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PROGRESS REPORT ON METAL REDUCTION, OCTOBER 1943

WORK DONE BY:
R. D. Baker
C. R. Maxwell
M. Kolodney

REPORT WRITTEN BY:
R. D. Baker
M. Kolodney
C. R. Maxwell
Cyril Stanley Smith

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ABSTRACT

Yields of 94 to 95 per cent of clean metal are consistently obtained by the bomb reduction method with 109 grams of UF$_4$ with 12.7 grams (1/7 mole) iodine and 36.7 grams (25 per cent excess) calcium. The bomb is lined with a hard magnesia liner, previously fired at 1700° to 2200° C., and the charge ignited by heating in the field of a high frequency coil in a total time of less than five minutes. Under these conditions the slag collects on the sides of the liner, while the metal runs cleanly to the bottom in a single button. Even greater yields - 93.8 to 96.8 per cent, - are obtained by the same technique with charges of 10.6 grams of fluoride, with iodine and calcium in proportion. Soft, unfired, liners of magnesia and hard liners of zirconia give inferior results for reasons that are being investigated.

Preliminary experiments with hot wire and atomic hydrogen reduction have been carried out, using halides relatively easily reduced, to permit development of the techniques.

Electrolytic cells have been set up, and small yields of uranium metal obtained by electrolysis of fused mixed uranium and sodium fluorides, in graphite cells, at temperatures in the neighborhood of the melting point. Uranium dioxide was found to be insoluble in sodium fluoride or barium fluoride. The tetrafluoride was found to be soluble in both these salts, but segregation occured when aluminum or magnesium fluoride was added.

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INTRODUCTION

Experiments on the reduction of uranium are being carried out by the metallurgy group at Y for the two-fold purpose of developing in detail methods that can be applied directly for the reduction of 25 when it becomes available, and to provide experience with a variety of methods, one or more of which will eventually be adaptable to work on 49. For the former, though relatively high purity metal is needed, the composition specifications are not extreme, and relatively high recovery is the prime requisite. Improvement of the existing bomb method to give better yields seems to be the most likely approach. For the preliminary work on 49, a scale of operations of one gram has been arbitrarily set as the smallest scale that the metallurgists should work on, though they will collaborate with the chemists and microchemists whose work on the microgram and milligram scale will provide the essential basis for later production. It seems likely that the conventional bomb method will not give sufficiently high purity, and attention is being particularly devoted to the study of gas phase reactions in which the purity of the components are more easily maintained, and in which there is little or no contact with refractory surfaces. At present two methods in particular seem promising—hot wire reduction and atomic hydrogen reduction—and both are being studied with easily reduced materials to develop the techniques concerned.

This report is the first of a series of progress reports that will be issued at monthly intervals: It is not a report of completed investigations, and its deficiencies must be weighed against the advantage of prompt reporting of the status of the work.

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I. EXPERIMENTS ON LINERS FOR BOMB REDUCTIONS

By R. D. Baker

The chemical and physical properties of the liner used are factors of extreme importance in the production of coherent metal on a small scale of bomb reduction. In the work described below, the composition of the charge and the method of firing were not varied. Two different size charges were used, 109 grams or 9.6 grams of UF_4 with 1/7 mole of I_2 per mole of UF_4 and 25 per cent excess calcium metal. The calcium was ground in a Wiley mill and sieved to -20, +30 mesh. This removed the fine material and, with it, most of the calcium oxide. All reactions were started by heating the steel bombs in a 3 KW induction furnace. When the charge ignited, the lower portion of the bomb became red, at which time heating was immediately discontinued. The total heating time for either size bomb was approximately five minutes.

Two types of liner were used, namely dry-packed and sintered. The dry-packed liners were formed in the bomb by introducing the pulverized refractory around a core and bumping the assembly on the table. The core was carefully removed and the well-mixed charge introduced into the space left. Loose liner material was pressed firmly in by hand above the charge to fill the bomb.

