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COATED MOLD FOR CASTING PLUTONIUM

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The present invention relates to methods and means for casting plutonium and plutonium base alloys, and is more particularly concerned with a novel coating for such molds whereby the disadvantages of prior art molds for casting plutonium are avoided.

Reasonably good solid castings or ingots of plutonium and its alloys can be obtained either by casting the molten metal into a thick-walled mold of a non-reactive metal such as tantalum at room temperature, or by chill casting in a hollow mold of copper or Monel metal, utilizing a coolant to conduct away the heat liberated by the cooling plutonium. Such massive castings are not in great demand, however, as the more common applications of plutonium are in the form of long rods suitable for use as fuel elements in a fission reactor. The molten plutonium cannot be chill cast into molds providing such thin casting sections, as the molten material cools too fast and freezes across the narrow opening, the result being a porous casting filled with "blow holes." For such thin sections, e.g., ½ inch or less in diameter, it becomes necessary to preheat the mold above 450° C. to obtain castings conforming accurately to the shape of the mold. Copper or Monel molds cannot be used because they react with the plutonium at such temperatures. Refractory metals such as tantalum and tungsten are unsatisfactory because they are wetted by the molten plutonium, with the result that the solidified casting sticks to the mold and can only be removed by leaching or forcible separation or a combination of both. Even where such refractory metal molds produce satisfactory castings, they are unsatisfactory in that they are expensive to obtain and are frequently ruined in the process of separating them from the castings.

The prior art molds which have been found most practicable and have heretofore been used for regular production work are graphite or metal molds coated with a refractory oxide, usually MgO or Al_2O_3. With graphite bases, such coatings are usually applied by air spraying and heating to set the coating, or by flame spraying. In the case of a metal mold base, the oxide is more accurately described as a liner or crucible, as it is separately formed and then fitted to the metal base. This has been necessary because a greater thickness of oxide is required to prevent penetration of the plutonium to the metal. The use of such molds, with such coatings or liners, has several disadvantages, namely:

(1) The plutonium reacts with the coating, resulting in a very hard refractory surface on the solidified metal. This makes it very difficult to remove the casting from the mold, and it is usually necessary to break the mold off in pieces. The hard refractory surface on the casting must be machined off with tools equipped with very hard cutting edges.

(2) Some of the plutonium penetrates the mold coating and, where graphite is used as the mold base, penetrates into the graphite itself. The quantity of plutonium thus lost from the casting represents such a high loss that the entire mold (or liner, where a metal base is used) must be processed to recover the plutonium, a process which adds considerably to the over-all cost of obtaining castings of plutonium.

(3) During the casting process, pieces of the oxide coating frequently flake off and become trapped in the casting. Such entrapped materials reduce the purity of the material and must usually be removed by further processing.

When such oxides have been used in the prior art, it has been impossible to use a steel base unless the oxide is used as a liner, e.g., of ¼-inch thickness. This has been necessary because plutonium and iron alloy readily, and thin coatings of the oxide permit sufficient penetration by the liquid plutonium to allow such alloying to take place. The result, where the oxide coating is of the order of 10 mils, is a complete seizure of the casting to the mold, a condition which can be remedied only by completely machining away the steel mold base or removing the entire casting by acid leaching.

It is an object of the present invention to provide a mold material which may be applied as a coating on various mold bases and can be used for precision casting of plutonium and plutonium alloys without reacting with the cast material.

It is another object of the present invention to provide such a mold coating material which may be applied in very thin coatings to steel molds without reaction of the coating with the plutonium being cast and without permitting penetration of such plutonium to the steel base material.

An additional object is to provide molds for the casting of plutonium and plutonium alloys wherein there is no reaction between the mold and the material being cast, such molds requiring no processing for the recovery of plutonium and being re-usable for repeated casting.

