranium compounds in higher purity and with more complete analysis than has been published previously. However, uncertainties in the form of some of the impurities and the magnitude of the amounts of the impurities show that further improvements are needed. In this connection it should be pointed out that the method of expressing the analyses can be somewhat deceiving, because of uranium's high molecular weight. A particular sample of US (Sample S-40), for example, analyzed 0.21% C, which, although undesirably high, does not appear serious. However, if the C is assumed to be present as UC, this would amount to 4.8% contamination with this compound.

The uranium-aluminum compounds UAl_2, UAl_3, and UAl_4 were prepared by solid-solid reaction of aluminum powder and uranium hydride. The X-ray diffraction patterns showed that single phases of UAl_2, UAl_3, and UAl_4 could be achieved. Impurities need further study.

The uranium-beryllium compound, UBe_{13}, was prepared by solid-solid reaction of beryllium powder and uranium hydride. The analytical method for oxygen needs further development.

The uranium-boron compounds, UB_2, UB_4, and UB_{12} were prepared by solid reaction, and single borides were obtained. Carbon contamination was especially serious in these samples.

The uranium-carbon compounds, UC and UC_2, were prepared by solid-solid reaction at temperatures up to 1200°C. The X-ray diffraction patterns showed a mixture of phases, and higher temperatures are probably required.

The uranium-nitrogen compounds, UN and UN_2, were prepared by reaction of uranium with ammonia at 850°C for UN_2 and subsequent heating of that product in vacuum for UN. The relative amounts of UO and UO_2 in the UN need to be determined.

The uranium-selenium compounds, USe and USe_2, were prepared in very small samples. The violence of the reaction of selenium with uranium hydride and the lack of availability of hydrogen selenide will limit the size of preparations.

The uranium-silicon samples, USi_2 and USi_3 were prepared by solid-solid reaction of UH_3 and Si. Numerous attempts were also made to prepare USi. One of the USi_2 samples was α-USi_2 and the other was β-USi_2.

The uranium-sulfur compounds, US and US_2, were prepared. US_2 was prepared by forming uranium hydride in a flow furnace and then reacting the hydride with hydrogen sulfide. US was prepared by reacting some of the US_2 with UH_3.

III Experimental Methods

A literature survey on the preparation and phase diagram and analysis of the compounds led to the choice of gas-solid and solid-solid reactions for producing the compounds. Admittedly, a few of the compounds could be made by melting techniques, possibly better than by solid-solid reaction. However, most of the compounds were not stable at their melting points and homogenization would be required to obtain the desired stoichiometry. Also, the solid-solid type of reaction produced a sintered material which was much easier to grind to pass a 100-mesh sieve than products from melting. Further, reaction of the compounds with crucible materials was minimized by solid-solid reaction.

A. Equipment

The solid-solid reaction required that special techniques be adopted for handling uranium hydride and potentially reactive compounds.

1. Uranium Hydride Apparatus

A Pyrex apparatus was used to prepare uranium hydride. It consisted of a reaction flask 2-1/2 inches in diameter, which could hold one to four 110-gram pieces of uranium metal cut from a rod. The pre-purified hydrogen (Matheson Co.) was further purified with a Deoxo catalytic gas purifier, a column of anhydrous magnesium perchlorate (Dehydrite), and a column of calcium hydride at 500°C. The uranium metal was cleaned with dilute nitric acid and then rinsed with water, acetone, and petroleum ether. The metal was then placed in the reaction flask, which was evacuated and filled with hydrogen. The flask was heated, and the reaction was monitored with a flow meter and a manometer. The reaction proceeded smoothly, with practically no induction period,[1] and had a maximum rate at a thermocouple reading of 240 to 250°C. After the reaction started, it was self sustaining, as the powdered uranium hydride did not slow up the reaction. After completion of the reaction and cooling to room temperature, the stopcock on the reaction flask was closed and the unit was transferred to the dry box.

2. Dry Box Operation

Maintaining an inert atmosphere in the dry box was a problem in the early stages of the project. The dry box was a conventional Blickman vacuum type with entry system. At first a 400-cc stainless steel beaker was filled with calcium metal turnings or uranium hydride and heated to 500°C, and this was partially effective in removing the oxygen and nitrogen. The disadvantages of this system were the heating of the work area in the dry box and the difficulties in replacement of the uranium hydride. Mass spectrometer analyses of the atmosphere gave about 0.2% oxygen and 3% nitrogen.

A gas circulating system was then used;[2] it consisted of a Model 4K Dynapump, a Hoskins Model FD303 tube furnace, and a ceramic tube filled with +20 mesh granular titanium (Catalog No. 501-5, Laboratory Equipment Corp.). The tube furnace, at 1000°C, was effective in removing oxygen and nitrogen. After 37 days, the argon contained <0.01% O_2, 0.27% N_2, and 0.72% H_2. A weekly analysis of the atmosphere was adequate. When the titanium began to be used up, the concentration of hydrogen would increase, and then the nitrogen would begin to increase. The titanium was replaced before the nitrogen reached 1%, and the oxygen was maintained at less than 0.01%.

3. Molybdenum Resistance Furnace

A 2-Kva molybdenum-wound vacuum furnace for growing single crystals was modified so that 3/4-inch-diameter alumina tubes could be passed from the dry box into the furnace while in an inert atmosphere. This was suitable for experiments up to 1400°C and amounts of material up to 25 grams. It was used in the experiments to develop experimental conditions for preparing silicides, borides, and other uranium compounds.

4. Graphite Resistance Furnace

A special 20-Kva furnace was designed and built for heating 200-gram mixtures of reactants up to 1800°C in vacuum or inert atmosphere. The furnace had a removable vacuum-tight transfer unit with a gate-type

valve which could be attached to the furnace. Large crucibles on a pedestal could be pushed up into the furnace with this transfer unit. It was used for all of the high temperature preparations.

5. Flow Furnace

A vertical tube furnace with an opening 2-1/4 inches in diameter and 8 inches tall was built to react uranium metal with ammonia or hydrogen sulfide. A Vycor tube with a Vycor grid supported the uranium metal, and the products dropped through the grid into the bottom part of the tube.

This furnace was also used with a Pyrex tube containing a fritted glass section. A piece of uranium metal was placed on the frit, reacted with hydrogen to form the hydride and then with hydrogen sulfide at 425°C to form uranium disulfide.

6. Accessory Equipment

A 400-cc micro ball mill was made from a 600-cc stainless steel beaker. Stainless steel, K-monel, and tungsten carbide balls were used. A small V-shell blender was also built to use the same motor and base. This unit was small enough to use inside the dry box, but the O-ring seals allowed us to load these in the dry box and operate them in the room.

The crucibles for the molybdenum resistance furnace included alumina thimbles (Norton RA7232) and zirconia thimbles (Laboratory Equipment Co. 528-208). The crucibles for the graphite resistance furnace were made from zirconia (Laboratory Equipment Co. No. 528-105), magnesia (Norton 70149 Magnorite K), berrylia (Brush Beryllium Co. 2-3/16 OD x 3-13/16 height) and graphite (made from National Carbon Co. AVC grade graphite).

B. Chemicals

The uranium metal was obtained from the Davidson Chemical Co. in 1-inch-diameter rod cut into 1/2-inch lengths. The indicated U-235 content was 0.40%. Normal uranium has an atomic weight of 238.07 and an isotopic

composition of 99.27% U238 (238.125 mass), 0.72% U235 (235.117 mass) and 0.0055% U234 (234.114 mass), where the atomic weight is on the chemical scale and the values of mass are on the physical scale. The calculated value of the average mass on the physical scale of normal uranium is 238.093, and for depleted uranium (0.40% U235) 238.102. Such a slight difference does not require a correction in the analytical results.

The aluminum metal was obtained from the Reynolds Metals Company as a sample of their 1-841 atomized powder, in answer to our request for aluminum powder suitable for powder metallurgical purposes and containing a minimum of oxygen.

The boron metal (Grade AA) was purchased from Cooper Metallurgical Associates. The first shipment (lot 1414) had a labeled analysis of 99.60% B, 0.16% Fe, and 0.09% C. The second shipment (lot 0560) had a labeled analysis of 99.60% B, 0.12% Fe, and 0.09% C. These were vacuum-packed, and a letter from Walter M. Weil claimed that the boron was practically oxygen free.

The berrylium was the premium grade of beryllium metal powder in -200 mesh as obtained from the Brush Berrylium Co.

