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FLUIDIZED-BED COATING OF UO_2 POWDER
WITH NIOBIUM AND OTHER ELEMENTS

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FLUIDIZED-BED COATING OF UO_2 POWDER WITH NIOBIUM AND OTHER ELEMENTS

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The chemical vapor deposition of niobium, molybdenum, tungsten, chromium, carbon, and niobium-vanadium alloys in a fluidized bed of UO_2 powder particles has been used to provide uniform, dense, nonporous coatings on the individual particles. In the case of niobium, which received major attention, hydrogen reduction of niobium pentachloride vapor was used as the vapor-deposition reaction. The most serious problem was that of maintaining bed fluidity and avoiding agglomeration. This problem was overcome to permit routine operation of the coating equipment. In the entire program of 68 experimental runs, only 1.1 per cent of the product was lost by agglomeration. In routine operation, this loss should be even lower.

INTRODUCTION

In the ever-expanding nuclear-reactor technology, encapsulation of fuel elements has become an established method of maintaining mechanical integrity and assuring fission-product retention. In the case of particulate ceramic nuclear fuels, such as UO_2 , attention has been directed to the possibility of encapsulating the individual particles, with the aim of localizing radiation damage and improving fission-product retention, particle distribution, and particle "fabricability", and for the purpose of preventing reaction of the fuel material with other components of the fuel system.

The techniques of vapor deposition⁽¹⁾ and, more recently, vapor deposition of metals on a fluidized bed of seed particles^(2, 3) appeared applicable to the coating of nuclear-fuel particles. The first program undertaken was the coating of UO_2 particles with tungsten.⁽⁴⁾ Since that time, interest has increased, and other programs have been undertaken to include coatings of pyrolytic carbon, chromium, molybdenum, niobium, tantalum, zirconium, chromium carbide, niobium carbide, chromium oxide, vanadium oxide, yttrium oxide, and zirconium oxide, and the deposition of alloy coatings such as niobium-tin and niobium-vanadium. Interest in nuclear-fuel-particle coating and preparation⁽⁵⁾ by vapor-deposition techniques has spread to a number of other laboratories and, in the light of the promising results being obtained, it appears that coated fuel particles will have an important place in future nuclear-fuel technology.

The vapor-deposition reactions used in the work at Battelle include thermal decomposition or reduction of volatile halides, carbonyls, or alkyls for deposition of metals, and thermal decomposition of hydrocarbons for deposition of hard carbon. Alloys or carbides are formed by codeposition of the elements from suitable mixed-vapor feeds. In addition to the above reactions involved in fuel-particle coating programs current or concluded, many other vapor-deposition reactions could be employed to deposit a wide variety of coatings.

(1) References at end of text.

It should be recognized at the outset that, although some generalizations can be made, each fluidized-bed vapor-deposition reaction has its individual peculiarities, which, for optimization of the coating properties and process variables, could make it the subject of a separate intensive research program. However, the task of evaluating a given lot of coated powder for a potential fuel-element application is so great that optimization of the coating properties and process must be deferred until a decision can be made as to whether the value of a given particle-coating combination can justify the expense of such a systematic study. This places a difficult burden on the scientist devising the coating scheme, who, in order to satisfy an immediate need for quantities of various coated powders for fuel-element evaluation, must rely on past experience and a "feel" for the process rather than on a systematic knowledge or investigation of the effects of the many process variables. Reporting the results of such a program then becomes a recitation of what seems to work, or not work, with but a limited treatment of the fundamentals of the process.

However, such information is needed as background, particularly for those who may be attempting to duplicate or extrapolate the results. It is hoped that this report will satisfy that need, and that the importance of vapor-deposition reactions in fluidized beds of powder particles will become sufficiently great to justify systematic attention to fundamentals.

This report will describe the process of vapor deposition in a fluidized bed in a general way, pointing out important general considerations, and then will move to a discussion of the procedures and results for carbon, chromium, molybdenum, and niobium coatings.

FLUIDIZED-BED VAPOR-DEPOSITION PROCESS

In the fluidized-bed vapor-deposition process, the particles to be coated are fluidized in a heated reactor by a stream of gas which may or may not be one of the reactants in the reaction being used. The gas velocity required for fluidization depends primarily on the particle size and density and, to a lesser extent, on the gas viscosity and density, particle shape, and reactor design.

The reactant gases may be premixed with the fluidizing gas, or, in cases where premature reaction would otherwise occur, may be injected at separate points and mixed in the bed.

The fluidized bed is an almost ideal averaging mechanism. The problems of non-uniformity encountered in many vapor-deposition reactions are avoided. However, the use of the fluidized bed for this purpose is not without problems, the most serious of which is the greater limitation on conditions for maintaining bed fluidity. This results from the addition of several new mechanisms of particle-particle interaction to the normal adhesive forces between particles encountered in other nonaccretive fluidized-bed processes. The most obvious difference is that, while depositing coating material on individual particles, the coating also tends to bridge particles in contact. Prolonged particle-to-particle contact can then result in sintering of the bed. Thus, localized stagnation, caused by dead space in reactor design, or momentary general stagnation,

caused by interruption of gas flow, are to be avoided. Other more subtle factors may lead to adhesion of particles and loss of fluidization. These include the deposition of liquid reaction products, such as lower-valent halides in a halide-reduction process. Even in cases where intermediate reaction products are not formed at unit activity, the reactants may undergo activated absorption on the particle surface, and possibly increase the particle-particle interaction.

Whatever may be the mechanism of bed agglomeration, it can be shown to be strongly dependent upon particle size. If the contact area of radius R between spheres of radius r (see Figure 1) is defined as that part of the surface area of the particles within a distance d of each other, we have the relation for R :

$$R^2 = r^2 - \left(r - \frac{d}{2}\right)^2,$$

or

$$R^2 = rd - \frac{d^2}{4}.$$

FIGURE 1. CONTACT AREA BETWEEN SPHERES

Since d^2 is much smaller than rd , $R^2 \cong rd$. The contact area as swept out around the point of tangency by r , is equal to πR^2 or πrd . Thus, the area of contact is proportional to the first power of the particle diameter. Since the mass and hence the impact energy of a particle at a given velocity is proportional to the volume or third power of the diameter, the tendency to break a particle-to-particle bond on collision should increase rapidly with particle size. Conversely, the smaller the particle size, the greater the care that must be taken to avoid agglomeration. This conclusion has been borne out by qualitative observations in the course of the present work.

It is often difficult to identify the mechanism involved in a given incident of bed freeze-up. However, it is certain that each system has a characteristic minimum degree of agitation required to avoid agglomeration of the bed. In discussing the individual coating procedures, we shall treat some of the factors to be considered in maintaining continued fluidization. In the following section, discussion will be limited to the fluidization characteristics of the UO_2 powder particles involved in this work.

Fluidization Characteristics of UO_2 Powder

Most of the material dealt with in the present work consisted of spherical UO_2 shot of density of 80 to 95 per cent of theoretical and three particle-size ranges, 88 to 105 μ , 105 to 149 μ , and 149 to 177 μ . For the most part, coating was done in 100-g batches, this being a convenient quantity for coating as well as for subsequent evaluation. Quartz or Vycor reactors 1 in. in diameter, having the bed-support design of Figure 2a, were used predominantly. Later in the work, improved agitation of the smaller particles appeared to be obtained through the use of the design shown in Figure 2b. The fritted-disk support shown in Figure 2c has the disadvantage of incurring stagnation along the periphery of the seal between the tube and the fritted disk, since the pores of the disk are invariably constricted in the sealing operation. This support has the additional disadvantage of making it difficult to adjust the position of the "hot zone". The hot zone is the area in which the particles are maintained at a temperature sufficiently high to be coated with the desired product. It is obvious that most of the particles should be contained in this zone. At best, particles allowed to cool below the temperature of this zone will not be coated. At worst, they could become coated with intermediate reaction products leading to bed stickiness. On the other hand, the constriction upon which the bed is supported must not be overheated, or deposition will occur within the constriction and gas flow will be cut off.

