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Mike H. West
Michael M. Martinez
Jon B. Nielsen
Donald C. Court
Quentin D. Appert

Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545

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ABSTRACT

A new avenue for the production of uranium metal is presented that offers several advantages over existing technology. A carbon dioxide (CO_2) laser is used to initiate the reaction between uranium tetrafluoride (UF_4) and calcium metal. The new method does not require induction heating of a closed system (a pressure vessel) nor does it utilize iodine (I_2) as a chemical booster. The results of five reductions of UF_4, spanning 100 to 200 g of uranium, are evaluated, and suggestions are made for future work in this area.

INTRODUCTION

Uranium metal has numerous uses in conventional weapons (armor penetrators) and nuclear weapons. It also has application to nuclear reactor designs utilizing metallic fuels—for example, the former Integral Fast Reactor program at Argonne National Laboratory.[1] Uranium metal also has promise as a material of construction for spent-nuclear-fuel storage casks.

Uranium metal is traditionally produced by reaction of uranium tetrafluoride (UF_4) with calcium metal in the presence of an elemental iodine (I_2) booster, as shown below.

$$Ca^\circ + I_2 \longrightarrow CaI_2 \qquad (1)$$
ΔG°_{rxn} (398°C) = -118.7 kcal/mole; ΔH°_{rxn} (398°C) = -141.8 kcal/mole

$$2\,Ca^\circ + UF_4 \longrightarrow 2\,CaF_2 + U^\circ \qquad (2)$$
ΔG°_{rxn} (410°C) = -120.6 kcal/mole; ΔH°_{rxn} (410°C) = -128.7 kcal/mole

A crucible constructed of magnesia (MgO) is typically employed to contain both reactants and products under argon in a pressure vessel or "bomb." The pressure vessel is heated inductively until reactions between (1) calcium metal and I_2 and (2) calcium metal and UF_4 occur.[2] Baker et al. found that the reaction between calcium metal and I_2 starts at 398°C and that this reaction also determines the temperature for the starting point of the calcium metal–UF_4 reaction (410°C). The Gibbs free energies (ΔG_{rxn}) and enthalpies

(ΔH_{rxn}) for the above reactions, computed from data in Pankratz,[3] are quite negative, suggesting that the reactions are both thermodynamically favorable and exothermic. Baker et al. developed the above technique for the preparation of uranium metal in quantities ranging from 1 to 1000 g. Previous to the work of Baker et al., Ames Laboratory at Iowa State College, had prepared uranium metal on the 11.3-kg (25-pound) scale.[4]

In an effort to improve existing technology for uranium metal production, Los Alamos has explored laser initiation of the reaction between calcium metal and UF_4. The French have been successful in initiating the reaction between calcium metal and plutonium tetrafluoride (PuF_4) using a 25-watt carbon dioxide (CO_2) laser.[5] Success in the laser-initiated approach will eliminate both the need for induction heating of the pressure vessel and the use of I_2 as a booster. In fact, the reaction can then be performed under conditions that make it unnecessary to use a pressure vessel to contain the reaction products. Iodine is very corrosive in any downstream processing steps necessary for recovery of uranium from the slag (CaF_2 and CaI_2) and crucible residues. It can be considered corrosive even under normal storage conditions.[6]

In this report, preliminary results are described for small-scale, laser-initiated reductions of UF_4 by calcium metal.

EXPERIMENTAL APPROACH

The following description of the experimental apparatus and procedure employed during the small-scale, laser-initiated reduction of UF_4 by calcium metal is fairly typical of the approach.

An overall picture of the experimental apparatus for small-scale, laser-initiated reductions is shown in Figure 1. The vessel, which contains the reactants and products, is pictured in Figure 2 (Los Alamos Drawing Number 26Y-201487). The reduction vessel has one O-ring seal that is protected from any expelled reaction products. Two gallium arsenide windows, each with an accompanying O-ring seal, provide an optical path for the laser beam between the exterior and interior of the vessel. A polished copper mirror redirects the laser beam at 90° with respect to the incident radiation. A visible diode pointer (Synrad Model 48-DP), mounted on the front of the CO_2 laser, emits a visible red laser beam, which when coaligned with the CO_2 laser beam, is a convenient tool for aligning the gallium arsenide windows in the reduction vessel with the CO_2 laser beam. The CO_2 laser is a Synrad Model E48-5-115V-014.

