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A FEASIBILITY STUDY - FORMATION OF URANIUM NITRIDE COMPOUNDS USING CHEMICAL VAPOR DEPOSITION TECHNIQUES

W. C. Robinson, Jr., and W. R. Martin

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Oak Ridge, Tennessee
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A FEASIBILITY STUDY - FORMATION OF URANIUM NITRIDE COMPOUNDS
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ABSTRACT

The feasibility of the direct gas phase reduction of UF_6 to uranium metal according to the reaction:

was demonstrated. Nitrogen was then introduced into the chamber simultaneously with UF_6 and lithium vapor to form a uranium-nitrogen compound. At temperatures and pressures selected, thermodynamic data indicate uranium nitride to be stable. The reaction produced UN, UN_2 , U, LiF, and other complex (U, Li, F) compounds. It was proved possible to form uranium nitride by this technique; however, clean separation of the desired material and the reaction products was not feasible in our apparatus.

INTRODUCTION

Thermochemical reduction of uranium halides is being investigated at ORNL as an alternate route for fabricating refractory uranium compounds for fuel element applications. This work is performed under the auspices of the Fuels and Materials Branch, Division of Reactor Development and Technology, U. S. Atomic Energy Commission. Previously,¹ a process was developed for the direct fabrication of uranium dioxide, either as powder or a free-standing body, by thermochemical reduction of uranium hexafluoride. The feasibility of converting UCl_4 to uranium oxides has also been demonstrated.² Uranium carbide, uranium nitride, and other uranium ceramics are also being considered. The thermochemical

¹R. L. Heestand and C. F. Leitten, Jr., Nucl. Appl. 1(6), 584 (1965).

²F. H. Patterson, W. C. Robinson, and C. F. Leitten, Jr., Conversion of Uranium Chlorides to Uranium by Gas-Phase Reduction and Hydrolysis, ORNL-TM-1701 (in press).

conversion of UF_6 to the nitride or carbide by reduction with hydrogen in the presence of a carbonaceous or nitrogenous gas is not thermodynamically feasible due to the formation of a stable UF_4 intermediate.³ Therefore, it was desirable to develop another technique that could be utilized to directly fabricate a uranium nitride or carbide fuel from the uranium halides.

THERMODYNAMIC FEASIBILITY

The strongest reducing agents available are the alkali metals. Calculations were made to explore the feasibility of the reduction of UF_6 with the alkalis Cs, Rb, K, Na, and Li. The lithium reaction

offered equilibrium constants of about 2 orders of magnitude more favorable than its nearest competitor, sodium. Therefore, lithium was selected for investigation. The standard free energy of Reaction (1) as a function of temperature was calculated and is shown in Table 1. The standard free energy of the reaction

was also considered since UF_4 is a known stable intermediate. Since the reaction must be performed at low pressure to remove the LiF as a gas from the system at reasonable temperatures, the free energy of Reactions (1) and (2) were also calculated assuming that each gaseous component was at 1 torr. These numbers are also given in Table 1. We decided to first verify these reactions and to observe the behavior of the system and then to introduce nitrogen gas into the reaction chamber in

³J. D. Fleming, W. C. Robinson, and C. F. Leitten, Jr., Thermochemical Analysis of Vapor-Plating Process, ORNL-TM-1454 (July 1966).

Table 1. Free Energies of Reaction for Reduction of UF_6 with Lithium^a

Temperature (°C)	Reaction 1		Reaction 2	
	ΔF at 1 atm	ΔF at 1 torr	ΔF at 1 atm	ΔF at 1 torr
900	-208,500	-196,700	-62,500	-50,700
1000	-209,000	-195,800	-63,100	-50,000
1100	-209,200	-194,700	-65,700	-51,100
1200	-209,300	-193,500	-67,200	-51,400
1300	-209,700	-192,600	-68,600	-51,500
1400	-209,900	-191,400	-69,800	-51,400

