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THE PREPARATION OF URANIUM MONOCARBIDE
BY REACTION IN A
LIQUID-METAL MEDIUM

by

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and R. K. Steunenberg

Chemical Engineering Division

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THE PREPARATION OF URANIUM MONOCARBIDE BY REACTION IN A LIQUID-METAL MEDIUM

by

E. J. Petkus, T. R. Johnson,
and R. K. Steunenberg

SUMMARY

Uranium and plutonium monocarbides are promising fuel materials for fast breeder reactors because of their high melting points, good resistance to radiation damage, high thermal conductivity, and high density. Their principal disadvantages seem to lie in the difficulties of synthesizing the compounds and of fabricating the fuel shapes. This report describes a novel method of uranium monocarbide synthesis. Uranium monocarbide was produced on a 500- to 1000-g scale by reacting, at 800°C, uranium dissolved in a liquid zinc-magnesium alloy with finely divided carbon suspended in the liquid-metal solution. In a typical preparation, 500 g of uranium was dissolved in a melt consisting of 500 g of magnesium and 3,200 g of zinc. With vigorous agitation, the uranium was reacted with 30 g of degassed charcoal for 8 or more hours at 800°C. The reaction vessel was an 8-in.-diam tantalum crucible that was well baffled to promote mixing. The carbide formed an insoluble solid phase that was heavier than the solvent metal. After a settling period of 1 to 4 hr, the bulk of the zinc-magnesium supernatant liquid was transferred by pressure-siphoning through a tantalum tube into a graphite mold. The zinc-magnesium remaining with the UC precipitate was removed by vacuum retorting at 850-900°C.

The typical UC product had a carbon-to-uranium atom ratio (C/U) of 1.05 to 1.10 and contained 0.2 to 0.3 w/o oxygen and 0.2 to 0.4 w/o of magnesium and zinc. Uranium monocarbide was the only compound formed, but stoichiometric or hypostoichiometric UC could not be produced by this method because an excess of carbon was necessary to completely react the dissolved uranium with the suspended carbon. Long reaction times (8-19 hr) and a carbonaceous material with a high surface area (such as activated charcoal) were beneficial in effecting almost complete reactions.

The oxygen impurity in the final product was attributed to residual oxygen in the feed material, especially in the activated charcoal, and to the exposure of the extremely reactive product to impure helium atmospheres. The charcoal was vacuum-degassed at 800-900°C before use. Although the helium atmosphere of a vacuum glovebox, in which the experimental operations were conducted, usually contained less than 40 ppm oxygen and 10 ppm water, the UC product was contaminated significantly by exposure to this atmosphere.

Based on the amount of uranium metal charged, UC yields of up to 83.5% were obtained. Losses occurred through the incomplete reaction of the dissolved uranium and through the entrainment of UC particles with the zinc-magnesium liquid as it was transferred out of the reaction crucible. Yields were increased by using longer reaction times (up to 19 hr) and longer settling times (up to 4 hr). The settling period allowed the fine UC particles to settle to the bottom of the crucible so that they were less likely to be entrained. The yield of UC was increased substantially by using a transfer tube whose inlet was directed away from the crucible bottom. When a tube of this configuration was used to transfer the liquid supernatant from the reaction crucible, the UC particles, which were on the bottom of the crucible, were not swept into the transferring liquid.

I. INTRODUCTION

Of the major types of reactor fuels (metal, oxide, and carbide) being most actively investigated, uranium and plutonium monocarbides are promising candidates for use as high-performance nuclear fuel materials for advanced power and fast breeder reactors. Metallic alloys of uranium and plutonium¹ have relatively low melting points and have compatibility problems with most cladding alloys at high temperatures. Metal fuels, because of their relatively poor irradiation stability, must be reprocessed frequently, or a large void volume must be provided inside the fuel cladding to accommodate fuel swelling. The advantages of metal fuels are their high thermal conductivities and the high densities of fissile atoms. The dioxides of uranium and plutonium are being developed¹ to overcome some of the deficiencies of metal fuels. The oxides have high melting points, good compatibilities with many types of cladding, and good resistances to radiation damage. However, oxides have relatively low densities of fissile atoms and poor thermal conductivities. The monocarbides¹ more nearly resemble metal alloys in these latter respects, while retaining the advantages of ceramic materials. The high density and thermal conductivity of the carbides permit smaller reactor cores, larger-diameter fuel rods, higher power density, lower in-core inventory, and better breeding characteristics than the oxides. For these important reasons, the development of the carbides as fuel material has been pursued actively. Although the irradiation testing of uranium-plutonium carbide fuels has not been as extensive as that of oxide or metal fuels, their stability² to neutron irradiation appears to be comparable to the stability of the oxides. However, hyperstoichiometric uranium monocarbide has shown a tendency to carburize and embrittle cladding in the presence of a sodium bond.³

The most common methods of synthesizing UC can be divided generally into two classes,⁴ those using uranium metal for the starting material and those using uranium oxide, as shown below:

Preparation of refractory-metal carbides of iron, zirconium, and niobium in a metal matrix, in which carbon is soluble, has been reviewed elsewhere.¹² In these preparations, the carbides were isolated by dissolving away the matrix metal with acid. The formation of various compounds in liquid metals¹³ has been observed in the past during studies directed toward the development of recovery and decontamination processes for fissionable materials. For example, compounds such as uranium carbide or uranium silicide were precipitated from uranium-cadmium solutions by reaction with carbon or silicon present as impurities in the solution or in the container material. Uranium carbides have also been prepared by retorting mercury¹⁴ or zinc solutions¹⁵ in a hydrocarbon atmosphere and by reaction in a medium of liquid chloride salts.¹⁶

The method of synthesis described in this report can be classified as a direct combination of the elements to produce UC. A liquid-metal medium is used to promote the reaction between the dissolved metallic element and the suspended nonmetallic material, carbon. Agitation of the melt promotes intimate contact between the reactants and allows the reaction to proceed in the liquid-metal medium at the relatively low temperature range of 700-800°C.

In scouting experiments at ANL,^{17,18} the following compounds were synthesized in various liquid-metal media: UC, Pu₂C₃, Ce₂C₃, USi₃, U₃Si₂, and ThC₂. In addition, ZrC and a mixed UC-ZrC were prepared in a liquid-zinc medium. To synthesize compounds by this method, the following general requirements should be met:

1. The solvent metal must not form insoluble compounds with either of the reactants at the temperature at which the reaction is performed and in the concentration ranges used.
2. At least one of the reactants must be fairly soluble in the solvent metal.
3. If the other reactant is insoluble, it must be finely divided and suspended in the melt.
4. The solvent metal must be sufficiently volatile to permit its complete removal by retorting under reduced pressure.
5. The compound formed must be stable in the solvent metal at the temperature of the reaction.

Class I

Starting Material: Uranium Metal

Reaction 1. $\text{U} + \text{C} \rightarrow \text{UC}$ (usual reaction temp: 2500-3000°C)

Reaction 2. $\text{U} + \text{CH}_4 \rightarrow \text{UC} + 2\text{H}_2$ (usual reaction temp: 600-900°C)

Class II

Starting Material: Uranium Oxide

Reaction 3. $\text{UO}_2 + 3\text{C} \rightarrow \text{UC} + 2\text{CO}$ (usual reaction temp: 1500-2000°C)

Reaction 4. $\text{UO}_2 + 3\text{CH}_4 \rightarrow \text{UC} + 2\text{CO} + 6\text{H}_2$ (usual reaction temp: 1500-2000°C)

The direct combination⁵ of the elements (Reaction 1) is most commonly done in an electric arc at temperatures above the melting point of the carbide. Several hundred kilograms of UC fuel for the Hallam reactor⁶ were synthesized by arc-melting of the elements, and the fuel shapes were fabricated by arc-casting. Because of the high vapor pressure of plutonium at the arc, temperatures, this method has only limited applicability to materials containing plutonium. Methane, or other hydrocarbons, must be reacted with finely divided uranium metal (Reaction 2) at a temperature below which the metal particles begin to sinter. In a laboratory-scale fluidized bed, both uranium and uranium-plutonium monocarbides have been produced⁷ successfully by this procedure.