A further object is to provide coated molds for the casting of plutonium and plutonium alloys as bodies having large surface to volume ratios, such mold coatings (1) being non-reactive with the metal being cast and thereby producing castings free of the refractory coatings obtained with prior art castings in ceramic oxide molds, (2) not being wettable by the metal being cast and thereby permitting easy removal of the solidified castings, (3) being impervious to plutonium and thereby requiring no chemical processing for the recovery of plutonium, and (4) adhering tightly in itself, thereby preventing flaking into the molten metal, such molds being re-usable with no more than filling in of cracks and voids in the coating brought about by thermal stresses and producing castings requiring no mechanical or chemical treatment to obtain a pure metallic surface of the metal being cast.

The above and other objects are accomplished according to the present invention by the use of a very fine calcium fluoride (CaF_2) powder as the mold coating material. This material has been applied by the present inventors to widely differing mold base materials and has been used to obtain precision castings of plutonium and various plutonium alloys in very small sections with none of the disadvantages attending castings obtained in prior art molds. The castings did not react with such coatings, were easily separated by hand and picked up very little in the way of impurities. The mold material picked up very little plutonium and it was unnecessary to subject it to the chemical processing of the prior art for the recovery of plutonium. The only plutonium left in the mold was a small amount on the surface which was easily removed by the mild abrasive action of a wire brush. Such molds, when tested for plutonium content by a neutron detector, exhibit so little activity that it would be economically wasteful to process them, assuming that they were not then re-usable. In point of fact, they are usually re-usable immediately. Occasionally a coating cracks or a piece of the coating chips off, but such minor damage is easily repaired by additional treatment to replace the lost material. Such damage appears only during the cooling of the plutonium after solidification, and is believed to result largely from the negative temperature coefficient of expansion of this metal in the delta and delta prime phases. It is to be emphasized that such broken-away portions of the mold coating are not entrapped in the casting and hence do not serve as a source of impurities for the same.

While the particular means and method used to deposit the CaF_2 coating on the mold base varies somewhat with the nature of the base material, the general procedure is to deposit on the base an aqueous solution containing the CaF_2 powder in suspension and a water soluble, easily volatilized binder for such powder. The water serves as a vehicle in the process and is driven off at about the same time it is deposited on the surface of the mold base, the latter being held at the boiling point of water during the application. For some types of mold bases, in particular steel, the present results have been obtained by making the vehicle slightly acidic, the acid apparently promoting adhesion of the CaF_2 powder by its etching action on the steel surface and the binding action of the resulting iron phosphate. Attempts to coat steel without such etching action of an acid are unsuccessful because of the iron oxide formed, the latter preventing good adhesion of the CaF_2.

While CaF_2 is somewhat hygroscopic and is widely distributed in nature as minerals of various colors, the water absorption of the material appears to be only a surface phenomenon, i.e., the natural forms are not hydrates of CaF_2. The present inventors are aware that prior workers in the plutonium metallurgical art have investigated CaF_2 as a solid crucible material without success. The crucibles made used CaF_2 in the form of coarse powders and were both fragile and hygroscopic. Those that were used to obtain a single casting were not re-usable thereafter, owing to cracking, and absorbed considerable amounts of plutonium, requiring the usual chemical processing characteristic of the prior art. Such molds could not be permitted to stand for more than a day in ordinary atmospheres as they absorbed so much water that they crumbled to a powder. The present inventors, on the other hand, have found that their molds, coated with a very fine powder of CaF_2 to a very small thickness, exhibit no such porosity and can be allowed to stand at least for several weeks without ill effect in ordinary atmospheres.

To aid in a better understanding of the present invention, the following examples are furnished as illustrative:

Example.—Graphite Base

The mold consisted essentially of a graphite cylinder of 3⅞ inches diameter by 8⅜ inches height with a 2⅝ inches diameter coaxial cavity in the top 1⅜ inches to provide a header. Eighteen cylindrical casting cavities of 27/64-inch diameter were provided below the header, uniformly spaced and extending the full length of the graphite cylinder. This mold rested on a solid graphite base engaging the base of the mold to define a closure for each of the eighteen casting cavities. This assembly was placed inside one coil of an induction furnace, directly beneath a pouring crucible containing plutonium and heated by a second induction coil. The furnace construction permitted vacuuming of both the casting mold and the pouring crucible.