The carbon was special spectroscopic graphite powder, grade SP-2, from the National Carbon Company.

The nitrogen was a prepurified grade from the Matheson Co. and has a specification of 99.9964% purity and oxygen of about 8 ppm. Ammonia was also used to prepare the nitrides and was obtained from a large cylinder of liquid ammonia (Shell Chemical Corp.).

The selenium powder was Fisher Scientific Company No. S-137, with a certified analysis of residue-on-ignition 0.4%, nitrogen 0.004%, sulfur 0.1%, heavy metals (as Pb) 0.1%, and iron 0.04%.

Sublimed sulfur (Sulfur Flowers) was used in a few preparations, but caused a violent reaction. Hydrogen sulfide, purified grade, 99.5% minimum purity, from the Matheson Company, was used for most of the uranium-sulfur samples.

The silicon powder was obtained from Union Carbide Metals Company. The purified silicon metal had a specification of 99.7 to 99.9% silicon and 0.005-0.015% iron. A sample of -325 mesh silicon was obtained, with the analysis 99.7% silicon, 0.19% oxygen, and 0.003% iron. Samples of -150 to + 325 mesh silicon with a specification of 99.9% can occasionally be obtained, but the company would not guarantee this, and the -150 to +325 mesh material which was received had a specification of 99.8% silicon.

C. Analytical Methods

1. Analysis of Main Constituents

The choice of analytical methods was based on a literature survey and tests on suggested methods.

Uranium was analyzed for using a lead reductor and titration with a standard ceric sulfate solution.[3,4] The acid strength was increased above that given in AERE-C/R-1813. The ceric sulfate was standardized using the New Brunswick standard U_3O_8, and tests with added amounts of the other elements were satisfactory. The method of preparing the solution was varied to suit the particular compound.

Analysis of aluminum was by solution of the sample with acids, fusion of any insoluble residue, a double precipitation with ammonium carbonate, and ignition at 1050°C. The recovery of pure aluminum added to uranium was usually about 1 to 2% higher than the amount added.

Analysis for boron was by fusion with sodium peroxide in a small Paar bomb. The uranium was separated by double precipitation with sodium hydroxide. The titration with standard sodium hydroxide was done at a pH of 7 with added sodium oxalate and mannitol. The recovery of boron added to uranium was satisfactory.

Beryllium was determined by solution of the sample with HCl, precipitation with ammonium carbonate and hydroxylamine hydrochloride, reprecipitation, and ignition to BeO.

Carbon was obtained with equipment for micro carbon-hydrogen, analysis. Usually hydrogen was determined at the same time.

Nitrogen analysis was attempted by the Kjeldahl method, with a variety of preliminary treatments to dissolve the sample. Among the better modifications was the addition of methanol before addition of acids and also the addition of fluosilicic acid and selenium. A given modification did not appear to work equally well on all samples. Later, the Dumas method was tried, using equipment for organic microanalysis. The results were in the correct range but the precision was poor. Thus, the nitrogen analysis is probably the least satisfactory of the methods. The Dumas method is preferable to the Kjeldahl method, but a special apparatus might be required to obtain adequate precision.

Selenium was analyzed by dissolving the sample, using a solution of sodium chlorate and careful addition of nitric acid. The selenium was precipitated using hydroxylamine hydrochloride and weighed as the element.

Silicon compounds were preheated to 600°C in a platinum crucible before the fusion with sodium carbonate. The preheating eliminated a vigorous reaction which would occur if a fresh sample was fused with sodium carbonate. The silica was dehydrated in the usual manner, and the weighed silicon dioxide was volatilized with hydrofluoric acid to correct for impurities.

Sulfur was analyzed using a Paar bomb fusion and gravimetric determination as $BaSO_4$.

2. Analysis of Impurities

Oxygen was determined using the platinum bath method with a Leco Oxygen Analyzer (No. 534-300). In general the sample was wrapped in 1-mil platinum foil, and the accumulated platinum served as the bath. This particular instrument required calibration with a standard oxide, and the lead oxide also served to indicate possible interference from gettering. Aluminum compounds were suspected of interfering by gettering

and a few trials were made with other baths, one of the more attractive being a copper-nickel bath. It was finally found that a few samples of aluminum compounds could be analyzed satisfactorily using platinum after some other samples had been analyzed. Beryllium compounds were worse than aluminum compounds, as gettering occurred after two samples were analyzed. Oxygen in sulfur compounds was determined by weighing the UOS residue after boiling the sample with 4 N sulfuric acid.

Carbon and hydrogen impurities were determined using a micro combustion apparatus. Nitrogen in low concentrations was determined by the Kjeldahl method using selenium as a catalyst.

Metallic impurities were detected by spectrographic analysis done by the American Spectrographic Laboratories using the set of standard samples from New Brunswick Laboratory as reference samples. The results were reported as a possible range of concentration, such as 0.001 to 0.01%. In those cases where the indicated range was 0.01 to 0.1 or higher, the elements were also analyzed by colorimetric methods. In general, the colorimetric results were within the indicated range given by the spectrographic laboratory and closer to the lower limit, which indicated that the spectrographic results were quite good.

3. X-ray Diffraction

X-ray diffraction patterns were obtained on all samples. Separate patterns were obtained of the top and bottom sections of the samples. The X-ray patterns were analyzed in terms of known compounds and impurities. All lines were identified as completely as possible, and any unidentified lines were noted.

The instrument used was a Norelco diffractometer with a copper tube. A rotating specimen holder was used because the rotation increased the reproducibility of peak heights by a factor of 4 over a stationary sample holder. Even with special care in back-loading of samples and use of -325 mesh samples, the peak heights were not sufficiently reproducible

for quantitative comparison of different samples. The estimated penetration of a uranium compound is about 3 microns at an angle of 20^{o}.

Line broadening was determined on a few of the silicide samples. The slight penetration prevented an accurate determination of crystallite size, but a sample of USi_2 heated 1 hour at 1400°C had an estimated crystallite size of 6 microns. USi_2 heated 16 hours had a crystallite size of 18 microns. Line broadening was not a problem with uranium-silicon samples. The lines in other samples heated to high temperatures were sharp, but were not measured for line broadening.

A special sample holder was constructed for obtaining X-ray diffraction patterns of reactive samples. This holder could be loaded easily in the dry box and used with the diffractometer. A 0.5-mil film of polyvinyl chloride was used at first, and no weight gain or loss in intensity of diffraction lines was obtained on uranium hydride in 4 days. Later polyvinyl alcohol film was found to cause less loss of intensity and gave a smaller background.

IV Preparations of Uranium Compounds

The literature background, the preliminary research, the final preparations, the analysis, and the estimated composition are given below for each series of uranium compounds. "The Constitution of Uranium and Thorium Alloys"[5] was the most useful single literature source, but a thorough literature survey of Nuclear Science Abstracts was also made to obtain more recent literature.

A. Uranium-Aluminum Samples

UAl_2, UAl_3, and UAl_4 were prepared. Of these, the phase diagram[5] indicates that UAl_2 could be made by a melting technique,[7] but that UAl_3 and UAl_4 would require a peritectic type of reaction or homogenization.[8] Thus, solid-solid reaction appeared to be the most suitable general method. UAl_4 provides an example of a well-established lattice defect structure[6] in which the UAl_4 structure was obtained from 64.2 to 66.3% U by weight,

or from $UAl_{4.9}$ to $UAl_{4.5}$. The UAl_4 structure thus contains some uranium sites which are empty or contain aluminum atoms.

Preliminary research on the reaction of uranium hydride and aluminum powders at various mole ratios and temperatures (9 runs) indicated that UAl_4 could be prepared by solid-solid reaction at 1400°C, UAl_3 at 1300°C, and UAl_4 at 700°C. The ratios were adjusted to obtain the maximum amounts of the desired compounds. Runs Al-10 to Al-16 were 200-gram preparations. Run* Al-10, made in a zirconia crucible, had a low total metal analysis, for unknown reasons, and was discarded. Runs Al-11 to Al-16 were made in graphite crucibles (see Table I), and only run Al-13 had an excessive carbon impurity.

Samples* Al-13 and Al-14, of UAl_2, were made at 1300°C. The mixture of aluminum powder and uranium hydride was heated under vacuum for 4 hours while the temperature was being increased to about 700°C. Then argon was introduced and the temperature was rapidly raised to 1300°C and held there at least 13 hours. Samples Al-11 and Al-15, of UAl_3, were prepared similarly. Samples Al-12 and Al-16, of UAl_4, were made under vacuum with the temperature being increased to about 700°C in 5 hours and then held there an additional 18 hours. The final pressure was 5 microns.