Uranium oxide is a preferred starting material for UC production because it is considerably less expensive than the metal. The reaction of carbon (Reaction 3) or hydrocarbons (Reaction 4) with uranium oxides requires that the temperature be in the range of 1500-2000°C and that the partial pressure of the CO product gas be kept low.⁸ For the reaction with elemental carbon, a high pumping rate at low pressure is needed. Temperatures of 1700-1800°C are required to lower the oxygen content below 300-400 ppm for stoichiometric or hyperstoichiometric UC; temperatures of 1800-1900°C are needed to produce hypostoichiometric UC with an oxygen content below 500 ppm.⁹ Reaction 4 could be done in a high-temperature fluidized bed¹⁰ where carbon would be introduced as methane in the fluidized gas stream. The partial pressure of CO in the exit stream would be kept very low by the flow of the fluidizing gas.

A few other synthesis procedures have been reported. The reaction of UF_4 or UF_6 with SiC to form UC and SiF_4 has been attempted,¹¹ but with no practical success. Uranium fluoride is an advantageous starting material because enriched uranium is less expensive as the tetrafluoride than as oxide or the metal.

II. FIRST SERIES OF URANIUM MONOCARBIDE PREPARATIVE RUNS

Most of the work on the synthesis of compounds in liquid-metal media was directed toward the preparation of UC since it was the ceramic fuel of greatest current interest. A preliminary investigation was made to study the feasibility of synthesizing UC by reacting uranium with powdered carbon in a liquid-metal solution and to determine the characteristics of the product. This first series of runs was also intended to yield information helpful in the design of improved equipment. These experiments were done in available equipment that did not permit total protection of reactants and product from contamination by reaction with water vapor and oxygen in the air. For the second series of runs, a vacuum-inert gas glovebox was used to permit materials to be loaded and unloaded under a high-purity helium atmosphere.

The process steps used to prepare UC in both series of runs were:

1. Dissolution of the metallic uranium in a zinc solution containing 12 to 18 w/o magnesium.
2. Addition of a degassed solid carbonaceous material.
3. Reaction of the constituents at 740-800°C by stirring the liquid for at least 4 hr.
4. Separation of the bulk of the supernatant liquid metal from the product.
5. Vacuum distillation of the residual metals from the UC product.

The reaction furnace for the first series of runs was an induction-heated, tilt-pour furnace that had been modified to include a heated tantalum tube through which the supernatant liquid from the reaction crucible could be transferred into an unheated receiver. The reaction crucible, made of 30-mil-thick tantalum sheet, was 3.38 in. ID by 8 in. deep and had four 3/8-in.-wide baffles that were attached to the wall and extended to within 1/8 in. of the bottom of the crucible. The paddle-type agitator (2.13 in. wide and 1.10 in. high) and the thermocouple well were also made of tantalum. An induction-heated vacuum retort was used to evaporate the solvent metals from the product. The metal vapors were condensed as solids on a gas-cooled, stainless-steel sleeve that fitted into the top of the retort.

The conditions and results of experiments on the scale of 300-500 g of uranium are shown in Table I. Similar experiments on a smaller scale (less than 50 g of uranium) were also made to investigate specific areas of interest. To calculate the extent of the reaction between uranium and carbon, the amount of uranium remaining in solution was determined by analysis of filtered samples taken from the melt. This sampling procedure has been described in detail in another report.¹⁹ After the UC product had

been separated from residual solvent metals, the product in the reaction crucible was removed from the retort and transferred into a helium-filled glovebox, where samples were taken for the various analyses listed in Table I. For total-carbon determinations, 0.1- to 0.2-g samples were sealed under helium in tin capsules and analyzed by a combustion technique. A blank value of 75 μ g of carbon was found for empty capsules handled in a manner similar to those that contained UC. For oxygen analyses, samples were sealed under helium in platinum capsules and analyzed by a combustion technique. Samples encapsulated in aluminum were analyzed for nitrogen by a Kjeldahl procedure. Uranium analyses were made by a volumetric procedure, which had an estimated standard deviation of $\pm 1\%$. Magnesium and zinc were determined by colorimetric analyses, which had standard errors of about $\pm 5\%$. Other trace impurities were estimated to within an order of magnitude by emission spectrography.

TABLE I. Process and Analytical Data for Uranium Monocarbide (UC) Production; First Series of Runs

	Run										
	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10	P-11	P-12
Charge											
Uranium, g	535	528	530	528	525	530	390	527	300 ^b	302	306 ^b
Zn + Mg, g	2990	2980	2990	2970	2960	2970	2210 ^c	2980	2710 ^c	2710 ^c	2960 ^c
C/U (g atom/g atom)	1.50	1.84	1.50	1.50	1.51	2.00	2.03	1.88	1.28	1.24	1.10
Type of carbon used ^a	Activated charcoal	Activated charcoal	Activated charcoal	Activated charcoal	Activated charcoal	Graphite	Graphite	Graphite	Activated charcoal	Activated charcoal	Activated charcoal
Reaction Conditions											
Time, hr	5.3	14	20	4	8	13	12	14	5.5	7.5	4.5
Temperature, °C	800	800	800	800	800	820	800	800	750	750	750
Phase transfer	UC settled 75 min, 60% of melt siphoned off	UC settled 30 min, 60% of melt siphoned off	Ingot surface cleaned	UC transferred as slurry	Melt partly frozen, liquid siphoned off	Supernatant solution poured off	Melt partly frozen, liquid siphoned off	UC transferred as slurry		Melt partly frozen, liquid siphoned off	
Results and Product Analyses											
Yield, % of U	64	44	92	46	80	93	90	-	93	98	89
Uranium, w/o	90.6	91.5	92.2	91.1	90.3	90.4	87.4	87.4	88.9	92.7	93.0
C/U, atom ratio	1.25	1.14	1.13	1.24	1.20	2.07	1.99	1.69	1.18	1.18	1.05
Oxygen, w/o	0.90	0.84	0.76	1.17	0.83	-	0.39	0.49	1.58	0.94	0.58
Mg + Zn, w/o	0.5	0.4	0.4	1.3	0.6	0.7	1.0	-	1.3	0.9	0.6

^aAll carbon used had particle sizes less than 74 μ . The total amount of carbon charged as shown was added to the melt in two steps in some runs.

^bSodium charged: ~35 g.

^cMagnesium content of solvent alloy was 20 w/o for these runs. For all other runs, it was 12 w/o.

