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PROCESSING OF URANIUM CARBIDE REACTOR FUELS. I. REACTION WITH WATER AND HCl

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ABSTRACT

High-purity uranium monocarbide reacted with water at 80°C to produce a finely divided, brown U(IV) compound, and 92 ml (STP) of gas per gram consisting of 11 vol % hydrogen, 86 vol % methane, 2 vol % ethane, and 0.6 vol % propane. At 90°C, the products were the same, but the reaction rate was higher. Reaction with 5.6 M HCl was slower than with water, but the gaseous products were essentially the same. In preliminary experiments at 80°C with UC-UC_2 mixtures containing less than 2 wt % free carbon, the volume of gas evolved per gram of sample hydrolyzed decreased from 92 to 32 ml (STP) and the methane concentration from 86 to 14 vol % as the UC_2 concentration in the mixture increased from 0 to about 63 wt %. An attendant increase in the hydrogen and ethane concentrations to 23 and 38 vol %, respectively, also occurred.

CONTENTS

1.0 INTRODUCTION

Studies to determine the stoichiometries and rates of the reactions of UC and UC_2 with water (both liquid and vapor), nitric acid, the common aqueous decladding solutions, i.e., aqua regia, sulfuric acid, and sodium hydroxide and such gases as oxygen and chlorine were started as part of a program to develop chemical processing techniques for carbide reactor fuels. Ultimately, the work will be extended to include mixed carbides of uranium with thorium and plutonium. Such materials as UC-ZrC and UC-NbC could also become important in reactor fuel technology because of their thermionic properties (1).

Interest in carbide reactor fuels has developed because of their stability at high temperature, favorable heat transfer characteristics, and high burnup potential. Since the uranium carbides react with most aqueous reagents and with a number of gases, a variety of processing methods is potentially available. The processes selected will depend primarily on the type of cladding and bonding used in specific fuel elements, safety aspects, and reaction rates. As cases in point, mechanical decladding of stainless steel—clad sodium-bonded fuels such as proposed for the CPPD-2 (2) will also result in reaction of the carbide fuel if water or steam is used for sodium disposal; and the practicability of using the 90% HNO_3 process (3) for graphite fuels containing carbide is dependent somewhat on the safety of reacting the carbides with concentrated nitric acid. This report contains a summary of the experiments conducted on the stoichiometry of the reactions of uranium carbides with water between July 1, 1960 and December 31, 1960.

The authors wish to thank D. T. Bourgette of the ORNL Metallurgy Division for preparing the carbide specimens, and A. D. Horton of the ORNL Analytical Chemistry Division for analysis of the gaseous hydrolysis products. Other chemical analyses, x-ray analyses, and metallographic examinations were provided by the groups of W. R. Laing, Analytical Chemistry Division, R. L. Sherman, Analytical Chemistry Division, and R. J. Gray and C. K. H. DuBose, Metallurgy Division, respectively.

2.0 EXPERIMENTAL

2.1 Results

2.1.1 Reaction with Water at 80°C

When uranium monocarbide was hydrolyzed with water at 80°C, the principal products were a finely divided brown solid U(IV) compound, methane (86 vol %), and hydrogen (11 vol %) (Table 1). Ethane and propane were also found. The gas-chromatographic analytical technique used was not very sensitive for the higher hydrocarbons. Recent experiments with a silica gel column indicated that the off-gas also contained about 1 vol % of compounds containing 4 to 7 carbon atoms per molecule. No acetylene was ever found. The CO liberated from specimens AI-1 and AI-4 was probably trapped in voids during sample preparation, and consequently was not a product of the reaction with water. Duplicate experiments with ORNL-2 specimens gave good agreement. There was, however, some variation among runs with ORNL-1A and AI-1; e.g., the hydrogen concentration varied between 9 and 14 vol % but was constant during each run as expected from results with ORNL-2 samples. Results with specimen AI-4 not only varied considerably between runs, but also showed considerable fluctuation within runs. In one experiment the hydrogen concentration increased from 12 vol % in the first third of the gas evolved to 23 vol % in the last third while the methane concentration decreased from 80 to 60 vol %.