UF_4 was dried to a constant weight at 100°C and allowed to cool in a desiccator over silica gel. The UF_4 was prepared at the Paducah facility of Union Carbide by fluorination of uranium dioxide (UO_2) with hydrogen fluoride (HF). Ground calcium metal was maintained under an argon atmosphere. The mixing jar and MgO cover for the crucible were also dried at 100°C and allowed to cool to room temperature in a desiccator. The MgO crucible was usually dried at 100°C before use. Magnesium oxide sand (<35 mesh) was utilized to provide a cushion between the crucible wall and the pressure-vessel wall.

The UF_4 (depleted uranium, i.e., 0.20% ^{235}U) and ground calcium metal (a particle-size range of <0.40 mm to >35 mesh fraction) were mixed in a glass jar and transferred to the MgO crucible with the help of a glass funnel. The mixture was manually compacted in the crucible with a stainless steel compactor. Calcium metal granules were visible at

the top of the charge. The top section of the vessel (Figure 2) was then screwed onto the bottom section, and the inlet and outlet argon lines were connected to the vessel.

The argon flowed at 1.4 L/min for about three minutes before the firing of the laser. A setting of 3.6 (about 44 watts) was utilized for the laser power. Cooling water to the laser was maintained at 17.5°C.

The laser was allowed to fire for about 5 seconds, but a crackling sound was heard immediately after flipping the switch on the Model CA-48 Controller. No pressure spike was observed on the pressure gauge nearest the reduction vessel. Argon was left flowing during and after the reduction. The temperature, monitored by a thermocouple placed at the reduction vessel base began to rise immediately after firing the laser. The underside of the lower laser table was found to be warm just after the reduction. Deposits were observed in the Tygon tubing leading from the reduction vessel. An odor of hot plastics or combustion products was noted after the reduction step. However, no visible damage was found to the Tygon tubing.

The vessel was allowed to cool to room temperature before disassembly and removal of reaction products, including uranium metal, CaF_2 slag, and MgO crucible. Normally, a gray deposit was found on the inside wall of the crucible, the crucible cover, and the top section of the reduction vessel. A deposit was also located on the lower gallium arsenide window. A thin coating of slag was usually found along the crucible wall. The crucible adjacent to uranium metal often had a yellow coloration. The weights of uranium metal, sand, slag, and crucible were all recorded separately. The sand was passed through a 35-mesh sieve and saved for use in further experiments.

The gallium arsenide windows were cleaned with cotton balls or cotton swabs saturated with acetone. The lower window surface was cleaned after every reduction.

RESULTS

The results from the first reduction (100 g of uranium in the UF_4 feed) are given in the table on the next page. For the purposes of this study, the UF_4 feed and uranium metal product were considered to be pure. A straight-walled MgO crucible was used for this first reduction (Figure 3), and the crucible was not dried before the reduction. The uranium metal was well coalesced (Figure 4) although the presence of tiny droplets of uncoalesced metal is possible. The mass of uranium metal obtained corresponds to an 88.9% yield. Because of the much higher melting point of uranium metal (1132°C) compared with plutonium metal (640°C), the ability to form well-coalesced uranium metal by the laser-initiated reduction technique was a potential obstacle to its technical success. Other than the laser beam impinging on the compacted mass of UF_4 and calcium metal, there is no external source of heat compared to induction heating of the pressure vessel. The external temperature of the reduction vessel peaked in about three minutes at 124°C.

Table. Results from five UF_4 reductions.

