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CERIUM AND PLUTONIUM DIOXIDE — NOTES
ON REDUCTION TO MASSIVE METAL

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CERIUM AND PLUTONIUM DIOXIDE -- NOTES ON
REDUCTION TO MASSIVE METAL

INTRODUCTION

Plutonium metal is prepared at Hanford by thermal reduction of plutonium tetrafluoride with calcium. A small quantity of booster, calcium and iodine, is reacted with the charge of calcium and PuF_4 . This booster serves a two-fold purpose in the smaller reductions. First, additional heat is provided for melting the bomb contents and secondly, the adhesive forces between the plutonium metal and the calcium fluoride slag are reduced which allows the cold metal biscuit to be easily freed from the slag. In small charges, 10 to 50 grams of plutonium, the additional heat is the important factor in using the booster. However, as charge size increases, the booster content can be reduced. In charges of 100-300 grams of plutonium the primary role of booster is that of allowing one to easily separate the metal from the slag.

Metal obtained by the reduction of plutonium fluoride is produced in high yield and purity, consistently meeting specifications. The troublesome step in the process has always been the preparation of PuF_4 which includes the following steps. A plutonium nitrate solution is reduced to Pu-IV by hydrogen-peroxide and Pu-IV oxalate is then precipitated. The oxalate is calcined at low temperature to yield PuO_2 which is

subsequently fluorinated to PuF_4 with anhydrous hydrogen fluoride at elevated temperatures. The maintenance of the hydrogen fluoride line has been a constant cause of difficulty and has led to several experimental programs aimed at circumventing this operation. (1,2,3,4). All these methods were aimed at the preparation of a plutonium salt which could be reduced to metal and yet did not require anhydrous HF as a reactant. The most promising of the solid-gas reactions studied was the fluorination of PuO_2 with freon-12. Another approach was the precipitation of a double salt, plutonium calcium fluoride from aqueous nitrate solutions. The reduction of the oxides of plutonium appears to be the most difficult system of all from which to prepare useable metal. Generally, pyrophoric powders are obtained from the oxide reductions which present a definite fire hazard. Numerous reductions of the oxides of the heavy metals have been performed in this and other laboratories using varied low melting slag systems. The results have, in general, been the same. Massive metal is not obtained. Pelleted or powder metal is obtained which is often pyrophoric, depending on the metal and variables of the reduction. The direct reduction of plutonium oxide to useable metal is an attractive goal which would considerably lower the present costs of converting a plutonium nitrate solution to the metal.

OBJECTIVE

Considerable experience has been gained in this laboratory on the reduction of the varied salts and oxides of uranium to metal. (5,6,7,8,9,10). A more accurate picture of the mechanism of oxide reduction reactions and some theories as to why massive metal is not easily obtained from such reductions have been forthcoming from this program. (11) The object of this work was to apply some of this uranium experience to the problem of recovering useable plutonium metal from plutonium dioxide by reduction with calcium. More exactly, the objective was to determine the effect on metal coalescence of coupling a low frequency vibratory energy source to a bomb during the reduction cycle. Since plutonium facilities were not available, all work was done with cerium as a stand-in material.

SUMMARY AND CONCLUSIONS

In small scale reductions of cerium dioxide, the use of vibrational energy has been shown to have a marked effect on the yield of coalesced metal. Buttons of 40 to 50 percent theoretical yield have been obtained from the vibrated reductions. This represents an increase of 33 to 67 percent over the massive metal yield of an identical unvibrated charge. A large amount of a suitable fluxing agent, in these runs calcium chloride, has been employed. This flux is necessary to dissolve the calcium oxide formed during the reduction reaction. As flux concentration is decreased, the slag becomes more viscous containing undissolved calcium oxide. It appears that from the highly diluted charges from which reasonably good coalescence is obtained the completeness of reduction of CeO_2 with calcium is seriously hampered. However, complete reduction is easily obtained from the less dilute charges, those containing considerably less flux, but the undissolved calcium oxide along with a more viscous slag prevent the metal from falling to the bottom and agglomerating into a solid mass.

A two-cycle process may have promise as a method of obtaining plutonium metal from the oxide. In such an operation the reduction can be completed with a smaller amount of flux which assures essentially one hundred percent reduction to a powdered metal. Vi-

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brating the reaction vessel will cause most of the metal to settle out of the slag. The undissolved calcium oxide present will prevent the metal from completely coalescing, but larger pellets of metal which can be handled in air are obtained. The metal particles can be recovered from the easily dissolved slag and coalesced under calcium chloride containing a small amount of calcium to reduce any oxide skin present (10). In the case of cerium, yields of 50 to 60 percent solid metal have been obtained by this procedure. The cerium metal pellets were not difficult to handle in air. Plutonium is less pyrophoric than cerium and therefore should offer no special difficulties. It is believed that less than one hundred percent button yields were obtained by this two-cycle method for several reasons. First, all of the fine metal powder which formed as a fog was not coalesced to small sized pellets. Secondly, the cerium fines apparently oxidize to some extent in the leaching operation and are lost as oxide. In the case of plutonium this oxidation during leaching should be greatly reduced, and due to the higher density of plutonium, a more complete pelletization of the metal powders should occur.

