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THE USE OF CALCIUM FLUORIDE AS A COATING FOR PLUTONIUM MELT AND MOLD CRUCIBLES

Supplement to LA-2315

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Supplement to LA-2315

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ABSTRACT

The initial use of CaF_2 as a protective coating for Pu casting molds has been described in Los Alamos Scientific Laboratory Report LA-2315. The introduction of "colloidal" CaF_2 during the past year has made obsolete the various recipes described in LA-2315. This report presents new coating recipes based on present use.

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INTRODUCTION

Practically all of the melt and mold crucibles used in Pu metal casting operations at the Los Alamos Scientific Laboratory are coated with a thin layer of CaF_2. Calcium fluoride neither reacts with nor is wet by Pu metal under the conditions used; therefore, excellent protection is afforded a base material, such as steel or nickel, which, when unprotected, will rapidly alloy with Pu at required casting temperatures. Consequently, these materials are made into suitable molds if protected with a 0.001-in.-thick layer of CaF_2.

The initial use of CaF_2 as a coating for Pu casting molds has been described in Los Alamos Scientific Laboratory Report LA-2315.[1] During the past year, significant improvements have been made in certain physical properties of the CaF_2 used and in the methods of application.

This supplemental report describes current coating mixtures and methods of application to a variety of melt and casting mold materials.

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COATING DEVELOPMENT

Regardless of the method used in applying a protective coat, smaller coating particles make it easier to apply a thin, impervious layer and, as a rule, a thin layer optimizes desirable coating characteristics. Also the low solubility of CaF_2 in most acid and basic media permits suspension of the fluoride in a solution which will etch metal and give a firmly adhering, impenetrable layer to the metal surface.

The Acheson Colloids Co. of Port Huron, Michigan, was contacted in January, 1959, and asked to prepare colloidal CaF_2 solutions which would be stable in acidic and basic media. Samples of their mixtures EC 1709 and EC 1769 were submitted to us in April, 1959, for evaluation. The EC 1709 is a water concentrate which contains 42% solids and is amenable to dilution with water and/or acid to a normal working consistency containing 5 to 10% solids. The EC 1769 concentrate contains 24% solids and is suitable for dilution with water and/or basic solutions. Both mixtures have a water base; i.e., they contain no organic reagents.

Test coatings prepared from these materials were far superior to previous ones. They adhered better and the mold surfaces could be covered completely with thinner layers. These two materials now form the base of all of the CaF_2 coating recipes.* As noted in LA-2315, the

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*Colloidal CaF_2 concentrates EC 1709 and EC 1769 are commercially available from the Acheson Colloids Co., Port Huron, Mich.

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preferred method of coating is to spray-coat on a warm mold surface. However, mold materials and design sometimes make application by brushing or flushing necessary. Continued developmental work using EC 1709 and EC 1769 materials resulted in the present recipes.

COATING METHODS

Graphite Molds

An unusually porous mold surface is often encountered when working with graphite molds. In order to effectively seal this type of surface from casting metal penetration, a pre-treatment of the surface with the aqueous colloidal concentrate of CaF_2 as received from the Acheson Colloids Co. has proven to be quite effective. Application is ordinarily by brush, and excess solids are removed from the surface by vigorously rubbing with a porous cloth. The final coating is then applied by one of the following methods:

a. Spray Coatings

Graphite molds are satisfactorily coated by spraying a suspension of the colloidal CaF_2 with a Thayer and Chandler artist's spray gun. The spray solution is prepared by diluting 155 g of EC 1709 or 300 g of EC 1769 with demineralized water to make 1 liter. This dilution gives a mixture containing 65 to 72 g of solids per liter.

The Acheson Colloids Co. reports that the EC 1769 contains a larger per cent of an undissolved binder material which gives better

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adhesive qualities to the CaF_2 coating than are obtained with EC 1709. Although well-adhering coatings have been obtained with both mixes, the EC 1769 is preferred because its adhering quality is superior.