As the amount of dicarbide in the specimen increased, the volume of gas (STP) evolved per gram of carbide hydrolyzed decreased from 92 ml with high-purity UC to 32 ml with the specimen containing about 63 wt % UC_2 (Fig. 1). The methane concentration decreased from 86 to 14 vol % while the ethane concentration increased from 2 to 38 vol % (Table 1). The specimens containing dicarbide also yielded an unidentified brown wax, which was soluble in alcohol, carbon tetrachloride, and ether but not in water or 6 M HCl. The nonvolatile hydrolysis products of the monocarbide specimens were completely soluble in 6 M HCl; in addition to the wax, the AI specimens yielded a trace (<0.01 mmole/g) of free carbon, and the UC_2-ORNL-1A piece a large amount of free carbon which presumably was unreacted in the original specimen.

Table 1. Reaction of Uranium Carbide with Water at 80°C (Helium Atmosphere)

Sample	Volatile Products: Average Composition of Gas, vol %: H_2	CH_4	C_2H_6	?[a]	C_3H_8	C_4H_{10}	CO	Total Vol of Gas, ml/g	Total C, mmoles/g	Total H, mmoles/g	H/C mole ratio	Nonvolatile Products, mmoles/g: Soluble in 6 M HCl: U	C[b]	Wax[c]	Total[c] C, mmoles/g
ORNL-2A	11.0	86.4	2.0	0.1	0.5	<1	-	90.6	3.73	15.56	4.17	3.98	-	-	3.73
ORNL-2B	10.8	86.5	2.0	0.08	0.6	<1	-	91.8	3.78	15.78	4.16	4.02	-	-	3.78
ORNL-1A	12.2	84.3	2.6	0.2	0.7	<1	-	92.7	3.82	15.85	4.16	3.98	-	-	3.82
AI-1	12.5	81.1	5.4	-	0.9	<1	0.1	85.3	3.62	14.77	4.07	3.91	0.11	0.23	3.96
AI-4	13.8	75.2	8.2	0.4	1.0	1.4	0.12	76.6	3.40	13.58	3.98	3.93	0.23	0.56	4.19
UC_2-ORNL-1A[d]	23	14	38	3.3	1.5	8.4	0.27	31.7	3.1						present

[a] Peak occurred at C_2H_4 on Molecular Sieve, but on silica gel no C_2H_4 peak occurred; probably this is one of the paraffin C_4 to C_7 isomers for which no standard is available.

[b] In analytical procedure most carbon compounds which steam-distill were lost.

[c] Assuming that wax is $(CH_2)_x$.

[d] Based on one incomplete experiment; the gas phase may also contain pentanes, 5 vol %; hexanes, 2.9 vol %; heptanes 1.3 vol %; and octanes 2.4 vol %.

High-purity monocarbide specimens weighing 12-15 g were completely hydrolyzed in 2 hr, whereas 4 g of the sample containing about 63 wt % dicarbide was only 80% hydrolyzed after 5 hr.

Results given (Table 1) for the sample containing about 63 wt % UC_2 (UC_2-ORNL-1A) must be regarded as very preliminary. Gas chromatographic analysis of the gaseous products with Molecular Sieve and silica gel columns yielded 25 peaks, of which 7 could be positively identified, viz., hydrogen, methane, ethane, ethylene, propane, 2-methylbutane, and CO. Five of the peaks corresponded to the n-isomers of butane, pentane, hexane, heptane, and octane but probably also represent other isomers of the same carbon content. The other 13 peaks occurred where other hexane, heptane, and octane isomers were expected. Since standards for these isomers were not available, the gas composition was calculated on the assumption that the 13 peaks actually represented C_6-C_8 isomers.

