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PREPARATION OF TERNARY PLUTONIUM ALLOYS FOR CORE TEST FACILITY PROGRAM

by

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ABSTRACT

Ternary plutonium-cerium-cobalt alloys are of interest as molten nuclear fuels. In preparing test fuel rods of such alloys, severe segregation of the components occurs unless special rod casting methods are applied. This report summarizes small-scale development work that was done to eliminate the problems associated with alloy segregation. These procedures have been incorporated into large scale fabrication of fuel pins.

ACKNOWLEDGMENTS

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INTRODUCTION

Ternary plutonium-cerium-cobalt alloys of the compositions shown in Table 1 are required for the Core Test Facility development program. However, attempts to prepare uniform rods of these alloys on the multikilogram scale have resulted in severely cracked and broken rod segments of variable composition. These rods had been formed by alloying the three elements in calcium fluoride coated[1] crucibles, and pouring into calcium fluoride coated molds.

A series of three small scale chill casting experiments have been done to eliminate macroscopic segregation in the alloy, and to produce uniform solid rods. The findings from these experiments are now being incorporated in the procedures for multikilogram scale production of alloy rods.

Table 1

Ternary Plutonium Alloys

Alloy Type	Pu density at reactor temp., g/cc.	Composition, percent by wt. Pu	Co	Ce
I	5.0	50.6	10.0	39.4
II	6.2	57.7	9.4	32.9
III	8.0	68.2	8.3	23.5

EXPERIMENTAL PROCEDURE

The feed stock for each experiment was Pu-Ce-Co alloy Lot No. JCC-1463, in the form of 0.35-in.-diameter rods.

This feed alloy had been prepared in the Metal Fabrication plant on the multikilogram scale by remelting for 10 min. at 600-650°C in a CaF_2-coated crucible, followed by pouring into a 0.39-in.-diameter CaF_2-coated mold that had been preheated to 375°C at the top and 325°C at the bottom. Typical compositions of this alloy are shown in Table 2.

Table 2

Chemical Composition of Alloy Lot JCC-1463

Region of Casting[1]	Composition, percent by wt. Pu	Ce	Co
Rod top	48.89	40.1	10.00
Rod bottom	50.26	38.7	10.12
Rod top	49.14	40.2	10.03
Rod bottom	50.37	38.3	10.08

(1) The top samples are not from the same rods as bottom samples because only broken rod segments were obtained from the casting.

Although this procedure produces uniform alloys of plutonium-iron eutectic composition,[1] it obviously results in segregated ternary alloy.

