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ABSTRACT

Many ceramic materials are inert to molten plutonium, but fragility and porosity of ceramic crucibles make them impractical for use in the plutonium foundry. Oxidized tantalum crucibles are inert to pure plutonium and to some of the low-melting-point alloys of plutonium. To take advantage of the ruggedness of metal crucibles, ceramic coatings inert to plutonium alloys at high temperatures that can be applied to metal or graphite crucibles and molds were developed. This report describes these coatings and the processes by which they are applied.

INTRODUCTION

Molten plutonium is a very corrosive substance that rapidly dissolves most metals in the periodic table. Of these metals, tantalum and tungsten are the most inert to plutonium, and tantalum crucibles are widely used in the plutonium foundry. The reaction between plutonium and tantalum rapidly increases above 1800°F, thus limiting the use of tantalum crucibles to low-melting-point alloys. In preparing high-melting-point alloys or alloys containing high-melting-point elements, it is necessary to use either an inert ceramic crucible or a ceramic coating on the tantalum crucible. Ceramic crucibles made from CaF_2, ZrO_2, or Y_2O_3 are inert to plutonium and to most of its alloys; however, they are difficult to use and all plutonium residues that penetrate the porous ceramics must be recovered.

Two different CaF_2 coatings were developed several years ago mainly for use on graphite molds.[1] These coatings had little abrasion resistance and tended to be easily washed by the movement of the molten plutonium. The low sublimation temperature of CaF_2 (2480°F) makes these coatings unusable at temperatures above 1800°F. To take advantage of the ruggedness of a metal crucible, a joint endeavor was undertaken by the Los Alamos Scientific Laboratory (LASL) and the Acheson Colloids Company to develop ceramic coatings that could be used above 1800°F.

This report deals with the ceramic coatings developed for use on crucibles and molds used in casting plutonium and its alloys.

COATING MATERIALS

The coating solutions were prepared by Acheson Colloids Company and the environmental testing was done at LASL. Several different coating materials, including ZrO_2, Y_2O_3, CaF_2, ZrC, and NbC were prepared and tested. These materials were prepared as aqueous solutions of the colloidal powders to which different binders were added. The coatings that exhibited good adhesion properties and resistance to spalling under thermal shock conditions were further tested as to their compatibility with high-melting-point plutonium alloys.

A NbC coating that can be applied to a graphite surface by the high-temperature reaction of a $NbCl_5$ gas with graphite was also evaluated.

COATING PROCEDURE

After each coating solution was received, thin (1 to 3 mil) coatings were built up on metal and graphite surfaces to determine their adherence. For evaluation all coatings were applied by spraying the diluted mixture (2 parts distilled water to 1 part solution) onto the heated part. The coating is applied by the following procedure. The graphite or metal surface is first thoroughly cleaned and then heated to 200 to 300°F on a hot plate. The diluted solution is sprayed with an artist's spray gun using an inert gas. A fine spray is used, which dries as it hits the heated surface. Care must be taken so that the solution does not form a puddle on the part being coated because the coating will then blister and come off where the puddle forms. Any loose powder that forms during coating is rubbed off with steel wool. Once the coating is built to the desired thickness (1 to 3 mil), it is given a final rubdown with steel wool.

Coatings that could be applied by spraying could also be applied by brushing the solution onto the heated part. When brushing the solution, it is necessary to use quick, light strokes so that thin layers of the coating can be built up. The final coating is then smoothed by rubbing it with steel wool.

COATING EVALUATION

Preliminary evaluation of how well the coating solutions adhered to the substrate, and the ease to which the coatings could be applied, eliminated both ZrC and NbC. The most effective binder used in the coating solution was K_2SiO_3. This binder was not used in the original CaF_2 coatings. The adherence and especially the abrasion resistance of the ZrO_2, Y_2O_3, and CaF_2, using this new binder, were far superior to the former CaF_2 coatings. The fact that these coatings, once applied, can be rubbed with steel wool testifies to their toughness.

Thermal cycling experiments were performed to determine the resistance of Y_2O_3 and CaF_2 coatings to spalling during heating and cooling. As is the case for all coatings, a thin coating of < 3 mils is preferable to thicker coatings that spall during heating and cooling because of differences in the coefficient of thermal expansion between the coating and the substrate. The CaF_2 coating could be cycled to 1800°F with no loss of integrity, and the Y_2O_3 coating was intact after heating as high as 2900°F.

Next the compatibility of the Y_2O_3 coating with molten plutonium and with high-melting-point U-Pu-Zr alloys was determined. In all cases, the coating was unwetted by the melt and only the U-15 w/o Pu-10 w/o Zr alloy, heated to 2700°F, showed any increase in impurities during casting. The silicon and oxygen content of this alloy increased by about 100 ppm. The Y_2O_3 coating on the tantalum crucibles proved to be virtually inert to all plutonium alloys below 1800°F, and the coating was intact after several runs and even then required only a minor touch up.

The CaF_2 mold coating was evaluated for use at temperatures below 1500°F; the Y_2O_3 coating was used on graphite molds at higher temperatures. These mold coatings were used at temperatures as high as the melting point of the plutonium alloy being cast, and in no case was the coating washed away by the metal flowing into the mold. The impurity level of the casting was never greater than the impurity level of the melt.

Evaluation of the NbC-coated graphite crucibles was carried out only on the high-melting-point U-Pu-Zr alloys between 2500 and 2900°F. The coating was extremely resistant to abrasion and was unaffected by thermal cycling. A tight vacuum system was necessary to avoid rapid oxidation of NbC at temperatures above 550°F. One problem in using these crucibles was complete wetting of the coating by the melt. This limited the use of the crucibles to one run because of the build-up of a casting skull and the problem of resetting the stopper plug in the pour spout. The only impurity added to the melt when using these crucibles was about 25 ppm of niobium.

SUMMARY

Two new ceramic crucible coatings have been developed for use at temperatures up to 2900°F. A Y_2O_3 coating, now commercially available as a spray solution, can be easily applied to either a graphite or metal crucible. Once applied, this coating exhibits good abrasion resistance and is not wetted by the plutonium alloy melts. This coating is virtually inert to all plutonium alloys, and can be reused several times. The second coating, NbC, can be applied to a graphite surface only by a special high-temperature process. This coating has excellent abrasion resistance and thermal shock properties, but it is wetted by the melts, which limits its use to one run. The NbC coating is the more inert of the two for high-temperature alloys that contain substantial amounts of oxygen gettering materials such as zirconium.

A new CaF_2 mold coating has also been developed. It is commercially available as a spray solution and can be easily applied to either a graphite or metal mold. The use of K_2SiO_3 as a binder in the solution makes this new mold coating far superior to the CaF_2 coatings previously used.

REFERENCE

1. J. W. Anderson, F. Miley, and W. C. Pritchard, "Coated Mold for Casting Plutonium," U. S. Patent No. 3,023,119 (1962).

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