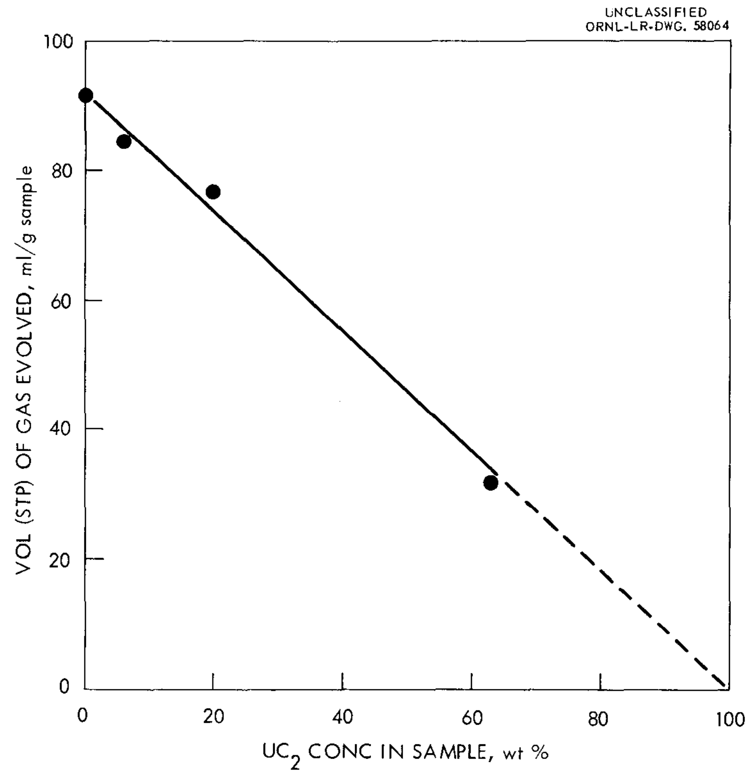

Fig. 1. Volume of gas evolved from UC-UC_2 mixtures containing <2% free graphite as a function of the UC_2 concentration.

2.1.2 Reaction with Water at 90°C

Specimen ORNL-1A, when hydrolyzed at 90°C, yielded an average of 92.4 ml (STP) of gas per gram of sample. The gas consisted of 11.3 vol % hydrogen, 85.6 vol % methane, 2.5 vol % ethane, and 0.7 vol % propane. These were essentially the products found at 80°C.

2.1.3 Reaction with 5.6 M HCl at 80°C

Specimen ORNL-2B, when reacted with 5.6 M HCl at 80°C, yielded essentially the same gaseous products as obtained with water. The resultant solution was green, with more than 99% of the uranium in the tetravalent state. For each gram of carbide hydrolyzed, an average of 91.6 ml (STP) of gas was evolved, which consisted of 9.9 vol % hydrogen, 87.7 vol % methane, 0.9 vol % ethane, 0.3 vol % propane, 0.4 vol % butane, and 0.3 vol % pentanes. In one experiment about 0.16 vol % hexanes and 0.07 vol % heptanes were also found.

The rate of hydrolysis was much lower in 5.6 M HCl than in water. For example, four specimens weighing a total of 3 g were only about 75% hydrolyzed in 5 hr at 80°C in hydrochloric acid, whereas hydrolysis in water of a 14-g specimen was complete in 2 hr at the same temperature.

2.2 Samples

Specimens ORNL-2A and -2B were prepared from high-purity uranium metal and carbon by the best arc-melting technique yet developed at ORNL, and appear to be nearly stoichiometric UC (Table 2). The other ORNL specimens were also prepared by arc melting. The method of preparation of the AI specimens is not known although the physical appearance of the material suggests that it may have been arc-cast into a graphite mold. Chemical analysis alone does not define the composition of the sample; e.g., an equimolar mixture of uranium and UC_2 yields the same chemical analysis as UC. Metallographic examination and x-ray analysis do not yield quantitative results, but are helpful in identifying the various phases present. For further details of the analytical procedures see the appendix.

Table 2. Analyses of Uranium Carbide Specimens

Specimen No.	Elemental Analyses: U, mmoles/g	Total C, mmoles/g	Free C, mmoles/g	N, ppm	Composition, mole %: UC	UC_2	U	Free C
ORNL-2A	3.99	3.95	-		>99.7	<0.2[a]	<0.1[a]	-
ORNL-2B	3.96	3.95	-	60	>99.7	<0.2[a]	<0.1[a]	-
ORNL-1A	4.00	3.91	-		98-100	-	0-2%[b]	-
AI-1	3.99	4.22	<0.01		94.2[c]	5.8[c]	-	-
AI-4	3.93	4.71	<0.01	260	80.2[c]	19.8[c]	-	-
UC_2-ORNL-1A	3.81	7.57	1.35	35	27.1[d]	46.7[d]	-	26.2[d]

[a]Metallographic estimation.

[b]Metallographic examination showed uranium as a nonhomogeneous dispersion.

[c]Based on chemical analyses; metallographic examination showed a fairly homogeneous mixed of UC and UC_2 except around the numerous cracks where pure UC_2 was present; confirmed by x ray.