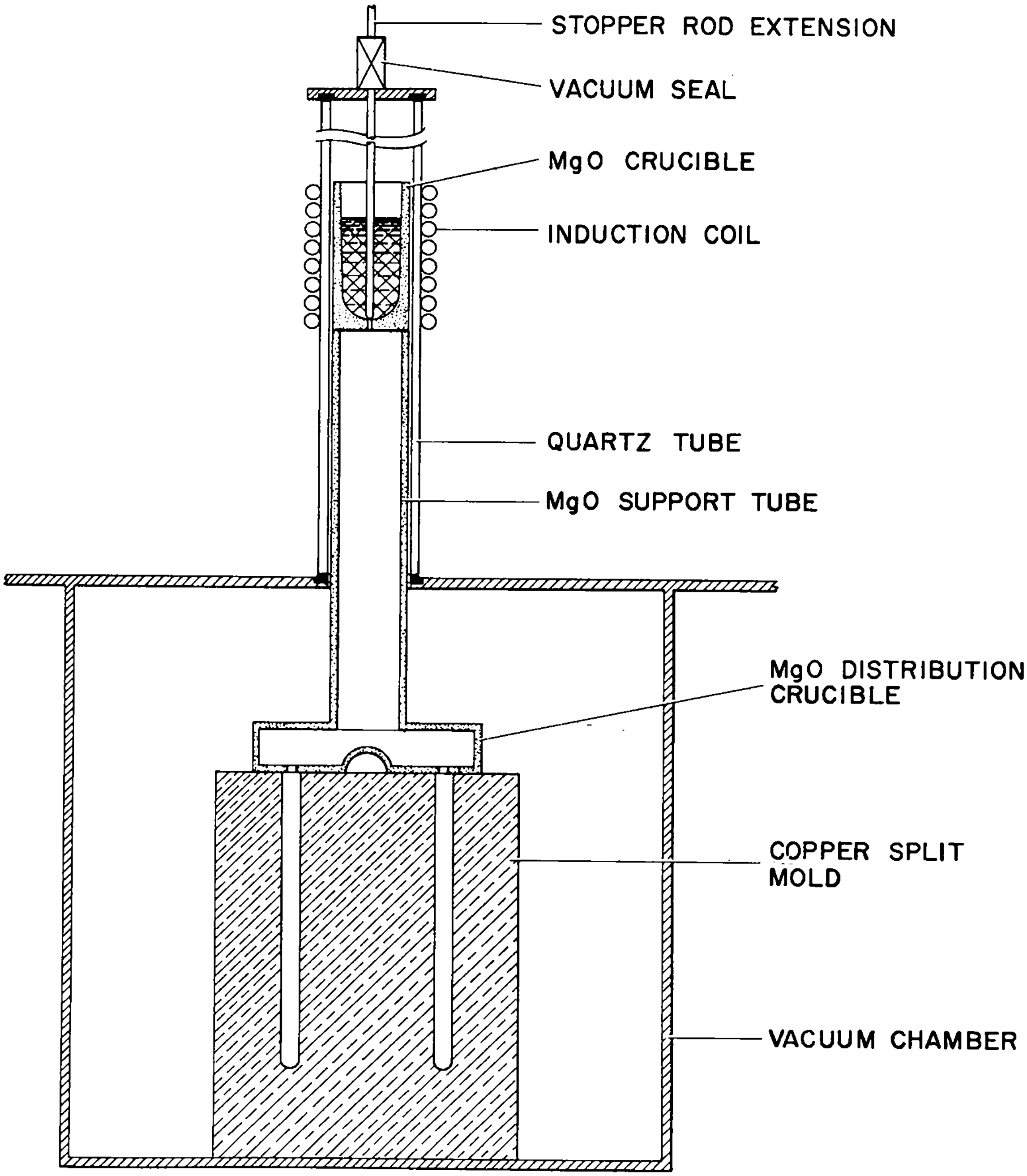
For the small scale chill casting experiments, the required amount of the above alloy was wire-brushed to remove adherent surface contaminant, then loaded into the magnesia melt crucible (Fig. 1).

The alloy charge was heated slowly to melting, then to 900-960°C in the vacuum induction furnace,and held at this temperature to redissolve the soluble phases. After this high temperature treatment the alloy was cooled to the desired pour temperature and held at temperature for the desired time. Pouring from the melt crucible into the copper mold was accomplished by pulling up on the stopper rod. Temperature-time cycles are shown in Table 3.

After casting the alloy, the mold was cooled to room temperature and opened to recover the cast rod.

In all cases the rods were smooth and shiny, with no indication of interaction with the mold or casting flaws.

A typical casting is shown in half of the copper mold in Fig. 2. (In the plutonium-copper binary system the lowest melting eutectic temperature is 419°C). The diameter of each rod was measured at several places along the rod for dimensional uniformity. The rod was then sampled at the top, middle, and bottom for both chemical and metallographic analysis.



ALLOY CASTING EQUIPMENT

Figure 1. Chill casting equipment, schematic drawing.