The configuration of the bed-supporting constriction is important not only from the standpoint of operating temperature, but from the standpoint of the dynamics of fluidization. A certain amount of "slugging" is thought to be useful in breaking up potential agglomerates. However, with little pressure drop across the bed-supporting constriction, and depending upon the upstream volume of the apparatus, a resonant condition can develop in which the stagnant part of the slugging cycle may be of sufficient duration to result in particle-to-particle adhesion and loss of fluidization in sensitive systems. On the other hand, the constriction should not be placed in such a way as to send a high-velocity jet of gas into the bed which would result in central channeling and relative stagnation at the walls.

Figure 3 gives data on the fluidization characteristics of spherical UO_2 powder in hydrogen determined as a function of temperature in a reactor of the design shown in Figure 2a. "Operating Level of Fluidization" is a term used to denote the condition in which the maximum bed height is about four reactor diameters above its static height.

The requirement of greater gas flow for larger particles is clearly illustrated. As would be expected, a lower flow (STP) is required at higher bed temperatures owing to the increased velocity of the expanded gas. Increased viscosity at higher temperature would also contribute to the lowered requirement. Attempts to treat the data of Figure 3 quantitatively with respect to these factors have not been rewarding because of the complexity of the system.

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FIGURE 2. BED-SUPPORT MODIFICATIONS

FIGURE 3. FLUIDIZATION CHARACTERISTICS OF SPHERICAL UO_2 POWDER

A 100-g bed was used in a reactor of the design shown in Figure 2a.

Although the bed cannot be observed directly during the coating operation because coating material is deposited on the walls, the operator develops a "feel" for the behavior of the bed by watching such pressure fluctuations as are recorded by the manometer on the fluidizing-gas feed line. (Care must be taken that the constriction just ahead of the bed is not made so small, and the pressure drop so large as to damp out fluctuations resulting from bed activity.) The amplified signal from a contact microphone attached to the reactor is also helpful in monitoring the fluidization.

Heating of Fluidized Bed

With rare exceptions, the vapor-deposition reactions of interest in applying coatings to nuclear-fuel particles are carried out at elevated temperatures, which range from 150 C for organometallic decompositions to 1200 C and higher for pyrolytic carbon formation. Heating of the small-scale fluidized-bed reactor is most conveniently done with an external resistance furnace. The furnace is preferably of the split variety, so that, in event of operational error, or improperly chosen conditions leading to bed agglomeration, the furnace can be opened to cool the reactor quickly. In this way, the extent of sintering can be minimized and the friable agglomerates can be broken up on a screen for re-use.

The temperature of the bed can be measured by a thermocouple in a well extending into the bed from the top of the reactor. This technique is somewhat disadvantageous in a small reactor, since it frequently results in a serious decrease in the cross-sectional area of the reactor. Moreover, unless the well is anchored, its clattering against the reactor walls masks the sound of the bed picked up by the contact microphone. In the deposition of alloys or compounds requiring separate inlets for two vapor streams, the position of the central thermocouple is usually taken by a vapor injector. Although it might be possible to miniaturize the design and include both without prohibitively constricting the reactor, the temperature of a 1-in.-diameter reactor is usually monitored by a thermocouple on the outer wall, placed so that it is not directly beneath a heating element. The acknowledged superior heat-transfer characteristic of the fluidized bed tends to minimize the error involved.

Figure 4 gives data on the temperature drop between the outside wall and a central well of a 1-in.-diameter reactor in which 100 g of UO_2 was fluidized with hydrogen. The data show the greater net heat-transfer rate of the more numerous smaller particles, resulting in a lower temperature difference between bed and furnace. At low gas flows, a greater fraction of the bed is in the relatively cold lower end of the reactor. As the flow is increased, heat is transferred to a greater extent from the hot zone and ΔT is decreased. As the flow is increased further, the greater sensible heat requirement of the gas takes over, and ΔT is again increased.

NIObIUM COATINGS

The deposition of niobium by hydrogen reduction of niobium pentachloride on a fluidized bed of "seed" particles is described by Oxley, et al. ⁽⁶⁾ Details of the process, as adapted for fuel-particle coating in the present work, are given in a later section of this report for the benefit of those who may be interested in its duplication.

FIGURE 4. TEMPERATURE DROP (ΔT) BETWEEN WALL OF FLUIDIZED-BED REACTOR AND CENTRAL THERMOCOUPLE

100-g beds of spherical UO_2 , 80- μ and 125- μ average diameter, were used with a reactor of the design shown in Figure 2a.

The coating reaction, which is followed by titration of the HCl produced by reduction of the chloride, is continued until the desired quantity of niobium has been deposited on the bed. Figure 5 gives the amount of niobium necessary to form a given thickness of coating on fully dense spherical UO_2 particles of various sizes. The equation

$$\frac{w}{w_0} = 0.855 \left(\frac{d}{d_0} \right)^3 + 0.145$$

gives the ratio of the weights of coated (w) to uncoated (w_0), 92 per cent dense UO_2 powder as a function of the final and initial diameter, d and d_0 , respectively.

The rate of deposition of niobium on a 100-g bed of UO_2 in a 1-in.-diameter reactor has been limited tentatively to about 5 g per hr on the basis of the observation that deposition at higher rates has often led to greater porosity in the coating and to increased surface roughness. Since some of the variables are inseparable, it is difficult to account for this phenomenon. It may be either the result of the lag in crystal nucleation at the higher deposition rate, or it may be related to the lower excess-hydrogen ratio which must be accepted in increasing the rate of NbCl_5 feed. Another explanation which is receiving current attention is the possibility that the porosity and surface roughness result from an increased rate of dusting of partially reduced chloride from a condensation zone above the bed into the bed itself. It is known from work with other systems that the introduction of feed materials as solids and their reduction on fluidized-bed particles results in a structure which is quite porous by comparison with that obtained on direct reduction of gaseous reactants. Although it was not possible to develop a correlation of surface roughness with coating conditions, characterizations of the coatings with reference to surface roughness are included in Table A-1 of the Appendix for the purpose of completeness.

Although the rate of 5 g per hr [2 lb/(hr)(ft²) of reactor cross-sectional area] is acceptable on a laboratory scale, and may be practical on a commercial scale, it would be highly desirable to increase this rate as a means of reducing coating costs. The first step contemplated is the use of a reactor having a smaller diameter disentrainment section which is heated above the dew point of the lower chlorides to prevent their condensation in the vertical leg. This would reduce dust recycle and its attendant potential difficulties. Further reduction in the dusting problem is expected to result with a larger diameter bed in which a greater bed height can be used, leading to improved reduction efficiency and minimization of lower chloride production.

A more thorough investigation of operation at higher temperatures should also be made as a means of increasing the efficiency of chloride utilization and preventing dusting of lower chlorides. Deposition of niobium has been limited to below 900 C in the past on the basis that some difficulty had been experienced in attempting to maintain fluidization at temperatures of 900 C and above. With so many other variables involved, it is quite possible that the temperature level alone was not responsible for the difficulty, and that conditions may be found for operating above 900 C. However, the pressing need for quantities of material for subsequent evaluation led to a reluctance to explore coating conditions which might jeopardize the successful preparation of a given lot of coated material. Thus, the use of reaction temperatures above 900 C has not been evaluated critically.

Two aspects of the niobium-coating procedure deserve special attention. These are (1) reactant purity, and (2) the technique for initiating and terminating a run.

FIGURE 5. NIOBIUM-COATING WEIGHT AS A FUNCTION OF THICKNESS

During the course of the present work, a minimum of attention was given to the purity problem, since the coatings being prepared were of the right order of hardness for the application. However, such observations as were made are included here for the benefit of those who may be seeking softer coatings.