[d]Based on chemical analysis and assuming no U_2C_3; metallographic examination showed UC_2, sheets of graphite, and a third unidentified phase; x-ray examination showed mostly UC_2 with a small amount of UC.

2.3 Procedure

The hydrolysis experiments were conducted as follows: The carbide specimen was placed in the reaction vessel, water was placed in the funnel, and the apparatus was assembled as shown in Fig. 2. The reactants were preheated to the desired temperature in a water bath controlled to ±0.05°C. During the equilibration period of 1.5 to 2 hr, helium was swept through the system to remove most of the air. Then the helium flow was stopped and the reaction vessel was isolated from the pressure equalizer. The gas buret was connected to the reaction vessel and water added to the carbide. The system was maintained near atmospheric pressure by adjusting the leveling bulb so that the mercury levels in the gas buret and open-end manometer were equal. Gas could be transferred from the buret to an evacuated sample bulb by raising the leveling bulb. A correction for the expansion caused by

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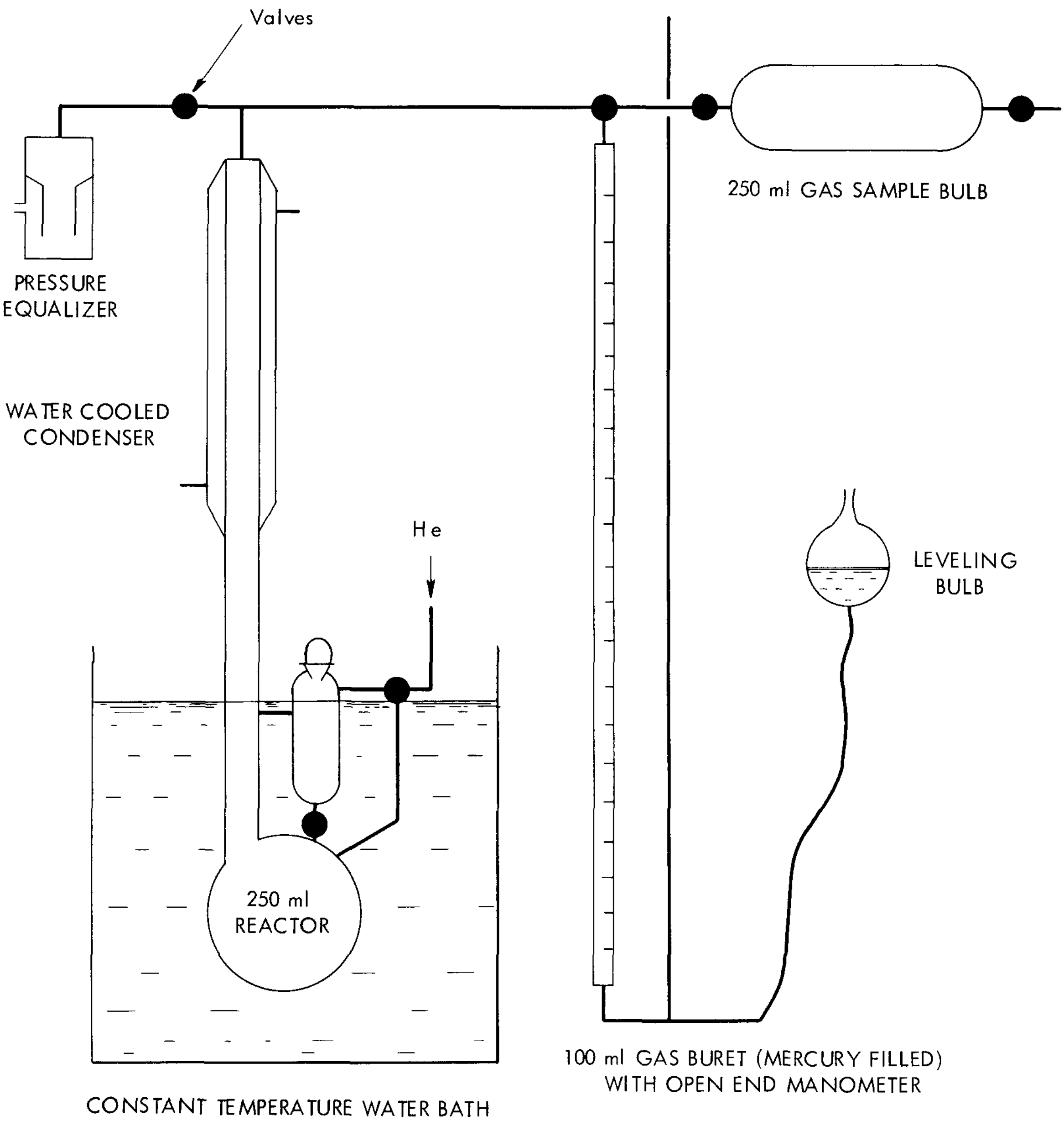