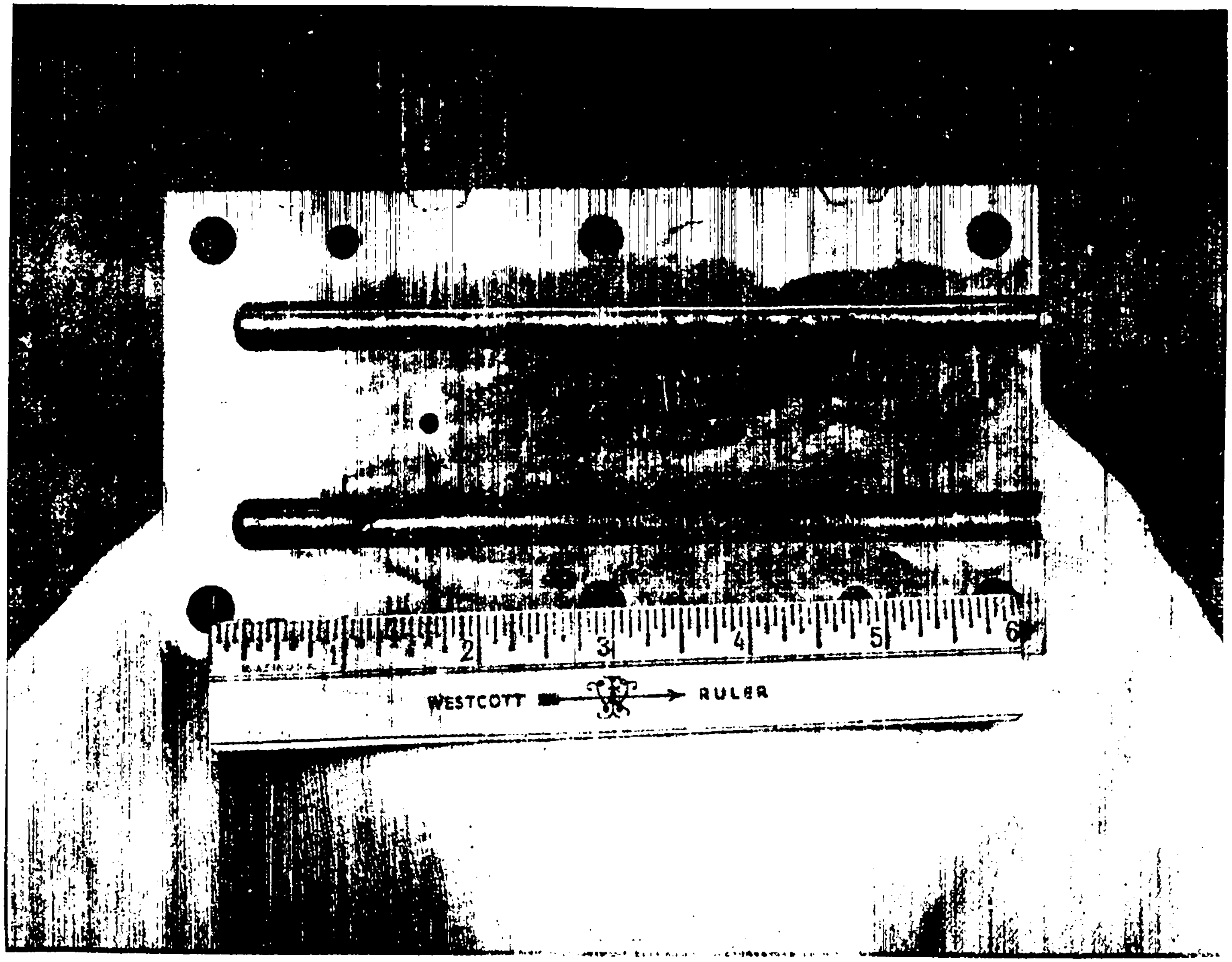


Figure 2. Pu-Co-Ce rods in copper mold.

RESULTS AND DISCUSSION

The heat cycles used in each experiment are shown in Table 3.