The sintered liners were formed by bumping in a similar manner in a graphite mold and were fired in the mold by high-frequency heating to the designated temperatures. The magnesia liners (prepared from 325 mesh periclase) when fired to 1750° C. for 10 minutes were hard and firm, but those fired at 2100° - 2200° were harder and less porous. The zirconia liners fired to 1800° C. were more dense and less porous than those of magnesia. The raw material was a commercial grade of 300 mesh electrically fused ZrO_2, containing considerable amounts of silica and other impurities. No appreciable difference was noticed in the zirconia crucibles fired at 1700° C., 1800° C. or those containing magnesia as a binder. After firing in graphite, the

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zirconia liners were black on the surface on account of the presence of carbide or carbon, which was removed by heating in an oxidizing atmosphere at 1000°C. Lids were made for all sintered liners. The significant data obtained to date are given in the following tables.

Table I

Calcium Reduction of Uranium Fluoride in 109 gram Charges

Charge: 109 grams UF_4
12.7 grams Iodine
36.7 grams Calcium

	Liner	Yield %	Remarks
1	Dry packed dolomitic quicklime	92.8	Well formed wafer of metal. Wafer covered with slag.
2	Same as 1	81.0	Poorly formed wafer of metal. Wafer covered with slag.
3	Dry packed thoria (not fused)	24.2	No wafer formed, only beads of metal. Liner collapsed.
4	Same as 3	36.3	Same as 3.
5	Dry packed electrically fused magnesia, 100F	87.0	Porous wafer formed. Wafer covered with slag.
6	Same as 5	84.5	Same as 5.
7	Dry packed 325 mesh periclase	92.0	Well formed wafer, wafer more clean than with dolomitic lime.
8	Same as 7	95.5	Same as 7.
9	Sintered (1750° C) 325 mesh periclase	94.5	Very well formed wafer. Wafer very free of slag.
10	Same as 9	94.0	Same as 9.

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Table II

Calcium Reduction of Uranium in 9.6 gram Charges

Charge: 9.6 grams UF
1.1 grams Iodine
3.2 grams Calcium

Liner	Yield %	Remarks
1 Dry packed 325 mesh periclase	32.0	Only beads of metal formed. Covered with slag.
2 Same as 1	78.0	Two pieces of metal formed, covered with slag.
3 Same as 1 or 2	66.0	One piece of porous metal formed. Covered with slag.
4 Sintered (1750° C) 325 mesh periclase	96.0	Well formed button of metal. Button free from slag.
5 Same as 4	96.7	Same as 4
6 Same as 4 or 5	93.8	Same as 4 or 5
7 Sintered (2100-2200° C.) 325 mesh periclase	96.8	Very well formed button. Better than in 1750° liner. Button free from slag.
8 Same as 7	95.0	Same as 7
9 Sintered (1800° C.) zirconia and 4% MgO	70.0	Well formed button. Beads of metal held in slag. Button free from slag.
10 Same as 9	73.8	Same as 9
11 Sintered (1800°C) zirconia	77.0	Well formed button. Beads of metal held in slag. Button free from slag.
12 Sintered (1700° C.) Zirconia	53.5	Poorly formed button. Beads of metal held in slag. Button free from slag.
13 Dry packed ZrO_2	63.0	Poorly formed button. Button covered with slag.

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The results obtained clearly indicate that a sintered liner is superior to a dry packed one. In the case of the sintered periclase liners, those fired at 2100° - 2200° C. are superior to those fired to 1750° C. The yields are of the same order of magnitude for either firing temperature, but the buttons formed in the higher fired liners are much cleaner. In either type of sintered liner, the slag forms a uniform layer on the inside of the liner, leaving the button of metal free of slag. The slag does not appear to penetrate or to be absorbed by the liner to any extent, a fact due partly to the density of the latter and partly to the short time available after the reaction before the inside surface of the liner is cooled to below the melting point of the slag.

An analysis of the metal formed in the small bomb with a 1750° C. sintered periclase liner gave the following results:

U - 100.0%
Si - Order of 1 ppm (spectrographic estimate)
B - Order of 0.1 ppm " "
Mg - <50 ppm " "
Ca - 100 ppm " "

Since analyses of the raw materials used for the reductions are not yet available, it is not known whether the Mg was obtained from the liner or from the raw materials. The results do indicate, however, that sintered periclase liners may be satisfactory for the preparation of 25. They will not be considered for 49 reductions.