Experiment Number	Feed (g)			Product (g)			
	UF_4	Ca Metal	MgO Crucible	MgO Crucible	MgO Sand	CaF_2 Slag	U Metal
1	131.9	42.1		210.6	120.9	79.2	88.9
2	131.9	42.2		193.8	112.9	75.0	93.2
3	131.9	42.1		242.8	92.1	74.8	95.0
4	197.9	63.2	189.1	191.7	121.5	118.8	136.8
5	263.9	84.2		233.7	136.2	139.4	181.8

The second experimental reduction was identical to the first except that the straight-walled crucible was dried at 100°C for several days. The yield of uranium metal at 93.2% was improved somewhat over the first experiment.

Because the uranium metal did not cover the entire surface of the crucible bottom in the first two reductions, a dried, tapered MgO crucible (Figure 3) was used for the third experiment. Otherwise, the third experiment was identical to the previous reductions. At the completion of the reduction, the slag was located 12.4 cm (4-7/8 in.) from the crucible lip. The uranium metal, formed as a result of the reduction, still did not occupy the entire bottom of the crucible. The yield of uranium metal was satisfactory at 95.0%.

The last two experiments explored the feasibility of UF_4 reductions at 150 and 200 g of uranium, respectively. A charge of 200 g of uranium is probably the upper limit for the reduction vessel used in this study. Dried, straight-walled crucibles were employed for both reductions. A yield of 91.2% resulted from the fourth experiment. The slag was about 3.8 cm (1-1/2 in.) tall. For the fifth reduction, the temperature at the reduction vessel's base peaked between 162 °C and 163°C (6-1/2 minutes after completion of the reduction). In the case of the fifth reduction, the uranium metal occupied the entire volume at the bottom of the crucible. The metal disk was about 0.95 cm (3/8 in.) thick (Figure 5). The yield was 90.9%.

FUTURE WORK

Several improvements to the laser-initiated reduction of UF_4 by calcium metal are desirable. First, the reduction technology must be demonstrated for up to 2 kg of uranium as UF_4. A larger reduction vessel is presently being designed to accommodate this goal. Second, improvement in the yield of uranium metal from the reduction reaction would be very helpful. The yields observed in the present study are similar to those reported by the French for the comparable laser-initiated reaction of PuF_4 with calcium metal.[5] Third, UF_4 is also being prepared by the thermal decomposition of $(NH_4)_4UF_8$. It is important to show that UF_4 synthesized in this fashion can be reduced to uranium metal with yields comparable with those from reduction of UF_4 prepared by fluorination of UO_2 with HF. $(NH_4)_4UF_8$ is prepared by the reaction of UO_2 with ammonium bifluoride (NH_4HF_2).[7,8]

ACKNOWLEDGMENTS

The crucibles were fabricated by Lalo Trujillo of the Materials Science and Technology Division, Ceramic Science and Technology Group (MST-4). A circular hole for the laser beam was ultrasonically cut in the MgO crucible cover at the Materials Technology: Metallurgy Group (MST-6) machine shop under the direction of Gerry Leeches. The tapered crucibles were designed by Jim Reavis of the old Plutonium Metal Technology Group (MST-13) in 1985. Federico Martinez of the Engineering Sciences and Applications Division, Design Engineering Group (ESA-DE) made the engineering drawings of the small-scale reduction vessel.

