

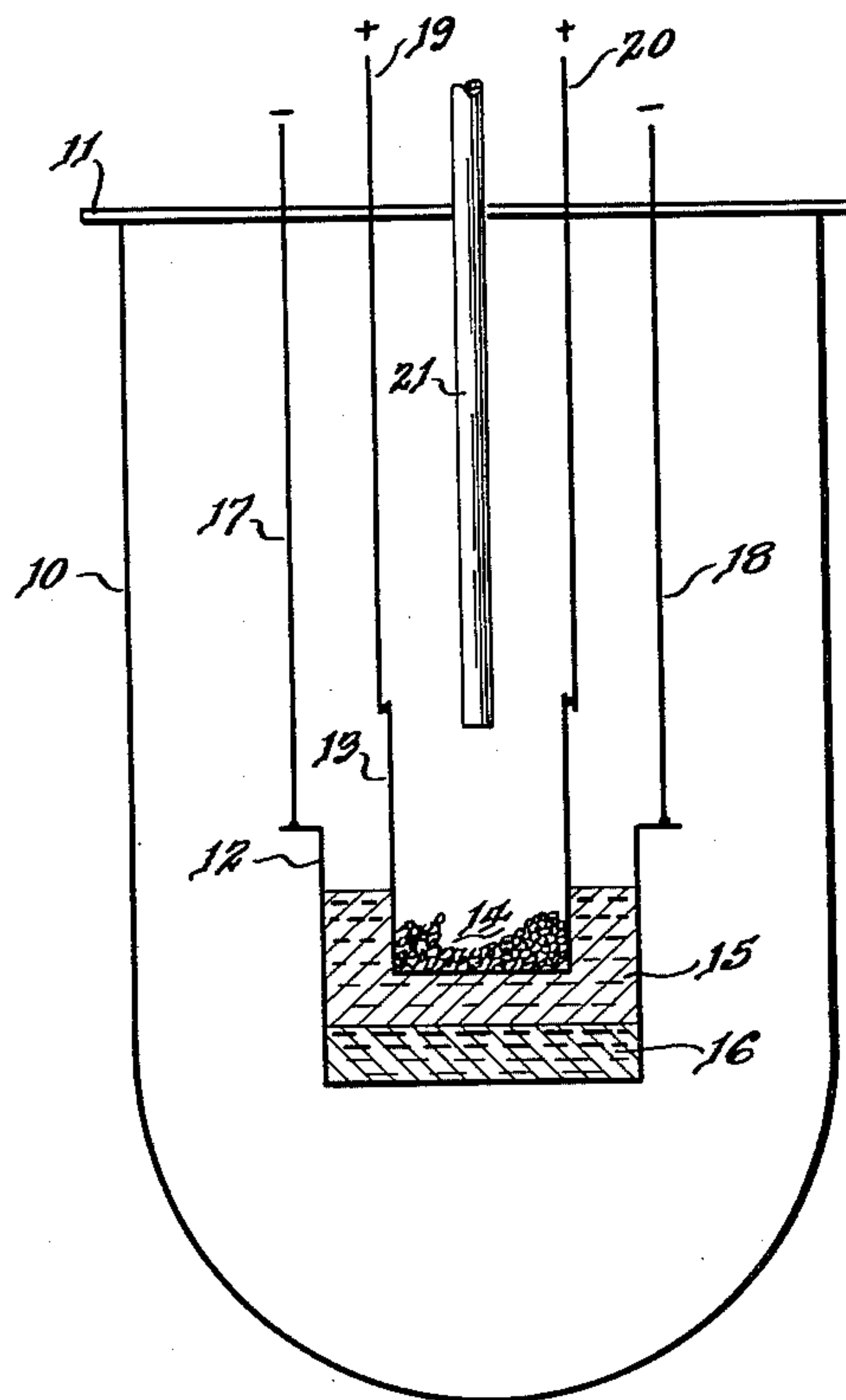
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METHOD OF PRODUCING URANIUM METAL BY ELECTROLYSIS

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METHOD OF PRODUCING URANIUM METAL BY ELECTROLYSIS

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4 Claims. (Cl. 204—1.5)

This invention deals with the production of uranium metal by electrolysis and in particular by electrolysis of uranium oxide using a fused electrolyte. The process is also applicable to the treatment of oxide-contaminated scrap uranium for the recovery of pure uranium metal.

