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PREPARATION OF REFRACTORIES FROM URANIUM DIOXIDE

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by

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W-142-1

PREPARATION OF REFRACTORIES FROM URANIUM DIOXIDE

The compounds of uranium have long been regarded by the ceramist as coloring agents for ceramic glasses, giving beautiful yellows and browns which have been difficult to duplicate, however, attention is now being drawn to the refractory properties of the pure dioxide of uranium, which make it suitable for special applications.

PROPERTIES OF URANIUM DIOXIDE

Proper fabrication of UO_2 refractories is contingent upon consideration of certain characteristic properties of the raw material which indicate the fabrication techniques that can be employed. UO_2 is a dark brown, granular, non-plastic material. It is quite active chemically and is, of course, radioactive since it contains uranium.

Of major consideration from the fabrication standpoint, however, are the erratic oxidation properties of UO_2 . Uranium forms a continuous monophasic series with oxygen from $UO_{1.75}$ to $UO_{2.3}$.¹ This means that uranium dioxide can take up more oxygen than the stoichiometric formula indicates up to a composition of $UO_{2.3}$ without changing from the face centered cubic lattice except for slight changes in lattice dimensions. While the members of this series are reasonably stable at room temperature in contact with air, this stability decreases with increasing temperature and oxidation proceeds rapidly even at comparatively low dryer temperatures. The blueish-black oxygensaturated form of the series, $UO_{2.3}$, is reached at the low temperature of $150^{\circ}C$. At higher temperatures in air oxygen content increases further thru a diphasic region up to a composition corresponding to U_3O_8 . Then above $750^{\circ}C$ U_3O_8 begins to decompose again, losing oxygen. This radically unstable nature of the uranium-oxygen system precludes the determination of moisture content by forced drying to constant weight, it limits drying temperature of finished ware to room temperature only, and it makes a vacuum or neutral atmosphere mandatory for firing.

W-142-2

The chemical activity of UO_2 also presents some minor difficulty in fabrication. UO_2 should not be left in contact with dies or metal containers any longer than necessary to avoid corrosion. Even though dies are cleaned immediately after use they soon show the inevitable signs of pitting. Chrome plating of dies and stainless steel containers are helpful in this respect, but are not permanent insurance against corrosion.

FORMING

Both pressing and slip casting techniques can be used for forming UO_2 refractories. Pressing offers the advantages of simple preparation of raw material and freedom from contamination, however wall thickness and design are limited. Slip casting supplements pressing in that it can provide the thin walls and some design features not possible with pressed ware.

Pressing

A -325 U. S. STD sieve fraction is used exclusively for pressing small crucibles up to about 2 inches in diameter. On larger crucibles up to about 5 inches in diameter a distribution of particles approximating a maximum density mixture is employed (see Table I). This particle sizing is quite roughly done, but it serves the purpose well for the larger crucibles which have thicker walls and can accommodate the larger particles.

Table I

Sieve Fraction U. S. STD	Percent
plus 30	25.3
minus 30 plus 200	36.7
minus 200 plus 325	32.8
minus 325	5.1

W-142-3

Tempering with 6 to 8 percent distilled water is the only step taken to prepare the UO_2 for pressing. The purity requirements of these pressed crucibles are very high and therefore no additives, lubricants, or binders of any type are used and since UO_2 has no plasticity it is essential that the proper amount of tempering water be added, if the pressing operation is to be successful. The proper amount of tempering water is not constant but varies from day to day depending, it is assumed on the relative humidity, and/or the original moisture content of the UO_2 . As stated above UO_2 gains weight due to oxygen absorption when subjected to dryer temperatures and it is therefore difficult to determine moisture content at least as a routine measure preparatory to tempering. The simplest procedure is to make several trial pressings until the optimum water content is determined and use this quantity in all subsequent pressings made the same day.

After tempering, the UO_2 is tamped in the inverted die using a uranium rod to minimize contamination, and the crucible is pressed in this inverted position using pressures from 6 to 20 tons/in² depending on the size of the die. Pressure is applied intermittently to allow escape of entrapped air and avoid "pressure cracking". After pressing the mandrel and base plunger are removed and the crucible extracted by pushing up on the base with an extraction ram.

The importance of proper die design should be emphasized when pressing without binders. Only a very slight taper can be tolerated so that when the crucible is extracted the sides will be in direct compression and will not shear from the base as will happen if the taper is too large.

The green UO_2 crucibles are extremely fragile, but with care and a little practice can be extracted readily. However, even the small pressure used in extraction is sometimes sufficient to crush the base, and it has been necessary to incorporate a support for the base in the form of a chrome plated brass ring (see Figure 1) which is beveled at a 45° angle where it meets the crucible.

This ring protects the base during extraction and allows the crucible to be handled without danger of breakage. The ring is easily removable after extraction and does not stick to the crucible. Extraction of the large sized crucibles ($4\frac{3}{4}$ " by $8\frac{1}{2}$ ") cannot be performed by hand because of the excessive weight of the die. A mechanical die stripper was therefore devised to perform this operation. It consists of a clamping arrangement for the crucible die and an extraction plunger actuated by a hydraulic bumper jack (see Figure 2). All pressed crucibles should be handled only by the extreme base to avoid breakage.

Slip Casting

The acid leaching technique commonly employed for slip casting of other non-plastic materials is used for preparing slips of UO_2 . The -325 U. S. STD sieve fraction is ground in a steel mill, four hours grinding being sufficient for heavy walled solid castings and as much as 16 hours required for thin walled castings. The mill product is then leached with 5N HCl for 24 hours after which the acid is decanted and the leaching repeated 3 or 4 times. The slip is then washed until the proper pH is obtained, four washings being usually sufficient. The specific gravity is then adjusted and any additives included.