The graphite mold is pre-heated to 95 to 100°C. The coating is then applied using a fine spray and several passes over the mold. Coatings 0.001 to 0.002 in. thick are adequate and display excellent adhesive characteristics. Before casting, any loose powder on the mold surface can be removed easily by means of an air brush.

b. Brush Application

Brush application of the coating is sometimes necessary because of a particular mold design. Although a coating which is completely uniform in thickness is not possible by this method of application, adequate protection is consistently afforded the mold surface. However, the resulting casting surface is not ordinarily as smooth as the surface obtained with spray-coated molds. The recipe described above for spraying is adaptable also for application by brushing.

c. Flushing Application

In some special mold designs, particularly multiple thin rod molds, even a satisfactory brush application is impossible. For this particular design, repeated flushing of the pre-heated mold with the above spray solution has afforded good mold surface protection.

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Metal Molds

a. Cast Iron and Mild Steel

For molds which contain Fe and for which repeated usage is anticipated, an adherent Cr coating, 0.002 in. thick, is initially applied to the mold surfaces. The Cr-Pu phase diagram[2] shows significant advantages over the Fe-Pu phase diagram[2] from a mold material protection consideration. The Cr-coated surface is first grit-blasted to effectively roughen the surface prior to the initial treatment with 4% H_3PO_4. This treatment is followed by heating at 200°C for 8 to 15 hr. The initial application of the acid suspension of colloidal CaF_2 is then applied, preferably by spray gun, to the pre-heated mold surfaces. The recommended acid coating formula is 155 g of the colloidal CaF_2 (EC 1709) diluted to 1 liter in an acid suspension of 4% H_3PO_4. A coating thickness of 0.001 to 0.002 in. is adequate for the initial application. The mold is again baked at 200°C for 8 to 15 hr. After this heating period, the mold surface is washed with 4% H_3PO_4 to remove any loose CaF_2. The colloidal CaF_2 spray-coating and heating cycle is again repeated for completion of the preliminary treatment.

For the final coating on cast iron, mild steel or Cr-coated molds, a spray solution of 310 g of the EC 1709 material diluted to 1 liter with 4% H_3PO_4 is used. The metal molds are pre-heated to 90 to 100°C, and spray coatings are applied in a manner similar to the graphite-mold applications. Normal coating thicknesses are < 0.002 in., but a coating of < 0.001 in. is satisfactory, particularly on previously used

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molds. If the mold is to be re-used, the present procedure is to re-coat prior to each run. Before re-coating, loose particles are removed by wiping the surface with a 4% H_3PO_4 solution. After coating, any loose powder on the coated surface can be easily removed by an air brush or a camel's hair brush.

Brush-coating the material on the metal mold surfaces is not recommended. In addition to the disadvantage of nonuniformity of coating thickness, the rate of application of a coating to a steel surface is more critical than on graphite. If the metal surfaces are wet for an appreciable period of time, blisters will subsequently form and cause rupture of the layer of protective coating.

b. Ta, W and Mo Molds

Colloidal CaF_2 (EC 1769), which is stable in a moderate to strong base, has been developed by the Acheson Colloids Co. specifically for metals requiring a basic-medium application. The coating procedures for a mold of this type will depend on the mold alloy and the mold design. Ordinarily, tubes of these metals are best coated by placing the tubes for 10 to 15 min in a hot (100°C) bath of EC 1769 diluted with concentrated basic solution. Other appropriate shapes may be spray or brush coated. The best technique will vary with the particular mold part. Coatings on Ta and W mold surfaces are used primarily to reduce wetting by Pu which results in sticking.

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Ceramic Molds

The value of a thin coating of colloidal CaF_2 is most readily demonstrated on ceramic surfaces exposed to molten Pu metal. Many unprotected ceramic surfaces are easily penetrated by molten Pu. However, by flushing ceramic crucibles for 5 to 10 sec with an aqueous solution of EC 1709 or EC 1769 and drying, the pores of the ceramic surface are effectively sealed, and the thin CaF_2 coating presents an impenetrable barrier to the Pu metal. The used crucibles are readily cleaned by moderate brushing. Flushing solutions used are 155 g of EC 1709 or 300 g of EC 1769 diluted to 1 liter with demineralized water. Effective protection to ceramic surfaces has been obtained with both materials.