The product was processed in the dry box. Small sections of the top and bottom were removed. The central portion, comprising the bulk of the sample, was ground to pass a 100-mesh sieve. A diamond mortar was used to break it to pass a 20-mesh sieve and the product was ground in the ball mill. The top and bottom portions were used for X-ray diffraction patterns to determine homogeneity, and were not combined with the central portion. Usually, the top had a greater intensity of UO_2 and any other impurities. The top of Al-11 and Al-13 contained an unidentified impurity

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*The word "run" in run-x indicates it was a preliminary sample and not shipped. The word "sample" indicates that it was shipped.

Table I

COMPOSITION OF URANIUM-ALUMINUM SAMPLES

Compound and Sample	U, %	Al, %	O, %	C, %	H, %	Trace Elements, %	Total, %
UAl_2							
Al-13	83.07	16.38	0.56	0.58	0.24	0.01	100.73
	83.02	16.23	0.52				
Al-14	82.85	16.98	0.16	0.04	0.11	0.21	100.49
	82.95	17.13	0.17				
UAl_3							
Al-11	74.01	25.45	0.14	0.14	0.25	(0.05)	100.00
	74.01	25.35	0.16				
Al-15	74.74	25.46	0.18	0.03	0.24	0.24	100.76
	74.73	25.19	0.18				
UAl_4							
Al-12	67.27	33.16	0.24	0.04	(0.20)[b]	0.05	101.09
	67.20	33.51	0.19				
Al-16	67.13	32.96	0.35	0.08	0.17	0.25	101.10
	67.20	33.19	0.35				

TRACE ELEMENTS BY EMISSION SPECTROGRAPHY AND COLORIMETRY

Sample	Fe, %	Si, %	Cu, %	Others, %
Al-13	--	0.001-.1 0.010[a]		--
Al-14	0.1-1 0.14[a]	0.01-.1 0.06[a]	0.01-.1 0.010[a]	Mn, Co, Ni 0.003-.03; Cr 0.001-.01; Ca 0.0003-.003
Al-11		0.03-.3 (.04)[b]	0.003-.03 (0.01)[b]	Cr 0.0003-.003
Al-15	0.03-.3 0.18[a]	0.01-.1 0.04[a]	0.01-.1 0.014[a]	Ni, Co 0.003-.03; Cr 0.001-.01; Mn 0.0003-.003
Al-12		0.03-.3 0.039[a]	0.01-.1 0.012[a]	Ni, Mg 0.003-.03; Cr, Co 0.001-.01
Al-16	0.03-.3 0.21[a]	0.01-.1 0.03[a]	0.01-.1 0.012[a]	Ni, Co 0.003-.03; Cr, Mg 0.001-.01; Mn 0.0003-.003

Table I (Concluded)

X-RAY DIFFRACTION (RELATIVE PEAK HEIGHTS)

Sample	UAl_2	UAl_3	UAl_4	UO_2	UC
Al-13	100	3		3	9
Al-14	100			< 3	4
Al-11		100	5		
Al-15	4	100			
Al-12			100		
Al-16		10	100		

CALCULATED CONSTITUTION OF URANIUM-ALUMINUM SAMPLES

Compound and Sample	UO_2,%	Al_2O_3,%	UC,%	X in UAl_X	UAl_2,%	UAl_3,%	UAl_4,%	Other, %
UAl_2								
Al-13	4.0		11.5	2.06	77.9	5.4		0.25
	1.6	0.4	11.5	1.95	(85.3)[c]			0.25
Al-14	1.3		0.8	1.81	(87.4)[c]			0.32
	0.5	0.1	0.8	1.78	(88.2)[c]			0.32
UAl_3								
Al-11	1.1		2.8	3.20		75.1	20.4	0.30
	0.4	0.1	2.8	3.15		80.7	15.4	0.30
Al-15	1.3		0.6	2.98	1.8	95.5		0.48
	0.5	0.1	0.6	2.92	7.2	90.9		0.48
UAl_4								
Al-12	1.6		0.8	4.32			(97.0)[c]	(0.25)
	0.5	0.2	0.8	4.29			(98.1)[c]	(0.25)
Al-16	2.6		1.6	4.49			(95.0)[c]	0.42
	1.6	0.3	1.6	4.31			(96.6)[c]	0.42

[a] Colorimetric

[b] Estimate

[c] This is the total of U and Al after correction for UO_2, Al_2O_3, UC, etc.

with lines at d-values of 2.44 and 2.79; but this was not present in the other samples. The top of Al-11 also had lines for Al_2O_3 as well as UO_2. The X-ray patterns did not show any UH_3, so the hydrogen was present either as dissolved or interstitial atoms which didn't alter the X-ray diffraction lines or was contained in this unidentified impurity.

The chemical analyses, trace elements, X-ray diffraction, and consitution are given in Table I.

The spectrographic analyses of the samples showed a considerable increase in metallic impurities (e.g., iron, copper, and silicon) in runs Al-14 to Al-16, compared with Al-11 to Al-13. The possible reasons for this have not been tested, but it may have been caused by an impure sample of aluminum.

The weight gain in air of these samples was less than 0.1% in 1 week.

The calculated constitution of the aluminum samples for percentages of compounds can be based on the assumptions that oxygen is present as UO_2 and carbon as UC, which is supported by the fact that these appear in the X-ray patterns of the UAl_2 samples. An alternative assumption is that Al_2O_3 is present because the heat of formation of Al_2O_3 per oxygen atom is nearly the same as that of UO_2. Low concentrations of Al_2O_3 would not show in the X-ray pattern. For the second assumption, the UO_2:Al_2O_3 ratio is taken as that corresponding to the U:Al ratio in the sample. The calculated constitution of the U-Al samples is given for both assumptions. The silicon, iron, copper, etc. are assumed present as elements, but are probably present as U-Si, U-Fe, and Al-Cu compounds. The analysis has been adjusted to 100.00% by lowering the percentages of aluminum, because the totals were usually high and the analytical tests on aluminum usually ran 1-2% high.

B. Uranium-Beryllium Samples

The compound, UBe_{13}, is the only one indicated in the phase diagram.[5] It has a melting point of about 2000°C and has been made only by solid-solid reaction[9,10,11] at temperatures from 1000 to 1500°C.

Three preparations were made, the first being a 50-gram sample and the others 100-grams each. The beryllium and uranium hydride powders were mixed and added to a beryllium oxide crucible. For run Be-3 the mixture was heated to about 700°C in 1-1/2 hours in an argon atmosphere, heated under vacuum for about 1/2 hour, refilled with argon, heated to 1400°C in 1 hour, and held at 1400°C for 16 hours.

The analysis, diffraction results, and constitution are given in Table II.

The chemical analysis for oxygen was not completed because of interference from gettering after the first sample was completed. Iron would have been determined colorimetrically if the spectrographic analysis had been completed earlier.

The X-ray diffraction showed a minor amount of an unidentified impurity with lines at α-values of 2.45 and 2.84.

The weight gain in air in one week was less than 0.1% on these samples.

The constitution of the samples is only approximate because oxygen was only determined on the first sample. The oxygen could be present as BeO because it has a higher heat of formation per oxygen atom than UO_2. However, the X-ray diffraction indicated that some UO_2 was present in the first sample. The calculations gave a higher ratio of Be to U than the 13.0 which was desired, although the ratio used in the preparation was 13.0.

Table II

COMPOSITION OF URANIUM-BERYLLIUM SAMPLES

Compound and Sample	U,%	Be,%	Total of U and Be	O,%	Other,%	Total
UBe_1						
Be-1	66.84	32.71	99.69	0.24	(0.06)	(99.97)
	66.95	32.85		0.20		
Be-2	66.61	33.05	99.80	(0.1)[b]	(0.11)	(100.01)
	66.62	33.30				
Be-3	66.33	33.58	99.93	(0.1)[b]	(0.11)	(100.17)
	66.44	33.49				

TRACE ELEMENTS BY EMISSION SPECTROGRAPH

Sample	Fe,%	Others
Be-1	0.03-0.3 (0.03)[b]	Mn, Si, Cu 0.003-.03; Al 0.001-.01
Be-2	0.1-1 (0.1)[b]	Mn, Si, Cu 0.003-.03; Al 0.001-.01
Be-3	0.1-1 (0.1)[b]	Mn, Si, Cu 0.003-.03; Al 0.001-.01

X-RAY DIFFRACTION (RELATIVE PEAK HEIGHTS)

Sample	UBe_{13}	UO_2	?[c]
Be-1	100	1	1
Be-2	100		1
Be-3	100		1

CALCULATED CONSTITUTION OF URANIUM-BERYLLIUM SAMPLES

Sample	UO_2,%	BeO,%	X in UBe_X	UBe_X,%	Other, %
Be-1	1.8		13.7	97.9	0.3
		0.3	13.4	99.4	0.3
	--	--	(13.5)	(99.5)[d]	0.5
Be-2	--	--	(13.6)	(99.8)[d]	0.2
Be-3	--	--	(13.8)	(99.8)[d]	0.2

[a]Colorimetric [b]Estimate [c]Unidentifed impurity

[d]Calculated values with no correction for oxides.