The sintered zirconia liners are inferior to sintered periclase liners under the same experimental conditions. The slag layer is formed on the inside of the liner, but small beads of metal remain trapped in the layer. The yields reported are on the basis of the one piece of coherent metal formed. Work is being continued in an effort to increase the yield in sintered zirconia liners.

Various other liner materials are to be studied. Investigations on producing uranium metal in one gram amounts will be started in the near future.

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II - HOT WIRE REDUCTION

By C. R. Maxwell

Several experiments with the deposition of zirconium from the iodide on a hot wire were made to familiarize the experimenters with the technique. A 2 in. diameter pyrex tube through which was strung a 6 in. filament of 10 mil refractory metal wire was charged with a mixture of zirconium and zirconium iodides and the apparatus evacuated and sealed off. The tube was then placed in a tube furnace and raised to the appropriate temperature before deposition was started by passing current to heat the filament to the desired temperature.

The charge of mixed metal and iodide had been previously prepared by heating a large excess of zirconium with a small amount of iodine in a closed vessel to 250° or 430° C respectively to form ZrI and ZrI_2. The apparatus could then be evacuated without the removal of volatile iodine.

The experiments are summarized in Table III.

Table III - Hot wire deposition of Zirconium

	Charge	Oven temp.	Filament	Filament Temp.	Duration of Experiment	Product
I.	4 grams Zr 2 grams I_2 Heated to 430°	480° C	10 mil tungsten	1200 to 1300° C	4 1/2 hrs.	30-40 mil wire
II.	Unused charge from exp. I.	480° C	10 mil molybdenum	1400 to 1500° C	11 min.	13 mil wire with beads of molten alloy
III.	1.7 grams Zr 0.7 grams I_2 heated 250°	280° C	10 mil tantalum	1300 to 1060° C	3 1/2 hrs.	30 mil wire

The metal deposited on tungsten and tantalum was smooth, uniform, and finely crystalline. A low melting point alloy evidently exists in the molybdenum-zirconium systems, for when using the molybdenum filament, beads of molten alloy

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formed at the temperature of operation, which caused local reduction in diameter of the wire and rapid failure.

Experiments in the near future will be carried out with the deposition of boron from boron trichloride and hydrogen and this seems to be one of the most easily carried out thermal deposition reactions. In particular, apparatus is being devised to deposit the element on large carbon or metal surfaces, heated by high frequency induction, to test the feasibility of depositing metal directly in final usable shapes and sizes, without the necessity of subsequent remelting and casting.

III - REDUCTION IN AN ATOMIC HYDROGEN ARC

By C. R. Maxwell

The great reactivity of atomic hydrogen as indicated by the equation

$$2H \rightarrow H_2 + 100 \text{ KCal}$$

indicated that suitable halides of almost any metal might be reducible by atomic hydrogen. As a source of atomic hydrogen at high temperatures, the tungsten arc operated in a hydrogen atmosphere was selected. It is conceivable that the reduced metal could be condensed in massive form upon a target maintained slightly below the melting point of the metal and thus shaped bodies prepared directly.

A hydrogen arc has been constructed which operates off a 220 v., 60 cycle, AC line with a 3.5 ohm resistance in series. The electrode holders are so constructed to introduce the hydrogen in an annular space around the tungsten rod electrodes. Tungsten rods, 60 mil diameter, operating on 30 amperes were found to be best. The electrodes make an angle of about 25° with each other and when operating smoothly are about 3-4 mm apart at their tips. The halide to be reduced is introduced into the arc as a vapor from a glass or metal tube between the electrodes and as near the arc as possible. The

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hydrogen flow is so adjusted that there is a minimum oxidation of the electrodes. Even so the electrodes lose from 10 to 20 mg of tungsten per minute; most of this is found as finely divided powder on the target placed in front of the arc.

The arc was first operated in air with a water cooled target. A water cooled metal box to contain the arc with the exclusion of air has been constructed, though much difficulty has been encountered with the cracking of observation windows. The arc is harder to strike, but runs more smoothly than in air.