Finely divided, activated charcoal was used as the source of carbon in most of the runs, but in Runs P-7, P-8, and P-9, a powdered graphite was charged. Both types of carbon had similar average particle size (less than 140 μ), but the specific surface area of the activated charcoal was higher than that of the powdered graphite (1100 m²/g compared to 4.6 m²/g). Surface-area measurements were made by a standard BET technique. For the same C/U charge ratio, the reaction rate and the degree of completion of reaction were higher when activated charcoal was used, as shown in Fig. 1 by the comparison of the reaction curve of Run P-6 and that of the first part of Run P-7. These experiments were made under similar conditions, except that activated charcoal was used in Run P-6 and graphite in Run P-7. In the latter run, additional graphite was added to the melt after

6 hr to complete the reaction. The difference was attributed to the much higher surface area of the charcoal. The mechanism of the reaction between the uranium and carbon evidently involved the reaction of uranium with the surface of the carbon, followed by diffusion of uranium into the bulk of the carbon (see p. 23 and Fig. 8 later).¹¹ Because the latter step was rate-limiting, the reaction rate and the extent of reaction were strongly influenced by the surface-to-volume ratio of the solid carbon, which also was indicative of the diffusion-path length for uranium into the carbon matrix.

Fig. 1. Effect of Type of Carbon; First Series of Runs

A charge of powdered graphite of about 100% in excess of stoichiometry was required to react the uranium completely in a Zn-12 w/o Mg solution, but only about 50% excess activated charcoal was needed. The reaction curves of experiments during which different amounts of activated charcoal were charged are compared in Fig. 2. The initial reaction rates in all

Fig. 2. Effect of Amount of Carbon; First Series of Runs

three runs were similar, but in the run with the lower C/U ratio, the reaction stopped before the uranium had been completely reacted. To complete the reaction of the dissolved uranium in Run P-4, additional charcoal was added to the melt after 11 hr.

Poor contact of the solid carbon with the metal solution was a contributing cause of the slow and incomplete reaction between the dissolved uranium and the solid carbon. After several hours at temperatures near 800°C and with agitation, loose, unwetted carbon generally was present on the surface of the Zn-12 w/o Mg melt. Slow agitation was required during the first few hours of a run to prevent this loose carbon from being thrown out of the crucible. To improve the wetting of the carbon by the melt, the magnesium content of the metal alloy was increased from 12 to 20 w/o in Runs P-8, P-10, P-11, and P-12. The addition of magnesium to zinc increased the ability of the molten alloy to wet solid surfaces, presumably because of the ability of magnesium to reduce surface oxides or to react with oxygen adsorbed on surfaces. In Run P-11, when the magnesium content was increased to 20 w/o, the reaction rate was higher than in a similar run (P-4), in which the magnesium content was 12 w/o (see Fig. 3). In addition, this rate increase was realized at a temperature that was 50°C lower. The increase in the magnesium content of the liquid-metal solution from 12 to 20 w/o increased the rate and extent of the reaction, but Martin and Wach²⁰ found that increasing the magnesium content of zinc alloys above a level of 10 to 12 w/o decreases the solubility of uranium in the liquid metal.

Fig. 3. Effect of Solvent Composition; First Series of Runs

The alkali metals are strong reductants and the heavy alkali metals (potassium, rubidium, and cesium) react with graphite to form lamellar compounds.²¹ The lamellar compounds may be desirable, since in effect they disperse the graphite particles and increase the surface area available for reaction. These heavy alkali metals are too volatile to be used near 800°C, and their solubilities²² in zinc and magnesium are low. However, at

800°C, sodium has a solubility²³ of at least 5 w/o in zinc and a vapor pressure²⁴ of only about 360 Torr. The sodium could be removed easily from the UC product by vacuum retorting. Sodium wets graphite well, and at elevated temperatures it exhibits some tendency to form compounds with graphite.²⁵

In small-scale runs, when sodium was added to the U-Mg-Zn melts, the rate and extent of the reaction of uranium with carbon was increased over comparable systems without sodium. In one such experiment, in which the C/U charge ratio was 0.90, and 6 w/o sodium was added to a Zn-10 w/o Mg-7 w/o U alloy, a homogeneous powdered product was recovered that had a C/U ratio of 0.89. The product with the lowest C/U ratio prepared in these small-scale runs without the addition of sodium was 1.05. Two large-scale experiments (Runs P-10 and P-12) were made with the addition of 1.3 w/o sodium to the Zn-20 w/o Mg alloy. Compared to Run P-11, in which no sodium was added, the reaction rate of Run P-10 was not significantly faster (see Fig. 3). In Run P-12, the decreased C/U ratio of 1.10 caused a slower reaction rate and an incomplete reaction of uranium. However, after 5 hr of reaction time, a homogeneous product was recovered. The surfaces of the metal ingots after these runs made with sodium were free of loose, unwetted carbon. After runs made without sodium, loose carbon was frequently found on the ingots.

Although the addition of sodium was helpful in the small-scale runs, the advantages of sodium addition were not proven by the few larger-scale experiments. The ineffectiveness of sodium on the larger scale was thought to be due to the lower sodium content of the metal alloy in these experiments.

Fig. 4. Effect of Sodium on the Solubility of Uranium in Zinc

In the equipment used for these preliminary experiments, sodium posed handling problems and was a major source of oxygen impurity. Sodium as well as magnesium decreases the solubility of uranium in liquid zinc. The effect of sodium on the solubility of uranium in zinc is shown in Fig. 4.

After the completion of the reaction between the uranium solute and the suspended carbon, the bulk of the solvent metal was separated from the precipitated uranium carbide. The purposes of this phase transfer were to reduce the heat required during retorting and to separate unreacted uranium and carbon from the product. Because of differences in their densities, the carbide product should settle to the

bottom of the vessel, and unreacted or partially reacted carbon should rise to the top of the melt. Unreacted uranium should remain dissolved in the metal solution. Various means of achieving this separation were tried. In Runs P-2 and P-3, the melt was allowed to remain quiescent for a time before the top portion of the melt was removed through the transfer tube. Large amounts of the carbide were entrained and transferred with the liquid. There was some improvement of product yield with increased settling time. In Run P-4, the entire melt was allowed to freeze in the reaction crucible, a thin surface layer of the ingot was removed, and the remaining metal was retorted. In Run P-5, the entire agitated melt was transferred into a cold mold, and the bottom half of this ingot was retorted to recover the product. The fraction of the product recovered was approximately equal to the fraction of the melt retorted. Apparently the UC particles did not have sufficient time to settle before the ingot solidified. These results indicated that the uranium carbide made from activated charcoal was easily suspended in the liquid metal. The carbide made from the powdered graphite apparently settled more rapidly, as shown by the high recovery obtained in Run P-7. In this run, after a quiescent period of 15 min, about half of the reaction melt was poured and the material remaining in the reaction crucible was retorted to recover 93% of the product.

In most of the other runs, the melt was cooled to about 500°C and the supernatant liquid was removed by pressure-siphoning. Product recoveries with this procedure were generally higher than with the other phase-separation procedures explored. Cooling the zinc-magnesium alloys caused the precipitation of $MgZn_2$, which had a higher density than the liquid phase. It was thought that this compound crystallized on the UC particles, caused the particles to settle to the bottom of the melt, and prevented them from being transferred from the crucible with the liquid. This procedure had the disadvantage that unreacted uranium would also precipitate when the melt was cooled, and thus free uranium metal would appear in the retorted product.

Because all the phase-separation procedures were relatively ineffective in separating unreacted carbon from the carbide product, they could not be used to control the C/U ratio in the product. The removal of excess carbon shown in Table I for Runs P-2 through P-6 was not primarily due to the liquid separation, but was due to the splashing of carbon from the melt or to the physical removal of carbon from the ingot before the retorting step.