C. Uranium-Boron Samples

Samples of UB_2, UB_4, and UB_{12} were prepared. Early phase studies[12] produced only UB_2 and UB_4, because UB_{12} was too unstable to obtain by a melting technique. UB_{12} has been obtained by an electrolytic method.[13] UB_2 has been prepared by solid-solid reaction, grinding, and sintering at 1680°C in a vacuum.[11]

Two small samples of UB_2 and UB_4 were purchased; they had analyses on the labels, with the theoretical percentages of boron, but the actual percentages were markedly different. The massive form indicated that preparation had been by melting, but serious segregation had occurred, as the X-ray diffraction showed that UB_2, UB_4, UB_{12}, and UO_2 were present in both samples.

In preliminary research in the first 12 runs, 20-gram samples were prepared in the molybdenum furnace. One of the difficulties which was noted was that the sample tended to sinter as a plug and rise to the top of the crucible, probably when the boron and uranium hydride reacted. Also, during two preparations of UB_4, the reaction was sufficiently violent to break the alumina crucible.

Sample B-13, of UB_{12}, was prepared by pelleting a mixture of uranium hydride and boron powder. The pelleting prevented the hydrogen evolution from lifting the sample out of the crucible, although the pellets did lose their shape during the run. The samples were heated in an argon atmosphere to 1400°C and maintained at that temperature for 14 to 16 hours. The products from three runs were combined for this sample. Its analysis is given in Table II along with the analyses of the other samples which were shipped.

Runs B-14 and B-15 were 100-gram preparations of UB_{12} in the graphite resistance furnace at 1400°C. UB_{12} was mixed with uranium hydride to prepare UB_2 for sample B-16. Sample B-17, of UB_4 was prepared using a mixture of UB_{12} and UH_3 in a zirconia crucible. The sample was heated

Table III

COMPOSITION OF URANIUM-BORON SAMPLES

Compound and Sample	U,%	B,%	O,%	C,%	H,%	N,%	Trace Elements %	Total,%
UB_2								
B-19	92.13	6.82	0.57	0.34	0.04		(.02)	100.06
	92.32	6.73	0.55					
B-31	91.63	7.18	0.49	0.31	0.07		(.05)	99.75
	91.58	7.25	0.49					
UB_4								
B-17	84.77	13.83	0.66	0.60	0.09		(.06)	100.06
	84.84	13.83	0.67					
B-21	83.56	14.32	0.44	0.76	0.04	0.05	(.04)	99.18
	83.50	14.34	0.41	0.76				
B-38	84.70	14.93	0.28	0.35	0.19		(.14)	100.60
	84.65	15.01	0.24					
UB_{12}								
B-13	63.94	33.27	0.79				(1.41)	99.76
	63.90	33.26	0.73					
B-23	60.22	36.97	0.65	0.62	0.30	0.07	(.36)	99.29
	60.23	37.18	0.60					
B-24	59.53	39.39	0.65	0.46	0.11		(.36)	100.43
	59.45	39.25	0.72					
B-25	60.21	38.43	0.34	0.68	0.02		(.30)	100.13
	60.22	38.53	0.42					
B-26	64.67	33.67	0.46	0.43	0.57		(.26)	100.05
	64.58	33.70	0.48					
Boron			0.9	0.24	0.34			

TRACE ELEMENTS BY EMISSION SPECTROGRAPH AND COLORIMETRY

Sample	Cu,%	Si,%	Fe,%	Other
B-19	.001-.01	.003-.03 (.01)[b]		Cr 0.0003-.003
B-31	.003-.03 (.01)[b]		.03-.3 (.03)[b]	Ca, Al 0.003-.03
B-17		.03-.3 .026[a]		Ca .01-.1
B-21		.003-.03 (.01)[b]		Ca .01-.1

Table III (Concluded)

Sample	Cu,%	Si,%	Fe,%	Other
B-38		.01-.1 (.01)[b]	.1-1 (0.1)[b]	Ni .01-.1
B-13	.03-.3 (.03)[b]	.3-3 .12[g]	.1-1 (0.1)[b]	Ca, Mg, 0.03-0.3; Al, Ni 0.01-0.1 Mn .003-.03 Cr .001-.01
B-24	.1-1 .053[a]	.03-.3 (.03)[b]	.3-3 (0.2)[b]	Ca, Mg 0.03-.3; Ni, Ti 0.01-.1 Al 0.003-.03; Mn 0.001-.01
B-25	.03-.3 (.03)[b]	.03-.3 (.03)[b]	.3-3 0.23[a]	Ca, Mg 0.03-.3; Ni 0.01-.1 Al, Ti 0.003-.03; Mn 0.001-0.1
B-36	.03-.3 (.03)[b]	.03-.3 (.03)[b]	.1-1 (0.1)[b]	Ca, 0.1-1; Mg 0.03-.3; Ni 0.01-.1 Al, Co 0.003-.03; Mn 0.001-.01
Boron	.01-.1 (.01)[b]	.03.-3 (.03)[b]	.1-1 (0.1)[b]	Ca 0.1-1; reg, Al, 0.01-.1

X-RAY DIFFRACTION (RELATIVE PEAK HEIGHTS)

Sample	UB_2	UB_4	UB_{12}	UO_2	UC	?
B-19	100			2	6	
B-31	100			5	11	3
B-17		100		8	4	
B-21		100		2		
B-38		100		2		2
B-13			100			1
B-23		1	100			
B-24			100			
B-25			100			
B-36		2	100			

CALCULATED CONSTITUTION OF URANIUM-BORON SAMPLES

Sample	UB_2,%	UB_4,%	UB_{12},%	B,%	UO_2,%	UC,%	B_4C,%	Other, %
UB_2								
B-19	89.7 $UB_{1.68}$				4.7	4.8	0.5	0.06
B-31	90.9 $UB_{1.80}$							
UB_4								
B-17	7.3	79.0			5.7	6.3	1.4	0.15
B-21	3.0	82.7			3.6	7.9	1.7	0.13
UB_{12}								
B-13			89.9	1.6	6.4	0.4	0.3	1.41
B-23			81.8	6.9	5.3	3.2	2.1	0.73
B-24			80.0	9.7	5.8	2.4	1.6	0.47
B-25			83.3	7.1	3.2	3.6	2.4	0.37
B-36			91.1	0.3	4.0	2.3	1.5	0.83

[a] Colorimetric analysis

[b] Estimate

in an argon atmosphere until the UH_3 had decomposed and the initial reaction had occurred; then the furnace was evacuated and refilled with argon and the sample held at 1400°C for 17 hours.

Runs B-18 to B-32 were made in a graphite crucible in an attempt to minimize the formation of oxide. However, it was later found that the borides are particularly susceptible to the pick-up of carbon and that all of these preparations contained a considerable amount of UC contamination. Some of these samples were shipped and may prove useful for preliminary development of techniques on determination of heats of formation. Sample B-19, for UB_2, was prepared using a mixture of UB_{12} and UH_3 in the same manner as for sample B-17. Sample B-21, for UB_4, was prepared similarly except that the system was evacuated during the initial heating. Then it was filled with argon at 800°C and maintained at 1400°C for 15 hours. Sample B-31, for UB_2 was prepared the same as for B-21.

The attempts to prepare UB_{12} which were made at 1400°C usually showed a considerable amount of UB_4 even though more boron was used than for stoichiometry. This indicated that UB_{12} would slowly decompose at 1400°C. Samples B-23 and B-24, of UB_{12}, were made by heating a mixture of boron and UH_3 in vacuum up to about 800°C, then filling with argon and heating at 1200°C for 22 hours and 14 hours respectively. Sample B-25, of UB_{12}, was prepared similarly except for use of an argon atmosphere during the initial heating in place of a vacuum, then evacuating, and heating in argon at 1200°C for 16 hours.