Uranium oxide has been electrolytically reduced heretofore using graphite electrodes and a fused electrolyte at a temperature above the melting point of uranium. However, the uranium oxide did not dissolve very well in the electrolyte, and a great proportion of it settled at the bottom of the container. Also, the presence of the oxide in the electrolyte interfered with the coalescence of the metal formed, so that metal shot was obtained rather than the massive piece of metal desired.

It is an object of this invention to provide a process for the electrolytic production of uranium metal from oxide whereby an oxide-free product is obtained which coalesces easily.

It is another object of this invention to provide a process for the electrolytic treatment of scrap uranium metal whereby a massive piece of high-purity uranium is obtained which is suitable for use in nuclear reactors.

It has been found that, if the uranium oxide to be treated is incorporated in the anode instead of in the electrolyte and an anode of the consumable type is used, the drawbacks enumerated above are overcome. The base material preferred for the consumable anode is carbon. It was also found that a further improvement is brought about if an oxide-free electrolyte is used and if it is at a temperature above the melting point of uranium and preferably between 1150 and 1175° C.

The process of this invention thus broadly comprises electrolyzing a system of a carbon- and uranium-oxide-containing anode, a cathode and an anode-free molten electrolyte at a temperature of between 1150 and 1175° C.

Uranium dioxide, uranium trioxide and U_3O_8 are suitable for the process of this invention. If the oxide is the dioxide, it is electrically dissociated or ionized at the anode, and the uranium cations formed travel to the cathode where they are deposited as the metal. In the case of either uranium trioxide or U_3O_8 , the carbon of the anode, as will be described later, chemically reduces the higher oxide to uranium dioxide, which then is ionized by the electrolysis. Analogous reactions take place in the case of oxide-contaminated scrap metal, such as uranium turnings.

The electrolyte found best suitable consists of a mixture of barium or calcium fluoride, magnesium or lithium fluoride and uranium fluoride. A composition of between 40 and 75% by weight of barium or calcium fluoride, 10 to 20% of lithium or magnesium fluoride and from 15 to 45% of uranium tetrafluoride has been found satisfactory, an electrolyte containing lithium fluoride and barium fluoride in equimolar quantities and 25% by weight of uranium tetrafluoride giving especially good results.

Both lithium fluoride and magnesium fluoride have ad-

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vantages. While lithium fluoride normally brings about a better yield than magnesium fluoride, the latter is less volatile and therefore provides for a more constant composition of the electrolyte.

A low quantity of uranium fluoride, within the range indicated, is preferred, because then higher current efficiencies are obtained. A relatively high uranium tetrafluoride content, on the other hand, permits the use of a higher current density before the so-called anode effect starts. This anode effect is based on a decomposition of the electrolyte and formation of a nonconducting fluorocarbon film on the anode which, in turn, causes interruption of the current.

To prepare the anode, coal tar pitch, or other similar carbonaceous matter, is mixed with the uranium material to be processed; the carbonaceous matter is best used in the form of a solution; for instance, it can be dissolved in hot trichloroethylene; the uranium oxide is then added to the solution formed. Powdered graphite or carbon black can also be incorporated in addition to the coal tar pitch, as will be described more in detail later. After a homogeneous mixture has been obtained, the trichloroethylene is evaporated under stirring. The resulting powder is compressed into the shape desired for the electrodes, using a temperature of about 110° C. and a pressure of about 2000 p.s.i. The resulting "green electrodes" are then packed in graphite powder and baked at a temperature of 1100° C. for from one to six hours.

The gaseous reaction product in the electrolytic process of this invention is mainly carbon monoxide, and only little carbon dioxide is formed. Therefore the anode should contain slightly less than 2 moles of carbon per mole of uranium dioxide. However, in most instances described in this specification a ratio of 2 moles was employed in order to have an excessive amount. On the other hand, the coal tar pitch content has to be restricted to a maximum of 10%, because otherwise bloating and cracking of the electrode occur during the carbonization step. A 10% pitch content, upon baking, yielded a carbon content of about 6.5%, and two moles of carbon per one mole of UO_2 amount to about 8%; "fixed" carbon, such as carbon black and powdered graphite, were therefore added to bring the carbon content to the amount desired. Before the baking procedure, the anode mixture is shaped, for instance, into rods or pellets.