PURITY DATA

Qualitative analysis of the EC 1709 mixture as supplied by the Acheson Colloids Co. is shown in Table 1.

Table 1

COLLOIDAL CaF_2 MIXTURE EC 1709

Element*	Concentration, %
Ca	major
Al	1 - 10
Na	0.1 - 1
Si	0.1 - 1
Mn	0.1 - 1
Mg	0.01 - 0.1
K	0.01 - 0.1
Sr	0.01 - 0.1
Ba	0.001 - 0.01
Pb	< 0.001
Cr	< 0.001

*Li, Be, B, Ti, V, Co, Ni, Zn, Mo, Ag, Cd, Sn, La and Bi were not detected.

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The high amount of Al in the mixture was of some concern; however, runs in coated molds showed no detectable pickup of Al or other impurities in pieces of Pu cast at 900°C. Analytical data of a 7-in.-diameter disc cast in a CaF_2-coated graphite mold using a coated MgO-melt crucible are presented in Table 2.

Table 2

7-IN.-DIAMETER, 0.250-IN.-THICK Pu DISC RUN J-4274

Element	Concentration, ppm	
	Feed	Cast Disc
Li	0.2	0.2
Be	0.2	0.2
Na	10	10
Mg	60	30
Ca	5	5
La	10	10
F	2	2
O_2	500	500
Si	100	105
Pt	8	8
Cu	25	25
C	360	280
B	0.5	0.5
Cr	70	70
Fe	310	260
Ni	90	90
Al	30 - 80	45

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TYPICAL CASTING RUN

The casting of a 7-in.-diameter, 0.250-in.-thick pure Pu disc is described as follows:

The graphite mold is coated with CaF_2 using the spray method previously described. After coating, the two sections are assembled in a small laboratory press and the mold is ready for use. Figures 1, 2 and 3 are photographs of coated mold parts after partial and complete assembly.

The ceramic melt crucible is coated on the inside with CaF_2 using the flushing method previously described.

Figure 4 depicts a cross-sectional view of the casting unit showing the mold positioned in the vacuum chamber directly below the melt crucible which is located on top of the chamber lid inside of a Pyrex bell jar.

The mold is heated to 700°C then cooled and held at 650°C while the charge is heated to 750°C. With a vacuum in the range of 1 micron the melt is poured by lowering the melt induction coil and melting the Pu plug in the bottom of the crucible. Figure 5 is a photograph of the as-cast Pu disc.

SUMMARY

As pointed out in LA-2315, CaF_2-coated molds are far superior to previously used Al_2O_3- and MgO-coated molds. No reaction is detected between CaF_2 coating and Pu. As a result, the surface of the Pu casting has a bright metallic luster upon removal from the mold and is completely free of the hard oxide skin obtained with Al_2O_3- and MgO-coated molds.

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In addition to using the CaF_2 coating on casting molds, it is also used on ceramic and metal melt crucibles. Its use on ceramic melt crucibles has reduced the Pu pickup in the crucible, resulted in smaller skulls and extended melt crucible life from 1 to 3 runs to as many as 15. A CaF_2 coating on Ta melt crucibles prevents sticking, making removal of the skull easy. Also, materials not resistant to Pu because of alloying, such as cast iron or steel, can be used as melt crucibles if they are coated with CaF_2. Further, the use of CaF_2 coatings makes practical re-usable molds for thin rod or thin section castings. Mold materials formerly precluded because of alloying, such as cast iron or steel, can now be used.

The use of colloidal CaF_2 makes coating operations easier, gives complete mold coverage with less coating material and adheres better than previous coatings. These characteristics of the colloidal coatings result in better surfaces on the cast pieces and more precise and reproducible cast dimensions. For some applications, such as pressing, extrusion or spinning, the cast ingots can be used directly.