A zirconia crucible was used for samples B-33 to B-38. Sample B-36, of UB_{12}, had a better X-ray diffraction pattern and a lower carbon content than Sample B-33. The maximum temperature of 1070°C was maintained for 16 hours. Run B-37, for UB_2, was made in a zirconia crucible, using UB_{12} from sample B-33, but it had a higher carbon content than sample B-31, which was made in a graphite crucible. Sample B-38, of UB_4, was made similarly and the maximum temperature of 1400°C was maintained for 16 hours.

The X-ray diffraction patterns showed an unidentified phase in a few of the samples. This was present in the top at higher intensity than in the main section of the sample. In samples B-17, B-19, and B-31, the lines in order of decreasing intensity had d-values of 2.39, 2.92, 3.46, 2.99, 1.71, 2.66, 2.08, and 1.80. In samples B-21 and B-38, the only lines were at 2.92 and 5.06. The UB_{12} samples had no unidentified lines.

The weight gain in air in one week was less than 0.1%.

The calculated constitution of the boron samples depends mainly on the assumption about the carbon. Although UC is shown by X-ray diffraction, a proportionate amount of B_4C could be present without being detected. Also, the carbon originally present in the boron might be expected to be present as B_4C. This uncertainty might be solved by tests of the equilibria at 1400°C, using a mixture of the uranium borides plus carbon and of boron carbide plus uranium. For the present, the assumption will be used that the UC:B_4C is that corresponding to the U:B ratio in the sample. The oxygen is most likely present as UO_2, which is shown in the X-ray diffraction patterns and which has a relatively higher heat of formation than B_2O_3. The Si, Fe, Cu, etc. are assumed present as elements. For the constitution, the analysis was normalized to 100.00%. The U-B system has the same structure from UB to UB_2, so the U:B ratio is given for UB_2. Compositions from UB_2 to UB_4 and UB_4 to UB_{12} are assumed to be mixtures. Compositions above UB_{12} are assumed to contain UB_{12} plus boron.

D. Uranium-Carbon Samples

Three compounds, UC, U_2C_3, and UC_2 were originally requested. However, the preparation of U_2C_3 would require strain[14] produced by heat treatment at 2000°C and then at 1600°C. The phase diagram and conditions indicated that it would not be likely to be produced as a single phase, so only one attempt was made to prepare U_2C_3. The preparation of UC has generally been done by arc melting[15] or sintering at 1800°C.[11] UC_2

should be quenched rapidly to avoid forming some UC plus C[16]. UC has also been prepared by the reaction of methane with uranium at 625°C.[17] Graphite with U_3O_8 at 1800°C can give UC and at 2400°C can give UC_2.[17]

All preparations were made by sintering or the solid-solid reaction of spectrographic graphite powder and uranium hydride. Runs C-1 to C-4 were small scale, made at 1400°C, and demonstrated that the solid-solid reaction would probably be satisfactory. Runs C-5 to C-13 involved 200-gram samples prepared in a graphite crucible in the graphite resistance furnace at 1700 to 1800°C. The best of these preparations were shipped (see Table IV). Sample C-7, for UC, was heated under vacuum to 1100°C and then heated in an argon atmosphere at the maximum temperature of 1700°C for 16 hours. Sample C-10, for UC, was prepared similarly except that slightly less graphite was used and the maximum temperature of 1670°C was maintained for 15 hours. Sample C-9, for UC_2, was a reheat of C-8, with the first heating at 1650°C for 17 hours and the second heating at 1680°C for 16 hours. The reheating was done in an attempt to decrease the amount of UC and graphite shown by X-ray diffraction, but no change was seen in the X-ray pattern. Sample C-13, for UC_2, was prepared, and the maximum temperature of 1700°C was maintained for 15 hours.

The weight gain in air in one week was 0.15% on C-9 and 0.1% on C-7, C-10, and C-13.

The constitution of the carbides really requires a determination of the graphite content, which had not been done at the time of this report. The oxygen in UC is undoubtedly present as UO, which has the same crystal structure as UC. The oxygen in UC_2 in these samples was assumed to be present as UO stabilized by the UC impurity, but purer UC_2 might contain only UO_2 as the oxide impurity.

E. Uranium-Nitrogen Samples

The uranium-nitrogen system contains three compounds, UN, U_2N_3, and UN_2. Of these, UN and UN_2 were to be prepared. UN is usually prepared by forming uranium powder from UH_3 and reacting it with nitrogen at 500°C

Table IV

COMPOSITION OF URANIUM-CARBON SAMPLES

Compound and Sample	U,%	C,%	O,%	H,%	Trace Elements, %	Total, %
UC						
C-7	94.80 94.80	4.84	0.26 0.25	0.03	(0.11)	100.24
C-10	94.99	4.83	0.35 0.35	0.10	(0.1)	100.37
UC_2						
C-9	90.33 90.43	8.98	0.45 0.48	0.05	(0.11)	99.99
C-13	89.84 89.86	9.62	(0.3)	0.09	(0.1)	99.97

TRACE ELEMENTS BY EMISSION SPECTROGRAPH

Sample	Fe,%	B,%	Others, %
C-7	0.03-.3 (0.1)[b]	0.003-0.03	Al, Si, Ca 0.001-.01;
C-10	0.03-.3 (0.1)[b]	0.001-0.01	Al, Si 0.001-.01
C-9	0.03-.3 (0.1)[b]	0.003-.03 (0.01)[b]	Al 0.001-.01; Ca 0.0003-.003
C-13	0.03-.3 (0.1)[b]		Si 0.003-.03; Al 0.001-.01

X-RAY DIFFRACTION (RELATIVE PEAK HEIGHTS)

Sample	UC	UC_2	C
C-7	100	18	
C-10	100	12	
C-9	12	100	3
C-13	11	100	3

CALCULATED CONSTITUTION OF URANIUM-CARBON SAMPLES

Sample	UC,%	UC_2,%	C,%	UO,%	Other, %
UC					
C-7	90.8	5.0		4.0	0.14
C-10	87.5	6.9		5.4	0.2
UC_2					
C-9	?	(91.8)	(0.59)	7.4	0.16
C-13	?	(94.0)	(1.03)	4.8	0.19

[a] Colorimetric [b] Estimate

to form UN containing some U_2N_3. This is then vacuum-heated to 1550°C[18] or higher. Ammonia has also been used in the preliminary nitriding of uranium shavings at 400°C.[19] UN_2 is more difficult to prepare and the crystal structure is formed at high pressures at about $UN_{1.75}$ or higher.[20] Although UN_2 has been claimed, the average ratio established by analysis has been $UN_{1.75}$ with nitrogen at 1800 psi at 600°C.[20]

Runs N-1 to N-3, and N-8, were trials to prepare UN_2, using UH_3 in the Aminco micro reactor or bomb. For sample N-8, uranium hydride was placed in a crucible in the reactor and purified nitrogen added to 1000 psig. The sample was heated to 350°C for 5 hours. The reactor was then flushed 4 times to eliminate ammonia. Then nitrogen was added at 1450 psig and the sample heated to 500°C for 20 hours. The pressure at temperature was 3150 psig. The product was pyrophoric. The analyses and constitution are given in Table V for this sample and the other samples which were shipped.

A preliminary study was made to prepare UN_2 by direct reaction of nitrogen and of ammonia with pieces of uranium metal. These runs, N-4 to N-7 and N-9 established that ammonia was better than nitrogen, as a 5/16-inch pellet was 37% reacted with ammonia at 800°C in 4 hours and 7% reacted with nitrogen. Also, ammonia may have a second maximum, since 18% reaction was obtained at 650°C, and 6% at 700°C.

Runs N-10 to N-15 were made in the vertical Vycor flow furnace. The first two runs had air leaks and produced U_3O_8 and UO_2. Run N-12 with ammonia at 650°C didn't produce much product, but the X-ray diffraction of this and earlier flow samples had produced the UN_2 structure with no sign of the lines characteristic of U_2N_3. Runs N-13 to N-15 with ammonia at 800 to 850°C gave about 65% reaction of a 110-gram piece of uranium metal in 8 hours. The products from runs N-13 to N-15 were combined and heated under vacuum in the graphite resistance furnace with 10.5 hours 1300°C The final temperature was 1350°C at 150 microns of pressure. Sample N-19, for UN, was prepared by heating sample N-17 of UN_2 under vacuum in a graphite crucible in the graphite resistance furnace. The temperature of 1325°C was maintained for 2 hours, and the final vacuum was 230 microns of pressure.