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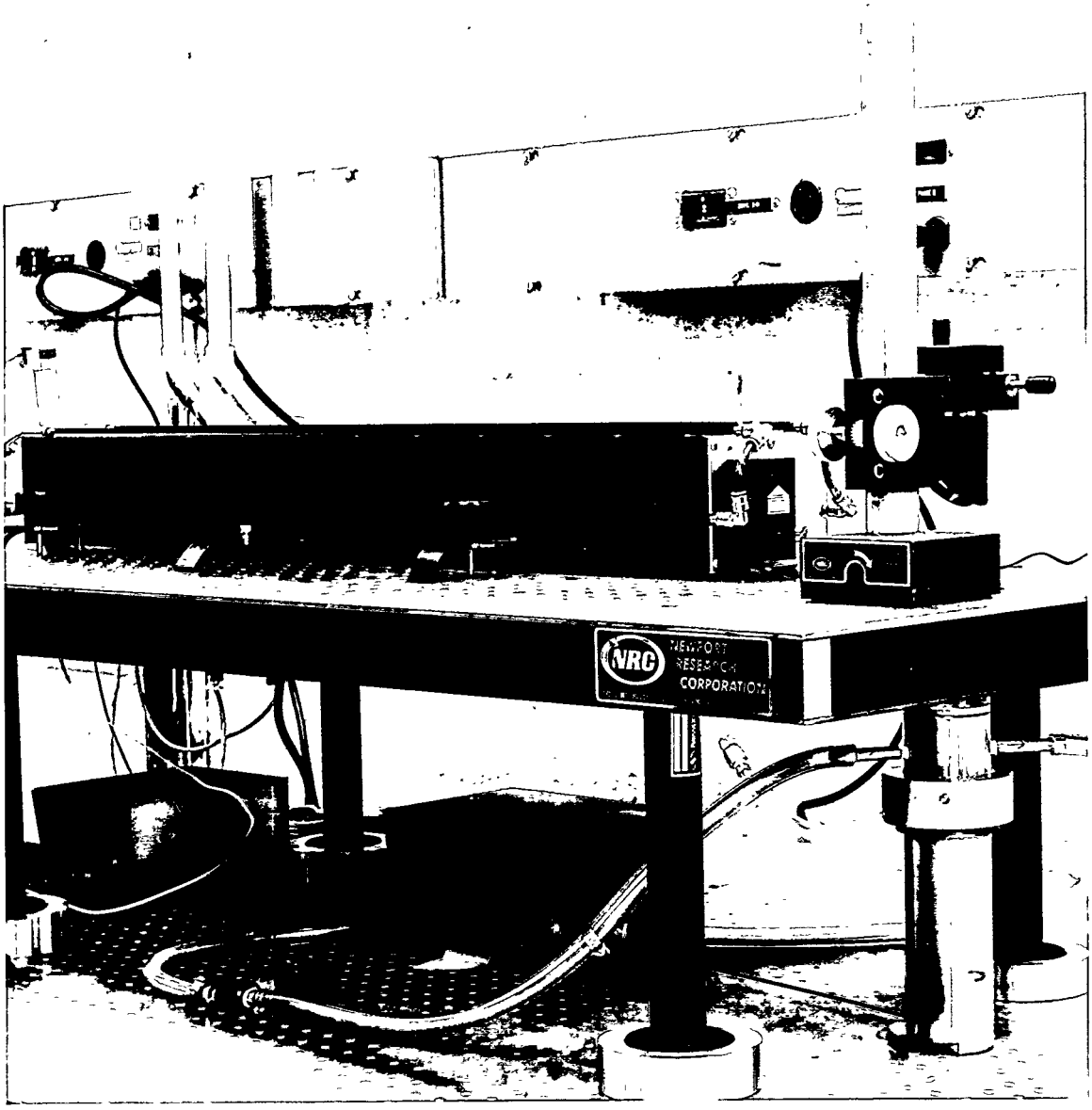

Figure 1. Experimental apparatus for small-scale, laser-initiated reductions. The CO_2 laser is shown sitting on the optics bench. Laser output is reflected by a copper mirror, attached to the top beam steering assembly in front of the laser on the right side of the photograph, and directed at 90° to the reaction vessel, shown here in the bottom right corner and in detail in Figure 2.