^aValues for free energies of formation of UF_4 and UF_6 obtained from Alvin Glassner, "The thermochemical properties of the oxides, fluorides, and chlorides to 2500°K," ANL-5750 (1957). Values for free energy of formation of LiF obtained from JANAF Interim Thermochemical Tables, Vol. 1, The Dow Chemical Company, Midland, Michigan.

the expectation that the uranium product would react with it to form uranium nitride. The purpose of the investigation was to establish the feasibility of forming uranium nitride by means of gaseous reactions. No provision for optimization of the process or to produce any quantity of material was made in design of the apparatus.

EXPERIMENTAL FACILITIES

In the initial experiments, it proved to be impossible to adequately control the flow of lithium vapor; it became apparent that the simplest possible apparatus was the best for a feasibility study. Therefore, the apparatus shown in Fig. 1 was constructed. A stainless steel tube coated internally with 0.005 to 0.010 in. of CVD tungsten was used to contain the reaction. The double-wound platinum furnace was arranged to have two heats zones, a 750°C zone in which the lithium boat was inserted, and a 900 to 1200°C reaction zone. The lithium metal was in a small stainless steel container. It was found by experience that the evaporation rate at 750°C and 15 torrs was sufficient to empty the container in about 5 hr. This was the only control on the lithium flow rate. The UF_6 and nitrogen

Fig. 1. Apparatus for Lithium Reduction of UF_6 .

gas were introduced at the other end via an injector of the type discussed previously by Heestand.¹ The UF_6 gas was metered by a Hastings mass flowmeter and the nitrogen gas by an ordinary Brooks rotameter. The pressure was monitored by a Wallace and Tiernan bellows gage and maintained by a mechanical vacuum pump. A cold trap cooled to approximately -50°C protected the pump from corrosive gases. The deposits were made on a removable stainless steel liner, which was replaced after each run.

EXPERIMENTAL PROCEDURE

The initial experimental apparatus was equipped with a sight glass on the water-cooled end of the reaction chamber. The lithium vapor and UF_6 gas both entered the reaction chamber from the heated end adjacent to the lithium vaporization chamber. One could observe the lithium

beginning to condense in the cold end of the reaction chamber after the lithium vaporization chamber was heated to 700°C under a pressure of 1 torr. At this time the UF_6 was introduced via the injector adjacent to the vaporization chamber. Within minutes the UF_6 injector invariably became plugged with uranium metal at the injector tip. This verified the feasibility of Reaction (1) but required modification of the apparatus to that shown in Fig. 1. There was no way to observe the lithium vapor transfer in the modified equipment, therefore, several runs were made to establish conditions at which a fairly constant transfer of lithium was obtained. It was noted that the lithium metal had to be outgassed at pressures of less than 0.5 torr at room temperature for several hours before it was heated and vaporized. If this was not done, a black film covered the material and prevented vaporization even at temperatures above 1000°C. The film was identified as containing Li_2C_2 and Li_3N and is probably the result of the reaction of the metal and the kerosene in which it is stored. An overnight outgassing of the metal prevented the formation of this film.

After conditions for a constant rate of lithium transfer had been established, uranium hexafluoride gas and, in later experiments, UF_6 and nitrogen gas were introduced into the chamber from the cold end of the reaction chamber.

RESULTS

An initial experiment was prepared to verify that Reaction (1) could be forced to occur in the vapor phase of the reaction chamber. This reaction was performed at 750°C and produced a very reactive uranium metal powder that ignited to UO_2 on exposure to air. The LiF product of Reaction (1) was also present in the reaction zone because 750°C was not sufficient to vaporize it. In subsequent experiments the reaction zone was heated to 800 or 1000°C where the uranium metal powder formed was transferred through the system and collected in the cold trap. The LiF was collected at the cooled end of the reaction chamber and nothing remained in the reaction zone.