The contamination of the carbide product by oxygen and other impurities was unacceptably high. The oxygen contamination was caused by the oxygen content of the charge materials (principally the activated charcoal), by exposure of the fine retorted product to air and moisture during the transfer from the retort to the glovebox, and by exposure to the inadequately purified atmosphere in the glovebox. To minimize the oxygen

content of the charge materials, the metallic materials were acid-cleaned, dried, charged into the furnace, and heated to 300°C under vacuum before being melted, and the carbon was degassed by heating in vacuum at 800°C. Although the degassed carbon was then added to the metal ingot as rapidly as possible, some exposure to air and moisture was unavoidable. The powdered graphite contributed less oxygen to the product than did the activated charcoal. Analysis of one sample of the powdered graphite after degassing showed an oxygen content of 0.62 w/o. This amount would add only about 0.03 w/o oxygen to the carbide product.

The uranium carbide after retorting was pyrophoric when exposed to air, perhaps because the specific surface area of the material made from charcoal was in the range of 1 to 10 m²/g. To make the transfer from the retort to an inert-atmosphere glovebox, the tantalum reaction crucible in the argon-filled retort was covered with a stopper and placed in an argon-filled plastic bag. Once inside the glovebox, the powdered carbide was stored in tight containers. The product was sampled and handled with a minimum of exposure to the glovebox atmosphere. The atmosphere of this glovebox was purified by a continuous purge of helium and by exposing trays of phosphorous pentoxide and NaK to the box atmosphere. However, these purification procedures were inadequate. Samples of the atmosphere taken during a 7-hr period, during which carbide samples were being prepared, showed that the water in the box atmosphere rose from 700 to 900 ppm and the oxygen from less than 100 to 400 ppm. Water vapor is known to diffuse at a significant rate²⁷ through neoprene gloves, and the rate is greatly increased by the moisture from an operator's hands.

The presence of magnesium and zinc in the product was caused primarily by small particles of the distillate falling back into the crucible containing the carbide product, but some of the magnesium may have been present as the nonvolatile oxide. The other minor impurities in the product made from activated charcoal and their approximate concentration ranges are:

Nitrogen	100-300 ppm
Tantalum	1000-3000 ppm
Fe-Ni-Cr(total)	100-1000 ppm
Sodium	1000-2000 ppm (where sodium was added)

In all the large-scale runs, uranium carbide was the only crystal phase detected by X-ray diffraction analysis. If all the oxygen had been present as UO₂, this compound should have been detected also in some cases. Oxygen is at least partially soluble²⁸ in the UC structure, and little distortion²⁹ of the UC lattice results. The lattice parameter measured for the precipitated carbide agreed in all cases with the parameter given in the literature⁵ for UC (4.961 ± 0.001 Å).

Fig. 5. Density of Uranium Mono-carbide Compacts with Linearly Rising Temperature

Cold-pressing and sintering is an attractive method of fabricating ceramic shapes, because this procedure can produce fuel pellets from fine powders at low cost and at a rapid rate. The sintering characteristics of uranium carbides synthesized by this method were compared with those of material prepared by other techniques by White and Handwerk^{30,31} of the Metallurgy Division. Sintering characteristics were compared (see Fig. 5) by recording in a vacuum dilatometer the shrinkage of a pressed pellet versus a linearly rising temperature (4°C/min). The other carbides were prepared by arc-melting of the elements, reacting uranium metal powder with methane, and reacting UO₂ with carbon. In all cases, the synthesized materials contained about 1 w/o oxygen and had C/U ratios

in excess of 1.0. Each material was reduced to a particle size of less than 15 μ by ball-milling. The powders were cold-pressed into 3/8-in.-diam pellets with a binder and then isostatically pressed. The sintering characteristics of the various uranium carbides were similar. The precipitated carbide reached its maximum density at lower temperatures than did the carbides made by arc-melting and by the methane reaction. As expected, the final densities were higher for material with lower oxygen content, indicating that the oxygen contamination of the powders limited the final density of the fired pellet. Heating one batch of precipitated carbide powder to 1800°C before pressing lowered the oxygen content to 0.33 w/o and the C/U ratio to 0.95. This was due to volatilization of carbon and oxygen as CO. Upon pressing, this material showed superior sintering characteristics. It reached a relatively high final density (90% of theoretical) at a relatively low temperature (1200°C). The low green densities of pellets pressed from the precipitated carbide were a disadvantage, because the large shrinkage during firing led to distortion of the final pellet. The relative ease with which the precipitated carbide sintered was thought to result from the fact that the outer surfaces of the UC particles were rich in uranium and perhaps were coated with uranium metal. During the sintering process, the inhomogeneous particles became homogeneous.

The first series of runs demonstrated that improvements were necessary in the control of the C/U ratio and in the impurity content of the carbide product. The fact that this process produced hyperstoichiometric carbide was not considered a disadvantage, because excess carbon was thought to be desirable for reactor fuel to avoid the formation of metallic phases during irradiation. Excess carbon would provide carbon atoms for combination with metallic atoms formed by fissioning, but this carbon also

would cause carburization of the fuel cladding in a sodium-bonded element. However, excess carbon will be less detrimental in a gas-bonded fuel element, where the mobility of this carbon is decreased. Modest decreases in the C/U ratio of the product were required, and the ability to reproduce this ratio from run to run was necessary. Experimental equipment was needed that would prevent exposure of the charge materials and the product to oxygen and water vapor. These conclusions led to the construction of new equipment and the additional experiments that are described in the next section.

III. SECOND SERIES OF URANIUM MONOCARBIDE PREPARATIVE RUNS

The second series of runs was made with equipment that permitted a closely controlled atmosphere. All loading of charge materials and transferring, unloading, and sampling of the UC product were done in a high-purity helium atmosphere of a vacuum glovebox.

The two main pieces of process equipment (the transfer furnace and the retort) are shown in Fig. 6. All the process steps except the distillation step were done in the transfer furnace. Because of the corrosiveness of zinc, the molten liquid metal was allowed to come in contact only with tantalum. The same reaction crucible was used throughout the process and moved to the retort for the distillation step. The tantalum reaction crucible was baffled, 6 in. in diameter, and 10 in. high. The scale of operation was limited by the volume of the reaction crucible and the solubility of uranium in the zinc-magnesium alloy. The crucible was of sufficient size to hold 1 kg of uranium metal dissolved in 7.2 kg of zinc-magnesium. After the precipitation of UC, the bulk of the supernatant zinc-magnesium liquid was transferred to the graphite mold through the transfer tube by applying helium pressure to the reaction crucible, while the graphite mold was maintained at atmospheric pressure or at a partial vacuum. The molten zinc-magnesium rapidly solidified to an ingot in the unheated mold. The retort was operated at a reduced pressure of about 15×10^{-3} Torr to facilitate distillation of zinc and magnesium at moderate temperatures. The solid UC product was heated to 850°C in the tantalum reaction crucible to drive off the last of the volatile metals. The zinc-magnesium vapors condensed at about 400°C or lower on the upper surfaces of the retort, which were constructed of Type 304 stainless steel. Since the zinc-magnesium vapors rapidly solidified at these temperatures, there was no wetting or corrosion of the steel condenser surfaces.