Table 3

Time-Temperature Data for Chill Casting Experiments

Expt. No.	Wt. Alloy Feed	Pour Temp., °C.	Total Time above m.p., min.	Time at 900-960°C, min.	Time at Pour temp., min.
1	192	950	17	10	2
2	192	600	74	10	30
3	324	775	29	4.5	7

Because the mold did not fill completely, Experiments 1 and 2 each produced one 6-in.-long rod and a short rod 1.5 in. long. The larger alloy charge in Experiment 3 resulted in complete filling of both mold holes.

The external dimensions of the rods were the same as the mold hole dimensions, within less than 0.001 in. for Experiments 1 and 2, as shown in Table 3. The top sections of both rods from Experiment 3 were about 0.004 in. oversize in diameter.

Table 4

Dimensional Uniformity of Pu-Ce-Co Alloy Rods

Expt. No.	Days after Casting	Rod Diameter, in.		
		Top	Middle	Bottom
1	15	0.351	0.350	0.351
2	6	0.352	--	0.350
3 (Rod A)	4	0.355	0.352	0.352
3 (Rod B)	4	0.355	0.351	0.351

Chemical analyses of the chill-cast rods are shown in Table 5.

Table 5

Chemical Analysis of Pu-Co-Ce Rods Experiments 1, 2 and 3

		Composition, w/o		
		Pu	Ce	Co
Experiment 1				
Top Sample		49.60	40.17	10.03
Middle Sample A		49.62	40.12	10.10
Middle Sample B		49.65	40.10	10.09
Bottom Sample		49.63	40.11	10.04
	Average	49.63	40.13	10.07
Experiment 2				
Top Sample		49.72	39.91	10.17
Middle Sample		49.72	39.83	10.13
Bottom Sample		49.72	40.02	10.18
	Average	49.72	39.92	10.16
Experiment 3, Rod A				
Top Sample		49.82	39.44	10.19
Middle Sample		49.83-49.92	39.48	10.02-10.10
Bottom Sample		49.81-49.98	39.25	10.18-10.26
	Average	49.86	39.39	10.16
Experiment 3, Rod B				
Top Sample		49.88	39.38-39.62	10.10
Middle Sample		49.72-49.82	39.62	10.13
Bottom Sample		49.81-49.96	39.40	10.12
	Average	49.85	39.51	10.12

Notes:

1. Standard deviation of analytical method is ± 0.03% (absolute) for Pu analysis, ± 0.08% for Ce, and ± 0.02 for Co. Where a composition range is given, the sample was slightly segregated. The midpoint values were used in averaging segregated samples for average rod composition.

2. All samples contained some residue that was insoluble in the HCl used to dissolve samples. This may have been derived from coatings used for melt crucibles and molds in preparing the feed alloy, JCC-1463. The amount of residue in samples of the feed alloy was much greater than that in the rods from the small scale experiments.

The chemical uniformity of each rod from Experiments 1 and 2 is excellent, as shown by the insignificant deviations from average analyses. The differences in average composition between the rod from Experiment 1 and that from Experiment 2 are small but significant. This is due to the variation in feed alloy, Lot JCC-1463. From the results shown in Table 5 for Experiments 1 and 2 it was concluded that the actual pouring temperature has no effect on chemical uniformity within a given rod casting over the temperature range 600-950°C.

Chemical analyses of Rods A and B from Experiment 3 are more variable than those of Experiments 1 and 2, indicating that the cast alloy was somewhat segregated. This may be attributable to the shorter time at 900-960°C.

The microstructure of feed alloy JCC-1463 is shown in Fig. 3A. Comparison of this microstructure with that shown in Fig. 3B shows the marked decrease in size of the primary A-phase grains caused by chill casting in Experiment 1.

A portion of the metal poured in Experiment 1 was retained in the magnesia distribution crucible. This portion obviously cooled much more slowly than the portion that flowed into the copper mold. The microstructure shown in Fig. 3C indicates that the grain size was nearly as coarse as that of the segregated feed alloy (Fig. 3A).

The microstructures of portions of the 6 in. long rod from Experiment No. 2 are shown in Fig. 4. The grain sizes are similar from top to bottom, and this is reflected in the uniformity of composition shown in Table 5.