Owing to the large excess of hydrogen required for efficient reduction of niobium pentachloride, the maintenance of hydrogen purity is an important consideration. At an excess-hydrogen ratio of 100 over stoichiometric, 1 ppm by volume of water vapor in the hydrogen will contribute up to 250 atom ppm of oxygen in the niobium coating. Since analysis of gases for impurities in the low ppm range is very difficult, the best indication of gaseous purity is the quality of the niobium metal produced. This will be considered in greater detail in a later section. During the major portion of the work reported here, the process hydrogen* was purified by passing it through a catalytic converter** to convert the oxygen to water. The gas was then passed through a "molecular sieve" dryer*** and on to a titanium or zirconium getter furnace for the removal of nitrogen. Very late in the work, the hydrogen was purified by passing it through a palladium diffusion unit****. Since only hydrogen can diffuse through the walls of a leaktight palladium tube, the process hydrogen should contain <1 ppm of any given gaseous impurity. No striking decrease in hardness of the niobium coatings was observed as the result of the substitution of the palladium diffusion unit. This would indicate that most of the hardening came from sources other than impurities in the hydrogen.

At first thought, it would appear that the presence of impurities in the niobium chloride should be less significant than those in the hydrogen, because of the absence of the large multiplication factor. However, the presence of niobium oxychloride in niobium chloride is known to be a significant problem. In the present work, oxygen contamination can enter the niobium chloride by way of the niobium metal used in the synthesis. Tank chlorine used in the synthesis contains approximately 1000 ppm of oxygen, which may carry over into the niobium chloride. Since the niobium chloride is very hygroscopic, exposure to moist air results in oxychloride contamination. However, the use of careful handling techniques permits the control of this source of contamination. Niobium oxychloride is particularly harmful as a contaminant because of the comparable volatilities of the chloride and oxychloride. The vapor pressures of niobium chloride and niobium oxychloride are shown in Table 1. NbOCl_3 is probably soluble in liquid NbCl_5 . Whether it is soluble in the solid is questionable. Since a slight residue of NbOCl_3 is normally observed in the vaporizer at the end of a run, this compound is present as a separate phase at least during the later stages of the run. In this condition, with the assumption of equal saturation efficiency, the last column of Table 1 gives the contamination to be expected from this source.

When it was recognized late in this report period that most of the contamination of the coating was being introduced via the chloride, a study was initiated designed to improve the techniques of chloride preparation and purification. A preliminary discussion of this work is included in the section "Preparation and Purification of Niobium Pentachloride".

*Electrolytic Grade, Air Reduction Sales Company.

**Deoxo Purifier, Model "D" 100-50, Baker and Company, Inc., Newark 5, New Jersey.

***The Lectrodryer Dehumidifier, Type BAC, Size 25, Pittsburgh Lectrodryer Division, McGraw Edison Company, Pittsburgh, Pennsylvania.

****Hydrogen Purifier, Model HPD-150-400C (150 ft³ per hr), Engelhard Industries, Inc., Newark, New Jersey.

TABLE 1. VOLATILITY OF NbCl_5 AND NbOCl_3 ⁽⁷⁾

Temperature, C	P_{NbCl_5} , mm of mercury	NbOCl_3 - NbCl_5 Pressure Ratio	Oxygen-Niobium Weight Ratio, ppm
100	0.62	0.0037	630
120	2.46	0.0049	840
140	8.51	0.0066	1300
160	26.3	0.0084	1450
180	73.3	0.0106	1800
190	117.5	0.0120	2060

In order to avoid the permanent absorption of hydrogen, it is necessary to terminate a niobium-coating run by cooling the bed in an atmosphere of inert gas (helium is preferred). This operation requires special attention since, if not done carefully, it can lead to agglomeration of the bed. It has been observed that any abrupt change in operating conditions can lead to agglomeration of the bed. Therefore, it is necessary to reduce the chloride-feed concentration slowly before making the change from hydrogen to helium.

The procedure used to initiate a run takes cognizance of the ability of niobium to react with any oxygen that may be present in the oxide in excess of the stoichiometric composition $\text{UO}_{2.00}$. Although, on the basis of Glassner's data⁽⁸⁾, the reaction

is thermodynamically unfavorable, the fact that products of the above reaction will be in solid solution in the niobium must be considered. If it is assumed as a first approximation that the activity of the uranium in solution is one-half that of the NbO , the activity obtained for the NbO is $a_{1250 \text{ K}} = 0.0003$. Since the solubility limit for oxygen (see p 26) is only about 0.2 to 0.4 w/o, this activity represents a negligible contamination by oxygen.

In contrast, oxygen in excess of $\text{UO}_{2.00}$ is relatively loosely bound. On the basis of data published by Belle and Lustman⁽⁹⁾, even the reaction

is very favorable. Thus, to minimize contamination of the coating by nonstoichiometric $\text{UO}_{2.0X}$, the material is fluidized in hydrogen at temperature for about 1/2 hr before the niobium chloride feed is introduced. No quantitative data are available on the need for such a treatment. It has been adopted as a simple precaution against one form of contamination.

Fluidizing in hydrogen offers little problem when the bed is composed of uncoated UO_2 . However, if a bed of niobium-coated UO_2 is being subjected to another coating step, considerable difficulty may be experienced in getting the coating run started. Changing abruptly from helium to hydrogen at operating temperature inevitably results in agglomeration of the bed. If trouble is experienced, a useful procedure is to change from helium to hydrogen gradually at a low temperature, 700 to 750 C, and to initiate the chloride feed at a low rate before raising the reactor to operating temperature.

The problem of maintaining the fluidization of niobium-coated UO_2 in pure hydrogen is not fully understood. Nor have any attractive agglomeration mechanisms been suggested. The problem is not confined to coated particles prepared by the present process, but becomes characteristic of niobium particles from any source as the particle size is decreased. However, a bed containing residual chloride is more sensitive than a clean bed of the same particle size. The problem is one of violent slugging of the bed, or, in severe cases, loss of fluidization which can only be recovered by immediately switching over to helium. It is generally agreed among those having experience with this problem, that the presence of niobium chloride in the feed vapor tends to smooth out the action of the bed. Thus, it can be judiciously used as a "lubricating" agent. It should, however, be introduced only under reducing conditions to avoid formation of lower chlorides by reaction of NbCl_5 with the niobium of the bed.

Whether or not the variation in gas density is the only factor involved in this behavior is uncertain at this point.

Current Procedure for Coating Uranium Dioxide Powder With Niobium

The apparatus for coating uranium dioxide particles with niobium by hydrogen reduction of niobium pentachloride is assembled as shown in Figure 6. The niobium pentachloride vaporizer, charged as described under the section entitled "Preparation and Purification of NbCl_5 ", page 15, is purged with either hydrogen or helium during connection of the ball joint (D) to the mating part on the reactor. A flow of either hydrogen or helium is maintained at a rate of about 3 liters per min, while the cap (J) is removed and the UO_2 (50 to 100 g) is poured into the reactor. After the cap is replaced, the reactor furnace (N) is heated to 850 C at the bottom section and 800 C at the top section. The hydrogen flow rate is adjusted so that the level of the fluidized bed reaches the center of the furnace. A hydrogen flow equal to about one-tenth of the total is passed through the NbCl_5 vaporizer which is then heated to about 140 C. The exhaust gas is bubbled through 100-ml portions of water at L to collect the HCl formed in the reaction*. The solution is removed and replaced with water every 15 min. The HCl solution is titrated against 3 N NaOH using a phenolphthalein indicator. A titration of 15 to 25 ml of NaOH equivalent to 3 to 6 g per hr of niobium is considered to be the normal operating range. The NbCl_5 vaporizer temperature is increased or decreased to vary the feed rate as indicated by the titration. In general, a steady increase in vaporizer temperature (usually starting at 140 C and finishing at 165 C) is required, since the NbCl_5 powder sinters together, decreasing its effective surface area. This decreases the degree of saturation of the carrier gas.

When the desired amount of niobium metal has been deposited, as indicated by the titration (a 10 per cent allowance is made generally for the niobium deposited as a foil on the wall and for partially reduced chloride), the power to the NbCl_5 boiler is interrupted, and the boiler is allowed to cool slowly under a continued flow of hydrogen. The bed may stick if the boiler is cooled too rapidly. If this occurs, helium is immediately substituted for hydrogen and the reactor is cooled. The bed becomes fluid again on cooling

*A word should be said in defense of the absence of a trap to prevent back-diffusion of water vapor from the HCl absorber to the reactor. The flow of hydrogen through the system is sufficiently rapid to prevent back diffusion. This was demonstrated by the fact that NbCl_5 placed in the last dust trap was not discolored by hydrolysis during a run.