Ferric chloride vapor was rapidly reduced to a black magnetic powder. Boron trichloride was reduced when introduced into the arc, and the resulting boron formed a finely divided powder as the target placed for condensation was not heated to a sufficiently high temperature to permit coherent metal to grow.

IV - PROGRESS REPORT ON ELECTRODEPOSITION

October 6, 1943 to October 28, 1943

By M. Kolodney

This report covers work initiated on October 6, 1943, for the purpose of producing uranium in compact form by electrodeposition. The metal is at present being commercially deposited by the Westinghouse Company as a powder from fused salt baths. This requires cleaning, compacting, and vacuum melting before the product is suitable for use. The obvious modification of this method would consist of deposition of the metal in liquid form in much the same fashion employed for the production of aluminum. The major difficulty to be expected results from the relatively high melting point of uranium which is about 1100° C. This would require temperatures probably in excess of 1200° C. for satisfactory accumulation of the deposited metal. The high density of uranium, however, would appear to be a distinct advantage in securing sharp separation from fused salt.

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The present Westinghouse bath employs a base mixture of calcium and sodium chlorides. The boiling point of this mixture is probably in the vicinity of 1500° C. and its operation at 1200-1300° C. is likely to result in excessive evaporation and low yields. However, the melting and boiling points of alkali and alkaline earth fluorides are in general considerably higher than those of the corresponding chlorides, and furthermore fluoride baths have been successfully employed for the electrolytic production of aluminum, magnesium, and beryllium. In the latter instances, the oxide of the desired metal (or an oxygen-fluorine compound) is dissolved in the metal fluoride diluted with alkali and/or alkaline earth fluorides. Uranium forms a stable fluoride and a fairly stable dioxide, and these materials were considered most suitable for initial experiments. The work was first directed toward the determination of the solubility of uranium fluoride and dioxide in other fluorides and this was followed by exploratory electrolyses of suitable mixtures.

In all the experiments described below, heating was effected by a gas-fired furnace constructed of firebrick and equipped with a conducting hearth to facilitate electrical connections. D.C. power was secured from a motor-generator set capable of delivering a maximum of 50 amperes at 3 to 20 volts. The most suitable contained was graphite machined from solid stock. Clay-graphite and silicon carbide crucibles were readily attacked by the molted fluorides.

Solubility of UF_4 and UO_2 in Fluorides

In the experiments described by outline below, 50-60 grams of the dry materials were premixed and melted in graphite crucibles 1 1/2 in. in diameter. The melts were fluid at the temperatures reached unless otherwise stated. Heating time was 10-15 minutes. The solidified salt was broken out and examined for segregation. The results obtained are given in Table I.

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Segregation in the solid state is an indication that a similar condition probably existed in the liquid condition and the absence of segregation when solid proves the existence of miscibility in the molten state. The results indicate that uranium dioxide is insoluble in sodium fluoride and probably in barium fluoride. The tetrafluoride, however, is soluble in sodium fluoride, barium fluoride, and possibly in calcium fluoride, in the concentration used. However, the addition of magnesium or aluminum fluorides to sodium fluoride led to segregation in the solid. Magnesium fluoride had the same effect in the barium and calcium fluoride mixtures.