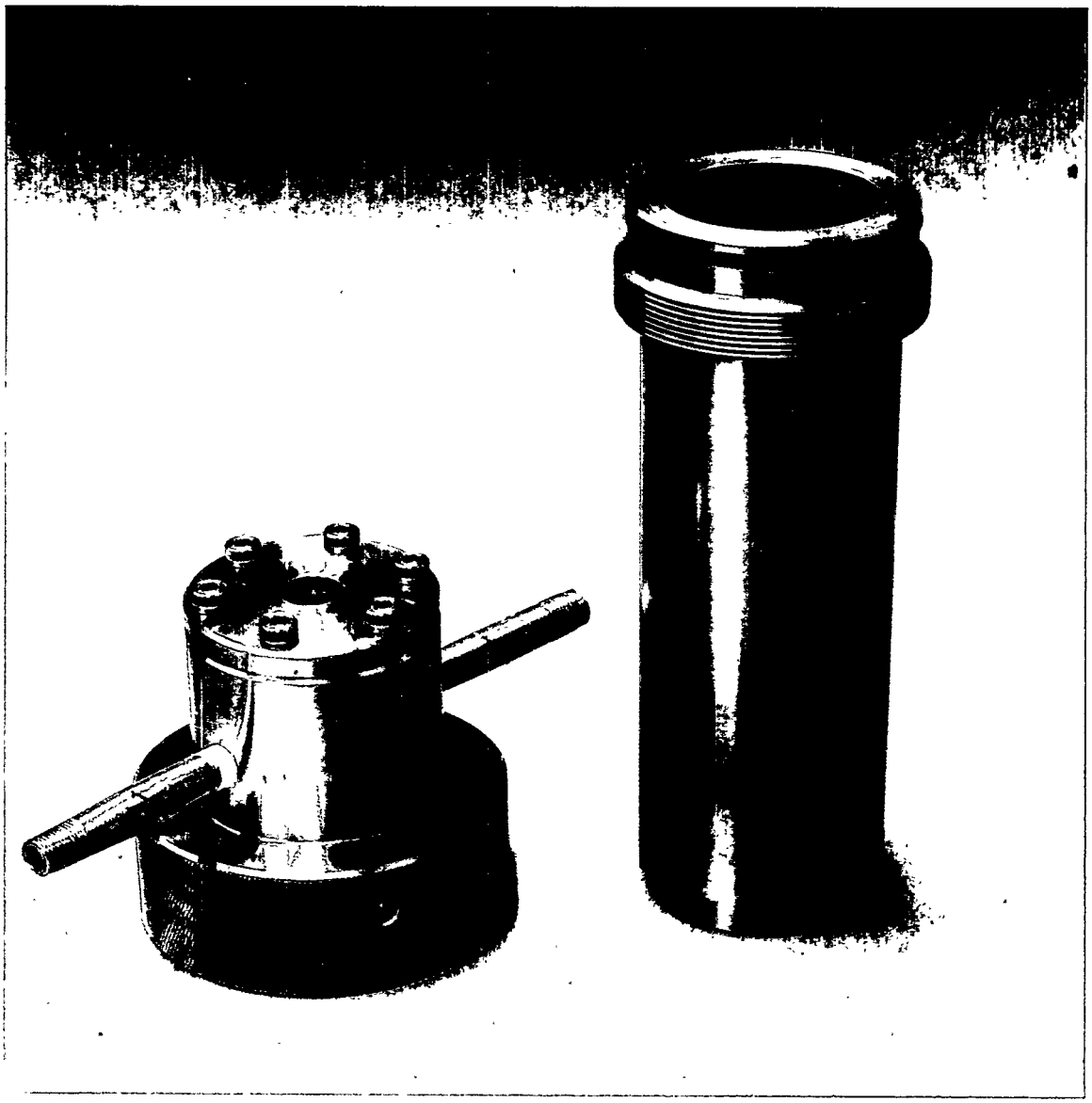

Figure 2. Stainless steel reaction vessel for small-scale, laser-initiated reductions. The top of the reaction vessel (left) contains two gallium arsenide windows, each with an O-ring seal, that provide an optical path for the laser beam. The bottom part of the vessel (right) has one O-ring seal that is protected from any expelled reaction products.