Fig. 2. Apparatus for measuring volume of gas evolved during reaction.

water vapor was determined from a blank run without carbide. The water bath was covered with a Lucite lid fitted around the apparatus to reduce the rate of evaporation from the bath. When necessary, water was added to the bath to maintain it at a constant level.

The gas samples were analyzed by gas chromatography with a 5-A Molecular Sieve column and a Burrell instrument modified with a Gow-Mac thermistor detector. Helium was the carrier gas, and peak areas were determined by the integrator on the Burrell instrument.

The solid uranium product was dissolved in chlorine-free 6 M HCl (prepared by flushing concentrated HCl with nitrogen just prior to use), and the solution was then filtered to test for free carbon. The filtrate was analyzed for U(IV) and total uranium potentiometrically, and for carbon by "concentrating" the solution on a hot plate before the residue was burned. The procedure for dissolved carbon was not satisfactory since volatile compounds were lost during the "concentration" step.

3.0 TENTATIVE CONCLUSIONS AND DISCUSSION

Gaseous products obtained from the reaction of uranium monocarbide with water were similar to those reported by Ockenden (4) at 20°C and by Litz (5) at 83°C. Litz, however, reported that the concentrations of the products changed markedly with temperature (Sect. 4.1). Preliminary results with samples containing about 63 wt % UC_2 were different from any reported in the literature.

A complete carbon balance was not obtained in any of the experiments. Carbon balances with the ORNL specimens were consistently 5% low. With specimen AI-4 the total carbon found by analysis was much too low to be attributed to the variations inherent in gas analysis. Considerable development work has been done on the combustion analysis used to determine total carbon in UC, and the method appears to yield results that are accurate and reproducible to within 1%. The gas-chromatographic analyses gave consistent results for the more volatile components. More recent results indicate that about 1 vol % of saturated hydrocarbons containing four to six carbon atoms per molecule were also present in the gas phase. In the future, gas samples will be analyzed chromatographically for hydrogen, methane, and ethane with a Molecular Sieve column. For the higher hydrocarbons, either silica gel or Apiezon L columns will be used. Standard mixtures of the isomers of hexane, heptane, and octane must be obtained to calibrate the columns.

The most difficult analysis appears to be that of determining carbon in aqueous solutions. In the experiments reported above, solutions were "concentrated" by evaporation on a hot plate and the residue was analyzed. The distillate was not collected. Pentane, hexane, and heptane isomers not volatilized at the reaction temperature would be lost by this procedure along with many other organic compounds which are steam-distilled. Analysts are working on a better method for analyzing the aqueous solutions.

4.0 LITERATURE SURVEY

Most of the prior data on the chemical behavior of uranium carbides were obtained with samples which were principally UC_2. Only a few references to work with UC are available. Uranium sesquicarbide (U_2C_3) is considered by the authors to be the material obtained by stressing $UC:2UC_2$ mixtures and is shown by x-ray and metallographic examination to be free of UC and UC_2. Virtually nothing is known about the chemistry of U_2C_3 since data reported for this compound in the older literature were obtained with samples prepared by a method that has since been shown to yield chiefly a mixture of 1 part UC and 2 parts UC_2.

4.1 Reactions with Water and Aqueous Acids

Uranium mono- and dicarbides react with water to produce a solid uranium oxide and a gaseous mixture of hydrogen and various hydrocarbons. The available data have been compiled in Tables 3 and 4. Considerable variation exists among the quantitative results of the various investigators, and few data on the purity of the starting materials are given. Estimates of the compositions, based on chemical analyses and the assumption that free carbon is carbon that did not react during sample preparation, have been included as footnotes to Tables 3 and 4. The UO_2-carbon reaction used by both Moissan (6) and Lebeau and Damien (7) to prepare their samples usually results in a carbide containing