Fig. 6. Equipment for Uranium Monocarbide (UC) Preparation by the Liquid-metal Method

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Fig. 7. Vacuum Glovebox for Uranium Monocarbide Preparation

The glovebox with a tilt-pour furnace attached is shown in Fig. 7. The helium atmosphere of the glovebox was purified by being evacuated overnight and refilled with high-purity helium in the morning. The advantage of this type of purification system was that the glovebox could be opened to the air atmosphere for construction or repairs of equipment and then closed and evacuated for rapid purification in a few hours. If a recirculating type of helium purification system³² were used, the box, after being opened to the air atmosphere, would have required purging with fresh helium and operation of the purification system for several days to obtain a satisfactory purity level. The average moisture content in a vacuum-helium glovebox was 10 ppm; the average oxygen level was 40 ppm. These figures represent the average oxygen and moisture impurities over a 9-hr working day. The transfer furnace and retort were attached to the glovebox through a gasketed flange in the floor of the glovebox. An inner cover sealed the glovebox from the furnaces, which could also be evacuated and filled with helium. The cover was then removed

to permit transfer of materials between furnaces and the box without exposure to air. A vacuum lock was used to transfer small items into the glovebox.

Activated charcoal was chosen as the source of carbonaceous material for this series of runs because the first series of runs had shown that a more nearly stoichiometric product could be made with charcoal. The charcoal was degassed in a stainless steel tube furnace for about 20 hr at an absolute pressure of 1 to 10×10^{-3} Torr at 850 to 900°C. To unload the degassed charcoal, the tube furnace was passed directly into the vacuum glovebox through the air lock.

Reaction conditions and experimental results of the second series of production runs are summarized in Table II.

TABLE II. Process and Analytical Data for Uranium Monocarbide Production, Second Series of Runs

	Run										
	UC-2	UC-3	UC-4	UC-5	UC-6	UC-7	UC-10	UC-11	UC-12	UC-13	UC-14
Charge^a											
Uranium, g	500	500	500	500	500	500	500	1000	1000	500 ^b	500 ^b
C/U, $\frac{\text{g atom}}{\text{g atom}}$	1.20	1.20	1.20	1.10	1.10	1.10	1.02	0.90	1.02	1.02	1.02
Reaction Conditions^c											
Time, hr	8	8	8	8	8	12	8	8	12	12	19
Results and Product Analyses											
Yield, g UC	393	233	474	398	332	407	343	444	714	388	471
Uranium, w/o	92.0	90.0	92.5	93.8	90.5	90.6	90.4	94.2	93.0	94.2	92.9
Total C, w/o	5.40	5.40	5.86	5.56	6.00	6.23	5.59	4.56 ^d	5.24	5.34	5.04
Oxygen, w/o	0.39	0.60	0.61	0.29	0.30	0.20	0.14	0.29	0.18	0.24	0.56 ^e
Nitrogen, ppm	380	380	60	10	180	220	120	20	190	230	300
Zn + Mg, w/o	0.71	2.51	0.78	0.46	1.02	0.95	0.42	0.09	0.28	0.21	0.31
Crystal Species	UC	UC, UO ₂ Minor	UC	UC	UC	UC	αU, UC	UC	UC	UC	UC
Lattice Parameter, $\text{\AA}$	4.959	4.959	4.959	4.959	4.959	4.960	4.959	4.960	4.960	4.960	4.960
Specific Surface Area, m^2/g	2.73	1.86	1.49	0.28	3.75	0.96	0.58	-	-	-	-

^aMetal charge composition: 80 w/o Zn, 11 w/o Mg, 9 w/o U^b93 w/o U²³⁵^cReaction temperature 800°C; phase transfer by pressure siphoning^dUnreacted U in product.^eInadvertently exposed to contaminated glovebox atmosphere.^fLattice parameter of UC = 4.961 Å.

The charge C/U atom ratio was decreased gradually from 1.20 to 1.02 and, for one run, to 0.90 to reduce the total carbon content of the UC. The UC product with the closest total carbon content to stoichiometric UC and without free uranium present was made in Run UC-14, which had a total carbon content of 5.04 w/o as compared to 4.80 w/o carbon for stoichiometric UC. This run also had the longest reaction time for any run (19 hr). Apparently, very long reaction times are necessary to produce UC with a very low carbon excess. Small areas of unreacted carbon, which were slowly decreased in size by diffusion of uranium, were probably left in the activated-charcoal particle. In one run, the total carbon content was reduced to stoichiometric or below by using a charge C/U atom ratio of 0.90 in Run UC-11. The total carbon content was reduced to 4.56 w/o in this run, but the product was nonhomogeneous as evidenced by particles of unreacted uranium metal throughout. A homogeneous UC product containing less than 5.0 w/o carbon can probably be obtained by using a small excess of carbon and long reaction times.

The presence of UC was confirmed by X-ray diffraction analysis, which showed UC as a major phase in the product from every run. X-ray analysis showed alpha uranium to be a major phase in Run UC-10. Metallic uranium that was seen in the product from Run UC-11 was separated from the sample submitted for X-ray analysis.

Activated-charcoal particles of less than 44 μ in size were used as the carbon source for Runs UC-6 through UC-12; particles of less than 149 μ were used in earlier runs. It was thought that if a fine charcoal powder were used the particle size of the UC product could be reduced so that further grinding of the UC product before fabrication might be eliminated. However, as shown later (in Table V) the particle sizes were

nonuniform from batch to batch and grinding would probably be required before fabrication. The specific surface area of the UC products varied from 0.28 to 3.75 m²/g, which is a reduction of about 300 or more from the surface area of the activated charcoal particles.

The yield of the UC product was increased from 61.6 to 83.5% over the last five runs, as shown in Table III. The total amount of uranium in the UC product was determined by analysis, and this total was used to calculate the yield as a percentage of the total uranium charged. The uranium losses occurred when the supernatant solvent metal was siphoned away from the precipitated UC, and the losses were caused by dissolved unreacted uranium metal and by entrained UC particles. For the last two runs (UC-13 and UC-14), the bottom tip of the supernatant transfer tube was bent upward away from the settled particles to minimize the entrainment of fine UC particles. This configuration prevented the sweeping of the magnesium-zinc melt over the particles before it entered the transfer tube. This transfer-tube configuration increased the yield about 11% in Run UC-13 over Run UC-12. An increase in reaction time to 19 hr and settling time to 3.75 hr in Run UC-14, as compared to 12 and 1 hr, respectively, in Run UC-13, increased the yield about 6%. In plant-scale operations, it is believed that a yield of over 90% could be obtained.

TABLE III. Process Variables and Yields for Uranium Monocarbide Production; Second Series of Runs

Run	U Charge, g	UC Yield, g	U (by analysis) in UC, w/o	Yield $\left(\frac{\text{U in UC}}{\text{U Charge}} \times 100 \right)$, %	Reaction Time, hr	Settling Time, hr	Type of Transfer Tube
UC-10	503	343	90.4	61.6	8	1	Straight
UC-12	1004	714	93.0	66.2	12	1.5	Straight
UC-13	470	388	94.2	77.8	12	1	Bent upward toward Zn-Mg melt
UC-14	524	471	92.9	83.5	19	3.75	Bent upward toward Zn-Mg melt

The main source of oxygen impurity in the UC product was the activated charcoal, as seen in Table IV. About 73% of the oxygen in the product was from the charcoal, and in all the runs, the charcoal contributed about 60 to 80% of the oxygen impurity. The major reasons that the charcoal used in the second series of runs had less oxygen than in the first series of UC runs were that the charcoal was degassed at a high temperature and that the degassed charcoal was never exposed to air.

Apparently, the oxygen content of the UC product cannot be decreased below 0.14 w/o (Run UC-10) with present degassing techniques for activated charcoal. The lower oxygen contents of the UC products of Runs UC-10 to UC-13 may have been partially a result of degassing of the transfer and retorting furnaces by heating and evacuation before each run.

