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REPORT

on

IDENTIFICATION OF REACTION PRODUCTS FORMED DURING MAGNESIUM REDUCTION OF URANIUM TETRAFLUORIDE

to

U. S. ATOMIC ENERGY COMMISSION

by

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ABSTRACT

This report describes the results of X-ray diffraction examination of reaction products from a series of experiments performed by Mallinckrodt Chemical Works as an aid in understanding the process of bomb reduction of UF_4. UF_4 is initially reduced to UF_3 by magnesium at 560° C., and subsequently to metal at 600° C. MgF_2 from the initial reaction forms a coating on the magnesium which retards the final spontaneous reaction.

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INTRODUCTION

The process for the production of uranium by bomb reduction of UF_4 with magnesium has been investigated by the Mallinckrodt Chemical Works, in an attempt to understand the mechanism of the reaction, and to obtain better control of the process. The reaction is strongly exothermic. The charge, consisting of UF_4 mixed with magnesium granules, is packed into a refractory-lined iron bomb. This is preheated to a temperature of about 650° C., at which temperature the reaction proceeds violently. The internal temperature rises rapidly above the fusion point of both reaction products, uranium and MgF_2. These separate, the latter rising to the top as slag. Good yield of massive metal depends, at least in part, upon the fluidity of the melt. For a given weight of charge, the heat supplied by the reaction is fixed, and the amount absorbed from external source during preheating depends upon the temperature at the instant of spontaneous reaction. The objectives of the present study were to investigate, in cooperation with Mallinckrodt, the causes of occasional failure to obtain fluidity, resulting in poor bomb yield, and to examine the mechanism of the bomb reaction.

Initial studies[1, 2] of slag from normal production bombs and experimental underfired bombs indicated that reduction was a two-step process. Later investigations[3] of reactions between magnesium vapor and UF_4 heated in partial vacuum or in helium confirmed the hypothesis of a two step reaction, as follows:

$$2UF_4 + Mg \rightarrow MgF_2 + 2UF_3$$

$$2UF_3 + 3Mg \rightarrow 3MgF_2 + 2U$$

Similarly, reactions between UF_4 containing intentional impurities and magnesium chips in the temperature range 550° C. to 600° C. caused a step reduction of UF_4 to UF_3 and then to metal.[4]

In the course of the above investigations, numerous samples were examined at Battelle by X-ray diffraction to determine the extent of reaction on the surface of the magnesium as well as in the UF_4. Separation of the samples into macroscopically different portions was made before analysis. The surface coating on the magnesium was studied to determine the composition of the coating and its possible effect on retarding the initial reduction of UF_4 to UF_3 in commercial bomb production of uranium. The reaction products adjacent to the magnesium particles and throughout the remaining powder were examined to determine their composition.

EXPERIMENTAL PROCEDURE

The apparatus used to carry out the reactions of magnesium with UF_4 at the Mallinckrodt Chemical Works has been described by A. E. Ruehle et al.[3, 4] Samples taken from the reaction chambers were submitted to Battelle for phase identification. Four general types of samples were studied: (1) products of reaction of magnesium vapor with UF_4 held for various times at approximately 560° C., (2) reaction products resulting from heating magnesium powder in contact with UF_4, in the temperature range 550° C. to 600° C., (3) reactions of magnesium chips with various uranium compounds or mixtures, and (4) reaction of magnesium sheet with UF_4 containing additives which might aid in filming the magnesium, and thereby retard the reduction of UF_4 to UF_3 at low temperatures. Electron-diffraction methods were employed to determine the composition of the outermost film on the magnesium sheet, while the phases present in the bulk coatings were identified by X-ray diffraction. Phase identification studies were also made of the bulk reaction products of magnesium vapor and magnesium powder with UF_4.

RESULTS

The reaction of bright green UF_4 with magnesium vapor at 560° C. caused a darkening of the green salt. Several of the reaction products were examined by X-ray diffraction, which showed that the UF_4 was reduced to UF_3 in a short reaction time. After extended treatment of the resulting UF_3 with magnesium vapor at this temperature (560° C.), oxides of uranium were the only phases detected by X-ray methods. These oxides are believed to have resulted from air oxidation of finely divided uranium metal. Table 1 describes the samples and the results of X-ray examination. It should be noted that, although the UF_4 was reduced by the magnesium vapor, no MgF_2 was detected. This suggests that the sensitivity of detection of MgF_2 in this case was too low or that during the reaction the temperature was increased by this exothermic reaction to a point where the MgF_2 was volatilized.