FIGURE 6. APPARATUS FOR COATING UO_2 WITH NIOBIUM

and, if these steps are taken quickly, little if any agglomeration occurs. To insure removal of excess chlorides it is desirable to treat an agglomerated bed with hydrogen. The material is removed, passed through an appropriate sieve, and transferred to a clean reactor and again heated to 850 C using a helium atmosphere during heating to avoid hydriding. When the reactor has reached operating temperature, hydrogen is substituted for helium, and the bed is fluidized for about 1/2 to 1 hr to remove residual chloride. It is interesting to note that the majority of the residual chloride is not removed by washing with water and/or ethyl alcohol. It is also noteworthy that a coated bed containing chloride residue is sticky and may slug violently when the hydrogen is substituted for helium at operating temperature. The residual chloride is removed slowly and the fluidization of the coated powder becomes smooth at least for $>75\text{-}\mu$ particles when the last trace of chloride is evolved (determined by checking a sample of solution from the water bubbler with AgNO_3). The coated powder is then cooled in a helium atmosphere to avoid hydriding.

The normal product will contain small pieces of foil and occasionally a few glass chips originating from fracture of the inner surface of the reactor wall by adherence of glass to the foil which separates from the wall as the reactor is cooled. The bulk of these contaminants can be removed by screening and by rolling the bed in a beaker. With the latter technique, static charges cause the foil and the glass chips to stick to the beaker wall. The coated particles are poured into a clean beaker and this is repeated several times.

Several more complicated cleaning techniques have been tried, such as funneling the particles through a capillary against a countercurrent of water. Since the glass and the foil are less dense or present greater surface than the coated UO_2 , the water flow can be adjusted so that most of the foil and glass will not fall through the capillary. Another technique is to funnel the coated particles (dry) through a capillary and let them bounce off of the bottom of an overturned 100-cm³ beaker which has been placed in a 500-cm³ beaker; the two being contained in a 2-liter beaker. The coated particles bounce farther than the foil or glass, and the cleaned fraction is caught in the 2-liter beaker; coated material richer in foil and glass is caught in the 500-cm³ beaker, and this is reprocessed. Several passes are required for a reasonable separation. In both of these latter methods, some glass and foil are carried along by collision with the coated powder and complete separation is not obtained. Consequently, the latter two methods are seldom used, in view of the simplicity of the technique of screening and rolling the coated bed in a beaker.

Preparation and Purification of Niobium Pentachloride

Niobium pentachloride is prepared by direct chlorination of niobium metal in the apparatus shown in Figure 7. About 600 g of niobium in the form of powder or pressed pellets is placed in the reactor. After purging with purified helium for 1 hr or more, the reactor and re-entrant tube are heated to 600 C. The helium flow rate is set at about 1/2 liter per min and then chlorine is introduced. The chlorine flow rate is increased until excess chlorine is evolved, as indicated by the rate of bubbling in the butyl phthalate trap. Niobium pentachloride condenses as a fine yellow "snow" in the condenser and falls into the attached flask. Occasional vibration of the condenser is required to loosen chloride powder from the walls.

FIGURE 7. NbCl_5 PREPARATION APPARATUS

A chloride production rate of about 100 g per hr is obtained under the above conditions. Since this rate was adequate to supply the required amount of niobium pentachloride, no attempt has been made to determine the optimum conditions for chlorination.

The niobium pentachloride is purified by use of the single-plate distillation apparatus shown in Figure 8. A flask, filled with niobium pentachloride from the preparation unit, and a receiver constituting the vaporizer to be used in the coating work are attached. After the system is purged with helium, the pentachloride and the line connecting the flask to the condenser are heated to 254 to 270 C. The helium inlet is closed and hydrogen is introduced. Hydrogen is used as a blanket during distillation because it is the purest gas available. The niobium pentachloride condenses as a yellow powder. About 75 per cent of the niobium chloride is boiled over and a 25 per cent heel is discarded.

The degree of purification obtained by this technique is not known, since no analytical techniques are immediately available for NbOCl_3 in NbCl_5 , and analyzing for oxygen in niobium-coated UO_2 has many problems. However, on the basis that NbOCl_3 is soluble in NbCl_5 and is less volatile, purification is to be expected. It was hoped that hardness of the coating would be an accurate indication of oxygen content of the feed material. However, as indicated on page 26, complications exist here and additional work is required to resolve the picture.

Coating Porosity

Figure 9 shows typical niobium-coated particles in the as-polished and etched conditions. In general, the coatings appear to be dense and impervious, consisting of 1 to 10- μ equiaxed grains.

Since moderate porosity short of incomplete surface coverage was permissible in the coated powder prepared in the present work, and since no incompletely coated particles have ever been observed in microsections of $\geq 8\text{-}\mu$ niobium-coated particles, only limited attention to coating porosity could be justified. However, it was thought desirable to devise a simple test which would measure the porosity of the coatings.

Since UO_2 is rapidly soluble in 50 per cent HNO_3 solution, to which niobium metal is inert, leaching in nitric acid and analyzing the leach solution for uranium appeared to be a useful procedure. In this procedure, a weighed sample (about 0.02 g) of the coated UO_2 was placed in a small test tube and covered with 6 or 7 cm^3 of 50 per cent HNO_3 . The test tube was permitted to stand in a water bath at 95 to 100 C for an arbitrary period of 7 hr for the purpose of dissolving any UO_2 dust that may have been picked up in removing the sample from the reactor*. After this preliminary leaching, the sample was washed and covered with 6 to 7 cm^3 of 50 per cent HNO_3 and was permitted to leach for 7 hr at 95 to 100 C. At the end of this time, the solution was decanted and subjected to uranium analysis by the fluorescent disk method.⁽¹⁰⁾ Table A-1 of the Appendix gives porosity data taken on 0.02-g samples of most of the lots of niobium-coated powder prepared in this program.

*Owing to the possible presence of contained dust and to the grinding action of fluidization, a small amount (<1 per cent) of UO_2 dust may be blown out of the reactor into the disentrainment section prior to the niobium-coating formation. Some of this material may be sifted into the product on its removal. The amount of dusting encountered at this point will vary with the past history of a given lot of powder.

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FIGURE 8. SINGLE-PLATE NbCl_5 DISTILLATION APPARATUS

In order to obtain information useful in minimizing coating porosity, a regression analysis of the effects of the process and product variables on the porosity was undertaken.

Among the variables which were thought to affect the porosity were the thickness of the coating, excess-hydrogen ratio, feed rates, particle size, bed weights, deposition temperature, and run number (insofar as it might reflect improvements in operating procedure). In the absence of a theoretical model to which a semiempirical equation could be ascribed, a simple linear effect of these variables on the film porosity was assumed. The final correlating equation is:

$$\begin{aligned}\epsilon = & -1.384 + 0.0011 N - 0.0034 R_{H_2} - 0.0121 W_{NbCl_5} \\ & + 0.0115 W_{H_2} - 0.0018 W_B - 0.0005 S_B \\ & + 0.0018 T_B + 1.867/t_f ,\end{aligned}$$

where

ϵ = porosity of coating, 0.000 to 3.620 per cent

N = number of experiments, 1 to 89

R_{H_2} = excess-hydrogen ratio, 29 to 211

W_{NbCl_5} = chloride feed rate, 8.3 to 39.0 g per hr

W_{H_2} = hydrogen feed rate, 15.4 to 66.0 g per hr

W_B = weight of bed, 44 to 101 g

T_B = bed temperature, 700 to 950 C

t_f = film thickness, 0.8 to 45 μ .