TABLE IV. Possible Contribution of Starting Materials to Oxygen Contamination of Uranium Monocarbide; Second Series of Runs

Material	Oxygen Content by Analysis	Grams of Starting Material in Typical Run	Total Oxygen, g	Percent of Total Contribution
Charcoal	1.92 w/o	30.4	0.584	73
Magnesium	64 ppm	510	0.032	4
Zinc	34 ppm	3160	0.107	13
Uranium	157 ppm	500	0.078	10
		Total	0.801	100

(Assuming that stoichiometric uranium monocarbide is formed, and that 500 g of uranium and 30 g of charcoal are used:

$$\text{w/o oxygen from starting materials} = \frac{0.801 \times 100}{525} = 0.15).$$

Sieve analyses of the product from the normal UC runs are shown in Table V. Each UC product was screened in a helium atmosphere by hand shaking for 10 min. In Runs UC-2 through UC-5, activated charcoal of less than 149 μ (100 mesh) was used. In Runs UC-6 through UC-12, activated charcoal of less than 44 μ (325 mesh) was used to decrease the particle size of the final UC product. A finer particle size of the UC product is desirable to enhance its sintering capability; i.e., a density of greater than 90% of theoretical density of UC is considered minimal. To obtain this particle size, UC material is normally ball-milled. The ball-milling step could probably be eliminated if the UC product was primarily less than 44 μ . Runs UC-6 and UC-7 showed a significant increase in smaller-size UC material (93.0 and 90.6 w/o less than 44 μ). Runs UC-10 and UC-11 are not representative because both products contained significant amounts of unreacted uranium. The product from Run UC-12 was not completely retorted.

TABLE V. Particle-size Distribution of Uranium Monocarbide; Second Series of Runs

Particle Size, μ	Batch Number								
	UC-2	UC-3	UC-4	UC-5	UC-6	UC-7	UC-10	UC-11	UC-12
	Particle-size Distribution, w/o								
>149	0.2	0.8	1.6	15.8	2.0	0.5	2.8	45.4	11.3
>74	13.7	14.5	6.0	37.5	3.6	1.5	9.4	59.7	25.2
>44	21.5	33.0	17.5	54.0	7.0	9.4	22.5	67.9	29.9
<44	78.5	67.0	82.5	46.0	93.0	90.6	77.5	32.1	60.1

Particles of UC from Run UC-12 were mounted, ground, and polished for electron-microprobe analysis. A photograph of the specimen taken from the microprobe is shown in Fig. 8. The particle shown in the center is about $65\text{ }\mu$ long by about $13\text{ }\mu$ wide. For a particle of this size, two distinct phases were detected by electron-microprobe analysis: an outer shiny phase, which is high in uranium concentration, and an inner grey phase, which is low in uranium. For the larger particles, the outer shiny phase appeared to be homogeneous and was assumed to be UC, since the microprobe analysis showed a uranium composition of 94-95 w/o. (Stoichiometric UC has a uranium composition of 95.2 w/o.) The inner grey phase varies in uranium composition from 20-60 w/o at the outer edge of the phase, which is also the center of the particle. The microprobe analysis thus indicated that the uranium atoms reacted first with carbon on the outer edge of the charcoal particle, and then the atoms moved inward by diffusion toward the core of the charcoal particle. Of course, the smaller particles were more completely converted to a high uranium concentration to give an overall uranium concentration for each batch of product of 90 to 94 w/o.

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Fig. 8. Electron-microprobe Photograph of Uranium Monocarbide Particle

IV. THERMODYNAMICS OF THE CARBIDE REACTION

The reaction of a component (M), which is dissolved in a liquid metal, with a second insoluble component (X) to form an insoluble product can be represented by the general equation,

If the standard states are chosen as the pure elements at the temperature of the reaction, if element X is pure, and if both X and the product MX are insoluble in the liquid, the free-energy change of the reaction is

$$\Delta G_R = (\Delta G_f)_{MX} - (\Delta G)_M,$$

where $(\Delta G)_M$ is the free-energy change accompanying the dissolution of M in the solvent alloy. For many metal solute-metal solvent systems, this free-energy change can be of the order of -10 to -30 kcal/mole, and it represents the free energy of formation of a compound between the solute and solvent at the saturation concentration. For the uranium-zinc system, the composition of the intermetallic compound³³ formed ranges from UZn_{12} at temperatures below 630°C to $UZn_{8.5}$ at temperatures above 800°C. The solid phases formed in the zinc-rich portion of the U-Zn-Mg ternary system have not been determined completely, but at high magnesium concentrations the solid phase becomes uranium metal.

At equilibrium, the free-energy change is zero. In a solution that is essentially pure zinc, the free energy of formation of UC can be calculated by

$$(\Delta G_f^\circ)_{UC} = RT \ln [(\gamma_U)_{Zn} (X_U)_{UC}],$$

where

$$(X_U)_{UC} = \text{atom fraction of uranium in the liquid phase in equilibrium with solid UC and carbon,}$$

and

$$(\gamma_U)_{Zn} = \text{activity coefficient of uranium in zinc.}$$

The uranium concentration in a liquid-zinc phase in contact with UC and free carbon was measured, and these data are shown in Fig. 9. The uranium concentrations in the liquid phase were determined by taking filtered samples of the liquid after agitation times of several hours and with both rising and falling temperatures. The amount of uranium present in solution

as UC was assumed negligible with respect to that dissolved as uranium metal. After this run was completed, the melt was frozen and the solid

phase was isolated by retorting the ingot. Uranium monocarbide was the only solid phase detected by X-ray diffraction.

Fig. 9. Uranium Monocarbide Solubility in Zinc

The solubility of uranium in zinc has been determined by Martin and Wach²⁶ and by Chiotti and Shoemaker.³⁴ The activity of uranium in saturated zinc solutions has been measured by Johnson and Feder.³⁵ If these activity and solubility data are combined, the following relation³³ gives the activity coefficient of uranium in a saturated zinc solution:

$$\log (\gamma_U)_{Zn} = \log \left(\frac{a_U}{X_U} \right)_{\text{sat.}}$$

$$= 3.950 - \frac{5,111}{T}.$$

This activity coefficient is felt to be accurate at the uranium concentrations in equilibrium with UC, because galvanic-cell measurements have indicated that Henry's law is valid in this system.

The liquid zinc used in the UC solubility measurements was not pure, but contained about 0.82 a/o magnesium. To correct the activity coefficient of uranium for the small effect of magnesium, the following approximate relationship can be used:

$$\log (\gamma_U)_{Zn,Mg} = X_{Zn} \log (\gamma_U)_{Zn} + X_{Mg} \log (\gamma_U)_{Mg},$$

where

$$(\gamma_U)_{Zn,Mg} = \text{activity coefficient of uranium in the zinc-magnesium alloy,}$$

and

$$(\gamma_U)_{Mg} = \text{activity coefficient of uranium in pure magnesium.}$$

The activity coefficient of uranium in magnesium can be estimated by³³

$$\log (\gamma_U)_{Mg} = 0.6886 + \frac{4,241.2}{T};$$

then

$$\log (\gamma_U)_{Zn,Mg} = 3.294 - \frac{5,024}{T}.$$

From the experimental data in Fig. 9, the amount of uranium dissolved in zinc in equilibrium with UC was expressed as a function of temperature by

$$\log (X_U)_{UC} = -2.392 - \frac{1,392}{T}.$$

The free energy of formation of UC is then

$$\begin{aligned} (\Delta G_f^\circ)_{UC} &= 2.303RT \log [(\gamma_U)_{Zn,Mg} (X_U)_{UC}] \\ &= -29,350 + 7.008T \text{ (cal/g mol UC).} \end{aligned}$$

Values of the free energy of formation of UC calculated from this expression are -22,300 cal/g mol at 1000°K and -23,700 at 800°K. Values of -23,500 at 1000°K and -23,800 at 800°K were calculated from an extrapolation of an equation presented by Frost,⁵ and values of -19,500 at 1000°K and -19,800 at 800°K were estimated from Huber and Holley.³⁶ Robinson and Chiotti³⁷ have made related studies of the systems U-C-Zn and U-C-O-Zn. In the present work, oxygen was present in the UC used, but the magnesium present in the zinc alloy would reduce uranium oxide to the metal.