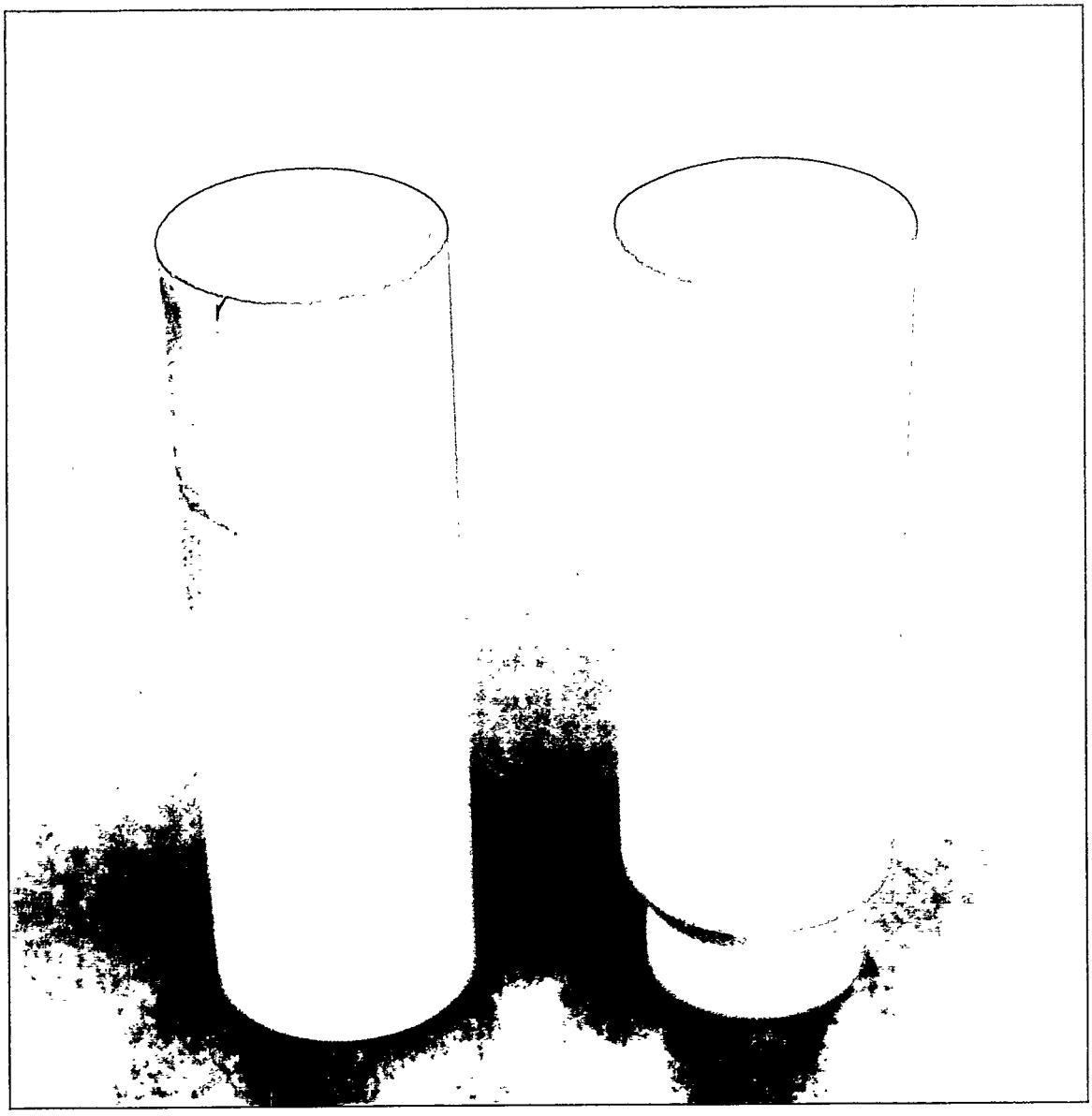

Figure 3. Magnesium oxide crucibles used for small-scale, laser-initiated reductions. The straight-walled crucible is on the left, and the tapered crucible is on the right.