Table V

COMPOSITION OF URANIUM-NITROGEN SAMPLES

Compound and Sample	U,%	N,%	O,%	C,%	H,%	Trace Elements, %	Total, %
UN							
N-16	94.40	4.87	0.16	0.03	0.03	(<0.01)	99.72
	94.45	5.26	0.15				
N-19	94.49	5.41	0.20	0.05	0.04	0.06	100.09
	94.56	5.10	0.20				
UN_2							
N-8	90.44	(8.56)	0.89			?	(99.96)
	90.44		1.03				
N-18	90.78	10.60	0.07	<0.01		0.12	101.34
	90.90	9.98	0.11				
N-23	90.77	8.76	0.07	<0.01		0.06	99.69
		8.79	0.08				
N-25	90.86	9.42	0.05			0.07	99.99
	90.91	8.56	0.03				

TRACE ELEMENTS BY EMISSION SPECTROGRAPH

Sample	Fe,%	Others, %
N-16	none	None reported
N-19	0.01-.1	Al 0.003-.03; Mn 0.0003-.003
	0.05[a]	
N-16	0.1-1	Cu, Ni 0.003-.03; Al 0.001-01;
	0.10[a]	Mn 0.0003-.003
N-23	0.01-.1	Al 0.001-.01; Mn, Ca 0.0003-.003
	(.05)[b]	
N-25	0.03-.3	Al 0.003-.03; Cu 0.001-.01
	(.05)[b]	

Table V (Concluded)

X-RAY DIFFRACTION (RELATIVE PEAK HEIGHTS)

Sample	UN	U_2N_3	UN_2	UO_2
N-16	100			1
N-19	100			6
N-8			100	
N-18			100	
N-23			100	
N-25			100	

CALCULATED CONSTITUTION OF URANIUM-NITROGEN SAMPLES

Sample	UO,%	UO_2,%	UC,%	X in UN_X	UN_X,%	Other, %
UN						
N-16	2.5		0.6	0.99	96.9	0.03
		1.3	0.6	0.97	98.1	0.03
N-19	3.2		1.0	0.98	96.8	0.04
		1.7	1.0	0.95	97.3	0.04
UN_2						
N-8		8.1		1.75	91.9	(0.01)
N-18		0.8		1.69	99.1	0.12
N-23		0.6		1.71	99.3	0.06
N-25		0.3		1.69	99.6	0.07

[a] Colorimetric [b] Estimate

Samples N-17, N-19, and N-20 to N-25 (Table V) were made with ammonia at 850°C, and a reaction time of 20 to 24 hours was used to obtain complete reaction of the uranium. Most of these samples were used in unsuccessful attempts to prepare the sulfides, using sulfur plus this UN_2. Samples N-23 and N-25 were shipped.

The weight gain in air in one week was less than 0.1% on all samples except for sample N-8, which was pyrophoric.

The calculations of the constitution of the samples requires a knowledge of the form of the oxygen. The oxygen in UN could be present as UO, which has the same structure as UN, but the X-ray diffraction shows some UO_2. Therefore, part of the oxygen is probably present as surface oxides as UO_2 and part is present as UO. The constitution is calculated for both assumptions, but both give low ratios for U to N. Probably an X-ray calibration of UO_2 is required to determine the relative amount of UO_2. Why the UN ratio appears less than 1.0 is not known, as the UN is sufficiently stable that free uranium would not be formed. For UN_2, the oxygen should be present only as UO_2. The nitrogen analyses are the least accurate, so the analyses have been normalized to 100.00% by taking nitrogen by difference. Carbon is assumed present as UC.

F. Uranium-Selenium Samples

The selenide, USe_2, and the telluride, UTe, were originally requested, but attempts were made to prepare USe and USe_2 before doing research on UTe. The uranium-selenium system[22] contains USe, U_3Se_5, αUSe_2, βUSe_2, USe_2, USe_3, and UOSe, with the same structures as the corresponding uranium-sulfur compounds. The potential compound, U_2Se_3, corresponding to U_2S_3, has not been reported. The compound USe has been prepared by reaction of uranium powder with selenium and has been reported as stable from 700 to 1300°C.[22] USe_2 has been prepared by heating USe_3 for 10 hours at 700° where the USe_3 was prepared by heating UCl_4 with H_2Se at 620°[21] or by reaction of uranium powder with selenium.

The reaction of selenium powder with uranium hydride was selected, but the runs were limited in size because of the violence of the reaction. Run Se-1, for USe_2 and run Se-2, for USe, were direct reactions in alumina thimbles at 350 and 500°C respectively. Sample Se-4, for USe, (Table VI), was a reheat of Se-2 at 1200°C for 16 hours to homogenize it, and it was the best USe preparation that was made.

Table VI

COMPOSITION OF URANIUM-SELENIUM SAMPLES

Compound and Sample	U,%	Se,%	of USe, %
USe			
Se-4	74.91	24.22	99.14
	74.88	24.26	
USe_2			
Se-11	-	-	

X-RAY DIFFRACTION (RELATIVE PEAK HEIGHTS)

Sample	USe	α-USe_2	β-USe_2	UOSe	UO_2
Se-4	100				4
Se-11		100	30	30	

Run Se-5, for USe_2 used a mixture of Se powder and UH_3 weighing only 20 grams. It was placed in an alumina thimble inside the Aminco micro reactor, but the violence of the reaction shattered the crucible. Runs Se-6 and Se-7 were unsuccessful attempts to react a mixture of Se and UN_2 powders. Run Se-8, for USe_3, was an attempt to prepare a higher selenide which could subsequently be used to prepare USe and USe_2. However, this reaction was also violent. Run Se-9, for USe, was prepared in a stainless steel holder, but flakes of material came off the stainless steel. Run Se-10 was conducted in an aluminum container made from solid aluminum rod with a 5/8-inch-diameter hole. The Al container with Al cap was placed inside the Aminco Micro reactor. With 25 grams of reactants, the aluminum container was satisfactory. The product was then heated in the tungsten furnace to 1200°C and designated as Sample Se-11. The X-ray pattern showed mainly α-USe_2 and some β-USe and UOSe (see Table VI).

Run Se-12, for USe_2, was made similarly to run Se-10, but 90 grams of reactants were added. In this case, the violence of the reaction caused melting of the aluminum cap, and the product could not be removed. The preparation of large batches of the selenides will require a suitable container material which does not react with selenium. The ceramics are too fragile, stainless steel corrodes, and aluminum has too low a melting point. The refractory metals should be considered.

The chemical analyses and X-ray diffraction data are given in Table VI for the two samples which were shipped. These are small samples useful only for preliminary experiments on combustion. No attempt has been made to estimate the constitution of the USe samples. Oxygen would need to be determined, possibly using the acid-insoluble residue method for UOSe in the same manner as UOS is determined in US.

G. Uranium-Silicon Samples

The compounds USi and USi_2 were originally requested, but USi_3 was substituted for USi. The uranium-silicon phase diagram shows U_3Si, U_3Si_2, USi, αUSi_2, βUSi_2, and USi_3.[23] The compound U_2Si_3 is shown in place of βUSi_2 in the phase diagram.[5] These were obtained by melting[23] but USi_2 has also been prepared by solid-solid reaction.[24]

The preliminary research on preparation of uranium-silicon compounds consisted of about 9 runs for USi_3, 9 runs for USi_2, and 18 runs for USi and lower silicon compounds. The research showed that USi_3 and USi_2 could be made easily by solid-solid reaction of silicon with uranium hydride, but USi could not. Most of the USi samples contained a considerable fraction of USi_2 or unidentified phases, although the Si content was lowered considerably below that for stoichiometry. Very small samples of USi were also melted in an arc melting furnace without producing a single phase. The lack of success in producing USi indicates that the phase diagram may need further study in the region between U_3Si and USi_2.

Sample Si-37, of USi_3, was obtained in the molybdenum furnace by combining the products from three 20-gram runs. In these runs, the mixture of uranium hydride and silicon was heated slowly in an argon atmosphere up to 1400°C and maintained at that temperature for about 17 hours. In the alumina crucible, some samples formed a plug which rose to the top of the tube, probably at the time of the exothermic reaction. The analyses, diffraction results and constitution are given in Table VII for this sample and the other samples which were shipped.