The significance of the variables can best be illustrated by referring to Table 2. The partial correlation coefficients are a measure of the dependence of the porosity on the process variables. The absolute value of the correlation coefficient lies between zero and unity, and the sign of the coefficient indicates whether or not the value of the dependent variables is increased or decreased by an increase in the value of the independent variable. When the coefficient has a value near zero, there is no linear correlation between the dependent and independent variable. If the coefficient has a value of approximately unity, a high degree of correlation is involved.

It can be seen that the only significant variable is coating thickness. By substituting the average value of the other variables into the general correlating equation, a simplified correlation for the effect of coating thickness (t_f) is obtained:

$$\epsilon = -0.221 + 1.867/t_f .$$

Thus, when the coating thickness is approximately 8.5 μ , the porosity of the film is essentially zero. The effects of the other variables can only be estimated as to whether

250X

N54535

As Polished

600X

N54843

Etched in 10 HF-10 HNO₃-30 Lactic Acid

- a. 12- μ Niobium Coating on Minus 100 Plus 140-Mesh
UO₂, Lot 15177-3

FIGURE 9. TYPICAL NIOBIUM-COATED UO₂ PARTICLES

250X

N59123

As Polished

250X

N59018

Etched in 10 HF-10 HNO₃-30 Lactic Acid

- b. 50- μ Niobium Coating on Minus 120 Plus 140-Mesh
UO₂, Lot 15177-37C

FIGURE 9. (Continued)

TABLE 2. EFFECTS OF VARIABLES^(a) ON COATING POROSITY

Variable	Variable		Regression Coefficient		Partial Correlation Coefficient, $r_{io.j}$	Levels of Variable		Porosity Change Due to Increase of Variable, $\Delta\epsilon_i$ at X_j ($i \neq j$)
	Average Value, $\bar{X}_i$	Standard Deviation, S_{X_i}	Average Value, b_i	Standard Deviation, S_{b_i}		Low, $\bar{X}_i - S_{X_i}$	High, $\bar{X}_i + S_{X_i}$	
Run Number	32.1	± 20.1	+0.0011	± 0.0045	+0.041	12.0	52.2	+0.045
Excess-Hydrogen Ratio	90.6	± 36.8	-0.0034	± 0.0044	-0.126	53.8	127.4	-0.250
NbCl ₅ Feed Rate, g per hr	19.7	± 5.9	-0.0121	± 0.0208	-0.095	13.8	25.6	-0.143
Hydrogen Feed Rate, g per hr	31.3	± 8.6	+0.0115	± 0.0134	+0.140	22.7	39.9	+0.197
Weight of Bed, g	87.4	± 20.7	-0.0018	± 0.0039	-0.073	66.7	108.2	-0.073
Particle Size, U.S. mesh	133.7	± 32.0	-0.0005	± 0.0024	-0.034	101.7	165.7	-0.032
Deposition Temperature, C	855.4	± 38.3	+0.0018	± 0.0021	+0.138	817.1	883.7	+0.137
Film Thickness, μ^{-1}	0.215	± 0.275	+1.867	± 0.307	+0.707	-0.060	0.490	+1.027

(a) The statistical terminology is of general usage; see, for example, Mood, A. M., Introduction to the Theory of Statistics, McGraw-Hill Book Company, New York (1950), 433 pp.

or not they increase or decrease the porosity, and the estimate itself is rather poor. This analysis points to the tentative conclusion that high excess-hydrogen ratios, high bed weights, and large particle sizes favor decreased porosity, and that high hydrogen feed rates, and high deposition temperatures, result in increased porosity.

The reason for the poor correlation of data from lots of thick-coated ($>8 \mu$) particles is evident from the data in Table 3, which show the variations among 0.02-g samples taken from the same lots of 8 to 10- μ niobium-coated particles. It is evident that the leaching of UO_2 from a sample results not from a homogeneous distribution of porosity, but from the occasional incidence of several uncoated or poorly coated particles in a sample of several thousand particles. These results imply that acid leaching may be a practical method of removing poorly coated particles from a lot prior to use, without the danger of general degradation.

TABLE 3. POROSITY OF SELECTED SAMPLES OF NIOBIUM-COATED UO_2

Lot	Sample	Coating Thickness, μ	Number of Particles in Original Sample	Equivalent Number of Particles Leached	UO_2 Removed, per cent
16490-1	a	8-10	1520	0.30	0.020
-1	b	8-10	880	0.15	0.017
-1	c	8-10	970	$<0.010^{(a)}$	$<0.001^{(a)}$
-1	d	8-10	1130	<0.011	<0.001
15177-27	a	8-9	1520	1.7	0.112
-27	b	8-9	1120	<0.011	<0.001
-27	c	8-9	960	<0.010	<0.001
-27	d	8-9	1090	0.011	0.001
15176-46	a	8	910	<0.003	<0.001
-46	b	8	590	<0.006	<0.001
-46	c	8	380	<0.004	<0.001
-46	d	8	400	<0.004	<0.001

(a) 0.001 per cent = lower limit of analysis.

To obtain data on the feasibility of this approach and on the progress of leaching as a function of time, samples were chosen from three lots which showed low, medium, and high porosity in the initial tests. These samples were leached in 50 per cent HNO_3 at 95 C for successive periods of 0.25, 0.75, 2, and 6 hr with intermediate decanting of the leach solutions and rinsing of the powder in distilled water. The leach solutions were analyzed for uranium as before with the results given in Table 4 and Figure 10.

These data show that a considerable fraction of the leaching occurs in the first few minutes, and that there is limited value in the results of the test described above in which a 7-hr unmonitored conditioning leach preceded the 7-hr leach period for which the data were taken. It is also obvious that a more gentle washing procedure should be used to remove occluded UO_2 dust prior to leach testing.

FIGURE 10. LEACHING OF NIOBIUM-COATED UO₂

TABLE 4. LEACHING OF NIOBIUM-COATED UO_2

Lot	UO_2 Particle Size	Niobium Coating Thickness, μ	Leach Period, hr	Per Cent UO_2 Leached	Leach Rate, per cent per hr	UO_2 Leached in Second 7-Hr Period, per cent
15177-31B	-140+270 mesh, 80- μ average diameter	24 (contained some 2 to 8- μ coatings)	0.25	1.75	7.0	1.38
			0.75	0.55	0.73	
			2.0	0.98	0.49	
			6.0	1.57	0.26	
15177-32B	-140+200 mesh, 90- μ average diameter	8 (contained some 2 to 3- μ coatings)	0.25	16.72	67	0.111
			0.75	0.89	1.2	
			2.0	0.69	0.34	
			6.0	0.43	0.07	
16490-3	-80+100 mesh, 160- μ average diameter	8 to 10 (normal product)	0.25	0.087	0.35	0.0039
			0.75	0.026	0.037	
			2.0	0.011	0.0055	
			6.0	0.002	0.0003	

It is interesting to note the difference in the rates of leaching of the powders with the porous nominal 8- and 24- μ coatings. It appears that the leaching of the particles with the nominal 8- μ coatings (containing some particles with 2 to 3- μ coatings), though high, had leveled off after 6 hr. The progressive leaching of the nominal 24- μ product is probably the result of the observed presence of 4 to 8- μ -coated particles in this lot. Its leaching would be expected to level off when the porous particles have been consumed.

Additional data would be needed to evaluate the nitric acid leach as a culling procedure. However, the method appears to be quite promising.

It is expected that, as the coating of UO_2 with $>8 \mu$ of niobium becomes routine, the incidence of more than 0.1 per cent of poorly coated particles will become rare. Indeed, of 34 lots of $\geq 8\text{-}\mu$ niobium-coated UO_2 for which data were available in the present work, only seven showed leaching in excess of 0.01 per cent in the 7-hr leach test described above. In each of these cases, an abnormality in the conduct of the preparation was noted. In three of these (Lots 15177-27, -28, and 16490-1), the run had to be terminated for one reason or another and the product removed, cleaned, and the coating completed in a second step. In two cases (Lots 15177-4 and -25) the reactor broke on shutdown, and the product may have been partially oxidized, or subjected to thermal shock. At least, the product was not relieved of absorbed hydrogen in an orderly manner. In one of the remaining runs (Lot 15177-31B), early sintering of part of the bed (17 g) occurred, with the result that some 2 to 3- μ -coated particles were included in the product. In the run with Lot 15177-31B, the niobium-foil deposit folded away from the reactor wall early in the run. A large portion of the bed was isolated from the mainstream of the feed vapor during the run, and many particles having coating thicknesses between 2 and 8 μ were observed in the product. In none of the other 27 runs were these troubles experienced.