The pH-viscosity relationship² for UO_2 in the acid range is shown in Figure 3. The minimum point occurs at about pH 3.6 and satisfactory castings have been made at this pH, however, the shrinkage of the cast crucible is barely sufficient for mold release and the finer particles in the slip tend to clog the mold pores. Both of these conditions improve toward the acid end of the curve and it has been suggested² that a satisfactory compromise can be made at pH 2.1 and this is recommended for a medium sized casting, however, with an acid leached slip the settling rate is not too high even at the extreme acid end and castings can be made at pH 1.5.

Small percentage additions of organic dispersion agents may be used to improve the dry strength and also help prevent cracking by slowing down the rate of water removal by the plaster. The addition of 2 percent (dry by dry weight of solids) of carbo-wax 4000W to the slip exerts a slight defloculating effect, aids in dispersion, as well as improving the dry strength. Using carbo-wax it is possible to cast very thin shapes such as thermocouple protection tubes and crucibles with walls $1/16''$ thick (See Figures 4 and 5).

FIRING

The urania refractories are allowed to dry slowly for several days at room temperature and are then fired in a molybdenum resistance furnace to a maximum temperature of 1750°C . A hydrogen atmosphere is used to prevent oxidation of both the furnace elements and the urania. The commercial hydrogen is purified by passing thru two puridryers and one catalytic unit for oxygen and water removal. The hydrogen atmosphere also serves the useful purpose of reducing oxygen in excess of $\text{UO}_{2.15}$, which may have formed on the surface (oxygen above $\text{UO}_{2.15}$ is comparatively loosely bound)¹ and may possibly reduce higher oxides to stoichiometrically pure $\text{UO}_{2.0}$. The urania pieces are set on alumina setting slabs with a thin sheet of molybdenum metal intervening to prevent any reaction between the alumina and urania. When slip cast ware containing carbo-wax is being fired the furnace temperature is raised slowly for the first 600°C to volatilize the carbo-wax. This requires about 8 hours. The furnace may then be heated fairly rapidly to reach 1750°C in about 20 hours. A nominal soak at temperature is allowed of about 2 hours to insure thermal equilibrium. The furnace must be cooled to essentially room temperature before the crucibles can be removed from the protective atmosphere. In practice, however, the crucibles are removed when the furnace has cooled to 50°C , but are immediately transferred to dessicators which are then evacuated for storage.

PROPERTIES OF FIRED WARE

Linear shrinkage measurements of pressed crucibles indicate an average 14.6 percent shrinkage in height and 14.9 percent shrinkage in diameter on ware fired to 1750°C. Shrinkage of slip cast ware is slightly higher averaging 15.2 percent for crucibles cast with a specific gravity of 4.0 and 16.2 percent for thermocouple protection tubes which were cast with a more fluid slip of specific gravity 3.8. All measurements are based on fired size.

Density measurements made on pressed ware fired at 1750°C indicate an average of 9.13 or 83.8 percent of the maximum theoretical UO_2 density taken as 10.9. With slip cast ware this average is 9.6 or 88.2 percent of theoretical.

The variation of density with firing treatment is shown in Figure 6. The effect of temperature is much more pronounced than soak time as would be expected. Ware fired at 2000°C was badly deformed.

The variation in density along the height of pressed crucibles caused by differences in pressure is not large, but is measurable. The effect is not as pronounced for crucibles fired at the higher temperatures.

HEALTH HAZARDS

UO_2 is, of course, radioactive since it contains the element uranium and definite precautions are necessary to avoid injury to health. Uranium is an alpha emitter of rather long half life and therefore the level of activity is quite low. Alpha particles cannot penetrate the skin so no direct radiation danger is eminent in ordinary handling, however, if UO_2 should become fixed inside the body it can cause serious radiation damage by its presence over a long period of time. For this reason all dusty operations must be performed in a hood or dry box and all operations performed outside the hood should be periodically checked for dust count. Open wounds also present a hazard and should be suitably protected by rubber gloves or fingers. Under normal conditions UO_2 passes quite readily through the

W-142-7

digestive tract, but sensible precautions are nevertheless advisable to prevent the contamination of food. The hands should be scrupulously washed when work is completed and care taken to prevent the contamination of street clothing. An alpha counter can be used as a check on cleanliness.

W-142-8

Figure 1 (Negative No. 106-433)
Expanded view of typical crucible die. Note the beveled brass ring which protects
the crucible base during extraction. Mandrel is hollow to reduce weight.

W-142-9

Figure 2

Hydraulic die stripper for extracting large crucibles. The hydraulic unit is an ordinary automobile bumper jack.

(This photograph has not been taken yet but is definitely unclassified)

W-142-10

**RELATIONSHIP BETWEEN pH
AND VISCOSITY
OF A UO₂ CASTING SLIP**

Figure 3 (Negative No. 106-469)
Relationship between pH and viscosity of a UO₂ casting slip.

W-142-11

Figure 4 (Negative No. 106-269)
Green slip cast crucibles. Note thinness of wall on small crucible.
Small tube in front of ruler is thermocouple protection tube.

W-142-12

Figure 5 (Negative No. 106-432)
Fired UO_2 crucibles and shapes. The two crucibles on the left are pressed.
All the other pieces are slip cast. Thermocouple protection tubes and large
crucible cover in the foreground.

W-142-13

Figure 6 (Negative No. 106-468)
Variation of density with firing treatment.

VARIATION OF DENSITY
WITH FIRING TREATMENT

W-142-14