Because the monocarbide was the only species formed in the liquid-metal solution even in the presence of excess carbon, either the monocarbide must be more stable than either the sesquicarbide or the dicarbide, or the higher carbides are formed very slowly in the heterogeneous, liquid-metal medium. An experiment was performed to determine if higher uranium carbides would form with long contacting times. An excess of carbon was contacted with a uranium-zinc solution at 800°C with agitation. The uranium disappeared rapidly from solution. After several 24-hr intervals, the melt was frozen and sections of the ingot were removed. These sections were retorted to recover the solid phase. In all cases, UC was the only solid phase detected by X-ray diffraction.

The carbides of other metals can be formed in liquid-metal systems, provided that the free energy of formation of the carbide is a larger negative value than the partial molar free energy of the reactant metal dissolved in

the solvent metal. Therefore, uranium monocarbide can be precipitated from liquid cadmium and magnesium. (However, the solubility of uranium in zinc or cadmium systems with high magnesium contents is impractically low.) Carbides of zirconium, niobium, and hafnium could be formed in zinc systems because the free energies of formation of these carbides are large compared to the free energies of solution of the elements in zinc.

Thermodynamic considerations rule out the formation of any of the carbides of plutonium,³⁸ thorium,^{39,40} and the rare earths^{41,42} in zinc or cadmium solutions because the activity coefficients of these elements in the liquid-metal solvents are exceedingly low. Carbides of these elements can be produced in liquid-magnesium solutions, because the activity coefficients of these elements in magnesium are greater than one.

The formation of plutonium carbides in zinc-magnesium alloys was investigated by Winsch and Cannon.⁴³ Magnesium was added incrementally to a plutonium-zinc alloy in contact with activated charcoal, and the fraction of the plutonium removed from solution was determined. The results are shown in Fig. 10. Plutonium sesquicarbide was formed, indicating that this compound is more stable than the monocarbide.

Fig. 10. Precipitation of Plutonium from Magnesium-Zinc Solutions by Reaction with Carbon

When the carbon was added to a solution of uranium and cerium dissolved in a Zn-20 w/o Mg alloy, the uranium was removed quantitatively from solution, while the cerium remained in solution. This system was then retorted to drive off the zinc and magnesium. As the liquid phase became progressively more concentrated in magnesium during the retorting, the activity of cerium approached one, and the cerium reacted with the free carbon present. Cerium sesquicarbide and UC were detected in the solid recovered after the retorting. When this mixed carbide was agitated with molten cadmium, the cerium was quantitatively dissolved in the cadmium,

while less than 1% of the uranium was dissolved. Cerium⁴¹ has a very low activity coefficient in cadmium; the uranium activity coefficient³⁵ is in the range of 10 to 100. The selective dissolution of certain carbides could perhaps be used as a process step in a fuel-recovery scheme. By contacting irradiated carbide fuel with cadmium, a liquid solution containing plutonium and the rare-earth fission products could be separated from uranium, zirconium, and other fission products because either they are insoluble in cadmium or their carbides are stable. The plutonium would then be separated from rare earths in a later step by liquid metal-liquid salt extraction.

V. CONCLUSIONS

1. Hyperstoichiometric UC was produced on a 500- to 1000-g scale by the reaction of uranium metal with degassed activated charcoal. An agitated liquid-metal medium of zinc-magnesium was used to dissolve the uranium metal and to promote the reaction between uranium and carbon. The UC product had 5.2 w/o carbon and about 93.0 w/o uranium in the final preparations, which is equivalent to a C/U atom ratio of 1.10.

2. The average oxygen-impurity level of the UC was 0.21 w/o for Runs UC-7 through UC-13. This level of oxygen impurity could be consistently reproduced in any future preparations of UC by this process. The oxygen content cannot be decreased substantially below 0.14 w/o with the present method of degassing activated charcoal. In its degassed state, activated charcoal contributed 60 to 80% of the total oxygen impurity in the UC product. The balance of the oxygen came mainly from the zinc and uranium metal used in the process.

3. Yields of UC of up to 83.5% were obtained by using reaction times of up to 19 hr, settling times of up to 4 hr, and a technique for removing the zinc-magnesium supernatant. The tantalum tube that was used for transferring the supernatant away from the precipitated UC was bent upward to avoid entrainment of the UC particles. This avoided a sweeping action of the zinc-magnesium liquid over the settled UC particles and thus minimized the entrainment of the fine particles.

4. Activated charcoal with a high surface-to-volume ratio was used as the source of carbon for UC preparation because it promoted a more rapid and complete reaction with uranium than did other forms of carbon.

5. Plutonium carbide could be made by this procedure only in solvents rich in magnesium. However, the less desirable plutonium sesquicarbide formed rather than plutonium monocarbide. Only uranium monocarbide was formed when attempts were made to coprecipitate uranium and plutonium carbides as the solid solution from zinc-rich alloys.

6. Uranium metal was used to prepare the liquid-metal solutions in this study. However, solutions of uranium in zinc-magnesium alloys can be made directly from uranium oxides or UF_4 by reducing these compounds with the solvent metals. The magnesium oxide or fluoride by-product can be separated efficiently from the metal solution by contacting the metal phase with a liquid chloride salt.

7. The liquid-metal method of producing UC was complex because several operations were required in two separate pieces of equipment. These complexities would make the preparation of UC expensive. Incorporating this preparative method into a liquid-metal fuel-reprocessing scheme

would reduce the cost. However, in the fast-reactor fuel program, the recycle of plutonium and the production of solid solution (U,Pu)C or an intimate mixture of UC and PuC are of prime importance. (The solid solution, (U,Pu)C, or an intimate mixture of UC and PuC on the micron level is of importance for safety purposes¹ in sodium-cooled fast reactors.) The solid solution, (U,Pu)C, or an intimate mixture could not be prepared by coprecipitation; therefore the liquid-metal preparative method was abandoned in favor of the fluidized-bed method of producing UC and (U,Pu)C. The fluidized-bed method produces UC or (U,Pu)C directly from the alloys by reacting finely divided metal with hydrogen-hydrocarbon mixtures.