REFERENCES

1. "The Use of Calcium Fluoride as a Coating for Plutonium Casting Molds," Report LA-2315, April 1959.

2. F. W. Schonfeld, private communication.

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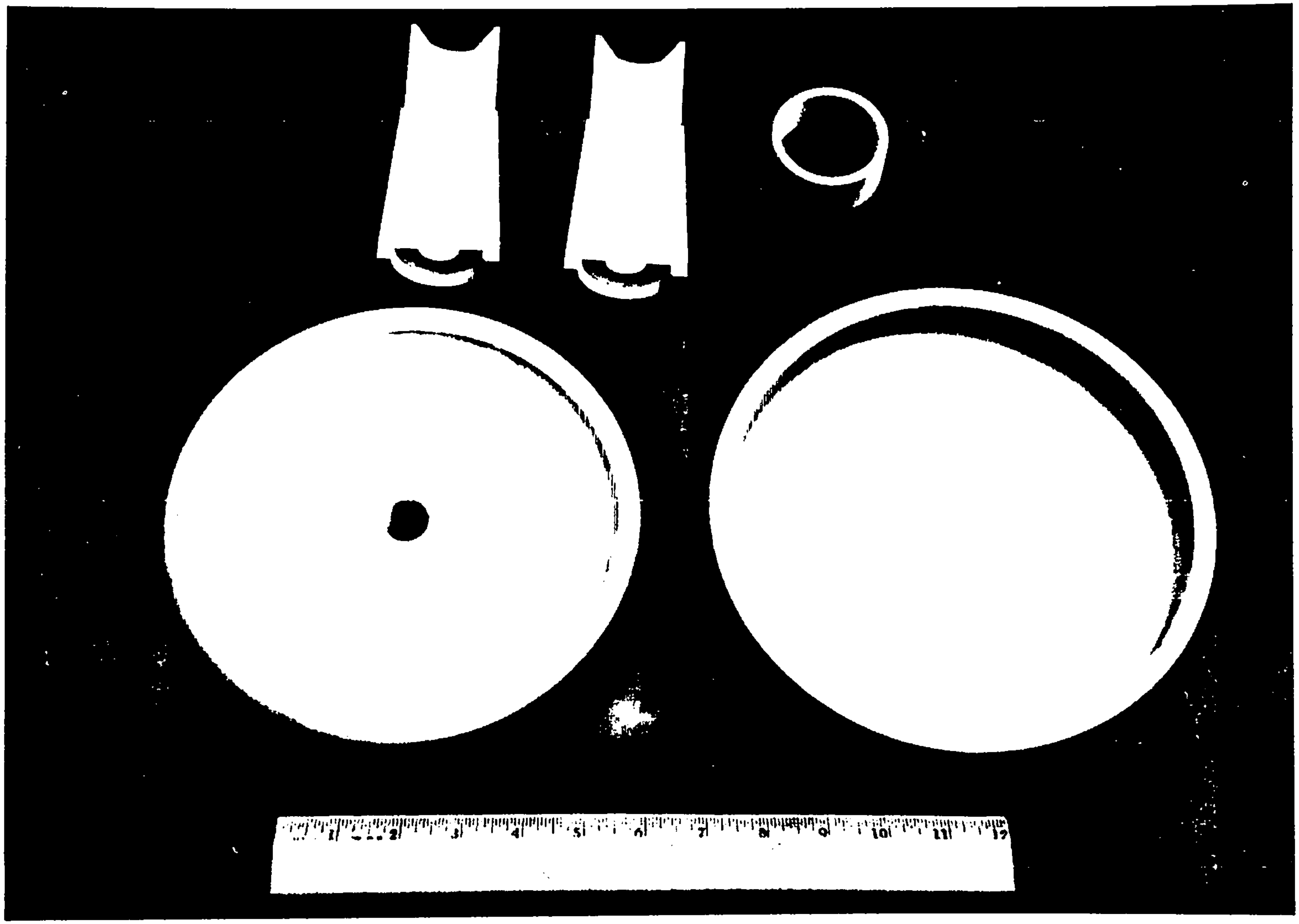

Fig. 1. CaF_2-coated graphite disc mold (before assembly).