The experiments involving the introduction of nitrogen gas into the chamber with the UF_6 -Li mixture produced solid deposits in the hot zone composed of uranium metal, uranium nitride (both UN and UN_2), and various lithium-uranium compounds including $\text{Li}_{17}\text{U}_6\text{F}_{31}$ and Li_3UF_7 . In one experiment, a fine powder was obtained in the cold trap. This powder ignited when exposed to air. X-ray analysis of the residue indicated a mixture of UN_2 and UO_2 . Typical powder patterns of the residue obtained for various conditions are given in Table 2.

Table 2. Reaction Products of UF_6 -
Lithium-Nitrogen Gas Reaction

Run Numbers	Phases Observed	Intensity
13-2	UN	S+
	αU	M+
	LiF	M+
	$\text{Li}_{17}\text{U}_6\text{F}_{31}$	M-
15-2	UO_2	S
	UN_2	S
	LiF	W
	$\text{Li}_{13}\text{UF}_7$	W+
	$\text{Li}_{17}\text{U}_6\text{F}_{31}$	W+
20-1	UN	S+
	LiF	S
	αU	M+
	$\text{Li}_{17}\text{U}_6\text{F}_{31}$	M-
	Unknown phase	M

S = Strong

M = Medium

W = Weak

Attempts were made to separate the uranium-nitride solid product from the LiF and the lithium-uranium compounds by heating the chamber, after reaction, to 1250°C under vacuum in an effort to remove the more volatile compounds from the deposit. This was only partially successful in obtaining purer product in the heated zone, with the UN being the strongest phase in the resulting powder patterns, but the LiF and lithium-uranium compounds were never reduced to below the detection of x-ray.

analysis. The injector was lengthened and placed above the lithium boat in an attempt to have the lithium vapor contact the UF_6 in the higher temperature zone. The injector was again plugged with uranium metal in minutes. Therefore, no pure solid deposit of UN was obtained. The cold-trapped UN_2 powder also had weak lines (see Table 2) that were tentatively identified as LiF and lithium-uranium compound.

DISCUSSION AND CONCLUSIONS

The feasibility of Reaction (1) has been definitely established. The fact that the introduction of nitrogen gas into the presence of UF_6 and lithium vapor will produce uranium nitride has also been established. It was shown as in previous systems^{4,5} that both a solid and powder product could be obtained but no attempt was made to control or optimize for production of a particular product. It is almost certain that a pure solid uranium nitride product could be obtained if one could have the initial contact of the gaseous streams in a zone of 1000°C or more at a pressure of less than 25 torrs. In the apparatus utilized here, the UF_6 gas encountered the lithium vapor at the lowest temperature at which the lithium remained as a vapor. This temperature was insufficient to vaporize the LiF or decompose the intermediate products. Attempts to inject the UF_6 directly into the hot zone resulted in the injector plugging as the lithium vapor could now reach the injector tip.

Since feasibility of the process was the objective of the study and this had already been established, it was decided that the time and effort necessary to solve the engineering problems for production of pure material were not justified. It has been noted, however, that the number of engineering problems could be drastically reduced by employment of a lithium-organic such as Li-NH_2 instead of lithium and nitrogen vapors. This will be investigated.

⁴R. L. Heestand and C. F. Leitten, Jr., Nucl. Appl. 1(6), 584 (1965).

⁵F. H. Patterson, W. C. Robinson, and C. F. Leitten, Jr., Conversion of Uranium Chlorides to Uranium by Gas-Phase Reduction and Hydrolysis, ORNL-TM-1701 (in press).

SUMMARY

Uranium hexafluoride may be reduced completely to uranium metal with lithium vapor. Performance of the reaction in the presence of nitrogen gas yields UN, UN₂, uranium metal, LiF, and a variety of Li-U-F compounds. The feasibility of the direct conversion of UF₆ to UN in a one-step operation was demonstrated but the technique necessary to produce a pure nitride product was not developed.

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