Sample Si-41, of USi_3, was prepared in the graphite resistance furnace, using a zirconia crucible. The mixture was heated in an argon atmosphere in 3 hours to 1000°C, evacuated, refilled with argon, heated up to 1400°C, and maintained at 1400°C for 13 hours. Sample Si-45, of USi_3, was prepared in a graphite crucible and heated under vacuum to 1000°C, then heated to 1350°C and held at that temperature for 17 hours.

For USi_2, Sample Si-42 was prepared in the same manner as for Si-41, and sample Si-44 was prepared like Si-45, with a final temperature of 1400°C instead of 1350°C. These two samples had different structures, Si-42 being the alpha form and Si-44 being the beta form.

The weight gain in air was less than 0.1% on samples Si-41, Si-42, and Si-44. Sample Si-45 had a 2% gain in weight.

The calculated constitution of the samples has been done by assuming that the oxygen is present as UO_2 and that carbon is present as UC. The total was normalized to 100.00%. The ratios of U to Si are not entirely consistent with the X-ray diffraction results, as Si-42 with $USi_{0.94}$ showed some USi_3 in the diffraction pattern, and Si-45 with $USi_{3.00}$ had some α-USi_2. Sample Si-44 with $USi_{1.82}$ might be reasonable for β-USi_2, which has been identified in some of the literature as U_2Si_3 or $USi_{1.5}$. That is, βUSi_2 may be stable at a lower ratio for U:Si than βUSi_2.

Table VII

COMPOSITION OF URANIUM-SILICON SAMPLES

Compound and Sample	U,%	Si,%	O,%	N,%	C,%	H,%	Trace Elements, %	Total, %
USi_2								
Si-42	81.45	17.40	0.76		<.005	<.005	.01	99.57
	81.38	17.36	0.78					
Si-44	81.97	17.21	0.13	0.02	0.03		0.01	99.46
	82.09	17.26	0.12					
USi_3								
Si-37	73.79	25.66	0.26				0.14	99.93
	73.82	25.77	0.25					
Si-41	74.57	25.52	0.20	0.02	0.02		0.01	100.31
	74.45	25.56	0.21					
Si-45	74.31	25.50	0.22		0.04	0.10	0.01	100.13
	74.18	25.52	0.20					

TRACE ELEMENTS BY EMISSION SPECTROGRAPHY AND COLORIMETRY

Sample	Cu,%	Fe,%	Others, %
Si-42	0.01-.1 0.011[a]		
Si-44	0.003-.03 (.010)[b]		
Si-37	0.01-.1 0.012[a]	0.03-.3 0.11[a]	Mn, Ni 0.003-.03; Al, Cr 0.001-.01
Si-41	0.01-.1 0.010[a]		
Si-45	0.003-.03 (.010)[b]		
Silicon			B, Al, Cr 0.001-.01; Fe, Ti, Cr 0.0003-.003 Mg, Cu 0.0001-.001

Table VII (Concluded)

X-RAY DIFFRACTION (RELATIVE PEAK HEIGHTS)

Sample	α-USi_2	β-USi_2	USi_3	UO_2	?[c]
Si-42	100		5	25	
Si-44	3	100		2	
Si-37					
Si-41			100	9	<2
Si-45	4		100	6	

CALCULATED CONSTITUTION OF URANIUM-SILICON SAMPLES

Sample	UO_2, %	UC, %	X in USi_X	Other, %	USi_X, %
USi_2					
Si-42	6.3		1.94	0.01	93.7
Si-44	1.1	0.6	1.82	0.03	98.3
USi_3					
Si-37	2.2		3.03	0.14	97.7
Si-41	1.7	0.4	2.98	0.03	97.9
Si-45	1.8	0.8	3.00	0.15	97.2

[a] Colorimetric

[b] Estimate

[c] Unidentified

H. Uranium-Sulfur Samples

The uranium-sulfur system[25] contains US, U_2S_3, U_3S_5, αUS_2, βUS_2, γUS_2, US_3 and UOS. The high temperature, or tetragonal, form of US_2 will be designated as "alpha" US_2 and the orthorhombic form as "beta" US_2.[25,26] Some reports[5,27] have alpha and beta reversed. The two compounds to be prepared were US and US_2. Uranium sulfide has been prepared by reaction of US_2 with UH_3,[1] H_2S with UH_3,[1,26] and U with S in a sealed tube at 600-800°.[25] The product can be heated at 1900 to 2200°C under vacuum for homogenization or annealing.[26] Uranium disulfide has been prepared by the reaction of UO_2 plus H_2S and C,[1] by UH_3 with H_2S,[1] and by H_2S on U_3O_8 at 1200 to 1800°C.[25]

In the preliminary research, runs S-1 to S-4 were the direct reaction of uranium hydride with sulfur. The reaction was sufficiently violent to break an alumina thimble, but a stainless steel holder seemed satisfactory for a small sample. A series of trials were made of reacting hydrogen sulfide with 5/16-inch-diameter pellets. The percent reacted appeared to have a maximum around 625°C of 25% in 3 hours. These trials were originally numbered H_2S-1 to H_2S-10, but later were renumbered as S-5 to S-14. Runs S-15, S-18, and S-20 were made with hydrogen sulfide in the Vycor furnace with a 110-gram piece of uranium on a Vycor grid. As the sulfide formed, it dropped to the bottom, and 88 grams of product were obtained in 94 hours in run S-15. Part of this was heated with UH_3 to form US_4 in run S-16, and part was homogenized by heating at 1400°C in run S-17.

Run S-19 was a test of the reaction of US_2 with sulfur at 600° to form US_3. This appeared successful, but the X-ray pattern showed no decrease in the intensity of the UOS lines.

Because the direct reaction of H_2S with pieces of uranium metal was so slow and the reaction of sulfur with UH_3 was violent, other methods were tried. Runs S-21 to S-29 were trials of reacting uranium nitride with sulfur. However, the X-ray patterns of the products contained unidentified phases, and the method was abandoned.

Next, runs S-30 and S-31 were made of the reaction of hydrogen sulfide in the Aminco micro reactor. Although 16 successive fillings were made in run S-31, the product still contained unreacted UH_3 as shown by X-ray diffraction. Sample S-32 was made by heating the US_2 from S-31 up to 1400°C for 19 hours. It was mainly U_3S_5, and was shipped. The analyses, diffraction results and constitution are given in Table VIII for this sample and the other samples which were shipped.

Then a Pyrex tube was designed and built to fit in the flow furnace so a 110-gram piece of uranium could be reacted with hydrogen and then with hydrogen sulfide. Run S-33 was made with a flow of hydrogen for about 4 hours at 250°C. Then a flow of H_2S was maintained while the tube was

Table VIII

COMPOSITION OF URANIUM-SULFUR SAMPLES

Compound and Sample	U,%	S,%	O,%	C,%	H,%	Trace Elements, %	Total, %
US							
S-34	87.71	11.94	0.38	0.25	<.005	(0.1)	100.41
	87.74	11.96					
S-40	87.90	11.89	0.25	0.21	0.04	(0.1)	100.42
	87.89	11.94					
U_3S_5							
S-32	81.15	18.60	0.38			(0.05)	100.17
	81.16	18.58					
US_2							
S-41	80.30	19.28	0.56			(0.03)	100.13
	80.22	19.28					

TRACE ELEMENTS BY EMISSION SPECTROGRAPH

Sample	Fe,%	Others, %
S-34	0.1-1 (.1)[a]	Si 0.01-1; Cu 0.001-.01; Ca 0.0003-.003
S-40	0.1-1 (.1)[a]	Si 0.003-.03; Al, Cu 0.001-.01; Ca 0.0003-.003
S-41	0.03-3 (.03)[a]	Mg 0.003-.03; Al, Ca, Cu 0.001-.01;

X-RAY DIFFRACTION (RELATIVE PEAK HEIGHTS)

Sample	US	U_2S_3	U_3S_5	α-US_2	β-US_2	UOS	?[b]
S-34	100	2				10	
S-40	100	2				8	
S-32			100		6	18	9
S-41				100	9	25	

CONSTITUTION OF URANIUM-SULFUR SAMPLES

Sample	US,%	U_2S_3,%	U_3S_5,%	US_2,%	UOS,%	UC,%	Other, %
US							
S-34	73.1	14.8			6.8	5.2	0.1
S-40	80.0	11.0			4.4	4.4	0.2
U_3S_5							
S-32			67.3	25.8		?	0.1
US_2							
S-41	(7.7)			(82.1)	10.1	?	0.1

[a] Estimate

[b] Unidentified

heated to 425°C for 6 hours. The product was β- and α-US_2. Sample S-34, of US was prepared by heating this US_2 with added UH_3 in a zirconia crucible in the graphite resistance furnace up to 1000°C in argon, evacuating, refilling with argon, and finally heating at 1400°C for 17 hours. Runs S-35, S-36, S-37, and S-39 were made in the same manner as run S-33 in order to prepare US_2 which was used in preparation of US. Sample S-40, of US, was made using US_2 from runs S-35 to S-37 plus UH_3 in the same way as for S-33.