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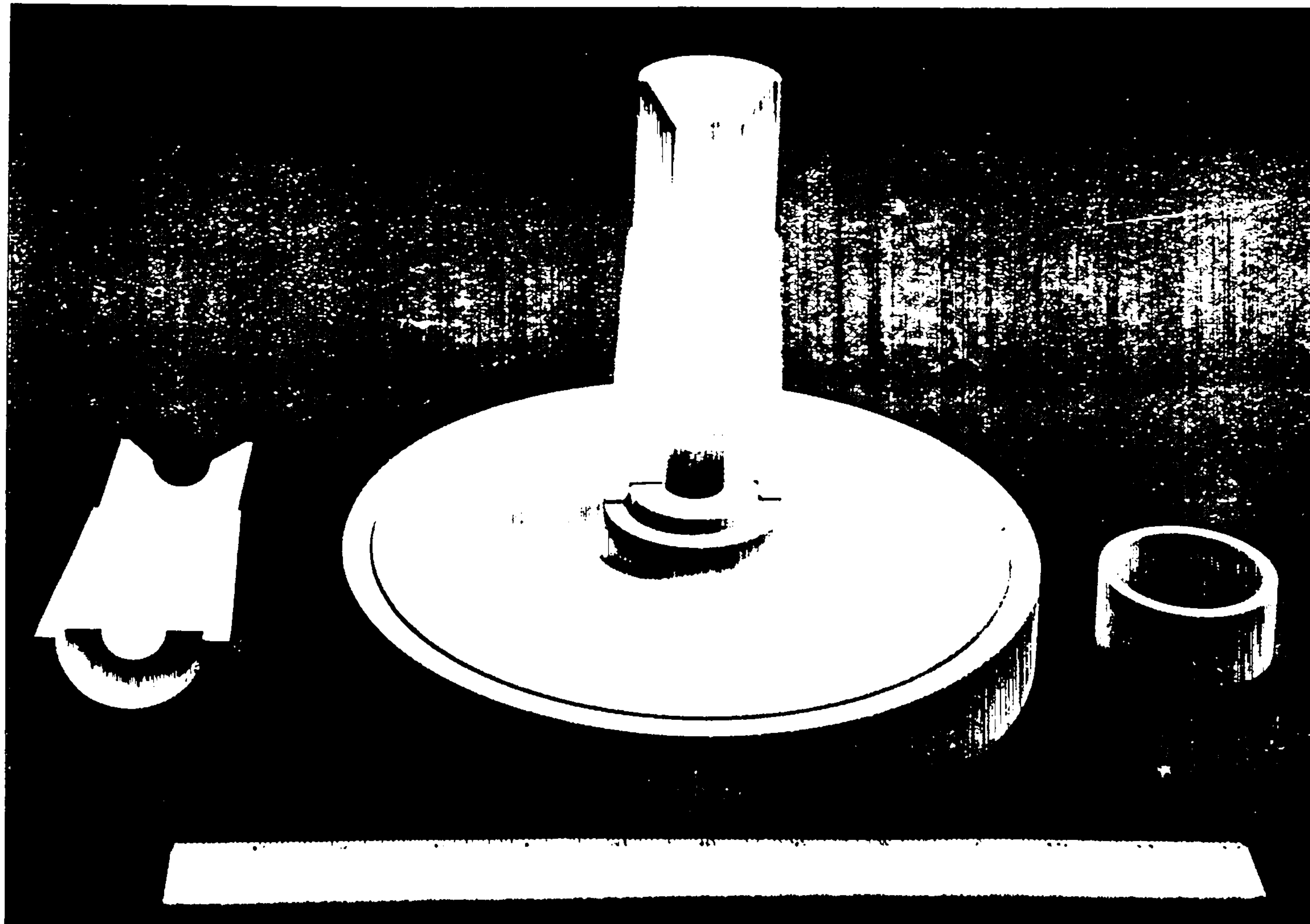

Fig. 2. CaF_2-coated graphite disc mold (partially assembled).