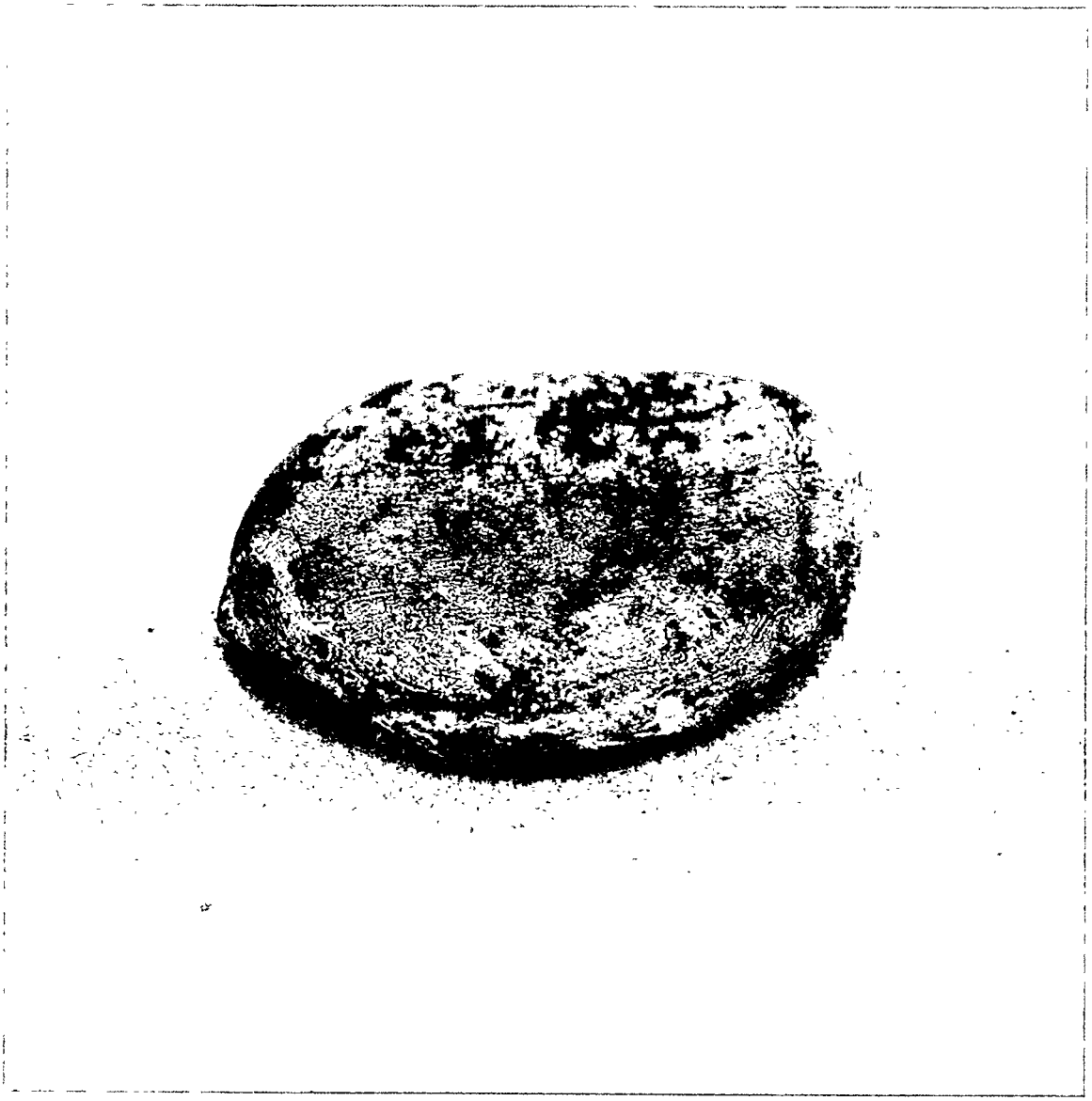

Figure 4. Uranium metal from a laser-initiated reduction of uranium tetrafluoride (100 g of uranium feed as uranium tetrafluoride). A straight-walled MgO crucible was used for this first reduction and the yield was 88.9% (see Table). Slag was removed with a wire brush to show uranium metal (silver) and uranium oxide tarnish (silver-grey in color).

Figure 5. Uranium metal from a laser-initiated reduction of uranium tetrafluoride (200 g of uranium feed as uranium tetrafluoride). This figure shows the results of the fifth reduction (see Table). The uranium metal disk is about 0.95 cm (3/8 in.) thick and occupied the entire volume at the bottom of the crucible. The copper-colored material is slag, the uranium metal is silver, and the tarnish is silver-grey.