Either a graphite crucible holding the electrolyte and also receiving the metal formed, or else a graphite rod extending into a fused-alumina cup containing the metal formed, were used as cathode.

While any apparatus using the above-described anode, cathode and electrolyte can be used for carrying out the process of this invention, an arrangement will now be described that has been found particularly well suitable for the treatment of scrap uranium. This device is illustrated diagrammatically in the drawing.

In said drawing, reference numeral 19 indicates a quartz tube which is closed by a lid 11. A graphite crucible 12 is concentrically arranged in said quartz tube, and an anode basket 13 again fits into the graphite crucible; the lower parts of the side walls and the bottom of the anode basket are perforated. Pellets 14 of a uranium oxide-carbon mixture are contained in said anode basket. An electrolyte 15 is present in the graphite crucible 12, and a metal pool 16 collects as it is formed at the bottom of the crucible 12.

The graphite crucible 12 is cathodically connected by means of cathode rods 17 and 18, and the anode basket

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13 is anodically connected by means of anode rods 19 and 20. A filling tube 21, for instance made of Vycor, extends into the anode basket 13; pellets of carbon-uranium oxide material, and also uranium tetrafluoride whenever the electrolyte is depleted, can be introduced through this tube 21. Heating coils (not shown) surround the quartz tube for the purpose of bringing the cathode crucible to operating temperature.

In operating the device just described, the electrolyte 15 is placed into the crucible 12. The apparatus is then evacuated and heated to about 500° C., and a vacuum of about 10⁻² mm. Hg is created and maintained at this temperature for approximately 30 minutes in order to outgas the crucible 12 and the electrolyte 15. Thereafter the system is filled with helium, and the temperature is raised to above the melting point of uranium and preferably to between 1150 and 1175° C. At this temperature the electrolyte 15 melts. The anode basket 13 containing the pellets 14 is then lowered into the crucible 12, and an electrical direct current is sent through the crucible, the electrolyte and the basket. Uranium metal forms at the cathode crucible 12 and collects in the form of the metal pool 16.

Even when the apparatus had been evacuated and subsequently flushed with helium, the electrolyte was found still to contain an undesirably great amount of oxygen so that the uranium metal formed did not coalesce satisfactorily. This drawback was overcome by subjecting the electrolyte to a pretreating process in situ prior to uranium production. This pretreatment consisted of electrolysis at reversed polarity whereby the graphite crucible was made the anode and the perforated basket the cathode. During this step the temperature was maintained at below the melting point of uranium, preferably at about 1075° C., so that uranium would not drip down to the then anodic surface. This reversed electrolysis was continued until erratic currents indicated a beginning decomposition of the electrolyte, and at this point the polarity was returned to normal, that is, the crucible 12 was made the cathode, the perforated basket 13 the anode, and the

temperature was raised to between 1150 and 1175° C. The current density may vary widely, but a higher cathode density was found to improve the current efficiency. With an electrolyte containing 25% uranium tetrafluoride, a cathode density of 15 amps./cm.² was found satisfactory. The anode density preferably is below 1.5 amps./cm.² in order to avoid decomposition of the electrolyte and the resulting anode effect. An anodic potential of between 8 and 12 volts was found advantageous, because at this high level a film formed which protected the anode basket from erosion. The uranium metal collected at the bottom of the crucible 12 may be directly cast into molds of the dimensions desired, and the ingots thus obtained may then be machined into cores for use as fuel in nuclear reactors. The turnings or other scrap obtained during the machining procedure can be recycled by using it as anode material in the process of this invention.

If scrap is to be recycled, it is first superficially cleaned by rinsing in trichloroethylene and air-drying. It was then added stepwise to the electrolyte at 1150° C. after treatment of the latter by reversed electrolysis while a current of from 250 to 400 amperes was maintained. In one instance, where 900 grams of uranium turnings were added in nine portions to an electrolyte consisting of 57% BaF₂, 20% MgF₂, and 23% UF₄ over a period of 2½ hours, 916 grams of good-quality metal were obtained. Of this amount 47 grams came from the decomposition of uranium tetrafluoride so that the metal recovery was about 97%. Twenty-seven liters of gas were evolved during the electrolysis, 77% of which consisted of carbon monoxide and 13% of carbon tetrafluoride; there were only 2% by volume of carbon dioxide, the remaining 8% being nitrogen. The analysis of the recovered metal is given in Table I.