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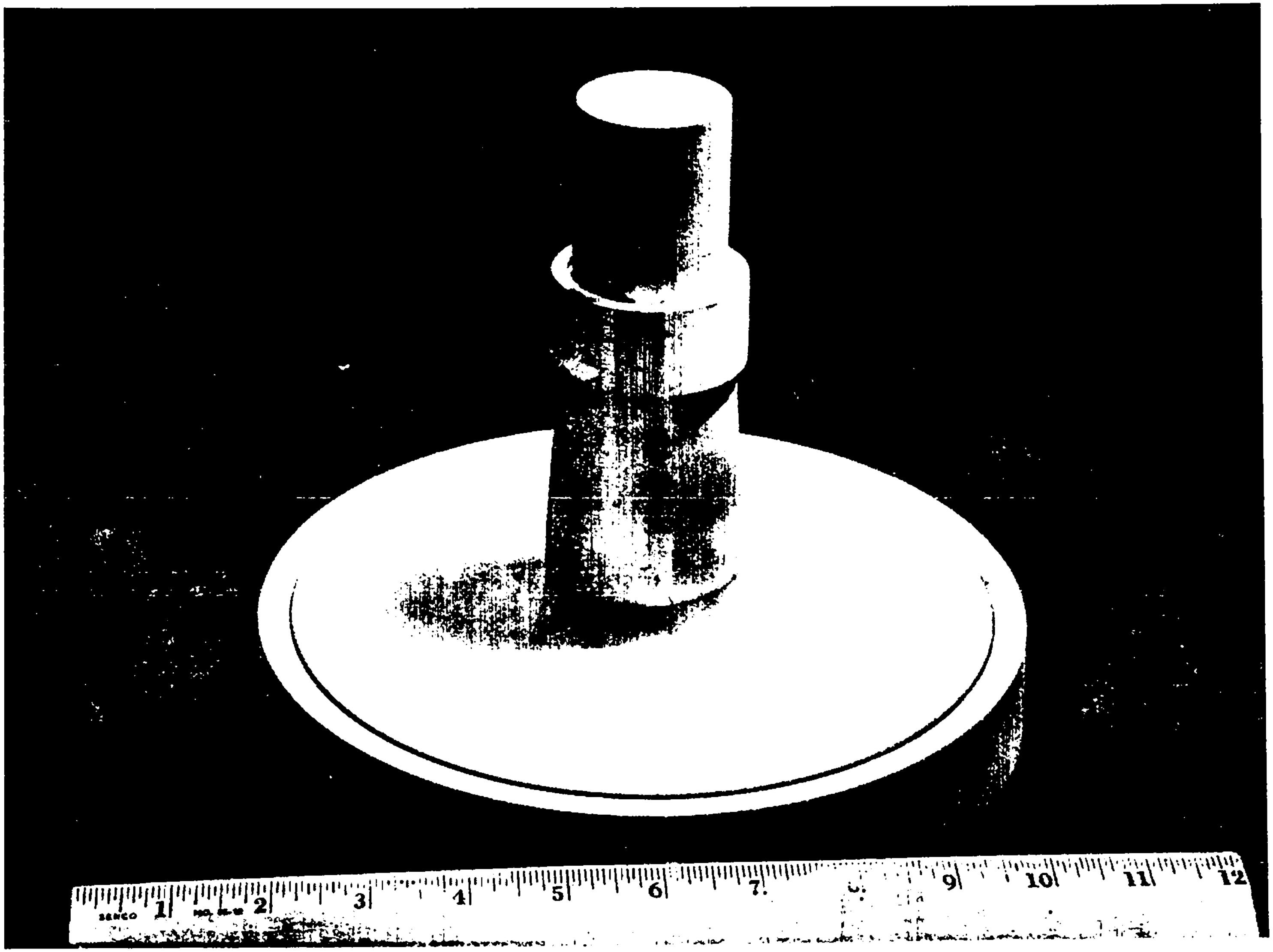

Fig. 3. CaF_2-coated graphite disc mold (assembled).