US_2 was prepared by homogenizing US_2 from the flow system by heating it at 1200 to 1400°C. Run S-38 was made by heating the US_2 in an argon atmosphere in a zirconia crucible in the graphite resistance furnace to 1400°C for 16 hours. Sample S-41 was made in the same way except the maximum temperature was 1200°. Sample S-41 had the lower oxygen content and was shipped.

The X-ray diffraction patterns of the samples contained unidentified lines in sample S-32, of U_2S_3, at d-values of 3.99, 5.44, and 2.30.

The weight gain in air in one week was less than 0.1% for the US samples, 0.5% for samples S-32 and 0.4% for sample S-41.

The calculated constitution of the samples has been obtained by assuming that the insoluble residue is UOS and that any carbon is present as UC. The latter assumption needs further study because no UC lines were found in the X-ray diffraction pattern. The percent total by analysis was normalized to 100.00%. Sample S-41 needed an analysis for carbon at the time this report was written, so the calculated constitution is incomplete.

V Discussion and Recommendations

The calculations of the constitution of the samples show very large effects from small concentrations of oxygen and carbon simply because of the high molecular weight of uranium. These impurities are especially troublesome when they may be present in two different forms; an example

being the amounts of UO and UO_2 in the samples of UN. The calibration of the X-ray diffraction analysis for UO_2 would undoubtedly be a help in resolving some of this uncertainty. A calibration on UH_3 would be helpful to determine the minimum UH_3 which is detectable. Also, some equilibrium determinations should be made by heating a sample with a relatively large amount of impurity to determine the equilibrium at the maximum temperature used in the preparations. Equilibrium determinations should be made to determine the form of such impurities as iron, nitrogen, etc. Further analyses are needed to determine the source of the iron impurity in some of the samples.

Thermodynamic calculations should be made on the samples to determine the effect of uncertainties in analysis or constitution on the final heats of combustion. Generally, the uncertainties have less effect than on the constitution, but the recent calculations on UN show that the uncertainty in the form of the oxide has very serious effects. The thermodynamic calculations provide the ultimate criteria for quality of the compounds.

For many of the compounds, it is believed that the impurities can be reduced markedly by an improvement in the vacuum of the graphite resistance furnace with a larger diffusion pump, and by reducing the oxygen in the argon atmosphere by using a circulating system similar to that used on the dry box.

A few of the analytical methods need further development, particularly the Dumas nitrogen method, and the oxygen method for UBe_{13}. A further improvement is required in the handling of samples for analysis. The samples which were shipped were kept in the dry box and received a minimum of handling in air if the weight gain in one week was less than 0.1%. The analytical samples received considerable handling in air, and even an 0.01% gain in weight is too high if it is due to the oxygen, moisture, or carbon dioxide in the air. This means that the samples for analysis of oxygen and hydrogen must be prepared in the dry box, using the same

precautions that have been used to store the large samples which were shipped. Thus the oxygen values are probably higher than the actual amount present in the samples which were shipped.

Contributors

The experimental runs were made by E. M. Carr and are recorded in SRI Notebooks 4458, 5606, and 5825. The chemical analyses were done primarily by O. D. Smith, L. J Salas, and H. H. Johnson. Dr. A. P. Brady was project supervisor. The helpful suggestions of Dr. R. C. Vogel, Dr. W. N. Hubbard and others in the Chemical Engineering Division at Argonne National Laboratories are gratefully acknowleged.

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REFERENCES

1. Eastman, E. D., et al.; Preparation and properties of the sulfides of thorium and uranium. J. Am. Chem. Soc. 72, 4019-23 (1950)

2. Gibbs, D. S., H. J. Svec and R. E. Harrington. Purification of the rare gases. Ind. Eng. Chem. 48, 289-96 (1956)

3. Casano, C. D., et al., editors. First conference, "Analytical Chemistry in Nuclear Technology" Nov. 4-6, 1957. TID-5555.

4. Bacon, A. and G. W. C. Milner. The Volumetric Determination of Uranium in Aluminum-Uranium Alloys AERE-C/R-1813 (March 21, 1956)

5. Rough, F. A. and A. A. Bauer. "Constitution of Uranium and Thorium Alloys" BMI-1300 (June 2, 1958)

6. Borie, B. S. Jr. Crystal structure of UAl_4. J. Metals 3, 800-2 (1951)

7. Gordon, P. and A. R. Kaufmann. The Alloys Systems U-Al and U-Fe. Trans. AIME 188, 182-94 (1950)

8. Snyder, M. J. and W. H. Duckworth. "Properties of Some Refractory Uranium Compounds." BMI-1223 (Sept. 7, 1957)

9. Williams, J. and J. W. S. Jones. "The Formation of Uranium and Beryllium Alloys by the Solid State Sintering of Mixed Elemental Powders." AERE-M/R-1974 (June 7, 1956)

10. Buzzard, R. W. Beryllium-uranium system. J. Res. N. B. Stds. 50, (2) 63 (1953)

11. Tripler, A. B. Jr., M. J. Snyder and W. H. Duckworth. Further Studies of Sintered Refractory Compounds. BMI-1313 (June 27, 1959)

12. Brewer, L., D. L. Sawyer, D. H. Templeton and C. H. Dauben. A study of the refractory borides. J. Am. Ceramic Soc. 34, 173-9 (1951)

13. Andrieux, J. L. and P. Blum. Electrolytic preparation and properties of uranium borides. Compt. rend. 229, 210 (1949)

14. Mallett, M. W., A. F. Gerds and D. A. Vaughn. Uranium sesquicarbide. J. Elect. Soc. 98, 505-9 (1951)

15. Farr, J. D., et al. The preparation of UC and its heat of formation. J. Phys. Chem. 63, 1455 (1959)

16. Rundle, R. E., et al. The structures of the carbides, nitrides and oxides of uranium. J. Am. Chem. Soc. 70, 99-109 (1948)

17. Litz, A. D., A. B. Garrett and F. C. Croxton. The preparation and structure of the carbides. J. Am. Chem. Soc. 70 1918-22 (1948)

18. Kempter, C. P., J. C. McGuire and M. R. Nadler. Uranium mononitride. Anal. Chem. 31, 156-7 (1959)

19. Chiotti, P. Experimental refractory bodies of high melting nitrides, carbides and uranium dioxide. J. Am. Ceramic Soc. 35, 123-30 (1952)

20. Rundle, R. E., et al. The Uranium-Nitrogen System, pp. 53-66 in Chemistry of Uranium-Collected Papers edited by J. J. Katz and E. Rabinowitch. TID-5290, Book 1 (1958). See also AECD-2247 and J. Am. Chem. Soc. 70, 99-105 (1948)

21. Khodadad, P. The selenides of tetravalent uranium. Compt. rend. 245, 934-6 (1957)

22. Ferro, R. Certain uranium-selenium and uranium-tellurium compounds. Z. anorg. u. allgem. Chem. 275, 320-6 (1954). cf. AERE-Trans 11/3/5/440.

23. Kaufmann, A., B. Cullity and G. Bitsianes. Uranium-silicon alloys. J. Metals 9, 23-7 (1957) or Trans. AIME 209, 23-7 (1957)

24. Loch, L. D., G. B. Engle, M. J.Snyder and W. H. Duckworth. Survey of Refractory Uranium Compounds. BMI-1124 (Aug. 7, 1956)

25. Picon, M. and J. Flahout. Sulfides of uranium. Bull. Soc. Chim. France 772-80 (1958). cf. AEC-Tr-3504.

26. Cater, E. D. The Vaporization, Thermodynamics, and Phase Behavior of Uranium Monosulfide. ANL-6140 (March 1960)

27. Zachariasen, W. H. Crystal chemical studies of the 5-f series of elements, X. sulfides and oxy-sulfides. Acta Cryst. 2, 291-6 (1949)