Microstructures of rods from Experiment No. 3 are shown in Fig. 5. There is no obvious structural difference between top, center, and bottom samples. However, the chemical compositions are slightly different, as shown in Table 5. Apparently variations of a few tenths of a percent in composition do not produce serious differences in microstructure.

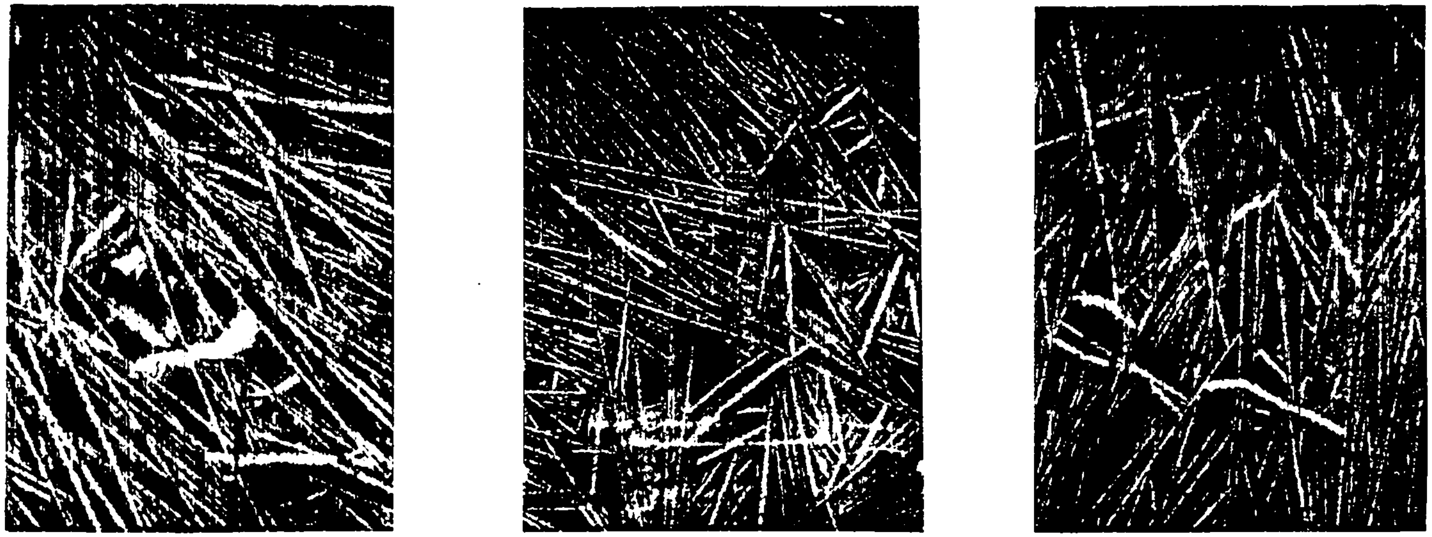
CONCLUSIONS

The conclusions drawn from this series of experiments are:

1. Uncoated metal molds can be used to chill-cast Pu-Ce-Co alloy into uniform rods, with no mold reaction. Even with only 160°C of superheat, the mold fills well, and no cold-shuts form. The rods can be cast to desired diameter in the 0.35-in.-diameter range.