It is felt that the results obtained in these scouting experiments with cerium are encouraging enough to warrant continued activity along this line with plutonium. The ratio of densities of Pu/Ce is 2.75. This difference in density may have an appreciable effect on the coalescence of plutonium from the slag in both the single and double cycle operation.

DISCUSSION

In reductions of the oxides and fluorides of uranium to yield massive metal it is usually necessary to take advantage of the exothermic nature of the reduction reaction, since temperatures above the melting point of uranium are necessary to form a solid button of metal. In general, construction materials do not permit operation at temperatures of 1200 to 1500 C unless special precautions are taken. However, plutonium which melts at 632 C permits operation well above its melting point using normal steel construction materials. Therefore, charges can be heated externally to the temperatures needed without dependence on the heat of reaction within the bomb to raise the charge to the desired temperature. Operation at these lower temperatures also allows one to soak the charges above the melting point of the metal and slag for long periods of time. For these reasons it was felt that the reduction of plutonium dioxide with calcium might be performed in a manner which would yield a solid metal piece. Since plutonium facilities were not available, cerium dioxide was used as a stand-in material. The melting point of cerium is essentially identical to that of plutonium; however, the densities differ by a factor of 2.75. It is felt that cerium is a fair stand-in for plutonium in these reduction experiments. Actually, as shown later in this report, the cerium probably results in poorer yields than can be expected with plutonium.

Previous work in this laboratory on the reduction of cerium dioxide with calcium has resulted in very poor metal button yields. Generally, powder or pellet material is obtained which is often pyrophoric. The following equation shows the products of the reduction reaction:

When no flux material is added to the charge, the high melting calcium oxide product

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forms a solid matrix preventing the cerium fines from coalescing. In this case extremely fine metal powder is obtained. Numerous experiments have been run using a flux material which partially dissolves the calcium oxide present resulting in a fluid slag. Again, pyrophoric powders are generally obtained. However, the metal is usually not as fine as that obtained without a flux. When enough flux is added to a charge to completely dissolve the CaO formed from reduction, and the charge is heated above the melting point of the metal and slag for 20 to 40 minutes, some solid metal is obtained. Yields have been low 10 - 30 percent, and some fine powders are also recovered. However, more of the large pellets which can be handled in air are found in the slag. It was also noted that much of the cerium fines did not settle to the bottom of the charge as expected and that many fairly large sized pellets which had settled out had not coalesced. This was true of 1/16 inch diameter pellets which were side by side. It has long been realized that a certain amount of oxide present in the slags tended to hinder coalescence. In the reduction of PuF_4 and PuF_3 with calcium approximately ten percent PuO_2 in the compounds would result in poor button yields. The metal generally was somewhat spongy and often pyrophoric. It was also realized that the calcium oxide from the CeO_2 reductions was in fact the troublesome component in the coalescence difficulties. However, this was quite vividly shown in some recent work by W. R. DeHollander of the Metallurgy Research Sub-Section (11). He has shown that small additions of calcium oxide to slag systems from which metal had previously been coalesced would actually prevent complete coalescence of the metal under identical conditions. Apparently, a film layer of CaO around a molten metal pellet is sufficient to halt or at least slow the growth of the pellet in contact with other oxidized metal particles. But charges in which enough flux was added to theoretically dissolve all of the CaO formed during reduction still failed to give satisfactory metal yields even when soaked for 20 to 40 minutes at temperatures well above the melting points of both the slag and the metal. It is postulated that the kinetics of dissolution of calcium oxide in the calcium chloride flux are slow during the reduction. The undissolved calcium oxide then prevents good metal agglomeration.