The casting cavities were coated with CaF_2 by a number of techniques, including hand brushing of both dry CaF_2 and aqueous suspensions containing CaF_2 and binders, flame spraying and air spraying of aqueous suspensions. Hand brushing was unsatisfactory in that uniform coatings could not be obtained with either the dry material or the suspension, and there was little adherence of the dry material. Flame spraying was more satisfactory, but the resulting coatings did not adhere so well as the air sprayed coatings, and exhibited rougher surfaces. In addition, the flame sprayed coatings were always thicker than the air sprayed coatings. Efforts were accordingly concentrated on air spraying techniques.

A coating suspension was prepared containing in each quart of water 32 grams of calcium fluoride and 10 grams of a water soluble polyethylene glycol binder. This suspension was sprayed on the casting cavities of the mold, which was preheated to 100° C., to a thickness of 5 mils. Spraying was carefully controlled to prevent running of the vehicle on the mold surface, thus promoting an even coating thickness. The mold surface was reheated to 100° C. between spray applications.

After applying the coating, the mold was vacuumed and then heated to 640° C. The plutonium in the pouring crucible was melted by heating it to 750° C., after which it was permitted to flow into the casting mold. The heat was then shut off and the cast material was allowed to cool and solidify under vacuum.

The cooled solid rods were removed from the mold at room temperature by hand. The surfaces of the rods exhibited a smooth appearance with a bright metallic luster, in contrast to the dull refractory finish of castings in magnesia or alumina lined molds. There was no flaking of the mold coating during the unloading. These rods were chemically analyzed, and compared with the feed plutonium as follows:

Element	Feed material, p.p.m.	Cast rods, p.p.m.
Li	<0.2	<0.2
Be	<0.2	<0.2
Na	25	<10
Mg	30	20
Ca	40	10
Al	20	20
La	<10	<10
Si	75	65
Pb	<1	<1
Cu	2	2
F	----------	<2
N	----------	6
C	100	105
B	<0.5	<0.5
H_2	----------	10
O_2	----------	70
B	<0.5	<0.5
Cr	20	20
Fe	65	50
Ni	60	60
Pu content, weight percent	99.9	

Various changes were made in the composition of the spray suspension in an effort to optimize such composition. Keeping the CaF_2 content per quart of water at 32 grams, the polyethylene glycol content was increased from 10 grams to 32 grams to yield a highly adhesive coating and good castings, but increasing the binder content to 64 grams under the same conditions made the suspension unusably thick and caused lumping of the CaF_2 powder. Satisfactory castings were produced with 16 grams of polyethylene glycol and 64 grams of CaF_2 per quart of water and with 32 grams of polyethylene glycol and 64 grams of CaF_2 per quart of water.

At the same time, the effect of varying the coating thickness was investigated. It was discovered that none of the above-mentioned compositions adhered satisfactorily to the mold surface prior to casting when the thickness was greater than 5 mils, and that a thickness greater than .002–.003 inch accomplished nothing that was necessary or desirable. The composition of 32 grams polyethylene glycol and 64 grams CaF_2 per quart of water flaked off the mold surface after casting in thicknesses greater than .005 inch but optimum casting results (least impurities in castings, smoothest castings and least flaking of coating) were obtained with this composition applied to a thickness of .002–.003 inch.

A suitable polyethylene glycol binder, and the one used in the above-described work, is sold under the proprietary name Carbowax 20–M. This particular compound has an average molecular weight of 15,000–20,000, is highly soluble in water, and has a viscosity of 450,000 Saybolt seconds at 210° F. There is no necessity to use this particular binder, however, the same having been used simply because it was readily available. Any water soluble binder which is readily volatilized in heating the mold to the temperature used in pouring may be substituted, although the optimum quantity and range of useful composition fraction will necessarily vary. An additional binder used to obtain plutonium metal and plutonium alloy castings as satisfactory as those described above is gum tragacanth.