In order to determine the effect of the preheat period on the reduction of UF_4, several runs were made by Mallinckrodt in vacuum with UF_4 and magnesium powder in the temperature range 550° C. to 600° C. Table 2 describes the samples of this series and gives the results of X-ray examination. The samples were sealed in evacuated tubes after reacting and not exposed to the atmosphere until after X-ray examination. The residual magnesium remained bright in these reactions and was removed before X-ray

TABLE 1. IDENTIFICATION OF PHASES FORMED BY REACTION OF URANIUM TETRAFLUORIDE AND MAGNESIUM VAPOR

Sample No.	Description of Samples	Intensity of Phases Identified			
		U_3O_8	UF_3	UO_2	Other
93A	Mg(vapor) + UF_4 at 560° C.; olive green		Strong	Faint	
M-2-14	Ditto		Strong	Very faint	Very faint MgF_2
M-2-16	Same as M-2-14, longer treatment	Strong	--	Medium(1)	Faint UF_4
M-2-17	Ditto	Strong	--	Medium(1)	--
M-2-19	"	Medium	--	Strong(1)	--

(1) These patterns of UO_2 were diffuse, indicating room-temperature oxidation of the reduced uranium metal.

TABLE 2. IDENTIFICATION OF PHASES FORMED BY REACTION OF URANIUM TETRAFLUORIDE AND MAGNESIUM POWDER

Sample No.	Time and Temperature of Reaction	Portion Examined	Intensity of Phases Identified				
			U	UF_3	UO_2	UO	MgF_2
M-2-37	4 hrs., 550° C.	Black aggregates	--	Strong	Very faint	--	Very very faint
		Brown powder	--	Strong	Medium faint	--	Very very faint
M-2-40	4 hrs., 570° C.	Black aggregates	--	Strong	Very very faint	--	--
		Black powder	--	Strong	Very very faint	--	--
M-2-42	3 hrs., 580° C.	Coarse particles	Very faint	Strong	Very faint	--	--
		Fine particle	Very faint	Strong	Very faint	--	--
M-2-45	3 hrs., 600° C.	Coarse particle	Strong	--	--	Medium	Medium
		Fine particle	Strong	--	--	Medium	Medium

analysis. The results show that below 580° C. only the first step of the reaction has been completed in 4 hours. However, at temperatures above 580° C., the reduction is complete and metallic uranium is obtained. These results indicate that considerable reaction takes place before the firing temperature (650° C.) is attained in normal bomb reduction. The bright magnesium particles remaining in the reacted powder indicated that any MgF_2 which formed during reaction was volatilized in the vacuum.

Earlier studies[2] of reaction products of underfired bombs showed that various colored coatings formed on the magnesium chips. This variation in coating appeared to be associated with the purity of the UF_4 and was believed to influence the firing and ultimate temperature attained in production bombs. A study was made of the surface coating produced on magnesium by heating it in contact with various uranium compounds known to be present in UF_4. Table 3 gives a description of the reacting materials, the coatings produced and the phases identified. It is of interest that, in the case of UF_3, the magnesium remained quite bright, indicating little or no reaction. The only samples in this series which showed reduction to metallic uranium were those of UF_4 and UO_2. Other samples showed only partial reduction. The presence of MgF_2 as the major phase on the surface of the Mg in partially reduced samples indicates that this coating retarded the final reduction step. However, it seems quite possible that the reduction of UF_4 to UF_3 in a small area around each magnesium particle contributes to retardation of the final reduction.

Since the X-ray method is not sensitive to detection of very thin coatings on the extreme surface, electron-diffraction studies were made on thin sheets of magnesium after reaction in underfired bombs. The thin sheets of Mg were inserted in the UF_4 and in UF_4 containing film-forming additives, such as $NaHF_2$, KHF_2, UO_2F_2, and HF, and heated to just below firing temperature, approximately 600° C. Phase studies of the coating on the surface of these magnesium sheets showed that MgO and $Mg(OH)_2$ were present on the extreme outer surfaces of the coating. Examination of the film by X-ray diffraction revealed that MgF_2 was also present below the MgO and $Mg(OH)_2$. However, in the case of UF_4 treated in HF, very little or no MgO or $Mg(OH)_2$ was detected, either by X-ray or electron diffraction. The only coating present was MgF_2. A study of the powder adjacent to the Mg sheet was not made for these runs, hence one cannot be certain as to the effect of these additives on retardation of the first step of the reduction.