Considering the facts that coatings of $<8\text{-}\mu$ thickness tend to be porous, and that a void structure is frequently observed between successive coatings, the porosity of the duplex $\geq 8\text{-}\mu$ coatings is easily explained. It would be interesting to subject some coated powder to thermal shock in a protective atmosphere to determine whether coated particles can be defected in this manner.

Hardness Measurements and Metallography
of Niobium-Coated UO₂

Knoop hardness measurements were made on cross sections of coated particles with a Tukon hardness tester. A 5-g load was used in all but the few cases in which it was impractical to do so. The as-deposited hardnesses are given in Table A-1 of the Appendix. Variation of hardness numbers with the load was determined on as-cast samples of niobium having hardness numbers ranging from 60 to 400 VHN as measured in a Vickers hardness tester (5-kg load). The data are given in Figure 11.

Samples of coated UO₂ were prepared for microscopic examination and hardness measurement by mounting about 0.1 g in Bakelite. The mounted samples were ground on 400- and then 600-grit silicon carbide paper, and given a fine polish on a cloth-covered wheel, using a water slurry of Linde B. The polished samples were given a light etch with an etchant consisting of 30 ml lactic, 10 ml nitric, and 10 ml hydrofluoric acids.

The coated samples were microscopically examined for roughness of the coating surface, uniformity, thickness, and porosity.

A discrepancy between the coating thickness, calculated on the basis of the weight of metal deposited, and that directly measured, was observed for some of the earlier lots. The microscopic thickness measurements indicated a coating thickness perhaps twice that of the weight-based thickness. This discrepancy was resolved when it was noted that coatings having an actual thickness of less than 5 μ could be folded over or smeared when polished causing a greater apparent thickness. This difficulty was circumvented by etching after polishing which readily removed the smeared and/or folded sections of the coating. Microscopic thickness measurements were then obtained which were in excellent agreement with the calculated thickness.

It would be highly desirable to use the as-deposited hardness as a measure of the coating purity. At the coating temperature, 800 to 1000 C, oxygen and nitrogen have limited solubility in niobium. The data of Seybolt⁽¹¹⁾ and of Elliott⁽¹²⁾ on oxygen solubility are conflicting. However, it is certain that oxygen or nitrogen contamination beyond the solubility limit would not be reflected in a hardness increase. Thus, since hardnesses in the range of the solubility limits were being obtained (up to 200 VHN, 5-kg load), it was desirable to determine whether or not undissolved contaminants were present.

Attempts to reproducibly heat treat samples wrapped in niobium foil at 1050 C (200 C above the preparation temperature) in vacuum gave considerable scatter in the observed hardening, presumably because of contamination of the coatings during the vacuum treatment. Although quantitative results were not obtained, it appeared from differences in the hardness increases of samples treated together, that solution hardening was indeed taking place.

As noted above, the coatings were of the right order of hardness for the intended use. Thus, no additional work on coating hardness was justifiable in this program.

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FIGURE 11. KHN VERSUS VHN FOR AS-CAST NIOBIUM

Purity of Niobium Coatings

As indicated in the section on coating-hardness measurements, a minimum of attention was given to the question of coating purity, since few problems arose during the evaluation of the coated powders which could be related to the purity of the coating. However, several analyses were made to obtain spot data for future reference. Table 5 gives spectrographic analyses of a niobium coating and the niobium metal from which the chloride was prepared.

TABLE 5. SPECTROGRAPHIC ANALYSIS OF NIOBIUM COATING

Impurity	Analysis of Lot 16490-3, ppm	
	Feed Metal(a)	Coating
Iron	100	100
Boron	<30	20
Silicon	<50	50
Magnesium	30	5
Vanadium	<30	300
Copper	70	30
Silver	<10	30
Aluminum	<30	500
Calcium	100	10
Tantalum	10,000(b)	3000-6000

(a) The NbCl_5 prepared from this feed material was used in Sample 16490-3 as synthesized without further purification.

(b) Estimated without standards.

It is believed that purification of the NbCl_5 , particularly with respect to boron and tantalum, can be accomplished by fractional distillation as the need arises.

Since analysis of the niobium-coated UO_2 powder for oxygen would be difficult at best, an effort was made to correlate the composition of the powder coating with that of the niobium foil that deposits on the reactor walls during a run and separates from the wall on shutdown. Table 6 gives the resulting data.

TABLE 6. ANALYSIS OF COATED POWDER AND FOIL FOR INTERSTITIAL IMPURITIES

Impurity	Analysis of Lot 15176-51, ppm	
	Powder Coating	Foil
Nitrogen	<177	220
Carbon	105	270
Oxygen	--	1660 (870) ^(a)
Hydrogen	--	36

(a) Corrected for 790 ppm of oxygen assumed to be associated as UO_2 with the analyzed uranium content of the foil.

In view of the questionable correlation of carbon and nitrogen analyses, it is doubtful that the oxygen content of the foil is equal to that of the powder coating. However, it is to be noted that the level of oxygen contamination is consistent with the assumption that it originates as NbOCl_3 in the NbCl_5 feed (see Table 1).

At one point in the present work, considerable concern was expressed over the possible effects of residual chloride in the coating. A limited and unsuccessful attempt was made at Battelle to develop a technique for the analysis for chlorine in niobium in the 100 to 1000-ppm range. This effort was abandoned when work outside of Battelle indicated that residual chloride was not a problem.

Reduction Efficiency and UO_2 Recovery

Since the primary objective of the work described in this report was the preparation of experimental lots of coated powder for subsequent evaluation, almost no effort was directed toward a systematic investigation of factors affecting the rate of deposition, and hence the efficiency of chloride reduction. Because of the urgent demand for the coated product, it was felt that operation at workable but not necessarily optimum conditions was preferable to the delays which might occur in attempting to define the optimum conditions.

Typical and near-average conditions for the great majority of the niobium-coating work were bed temperature, 850 C; excess-hydrogen ratio, 90; bed weight, 100 g; hydrogen feed rate, 30 g per hr; and particle diameter, 130 μ . However, considerable variations of all variables except bed temperature were used during the coating program. This variation in conditions provided a somewhat random set of data (see Appendix, Table A-1) for subsequent analysis by regression techniques.

A simple linear model was again assumed for the effects of excess-hydrogen ratio, bed weight, hydrogen feed rate, and particle size on fractional conversion of NbCl_5 feed to metal deposited on the UO_2 powder. The best correlating equation for this linear model is:

$$x = 0.554 + 0.000083 D_p + 0.002434 W_B + 0.000793 R_{H_2} - 0.007682 W_{H_2} ,$$

where

x = fraction conversion of chloride to deposited metal, 0.415 to 0.866

D_p = particle diameter, 88 to 196 μ

W_B = weight of bed, 56 to 131 g

R_{H_2} = excess-hydrogen ratio, 37 to 134

W_{H_2} = hydrogen feed rate, 15.4 to 41.2 g/hr range.