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TABLE I

		P.p.m.
	C	1,400
	H	1.1
5	Ag	0.2
	Al	37
	As	<10
	B	<0.10
	Be	<0.1
10	Bi	<5
	Cd	<0.20
	Cr	7
	Cu	<10
	Fe	>100
15	In	4
	Li	<1
	Mg	>100
	Mn	32
	Mo	<5
20	Na	<10
	Ni	>100
	P	<50
	Pb	<5
	Si	<10
25	V	60
	Zn	<20

Instead of using a graphite basket to hold the anode material to be treated, a so-called bare anode can also be used. Such an anode is made by the same method as is the basket, but it is a solid block which preferably has perforations on the sides and elongated slots in the bottom. The slots are for the purpose of causing any attack by the electrolyte in the bottom rather than at the sides so that the anode-cathode spacing remains as constant as possible. The anode can be lowered and immersed in the electrolyte as it is consumed. It was found that this bare anode has the considerable advantage over the basket-type anode that no reaction between graphite and electrolyte occurs. Consequently no carbon tetrafluoride is developed, and the composition of the electrolyte remains practically the same. Also, this bare anode has a considerably longer service life than does the anode basket.

In the following, a few examples are given of the process of this invention for illustrative purposes.

Example I

Five runs were carried out using uranium dioxide-carbon pellets as the anode and a graphite crucible as the cathode. The anode pellets of uranium oxide plus carbon were contained in a perforated graphite basket as is illustrated in the drawing. In runs 1-3 this basket was directly connected with the anode, while for runs 4 and 5 the anode proper was formed of a graphite rod which was in contact with the material to be processed in the basket. The electrolyte for the first run consisted of 45% by weight of barium fluoride, 15% of magnesium fluoride and 40% of uranium tetrafluoride, while for the other four runs the electrolyte consisted of 65% of barium fluoride, 10% of lithium fluoride and 25% of uranium tetrafluoride. The other operating conditions and the results are compiled in Table II.

TABLE II

Run No.	Current density, amp./cm. ²		Total current, amp./hr.	Amount of metal produced, g.
	Anode	Cathode		
1	~2	1.2	160	14
2	~2	1.2	140	33
3	~2	1.2	127	52
4	1.5	8	215	92
5	~1	15	428	370

All metals produced were sound, massive, and very clean pieces with no electrolyte trapped therein. The metal of run 5 was analyzed; it showed the following contents and density.

TABLE III

Chemical analysis:

Density	g./cc.	18.91
Hydrogen	p.p.m.	1.9
Carbon	p.p.m.	160

Spectrographic analysis (p.p.m.):

Ag	<0.1
Al	>100
As	<10
B	0.36
Be	<0.1
Bi	<5
Cd	<0.20
Co	<5
Cr	12
Cu	5
Fe	>100
In	<1
Li	>10
Mg	<10
Mn	<10
Mo	<5
Na	<10
Ni	11
P	<50
Pb	<5
Si	70
Sn	<5
V	<20
Zn	<20

Considering the relatively small quantity that was processed in these runs, the purity of the product was very high. This is especially true for the carbon content which was fairly low in spite of the fact that the metal was collected in a graphite container.

Example II

Another set of ten runs was carried out using a perforated anode basket with varying numbers and shapes of perforations. The uranium dioxide-carbon anode mixture had been crushed to a sieve size of $-\frac{3}{4}$ inch to $+\frac{1}{4}$ inch; this small particle size permitted a higher current flow and consequently faster rates of metal formation. The apparatus used was that shown in the drawing. The potential ranged between 4.5 and 5.5 volts in all runs with the exception of run 10. Run 10 was first operated at 4.6 volts and in the second stage at 11 volts; in the first stage the off-gas contained 15% CF_4 , while in the second stage no CF_4 could be discovered in the gas. The conditions and results of the ten runs are compiled in Table IV.