A satisfactory air spray mechanism used is the Thayer and Chandler air brush, either Model C or Model E. Air pressures of 10 to 20 p.s.i. were used. Any spray gun and any air pressure appear to be equally satisfactory, the important point being to apply the solution at such rate that there are no "curtains," i.e., no running of the vehicle on the mold surface.

The starting CaF_2 used in the work described in all examples herein was dry, —100 mesh. The particular lot employed, J. G. Baker Chemical Company Lot 2045, contained maximum impurities as follows:

	Wt. percent
Chloride	0.006
Sulfate	0.03
Heavy metals (as Pb)	0.005
Iron	0.002

Unscreened powder containing particles of larger size have also been used, the resulting coatings adhering well to the base material but exhibiting rougher surfaces as a result of the larger particles included. Such rough coatings are not suitable for precision castings, but are satisfactory for applications in which the casting will be remelted before final use.

Example.—MgO Base Crucible

The work summarized in the above example was repeated with an MgO crucible coated to a 5 mil thickness with an air spray of an aqueous suspension of 10 grams of polyethylene glycol and 32 grams of CaF_2 per quart of water. The resulting castings were readily separated and had the same bright metallic luster, significantly free of the dull hard surface characteristic of the prior art castings in uncoated MgO molds. The chemical analysis was essentially identical to that of the first example, and the mold was re-usable after only a wire brushing.

Example.—Tantalum Base Mold

The work of the first example was repeated by air spraying a composition of 10 grams of polyethylene glycol and 32 grams of CaF_2 per quart of water on a tantalum base to a .005-inch thickness. Again the cooled and solidified castings were readily separated from the mold by hand to exhibit a high metallic luster and a comparable chemical analysis, with no significant flaking of the mold coating and no significant plutonium absorption therein.

Example.—Steel Base Mold

The work of the first example was repeated with mild steel base molds coated with CaF_2 by two types of suspensions, one of CaF_2 in a mildly acidic aqueous solution containing 128 to 256 grams of CaF_2 per quart of 4% phosphoric acid solution, the other of a two step coating of 64 grams of CaF_2 per quart of 4% H_3PO_4 followed by air spraying of suspensions containing 64 grams of CaF_2 per quart of water and either 10 or 32 grams of polyethylene glycol per quart of water. Although all castings were satisfactorily pure and dense, and separated easily from the mold to exhibit bright metallic surfaces, the least outgassing was obtained with 128 grams of CaF_2 per quart of 4% phosphoric acid, applied to a .002–.003 inch thickness.

Graphite and steel molds defining a variety of thin casting cavities and coated as above have been re-used at least six times without any processing other than a surface cleaning with a wire brush to yield easily separated precision castings. In several instances, it was necessary to spray additional coating material on the mold between castings to repair thermal cracks; later a standard practice of spraying after each casting was adopted to avoid the possibility of overlooking minute cracks. The purity of the castings did not diminish with continued use of the mold, nor did it ever become necessary to remove any sort of coating from the surface of any casting. Even after the last casting, no mold had absorbed so much plutonium as to require processing.

What is claimed is:

1. A mold for the precision casting of plutonium and plutonium alloys in thin sections, comprising a base portion and a uniform, impermeable coating thereon, said base portion being of a material which remains solid and stable at temperatures as high as the pouring temperature of the metal being cast, said coating comprising finely divided calcium fluoride in which the maximum particle size is about 149 microns and said coating having a thickness not exceeding about 0.005 inch.

2. The mold of claim 1 in which said base portion is graphite and the thickness of said calcium fluoride coating lies in the range 0.002–0.003 inch.

3. The mold of claim 1 in which said base portion is a metallic material.

4. The mold of claim 3 in which said base portion is predominantly iron and the thickness of said calcium fluoride coating lies in the range 0.002–0.003 inch.

5. The mold of claim 1 in which said base portion is a refractory oxide material.

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