The significance of these variables can be best illustrated by reference to Table 7. The two most significant variables are bed weight and hydrogen feed rate, thus indicating the process is controlled by space velocity or contact time. Hence, the experimental

TABLE 7. EFFECT OF VARIABLES ON CHLORIDE CONVERSION

Variable	Variable		Regression Coefficient		Partial Correlation Coefficient, $r_{io,j}$	Levels of Variable		Conversion Change Due to Increase of Variable, $\bar{X}_j (i \neq j)$
	Average Value, $\bar{X}_i$	Standard Deviation, S_{X_i}	Average Value, $\bar{b}_i$	Standard Deviation, S_{b_i}		Low, $\bar{X}_i - S_{X_i}$	High, $\bar{X}_i + S_{X_i}$	
Particle Size, μ	128.4	± 32.5	+0.000083	± 0.000535	+0.024	95.9	160.9	+0.005
Weight of Bed, g	98.7	± 23.8	+0.002434	± 0.000871	+0.404	74.9	122.5	+0.116
Excess-Hydrogen Ratio	87.6	± 23.9	+0.000793	± 0.001064	+0.117	63.7	111.5	± 0.038
Hydrogen Feed Rate, g per hr	29.4	± 5.4	-0.007682	± 0.004925	-0.239	24.0	34.8	-0.083

conversions would be expected to be considerably below the equilibrium conversion levels which could be obtained in deeper beds. Previous data have shown that excess-hydrogen ratios of 92 and 62 should result in essentially complete conversions at bed temperatures of 800 and 950 C, respectively.⁽⁶⁾ Whether the present small-scale coating results are actually controlled by kinetic or heat-transfer effects is open to speculation. It seems reasonable to assume that both effects are at least partially controlling.

The following simplified approximate equation can be obtained from the general correlation by using average values of the experimental excess-hydrogen ratios, particle sizes, and hydrogen feed rates:

$$x = 0.408 + 0.002434 W_B .$$

This equation predicts that a bed inventory of approximately 243 g would be required for essentially complete conversion to deposited metal. This bed inventory corresponds to a bed height approximately two and one-half times that used in the coating program described herein.

Although insignificant in the coating of natural UO_2 , the loss of UO_2 becomes significant when the coating of enriched UO_2 is considered. Thus, the data collected on UO_2 loss during the course of this work have been analyzed.

In most cases, the recovery of UO_2 as coated powder from a given run could be determined to be practically 100 per cent by visual observation. No reaction of $NbCl_5$ with the UO_2 appears to occur and niobium coating is initiated on feeding the chloride. Thus, losses are limited to dusting, sintering, and spillage. During the course of this work, UO_2 analyses were obtained on 47 lots of niobium-coated UO_2 (see Table A-1 of the Appendix). In 32 cases, the results indicated 100 ± 2 per cent recovery. When the results for the other 14 lots are considered critically, their indication of loss is shown to be questionable. Table 8 gives comments on the data for the 14 runs in question.

Incomplete solution of the coated powder in H_2SO_4 -HF-HCl- HNO_3 and possible entrainment of uranium in a niobium-bearing precipitate during the analytical procedure have been problems. Moreover, it is suspected that insufficient attention has been given to sampling for analysis. Owing to the fact that particles of different diameters receive coatings of equal thickness, particle-size segregation before sampling can give misleading results. For example, the UO_2 content of minus 100 plus 140-mesh material with 8- μ coatings can vary from 70.5 to 78.4 per cent over the range of particle size involved.

Thus, it appears that a critical effort would be necessary before the analysis of the product could be used as an adequate basis (± 0.1 per cent) for recovery data. It would be more reliable on the present small scale to collect the residues (foil, lower chlorides, and UO_2 dust) and analyze for UO_2 content.

Another significant recovery problem is presented by the sintered bed. This material is not lost, but, if enriched, must be sent through expensive reprocessing, all of which must be charged against the coating operation. Although difficulty was experienced with bed agglomeration, as indicated earlier in this report, and as indicated in the "Performance" column of Table A-1, sintering was not a great problem. In 68 runs in which 7,834 g of niobium-coated UO_2 was prepared, only 12 runs yielded any permanently sintered material (that which did not break up on a shaking screen). This amounted to only 88 g or 1.1 per cent of the total. In a routine operation, this figure would be expected to drop considerably.

TABLE 8. POSSIBLE EXPLANATIONS FOR HIGH LOSS OF UO_2 IN 14 NIOBIUM-COATED SAMPLES

Lot	UO_2 Recovered, per cent	Remarks
15177-16	95.5	Analysis suspect; poor check, additional sample requested but not supplied
-24	79.5	Analysis suspect; bed-weight gain, coating thickness, and product HCl titration agree to predict high recovery
-25	92.0	Ditto
-26	94.7	Some bed trapped behind loose foil during run; sample analyzed probably was not representative
-29	89.1	No analysis was made of 16.5 g of sintered product; if sintering occurred early in the run, analysis of bed (136 g) was not representative
-35	95.2	Real loss, reactor broke
-37C	96.4	Sintered material (8.9 per cent) not analyzed, see -29
-40A	89.9	Sintered material (4.9 per cent) from niobium undercoating Lot -38 not considered in analysis, see -29
15176-45B	97.2	Analysis in error or nonrepresentative; weight gain, HCl titer and coating thickness predict 100 per cent
-49	96.5	See -45B
-50	91.3	5.2 g of 50-g bed sintered, see -29
-53	96.7	Real loss, reactor broke
16490-1	104	?
-3	87.6	See -45B

On the basis of the data and general observations, it is concluded that yields of coated UO_2 well in excess of 99 per cent of the UO_2 charged should be attained in routine operation.

MOLYBDENUM AND TUNGSTEN COATINGS

The apparatus and procedure used for deposition of molybdenum and tungsten were identical to those used for the deposition of niobium, except in accounting for differences in the volatilities of NbCl_5 , MoCl_5 , and WCl_5 . The volatilities of NbCl_5 and MoCl_5 are nearly equal. However, in feeding WCl_6 , the vaporizer temperature must be maintained 50 to 60 C higher to give an equivalent feed rate. In general, the rate of coating with tungsten and molybdenum was held lower than that used for niobium since, in most cases, it was desired to overcoat a niobium-coated UO_2 powder with a 1- μ -thick tungsten or molybdenum coating. Consequently, a low rate of deposition was used to avoid "over-shooting" the desired amount.

Figure 12 shows an 8- μ -thick tungsten coating on minus 100 plus 150-mesh UO_2 . In general, the tungsten coatings were brighter and smoother than the niobium coatings.

CHROMIUM COATINGS

Several methods of coating UO_2 with chromium were given cursory investigation. They were (1) hydrogen reduction of CrCl_3 in a fluidized bed, feeding the halide as a solid, (2) vaporizing the equilibrium $\text{CrI}_2(\text{g})\text{-I}_2(\text{g})$ mixture from a slurry of UO_2 and liquid CrI_2 , (3) vapor deposition in a rotating evacuated de Boer bulb, (4) pyrolysis of $\text{Cr}(\text{CO})_6$ in a fluidized bed, (5) thermal dissociation of CrI_2 vapor in a fluidized bed, and (6) hydrogen reduction of CrI_2 vapor in a fluidized bed. The most promising results were obtained with (4) and (6).

A continuous uniform layer of chromium could be deposited on UO_2 by pyrolysis of $\text{Cr}(\text{CO})_6$ in a fluidized bed. However, the coating was impure, containing about 10 per cent carbide and oxide even under optimum coating conditions. The impure chromium was not considered suitable for the intended application, and this method of applying chromium coatings was abandoned.

Preliminary work with the hydrogen reduction of CrI_2 and of CrCl_2 and the thermal dissociation of CrI_2 produced spotty discontinuous chromium coatings on UO_2 indicating poor nucleation characteristics of UO_2 for chromium. In the hope of improving the nucleation characteristics, chromium was applied on a substrate niobium coating. A continuous chromium coating such as that shown in Figure 13 resulted. It was found that surface contamination of the niobium undercoat resulted in a discontinuous chromium layer, but that continuous chromium could be obtained on bright, clear niobium underlays. Lot 15176-84, in which oxidized and carburized niobium-coated particles were mixed with clean niobium-coated particles from Lot 15177-3, resulted in discontinuous coatings on all particles but those from Lot 15177-3. The chromium coating on the latter resembled that shown in Figure 13.