Table 3. Gaseous Products of the Reaction of Uranium Monocarbide with Water

Gas	Gas Conc, vol % 20°C[a]	83°C[b]	90°C[b]	100°C[b]	200°C[c]	307°C[c]	400°C[c]
Hydrogen	8	12	22	37	93	96	99
Methane	85	81	72	57	5	3	0.5
Ethane	5						
C_3-C_5 paraffins	1	4	4	4			
Olefins		2	0.8	1.0	1.1	0.5	0.0
Acetylenes		0	0	<0.2			
CO_2		0.3	0.2	0.3	0	0	0
CO		0.4	0.2	0.9	0.4	0.4	0.3

[a]Reference 4; no chemical analyses of starting material given.
[b]Reference 5, liquid water; no chemical analyses of starting material given.
[c]Reference 5, water vapor; no chemical analyses of starting material given.

significant amounts of oxygen. Neither of these investigators used x-ray or metallographic examination to determine the purity of the samples. Litz (5) used these techniques on at least one specimen of UC and UC_2 as part of his proof of the compound UC, but failed to describe the material used in the chemical studies. Nothing is known about the purity of Ockenden's (4) samples. Ockenden was the only investigator to use gas chromatographic analysis of the gas mixtures; the other workers used vacuum-train separation in cold traps, a cumbersome procedure. Later observations showed that Moissan's "methane" analysis would also include the higher paraffins (7).

Moissan (6) reported that in the hydrolysis of UC_2 about 2/3 of the carbon went to liquid and solid hydrocarbons and 1/3 to gaseous products. Lebeau and Damien (7) studied only the gaseous products, finding 35.3 ml of gas per gram of carbide from specimen b and 32.1 ml/g from specimen c. Litz (5) also noticed in the hydrolysis of UC_2 some nongaseous hydrocarbons, which he presumed to be unsaturated as they darkened upon exposure to air.

Table 4. Gaseous Products of the Reaction of Uranium Dicarbide With Water

Gas	Gas Conc, vol %												
	a	b	c	81°C[d]	95°C[d]	100°C[d]	109°C[d]	125°C[d]	137°C[d]	148°C[d]	200°C[d]	248°C[d]	20°C[e]
Hydrogen	14	50	29	17	39	47	64	68	75	83	89	96	10
Methane	79[f]	13	20	30	18	10	10	8	7	6	4	1	60
Ethane		24	23	30	31	30	25	15	11	10	6	1.5	25
C_3-C_5 paraffins		4	10	8									4
Olefins	6	8	16	12	9	8		5	4		0.6	<0.2	
Acetylenes	0.5	2	3	2	1.1	2		0.3	2		0	<0.2	
CO_2				0.2									
CO				0.9	0.9	2	0.6	3	0.5	0.2	0.4	1.1	

[a]Reference 6, temperature not given; analysis of initial carbide: combined C, 7.3 wt %;U, 92.7 wt % (44 mole % UC, 56 mole % UC_2).

[b]Reference 7, temperature not given; analysis of initial carbide: 1.47 wt % free graphite (31 wt % UC, 68 wt % UC_2).

[c]Reference 7, temperature not given; analysis of initial carbide: no graphite, U 91.6 wt % (18 mole % UC, 82 mole % UC_2).

[d]Reference 5; no chemical analysis of initial carbide given.

[e]Reference 4; no chemical analysis of initial carbide given.

[f]Analytical procedure such that higher paraffins may also be present in "methane" fraction.

Heating the nonvolatile residue to 500°C after hydrolysis at 110-150°C yielded what he termed "residual" gas, consisting of 80 vol % H_2 with some carbon monoxide and hydrocarbons. Litz further reported that increasing the hydrolysis temperature of both UC and UC_2 increased the hydrogen concentration in the off-gas to nearly 100% at about 300°C while the amount of carbon in the residue also increased. No quantitative data on nonvolatile carbon were given.

The reaction of UC_2 with water vapor at 29 mm of Hg follows the linear rate law (8)

$$w = kt$$

with k = 0.044 $\mu g\ cm^{-2}\ sec^{-1}$ at 50°C, 0.66 at 150°C, and 3.2 at 200°C. The solid reaction products were identified by x-ray analyses as UO_2 and UC. The reaction of UC_2 with liquid water at 95°C was much more rapid than with steam at 250°C (5). Boettcher and Schneider (9) reported that uranium monocarbide (75% of theoretical density) was not attacked by liquid water below 50°C, attack was visible in 1 hr at 60°C, the rate was 600 mg $cm^{-2}\ min^{-1}$ at 65°C, and a violent reaction ensued at 100°C. Litz (5) stated that UC reacted more slowly with water vapor than UC_2, but that the carbides reacted with liquid water at about the same rate. Uranium sesquicarbide (crystallized under stress) did not react with liquid water at 75°C (10).