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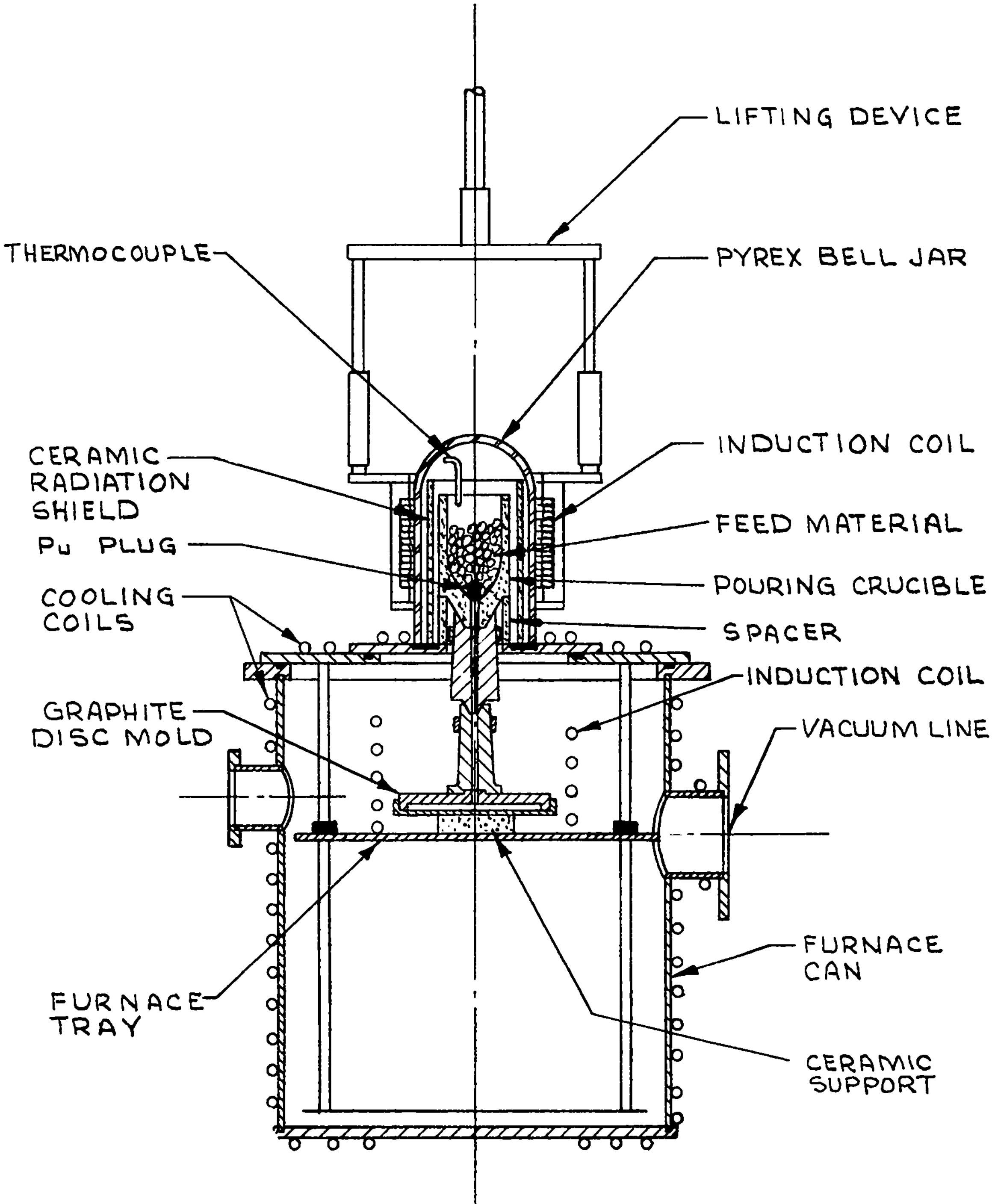

Fig. 4. Casting furnace (cross section).