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REFERENCES

1. J. H. Kittel, E. L. Zebroski, *et al.*, *Plutonium Fuel Development for Fast Reactors in the U.S.*, Nuclear Metallurgy Symposium A.I.M.E., Oct. 3-5, 1966.
2. L. A. Neimark, J. H. Kittel, and C. C. Crothers, "Irradiation of Pu-C and (U,Pu)C" pp. 864-878 in *Carbides in Nuclear Energy* Vol. 2, L. E. Russell, ed., The Macmillan Co., London (Nov 1963).
3. W. C. Hayes, "Uranium Carbide Development Program at Atomic International," in *The Fourth Uranium Carbide Conference*, East Hartford, Connecticut, May 20-21, 1963, TID-7676 (Feb 1964).
4. L. Jakesova and D. Jakes, *Carbides, Nitrides, and Silicides of Uranium as Promising Nuclear Fuel*, Atomic Energy Review 1(3): 3-46 (Sept 1963).
5. B. R. T. Frost, *The Carbides of Uranium*, J. Nucl. Materials 10(4): 265-300 (1963).
6. H. Pearlman and C. W. Wheelock, "Uranium Monocarbide Fuels," *Proceedings of the American Power Conference*, 26th Annual Meeting, Chicago, Ill. (April 1964).
7. E. J. Petkus, A. D. Tevebaugh, *et al.*, *The Synthesis of Stoichiometric Uranium Monocarbide in a Fluidized Bed by the Uranium Metal-Hydrocarbon Gas Reaction*, AIChE Symposium Series 62(67): 76-85 (1966).
8. R. Ainsley *et al.*, "New Nuclear Materials Including Non-Metallic Fuels," *Proceedings of IAEA Conference* Vol. 1, p. 349, Prague (1963).
9. S. Strausberg, *Preparation of UC by Carbothermic Reduction of U₃O₈*, NAA-SR-10486 (June 30, 1965).
10. R. C. Vogel, M. Levenson, J. H. Schraidt, and J. Royal, *Chemical Engineering Division Summary Report January-June 1966*, ANL-7225 (Nov 1966).
11. R. D. Reznik and R. M. Powers, *Direct Conversion of UF₄ to Uranium Carbide*, GTR-17 (May 1963).
12. P. Schwarzkopf and R. Keefer, *Refractory Hard Metals*, The Macmillan Company, New York (1963), pp. 60-63.
13. S. Lawroski, R. C. Vogel, and V. H. Munnecke, *Chemical Engineering Division Summary Report, July, August, September 1961*, ANL-6413, pp. 65-67.
14. W. N. Hansen, *Reprocessing of Uranium Carbide by Molten Salt Electrolysis*, NAA-SR-7660 (March 1963).
15. J. Bartos, private communication.
16. R. C. Vogel, Milton Levenson, and V. H. Munnecke, *Chemical Engineering Division Semiannual Report, July-December, 1963*, ANL-6800 (May 1964), p. 145.
17. A. Schneider, L. Burris, Jr., and S. Lawroski, *The Synthesis of Refractory Nuclear Feed Materials in Liquid Metal Media*, Trans. Am. Nuclear Soc. 4(2), 345 (1961).

18. S. Lawroski, R. C. Vogel, and V. H. Munnecke, *Chemical Engineering Division Summary Report, April, May, June 1961*, ANL-6379 (Oct 1961), pp. 79-85.
19. I. O. Winsch, K. R. Tobias, R. D. Pierce, and L. Burris, Jr., *Sampling of Liquid Metals*, ANL-7088 (Sept 1965).
20. S. Lawroski, R. C. Vogel, and V. H. Munnecke, *Chemical Engineering Division Summary Report, October, November, December 1961*, ANL-6477 (March 1962), pp. 93-94.
21. A. Herold, *Insertion Compounds of Graphite with Bromine and the Alkali Metals*, Bull. Soc. Chim, France 999-1012 (1955).
22. M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill Book Co., Inc., New York (1958).
23. I. Johnson and I. G. Dillon, *The Solubility of Metals in Liquid Zinc*, ANL-7083 (Nov 1965).
24. C. B. Jackson and J. W. Mausteller, "Liquid Metals" in *Modern Materials, Advances in Development and Applications*, Henry M. Hausner, ed., Vol. 3, p. 406-407 (1962), Academic Press, New York.
25. J. J. Gill, *Sodium-Graphite Interaction and Graphite Protective Coatings*, NAA-SR-6094 (May 1961).
26. S. Lawroski, R. C. Vogel, and V. H. Munnecke, *Chemical Engineering Division Summary Report, January, February, March 1961*, ANL-6333 (June 1961), p. 109.
27. J. E. Ayer, R. M. Mayfield and D. R. Schmitt, *The Engineering Aspects of the Water Vapor Permeability of Glove Materials*, Nuclear Sci. Eng. 8: 274 (1960).
28. S. Namba, S. Imoto, and T. Sano, *On the Formation of $UC_{1-x}O_x$* , Osaka Univ. Tech. Report 12: 429-434 (1962).
29. P. Magnier, J. Trouve, and A. Accary, "The Solubility of Oxygen and Nitrogen in Uranium Carbide," pp. 95-107 in *Carbides in Nuclear Energy*, Vol. 1, L. E. Russell, ed., The Macmillan Co., London (Nov 1963).
30. G. D. White, Trans. Am. Ceramic Soc., April 28-May 2, 1963.
31. T. R. Johnson, G. D. White, O. L. Kruger, R. K. Steunenberg, and J. Handwerk, "Uranium and Plutonium Carbide Developments at Argonne National Laboratory," in *The Fourth Uranium Carbide Conference*, East Hartford, Connecticut, May 20-21, 1963, TID-7676 (Feb 1964).
32. M. S. Foster, C. E. Johnson, and C. E. Crouthamel, *Helium-purification Unit for High-purity Inert-Atmosphere Boxes*, ANL-6652 (Dec 1962).
33. I. Johnson, "Thermodynamics of Plutonium, Thorium and Uranium Metallic Systems," pp. 171-192 in *Compounds of Interest in Nuclear Reactor Technology*, J. T. Waber and P. Chiotti, IMD Special Report No. 13 (1964).
34. *Semiannual Summary Research Report in Metallurgy for July-December 1957*, ISC-977, p. 31 (Aug. 15, 1958).

35. I. Johnson and H. M. Feder, "Thermodynamics of the Binary Systems of Uranium with Zn, Cd, Ga, In, Tl, Sn, Pb," in *Thermodynamics of Nuclear Materials*, I.A.E.A., Vienna, Austria (1962), p. 319.
36. E. J. Huber, Jr. and C. E. Holley, Jr., "The Thermodynamic Properties of the Actinide Carbides Including New Measurements of the Heats of Formation of Some Thorium, Uranium, and Plutonium Carbides," pp. 581-600 in *Thermodynamics of Nuclear Materials*, I.A.E.A., Vienna (1962).
37. W. C. Robinson and P. Chiotti, *Reactions of Uranium Carbide in a KCl-LiCl/Zn System*, J. Less Common Metals 10, 190 (1966).
38. I. Johnson, M. G. Chasanov, and R. M. Yonco, *Pu-Cd System Thermodynamics and Partial Phase Diagram*, Trans. Met. Soc. A.I.M.E. 233, 1408 (July 1965).
39. I. Johnson and M. G. Chasanov, *Thermodynamics of the Plutonium-Zinc System*, J. Inorg. Nucl. Chem. 26: 2059 (1964).
40. P. Chiotti and K. J. Gill, *Phase Diagram and Thermodynamic Properties of the Thorium-Zinc System*, Trans. Met. Soc. A.I.M.E. 221: 573 (1961).
41. R. C. Vogel, M. Levenson, and F. R. Masten, *Chemical Engineering Division Research Highlights, May 1964-April 1965*, ANL-7020, p. 74.
42. P. Chiotti and J. T. Mason, *Phase Relations and Thermodynamic Properties for the Cerium Zinc System*, Trans. Met. Soc. A.I.M.E. 233: 786 (April 1965).
43. S. Lawroski, R. C. Vogel, and V. H. Munnecke, *Chemical Engineering Division Summary Report, October, November, December 1961*, ANL-6477 (March 1962), pp. 55-57.