The reaction of UC with 4 N HCl and 18 N H_2SO_4 gave essentially the same gaseous products as with water (4). Uranium monocarbide was also separated from uranium metal by dissolving the metal preferentially in dilute HCl containing hydrogen peroxide (11). At 81°C, reaction of UC_2 with water, 0.15 N NaOH, 0.1 N H_2SO_4, 6 N HCl, and 0.5 M $FeCl_3$—1 M HCl resulted in the same gaseous products (5). Uranium dicarbide reacted slowly with cold hydrochloric and sulfuric acids to produce green solutions and with cold nitric acid to produce a yellow solution (6). Reactions with these acids were rapid when the solutions were heated. Uranium sesquicarbide did not react with concentrated acetic acid, concentrated KOH, or cold concentrated HCl; it reacted slightly with concentrated sulfuric and nitric acids at 75°C, and vigorously with concentrated HCl at 75°C (10).

Uranium monocarbide, when dissolved in 6 M HNO_3, yielded a brown solution and a black residue containing about 0.02% of the original uranium and 10% of the carbon (12). The gaseous products were mostly nitrogen oxides. Upon standing, uranyl oxalate separated from the solution.

4.2 Reaction with Oxygen

Both UC and UC_2 react readily with oxygen. The carbides are pyrophoric at room temperature if the surface area is sufficiently large: according to one source, when the particle size is 40 μ or less (13). The reaction of UC_2 with oxygen follows the parabolic rate law in the range 150-250°C:

$$w^2 = kt$$

where k is 6.1 $(\mu g\ cm^{-2})^2\ sec^{-1}$ at 150°C, 75 at 200°C, and 900 at 250°C (8). At 300°C the reaction proceeded anisothermally, with the temperature rising to 1000°C in less than 1 min. Both UO_2 and UC were detected in the product by x-ray analyses. Baker (14) reported U_3O_8 as a product of the reaction at 370°C.

4.3 Reaction with Carbon Dioxide

Uranium monocarbide with a bulk density of 10.98 g/cc was oxidized at a rate of 140 mg $cm^{-2}\ hr^{-1}$ over the range of 500 to 830°C (15). Sintered UC was about 0.6% oxidized after 6 hr at 500°C in a CO_2 atmosphere whereas uranium metal under similar conditions was 6% oxidized (16).

4.4 Reaction with Nitrogen

Nitrogen reacted rapidly with UC_2 at 1100°C to form uranium nitride (6). Between 400 and 700°C the reaction followed the parabolic rate law, $w = kt^{1/2}$, where k = 16 $(\mu g\ cm^{-2})^2\ sec^{-1}$ at 400°C, 260 at 500°C, 860 at 600°C, and 3300 at 700°C (8). The solid product was UN_x where x = 1.5 to 2.

4.5 Reactions with Halogens

Fluorine and UC_2 did not react at room temperature, but an explosion resulted when the system was heated slightly (6). Both UC and UC_2 reacted with BrCl, Br_2, or I_2 to produce carbon and the respective uranium tetrahalide (5).

The reactions were slow at low temperatures but rapid above 300°C (17). Uranium dicarbide burned in chlorine at 390°C to produce a volatile chloride (6). Uranium dicarbide burned in HCl gas at 600°C (6).