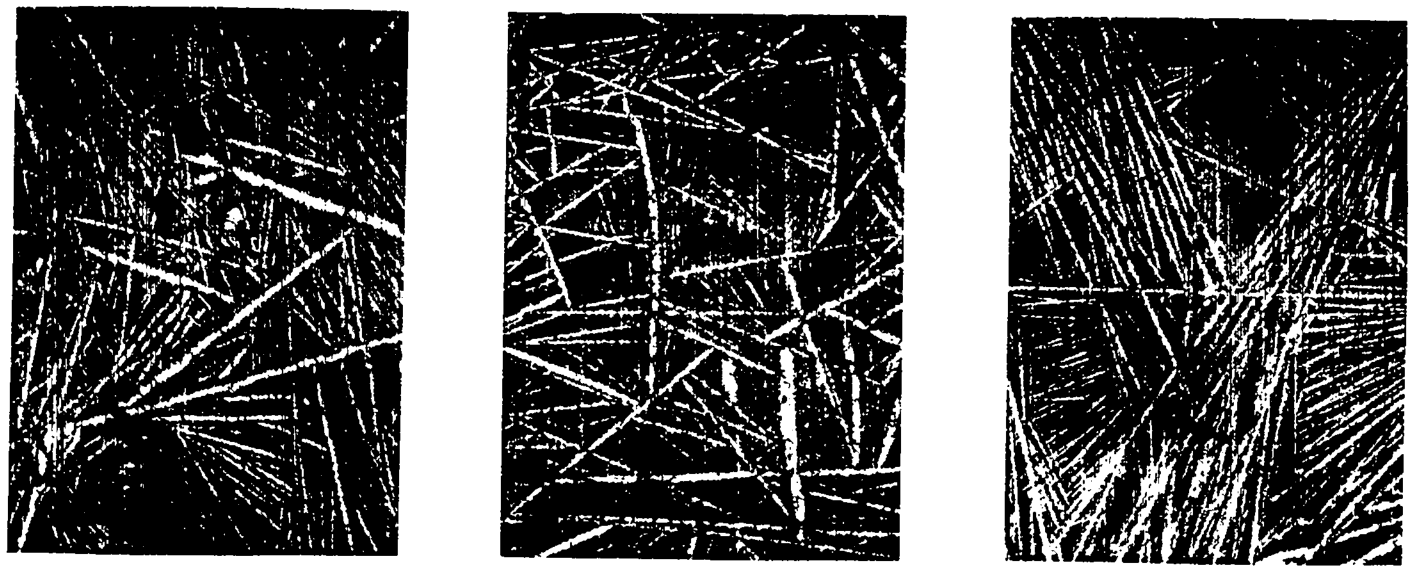
(3A) (3B) (3C)

Figure 3. Microstructure of feed alloy lot JCC-1463 (3A), chill-cast rod from Experiment No. 1 (3B), and magnesia distribution crucible metal (3C). Magnification 58X.



(4A) (4B) (4C)

Figure 4. Microstructure of samples from chill-cast rod, Experiment No. 2 top of rod (4A), center (4B), bottom (4C). Magnification 58X.



(5A) (5B) (5C)

Figure 5. Microstructure of samples from chill-cast rod B, Experiment No. 3, top of rod (5A), center (5B), bottom (5C). Magnification 58X. (Microstructures of Rod A regions are similar to corresponding Rod B regions.)

2. From the standpoints of Pu uniformity and rod appearance, the pour temperature is not important in the range 600° to 945°C.

3. Pu concentration is uniform along the length of the rod to within analytical error.

4. Chill-cast Pu-Ce-Co alloy has a fine-grained microstructure. However, cooling the same liquid more slowly in MgO produces very coarse segregated microstructures.

5. The chill-cast unsegregated alloys have less tendency to oxidize or crack.

6. Calcium fluoride coatings on melt crucibles and molds are undesirable for cerium alloys. The distillation of calcium from the melt crucible can be observed during melting under vacuum, presumably by the reaction

$$2\ Ce\ (\text{in liq. sol'n.}) + 3\ CaF_2 = 2\ CeF_3 + 3\ Ca\ (\text{gas})$$

Moreover, the mold coating is undesirable for two reasons; it reduces the rate of alloy cooling and it sticks to the cast rods, thereby adding impurities.

REFERENCE

1. J. W. Anderson and W. J. Maraman, "Multiple Casting of Fuel Pins for Molten Plutonium Reactor Experiment", Trans. Amer. Foundrymans Soc., Vol. 71, 427-432 (1963).