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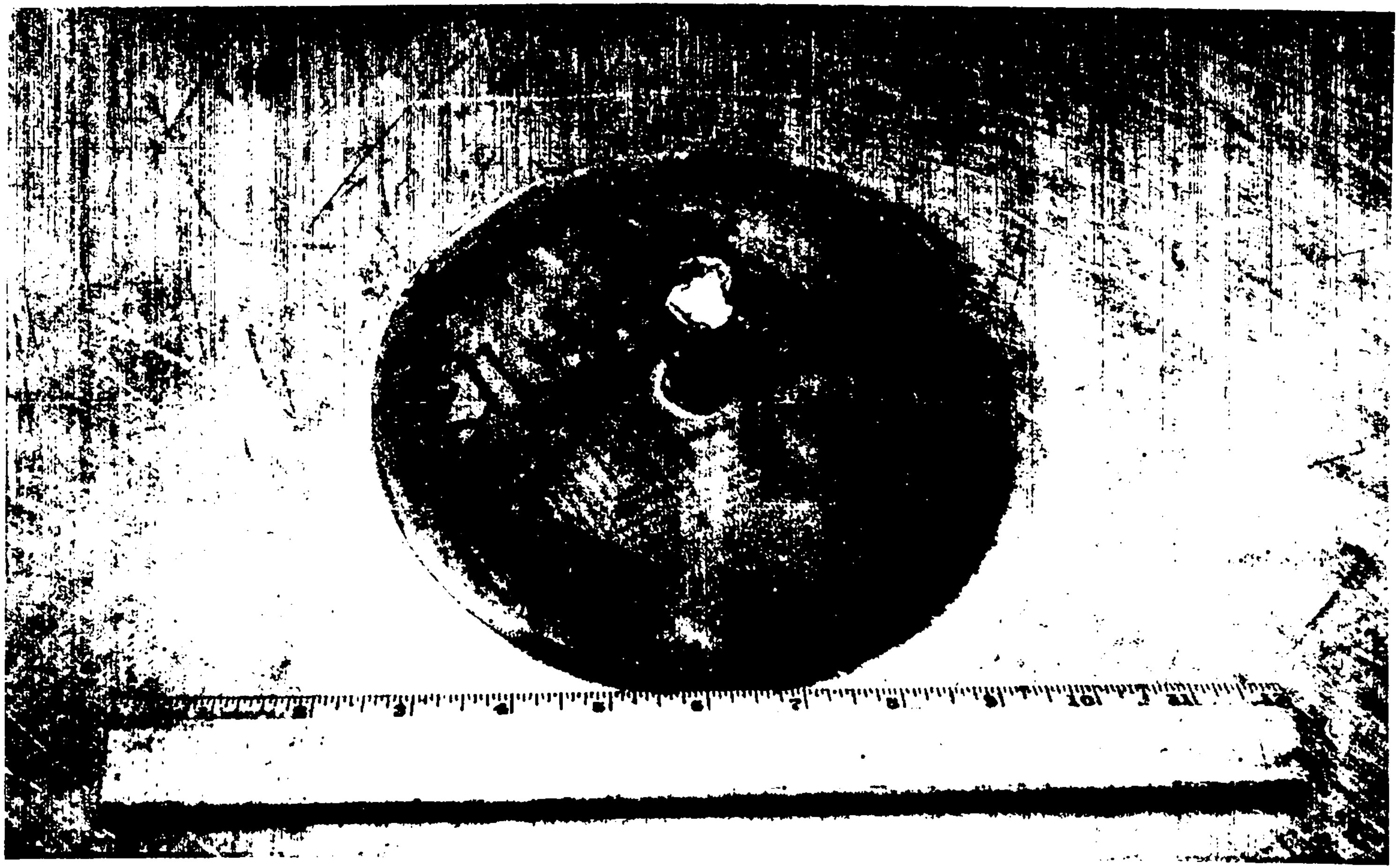

Fig. 5. Cast Pu disc (7 in. diameter, 0.250 in. thick).

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