5.0 REFERENCES

1. "Quarterly Status Report of the LASL Plasma Thermocouple Development Program for Period Ending September 20, 1960," LAMS-2473.
2. J. W. Ullmann, ORNL, "Consumers Public Power Reactor Data Sheet," personal compilation, Aug. 22, 1960.
3. M. J. Bradley and L. M. Ferris, Ind. Eng. Chem., 53: 279 (1961).
4. D. W. Ockenden, AERE, Harwell, personal communication, Dec. 14, 1959.
5. L. M. Litz, "Uranium Carbides: Their Preparation, Structure, and Hydrolysis," PhD Thesis, Ohio State University, NP-1453 (1945).
6. H. Moissan, Ann. chim. phys., (7) 9: 302 (1896).
7. P. Lebeau and A. Damien, Compt. rend., 156: 1987 (1913).
8. A. B. Tripler, M. J. Snyder, and W. H. Duckworth, "Further Studies of Sintered Refractory Uranium Compounds," BMI-1313 (1959).
9. A. Boettcher and G. Schneider, "Some Properties of Uranium Monocarbide," P/964, Proc. 2nd UN Interntl. Conf. on Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 6, p. 561, UN, New York.
10. M. W. Mallett, A. F. Gerds, and D. A. Vaughan, J. Electrochem. Soc., 98: 505 (1951).
11. R. E. Rundle, N. C. Baenziger, A. S. Wilson, and R. A. McDonald, J. Am. Chem. Soc., 70: 99 (1948).
12. A. M. Simpson and B. A. Heath, I. G. Memorandum 464 (D) (June 1959).
13. E. Barnes, W. Munro, J. Williams, and P. Murray, "The Preparation, Fabrication and Properties of UC and U-UC Cermets," AERE-M/R-1958 (May 1956).

14. J. Baker, "Uranium Carbide," NEPA-138-SCR-3 (Dec. 31, 1946).
15. P. Murray and J. Williams, "Ceramic and Cermet Fuels," P/318, Proc. 2nd Interntl. Conf. Peaceful Uses Atomic Energy, Geneva, 1958, Vol. 6, p. 538, UN, New York.
16. J. Dubuisson, A. Houyvet, E. Le Boulbin, R. Lucas, and C. Moranville, "The Preparation of Uranium—Uranium Carbide Cermets and Stoichiometric Monocarbide by Sintering under Stress," P/1162, Proc. 2nd Internatl. Conf. Peaceful Uses Atomic Energy, Geneva, 1958, Vol. 6, p. 551, UN, New York.
17. J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," pp. 224-226, NNES, VIII, 1, McGraw-Hill, New York, 1951.
18. M. W. Mallett, A. F. Gerds, H. R. Nelson, J. Electrochem. Soc., 99: 197 (1952).
19. D. W. Bourgette, ORNL Metallurgy Division, personal communication, January 1961.

6.0 APPENDIX

The following is a synopsis of the analytical procedures used in the present investigation.

Uranium. Uranium was determined gravimetrically after precipitation with carbonate-free ammonium hydroxide and ignition to U_3O_8.

Total Carbon. Total carbon was determined by combustion analysis. A 200-mg sample was burned in oxygen in an induction furnace at 1400-1600°C for 10 min with 400 mg of flux consisting of 1/3 tin, 1/3 low-carbon iron (to maintain the temperature of the specimen) and 1/3 CuO (to provide an oxidant at the site of the reaction).

Free Carbon. Free carbon was determined by combustion analysis after the original carbide sample was dissolved in 6 N HCl, the solution filtered through a porous combustion boat, and the residue washed with ether to remove any wax present.

Earlier workers (6, 18) assumed that any carbon found after hydrolysis of the specimen in dilute HCl represented carbon that had not reacted with the uranium to form carbide. This conclusion seems justified in the case of uranium monocarbide, since high-purity specimens have been made which yielded no free carbon on hydrolysis. However, it has not yet been proved that carbon is not a product of the hydrolysis of UC_2. There is still some question regarding the existence of pure UC_2 at temperatures below 1800°C (18); therefore proof of the origin of free carbon found on hydrolysis will be difficult. In this study it was assumed that free carbon was carbon that did not react during sample preparation.

Metallographic Examination. This technique, while not yielding quantitative results, is useful in determining the homogeneity and phases present in the samples. The purity of samples of nearly stoichiometric UC is best estimated by estimating the area covered by the insoluble, impure phases. Both uranium and UC_2 are reported to be insoluble in UC (18). A series of near stoichiometric UC specimens of constant uranium weight and differing in carbon weight by 50 ppm increments (i.e., 0.1 mole %) under metallographic examination showed detectable differences going from uranium-rich to carbon-rich specimens (19). Oxygen and nitrogen, which form solid solutions in UC, are not detected metallographically. The metallographic procedure was of no quantitative value for specimens containing 5% or more impurity.

X-ray Powder Pattern. This technique was also used to confirm the compounds present. At least 5% must be present before the compound is detected.

ORNL 3101
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