Table I - Solubility of UO_2 and UF_4 in Fluorides

No.	Composition, Weight percent	Maximum Temperature* ° C.	Appearance of Solidified Melt (UF_4 green, UO_2 brown, all other compounds white)
1	91 NaF; 9 UO_2	1000	White with thin brown layer at bottom.
2	45.5 NaF; 45.5 BaF_2; 9 UO_2	1115	White with thin brown layer at bottom.
3	84 NaF; 16 UF_4	----	Deep green, with greenish-white surface crystals.
4	45.5 NaF; 45.5 BaF_2; 9 UF_4	1025	Uniform dark green.
5	45.5 NaF; 45.5 CaF_2; 9 UF_4	1025	Uniform gray-green, yellowish crystals at surface.
6	45.5 NaF; 45.5 MgF_2; 9 UF_4	1015	Gray upper region with thin deep brown lower layer.
7	45.5 NaF; 45.5 AlF_3; 9 UF_4	1050	White upper region, thin brown lower layer, mottled with white.
8	45.5 BaF_2; 45.5 MgF_2; 9 UF_4	1100	White upper region with brick-red lower layer.
9	38.5 BaF_2; 38.5 MgF_2; 15.5 NaF; 7.5 UF_4	1025	White upper region with thin brown lower layer.
10	45.5 CaF_2; 45.5 MgF_2; 9 UF_4	1150	White upper half, brown lower half.
11	50 BaF_2; 50 UF_4	1075	Deep green throughout with white specks.
12	50 MgF_2; 50 UF_4	1150 (not fluid)	Deep green with brown center.
13	33.3 BaF_2; 33.3 CaF_2; 33.3 UF_4	1200	Green with black area at base.

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* Determined with optical pyrometer, not corrected for emissivity.

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Electrolytic Experiments

Since uranium tetrafluoride has been found soluble in sodium fluoride and in barium fluoride, most of the initial experiments were conducted in those menstrua, using charges of 200-300 grams. Since high cathode current densities could not be obtained on the relatively large area presented by a crucible, some experiments were performed using the crucible as anode, and a graphite rod as cathode. Very small quantities of uranium could be detected by the characteristic appearance of the spark obtained upon grinding the solidified salt that had been in contact with the cathode. The current densities, ampere-hours, and temperatures given in Table II, which summarizes the results, are in many cases approximate. The electrochemical equivalent of uranium in quadrivalent state is approximately 2.2 grams per ampere-hour.

It will be noted that no current flow could be obtained with UF_4 in calcium-barium fluorides, or with low concentrations in NaF. However, the bath containing equal proportions of NaF and UF_4 is an excellent conductor, and an increase in the tetrafluoride concentration to 57 per cent maintains these properties. Metal was deposited from the UF_4-NaF bath only when high current densities were employed. The failure to deposit any metal in runs such as nos. 6 and 12 may be accounted for either by the formation of a lower valence compound at the cathode or by the reaction of the deposited metal with anode products. Further experiments will be made to test these explanations.

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Table II - Summary of Fluoride Electrolysis

Run	Bath Composition Weight per cent	Cathode material	Approximate Cathode C.D. Amp./sq. in.	Ampere hours	Voltage	Temp. °C	Results
1	32.5 BaF_2; 32.5 CaF_2; 32.5 UF_4; 2.5 UO_2	Graphite crucible	0	0	20	1075	Anode effect prevented current flow.
2	95 NaF; 5 UF_4	Graphite crucible	0	0	20	1115	Anode effect prevented current flow.
3	45.5 NaF; 45.5 UF_4; 9 UO_2	Graphite crucible	2	12.5	4	1085-1115	No visible metal yield, but characteristic uranium spark from bottom of solidified sa
4	50 NaF; 50 UF_4	Molybdenum rod	32	2	3	----	Brown coating on cathode rod. Uranium has alloyed with molybdenum as shown by spark test on the rod.
5	50 NaF; 50 UF_4	Graphite rod	20	-	6	950 approx.	Small particles of metal visible in vicini of cathode. Metal in a matrix of brown material.
6	50 NaF; 50 UF_4	Graphite crucible	2	30	4	1100	No metal yield.
7	50 NaF; 50 UF_4	Graphite rod	100	3	-	1000	Treelike deposit containing visible metallic uranium particles.
8	50 BaF_2; 50 UF_4	Graphite crucible	4	5	4.5	1100	No metal yield.
10	28 NaF; 57 UF_4; 15 UO_2	Molybdenum rod	60	-	-	1000	Metal deposited in small amounts.
		Molybdenum rod	60	-	-	750	Purplish material deposited.
11	24 NaF; 47 UF_4; 29 UO_2	Graphite crucible	5.5	16.5	6	1100-1150	Faint traces of uranium.
12	27 NaF; 55 UF_4; 18 UO_2	Graphite crucible	4	38	6	1200-1300	No metal deposited.

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