DISCUSSION OF RESULTS

The results of the present investigation show that magnesium reduction of UF_4 to metallic uranium is a two-step process. Reduction of UF_4 to the

TABLE 3. IDENTIFICATION OF SURFACE COATINGS PRODUCED ON Mg CHIPS BY REACTIONS WITH VARIOUS MIXTURES OF U COMPOUNDS

Sample No.	Compounds Mixed with Mg for Reaction	Description of Particle Examined	Phases Identified Other Than Mg
B87-P85	UF_4	Gray-brown coating	$U + MgF_2 + UF_3$
B87-P96B	UF_4	Temper-color coating	$MgF_2 + UF_3$
B87-P34	UO_2F_2	Red-brown coating	$MgF_2 + UO_2 + UF_3$
Ditto	Ditto	Temper-color coating	$MgF_2 + UF_4$
"	"	Fine black powder	$U_3O_8 + UO_2$
B87-P36	UO_2	Gray-black coating	$U + UO_2 + MgO$
B87-P82	UF_3	No apparent coating	UF_3
B87-P90	$UF_4 + UO_2F_2$	Temper color coating	$MgF_2 + UF_3$
Ditto	Ditto	Green powder	$UF_4 + UO_2$
B2-P35	$UF_4 + U_3O_8$	Gold coating	$UO_2 + MgF_2$

trifluoride occurs at temperatures well below the firing temperature in commercial bomb reduction of uranium. The trifluoride produced in the first step of the reduction is stable at the lower temperatures. The rate of reduction of trifluoride to metal becomes more rapid at 600° C. and above. Reactions which are run in vacuum appear to go to completion at lower temperatures than in normal production bombs. The absence of a surface-film formation on the magnesium in reactions under vacuum suggests that films formed on magnesium in normal bombs retard the final reduction by restricting the vaporization of the magnesium.

A study of the above films on magnesium was made to determine differences in composition which may affect firing temperatures in normal production. All samples of magnesium heated in the presence of UF_4 were coated with a layer of MgF_2. MgF_2 is also formed on magnesium heated in UO_2F_2 or mixtures of UF_4 and U_3O_8. Electron-diffraction studies showed that a thin layer of MgO and $Mg(OH)_2$ covers the MgF_2 except when the UF_4 contains excess HF. The films on magnesium reacted with UO_2, UO_2F_2, or with mixtures of UF_4 and UO_2F_2 or U_3O_8, also contained UO_2. This UO_2 may have resulted from air oxidation of some reduced uranium metal or may have been produced during the reaction. The absence of any film on the magnesium heated in UF_3 suggests that the MgF_2 film forms during the first step in the reduction of UF_4. Attempts to retard this first step in the reduction of UF_4 were not conclusive. Addition of $NaHF_2$, KHF_2, or UO_2F_2 to the UF_4 charge did not change the composition of the films on the Mg. However, an addition of HF did seem to prevent the formation of MgO or $Mg(OH)_2$. Since none of the powder adjacent to the magnesium in these runs was examined, one cannot be certain whether reduction of UF_4 to UF_3 occurred. It would seem quite likely that the MgF_2 film could have formed through a reaction with the additives rather than with the UF_4.

CONCLUSIONS

1. The major portion of the film formed on magnesium during the first step of the reduction of UF_4 is MgF_2. Minor phases present are MgO, $Mg(OH)_2$, and UO_2.

2. Addition of HF to the UF_4 charge prevents formation of the minor phases.

3. Each magnesium particle reacts with UF_4 to produce the MgF_2 and a layer of UF_3 powder during preheat of normal production bombs.

4. No surface films are detected on the surface of the magnesium when reduction is carried out in vacuum, even though the first step of the reduction is complete.

5. UF_3 is quite stable against air oxidation or further reduction by magnesium below 560° C. but is reduced to metal when heated with magnesium in vacuum to 600° C. for 4 hours.

6. In bomb production of uranium, the delayed final reduction occurs when the vapor pressure of the magnesium is sufficient to break through the MgF_2 film, volatilizing magnesium throughout the UF_4 charge.

7. Delay of the spontaneous reaction allows more external heat to be absorbed by the charge, increasing the fluidity of the reaction products.

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