A low frequency air-driven vibrator, 60 cycle/second, has been coupled to the reaction vessel during the reduction. It was theorized that this vibratory energy may markedly increase the dissolution rate of the calcium oxide in calcium chloride, and secondly, the film layers of undissolved calcium oxide may be physically disturbed, allowing metal to contact metal and coalesce. Using calcium chloride as the flux, quite impressive results were obtained from reductions of cerium dioxide. A mole ration of $\text{CaCl}_2/\text{CeO}_2$ of 12.5 was employed in most reductions. This corresponds to an eight percent solution of calcium oxide in the calcium chloride slag after reduction has taken place. The solubility of calcium oxide in calcium chloride has been reported as 13.8 percent at 900 C so this is a large excess over the calcium chloride required for oxide dissolution.(12) The cerium dioxide, 100 percent theoretical excess of calcium metal and calcium chloride flux were mixed and packed in a fired magnesia crucible which was hermetically sealed in a steel bomb. The bomb was heated by induction to 1000-1050 C for periods of 20 to 40 minutes. During this heating period the bomb was vibrated for approximately two minutes at a time, these vibrations being repeated from five to ten times during the run. Cerium buttons of 40 to 50 percent theoretical yields were obtained. The unvibrated charges produced buttons of 10 to 30 percent yield. These vibrated yields represent an increase of 33 to 67 percent over the best yield obtained without vibrating the bomb. The bomb charge was heated to 600-700 C while vented, allowing a small amount of water vapor to be removed from the anhydrous calcium chloride. The bomb was then hermetically sealed with a pressure gauge. Pressures were negligible, two to five psi, if this procedure was followed. The low calcium vapor pressure prevents

a rapid reduction reaction. In these diluted charges the cerium dioxide and liquid calcium may not come in contact for reaction to occur. If there was an appreciable calcium vapor pressure, the reaction would be expected to go to completion much more rapidly. It is therefore felt that less than 100 percent yields may in part be due to incomplete reduction of the cerium dioxide. As previously mentioned, the difference in the density of cerium and plutonium may play an important role in the effective metal coalescence. In the cerium system the metal to slag density ratio is approximately 3.15, while in the plutonium system the ratio is 8.67. It is expected that better yields will be realized from the reduction of plutonium dioxide than have been obtained from the cerium system because of this density difference.

A second method of performing the oxide reduction has been briefly studied. If a lesser amount of calcium chloride flux is used, the reduction goes essentially to completion. However, the metal does not coalesce due to the undissolved calcium oxide present even though the slag may be quite fluid. It has been found that the cerium pellets can be increased in size by vibrating the bombs heated to a temperature of 1000 C. By this procedure metal particles can be grown to shot size which are not pyrophoric. The slag can then be easily dissolved and the metal particles coalesced under calcium chloride containing a small amount of calcium to reduce any oxide skin present⁽¹⁰⁾. With cerium dioxide, yields of 50 - 60 percent solid metal have been obtained. This operation is, of course, less desirable than a single cycle process. However cerium particles obtained by this method were large enough to be handled in air. If necessary, an inert atmosphere could be employed during the casting. During the slag dissolution step some of the cerium fines were oxidized by the aqueous solution and lost. Plutonium should be oxidized less rapidly than cerium, resulting in higher yields. However, some fines are always formed which will be partially oxidized during dissolution of the slag in water or dilute acids. These powders are often quite pyrophoric and would therefore cause difficulties if collected. In the case of cerium the fines were estimated to be 10 to 30 percent of the metal formed depending on the variables of the reduction. Due to the density difference the plutonium fines may settle to the bottom of the charge more readily than cerium. In such a case they may be more rapidly grown to a size which can be handled, resulting in a greater button yield.

The results with cerium dioxide have been encouraging. It is recommended that studies with plutonium dioxide be initiated. Several methods of dislodging the oxide skins could be studied. A range of frequencies from the low, 60 cycles/second through ultrasonics could be coupled to the reduction bombs. Jolting tables may find application and should be considered along with high temperature centrifugal casting equipment. The choice of a slag system may result in improved yields. The calcium chloride has been used since it could be easily leached away revealing the position, size, and shapes of the uncoalesced metal. However, several low melting fluoride slag systems thermodynamically compatible in a plutonium system might prove superior to calcium chloride^(13, 14). The use of magnesium metal as reductant may be a practical method of eliminating the incomplete reductions obtained in the dilute systems. Magnesium metal would have an appreciable vapor pressure at 1000 C approximately 280 mm of mercury. The reaction would then be a solid gas reaction instead of the liquid solid reaction which takes place with calcium and CeO_2 . Due to the solubility of magnesium vapor in the slag the reduction reaction should proceed rapidly to completion. Although it is impossible to predict the degree of success which may be obtained from the plutonium oxide reductions, results with cerium indicate some work should be encouraged. In fact if quality button yields of 70 to 80 percent could be obtained with plutonium, a pro-

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cess may be economically feasible based on the recovery of the uncoalesced metal fines and unreduced plutonium oxide as a recycling feed material for subsequent bomb reductions.

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