TABLE IV

Conditions	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Number of holes	80	80	~80	~80	~120	150	850	¹ 17	150	150
Diameter of holes, in.	$\frac{3}{16}$	$\frac{3}{16}$	$\frac{3}{16}$	$\frac{3}{16}$	$\frac{3}{16}$	$\frac{3}{16}$	$\frac{3}{16}$	² $\frac{3}{16}$	$\frac{3}{16}$	$\frac{3}{16}$
Electrolyte ³	A	A	B	A	A	A	A	A	C	B
Duration, mins.	300	315	360	1,414	2,327	497	332	414	406	334
Total current, amp.-hrs.	1,280	1,145	740	9,700	16,874	3,020	1,100	2,790	2,720	1,230
Total gas, liters	92	185	63	400	1,144	282	224	181	117	165
Metal produced, g.	270	775	245	2,550	6,800	1,475	1,190	675	530	725
Current efficiency, percent	10	30	15	12	18	22	49	11	9	27
CF_4 in gas, vol. percent, avg.	4	13	12	16	15	11	18	6	0	-----

¹ Slots. ² Wide.

³ Initial electrolyte composition: A—65% BaF_2 , 10% LiF , 25% UF_4 . B—57% BaF_2 , 20% MgF_2 , 23% UF_4 . C—40% BaF_2 , 15% MgF_2 , 45% UF_4 .

The metal obtained in run 5 was analyzed and so was the uranium dioxide-carbon anode material for comparison's sake. The data are listed in Table V.

TABLE V

	UO_2 -Carbon anode	Metal product
Density, g./cc.	~6	18.96
Carbon, p.p.m.	~80,000	320
H ₂	0.12	0.2
Ag	11	<0.1
Al	<10	~100
As	0.30	<10
B	<0.1	0.10
Be	<5	<0.1
Bi	<0.20	<5
Cd	<5	<0.20
Co	50	<5
Cr	2	12
Cu	>100	3
Fe	<1	60
In	6	<1
Li	32	1
Mg	<10	<10
Mn	<5	<10
Mo	12	<5
Na	50	<10
Ni	<50	<5
P	<5	<50
Pb	32	<5
Si	<20	<10
V	<20	26
Zn	<20	<20

The above analysis shows that an appreciable decontamination is obtained by the process of this invention.

The following example illustrates the application of the process of this invention to the treatment of uranium turnings as they were obtained in the machining of uranium pieces for dimensioning fuel element cores for nuclear reactors.

Example III

A graphite anode basket was used which had 440 holes of $\frac{1}{8}$ inch in diameter. Uranium turnings were washed with water and dried with acetone. An electrolyte was used consisting of 75% of equimolar lithium and barium fluorides plus 25% of uranium tetrafluoride. The temperature, as in all instances, ranged between 1150 and 1175° C. Two runs were carried out, the conditions and results of which are given in Table VI.

TABLE VI

Run No.	Amps.	Volts	Total gas evolved, liters	CF_4 in gas, percent	Turnings processed, gms.	UO_2 on turnings, w./o.	Yield, percent
1	500	8	65.2	13	638	25	91
2	¹ 120-500	¹ 10-12	35.6	<0.5	703	20	98.5

¹ Between.

The metal obtained in the first run was analyzed and found to contain—

TABLE VII

Element:	Metal recovered from core turnings, p.p.m.
Ag	<0.1
Al	>100
As	<10
B	>1.0
Bi	<5
Cd	<0.2
Co	<5
Cr	8
Cu	6
In	<1
Li	<1
Mg	<10
Mn	10
Mo	<5
Na	<10
Ni	19
P	<50
Pb	<5
Si	24
V	<20
Zn	<20
Fe	>100

It will be understood that the invention is not to be limited to the details given herein but that it may be modified within the scope of the appended claims.

What is claimed is:

1. A process of making massive uranium metal from

uranium-oxide-containing material, comprising electrolyzing with a direct current a system of cathode, anode and electrolyte, said anode substantially consisting of said uranium-oxide-containing material to be processed and about two moles of carbon per one mole of uranium dioxide and said electrolyte being at a temperature above the melting point of uranium and consisting of a mixture of from 40 to 75% by weight of alkaline earth metal fluoride selected from the group consisting of barium fluoride and calcium fluoride, 15 to 45% of uranium tetrafluoride and from 10 to 20% of a fluoride selected from the group consisting of lithium fluoride and magnesium fluoride whereby pure uranium metal deposits on the cathode, melts and settles separately below the electrolyte, and cooling the uranium metal for solidification.

2. The process of claim 1 wherein the temperature of the electrolyte ranges between 1150 and 1175° C.

3. The process of claim 1 wherein the electrolyte consists of 75% by weight of an equimolar mixture of lithium fluoride and barium fluoride and 25% of uranium tetrafluoride.

4. The process of claim 1 wherein the electrolyte is free from oxides.

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