250X

As Polished

N59016

FIGURE 12. 8- μ TUNGSTEN COATING ON MINUS 100 PLUS 150-MESH UO_2 PARTICLES, LOT 15177-41B

250X

Etched in 10 HNO_3 -10 HF -30 Lactic Acid

N57574

FIGURE 13. 1.9- μ CHROMIUM COATING APPLIED OVER 12- μ -NIOBIUM COATING ON MINUS 100 PLUS 140-MESH UO_2 PARTICLES, LOT 15177-3Cr

The method of depositing chromium by hydrogen reduction of chromous iodide consisted of feeding iodine carried by helium to an ampoule containing high-purity iodide-chromium crystals* attached to the bottom end of a fluidized-bed reactor. A fraction of the iodine reacted with the chromium metal forming an equilibrium mixture of chromous iodide and iodine. The rate of iodine feed was adjusted so that concentration of chromous iodide was below saturation to prevent its condensation. The conditions for the latter were determined by trial and error. The mixture of helium, chromous iodide, and unreacted iodine was contacted with hydrogen within the bed. Reaction of hydrogen with the iodine to form HI shifted the equilibrium in the direction of chromium deposition. Since the iodine content of the vapor leaving the chromium feed was unknown, titration of the HI produced gave only an upper limit for the rate of chromium deposition.

The apparatus used for coating niobium-coated UO_2 with chromium by hydrogen reduction of CrI_2 is shown in Figure 14. About 1 lb of resublimed iodine crystals was placed in the boiler (A) and 100 to 200 g of chromium crystals was placed in the bulb (D). Fifty to one hundred grams of niobium-coated UO_2 was added through the cap (L), while a flow of about 3 liters per min of helium was maintained through the reactor. The reactor and the chromium container were heated to 850 to 880 C using helium for fluidization. When the reactor was at temperature, hydrogen flow at a rate of 2.5 liters per min was started through the center tube (H). Helium was passed through the iodine vaporizer at a flow rate of 1 liter per min, and the iodine was heated to 60 to 90 C. The rate of iodine feed was monitored by bubbling the exhaust gas through water and periodically measuring the quantity of dissolved HI by titrating with 3 N NaOH. A titration of 4 to 8 cm^3 per 15-min period was considered normal. There was little correlation between the titration and actual quantity of iodine feed in several of the runs. This may be traced to variations in the CrI_2 reduction efficiency. However, the titration was informative as to whether the iodine feed rate was constant, increasing, or decreasing when an attempt was being made to hold the operating conditions constant during a run.

Coating runs were terminated by cooling the iodine vaporizer to room temperature and then interrupting the flow of helium through the vaporizer. At this point, the hydrogen flow was stopped, and the reactor was cooled under a helium atmosphere.

PYROLYTIC CARBON COATINGS

Exploratory work was done on the deposition of carbon coatings on UO_2 by the pyrolysis of hydrocarbons in a fluidized bed of the coated powder contained in the apparatus shown in Figure 15.

At the time of writing this report, data were being obtained on the rate of coating formation and on coating porosity as a function of process variables such as temperature and hydrocarbon type and concentration. This information will constitute the subject of a later report. However, it may be tentatively concluded that, at deposition temperatures in the range of from 1000 to 1200 C, acetylene is superior to methane, benzene, or propane in terms of coating rate and relative freedom from by-product soot which eventually plugs the reactor system downstream of the bed.

*High-purity iodide-process chromium crystals marketed as "Iochrome" by the Chromalloy Corporation.

FIGURE 14. APPARATUS FOR COATING UO_2 WITH CHROMIUM

AEA-33315

FIGURE 15. APPARATUS FOR COATING UO_2 POWDER WITH CARBON

The coating shown in Figure 16 is typical, with the exception of the peripheral void which does not always appear. It is suspected that this void resulted from the abrasion during polishing of loose UO_2 which had been formed by the reduction of non-stoichiometric surface oxide. It would be interesting to subject the powder to a preliminary hydrogen reduction in an effort to form an improved UO_2 structure or to permit the abrasion of the loose UO_2 before coating.

Owing to the difference in the thermal expansion of pyrolytic carbon (2×10^{-6} per C) and UO_2 (10×10^{-6} per C), approximately 1 per cent relative diameter shrinkage on cooling from coating temperature to room temperature can be expected. However, this does not account for the large void shown in Figure 16.

The latest data on the preparation of pyrolytic carbon show that the rate of carbon deposition is greatly increased by preheating the gases to a temperature just below that at which decomposition takes place. Moreover, the tendency toward soot formation is reduced by increasing the bed depth.

Porosity data were limited at the time of writing of this report. However, it may be stated that coatings of 5μ or less appear to be relatively porous, while $8\text{-}\mu$ coatings appear to be equivalent to the better niobium coatings.

NIOBIUM CARBIDE AND NIOBIUM-CARBON LAMINATED COATINGS

Several attempts were made (Lots 15176-60 through -69) to prepare various laminated coating structures of niobium, niobium carbide, and carbon by the hydrogen reduction of NbCl_5 with simultaneous or alternate introduction of various hydrocarbons. Under no conditions was it possible to produce a laminate structure at 850 C, carbon diffusion apparently being too rapid at this temperature.

A single attempt to prepare a Nb/NbC/Nb laminate at 700 C showed some promise. However, the need for such structures decreased, and this phase of the work was concluded.

ALLOY COATINGS

Exploratory work has been recently undertaken on the deposition of alloy coatings by the coreduction of mixed metal halide vapors. The first to be studied is the niobium-vanadium system. As in the case of the pyrolytic carbon coating, these results will be the basis of a separate report to be issued when more data become available.

Briefly, the preparation of niobium-vanadium-alloy coatings is accomplished in a quartz reactor of the design shown in Figure 6. However, in this case, the VCl_4 in a helium carrier is brought downward through an axial vapor-injector tube similar to the hydrogen inlet in the chromium-plating apparatus of Figure 14. Since VCl_4 is explosively reduced by hydrogen to a solid lower chloride, it cannot be premixed in the manner

250X

N66010

FIGURE 16. TYPICAL PYROLYTIC CARBON COATING ON MINUS 140 PLUS 230-MESH UO_2

of the NbCl_5 . It may be possible to use a helium carrier for the mixed chlorides, in which case the hydrogen fluidizing gas could be injected separately. However, this alternative has not been explored owing to a concern over potential difficulties.

One problem that deserves some mention is that of controlling the VCl_4 feed rate. VCl_4 appears to be a nonstoichiometric liquid as prepared by chlorination of vanadium metal. It is certain that excess vanadium volatility (probably as VOCl_3 , although VCl_5 is not completely ruled out) exists in the as-prepared material. This excess can be eliminated by purging a fresh vaporizer charge with helium prior to its use. VCl_4 has a significant equilibrium chlorine pressure at room temperature. As it is vaporized, solid VCl_3 accumulates in the vaporizer. This decomposition, apparently light-sensitive, is also evident in VCl_4 on standing in loosely sealed containers.

The presence of the second condensed phase, VCl_3 , stabilizes the Cl/V ratio in the vaporization product at constant temperature, and a steady feed is obtained once the precipitate is formed. Whether any solubility of VCl_3 in VCl_4 exists to give a region of variable vapor composition is uncertain. A study of the volatility and stability of VCl_4 is being undertaken to provide a basis for intelligent handling of this material.

Because of the greater stability of vanadium chloride as regards its hydrogen reduction to metallic vanadium, care must be taken to avoid the deposition of VCl_2 in the particle coating. This can be done by increasing the excess-hydrogen ratio over that used in niobium deposition, or by increasing the deposition temperature. The use of a deposition temperature of 1050 C is currently preferred for the formation of niobium-5 w/o vanadium alloy coatings.

COMPRESSION TESTS OF UO_2 PARTICLES

It was desirable to have a method of measuring the fabricability of the niobium-coated UO_2 powder. The data would be useful to determine the quality of the deposited metal. In addition, a comparison of the compressive strength of the coated particle and the uncoated particle could be made to determine the possible deterioration of the base material in the coating process.

The gross stress-strain characteristics of niobium-coated and uncoated UO_2 powder were measured by adaptation of a commercial tensile-testing unit. Figures 17 and 18 show details of the adaptation. The tensile-test unit was used to gradually supply and measure force on an individual particle placed between a stirrup and anvil. The stirrup was connected to the core of a differential transformer for electronic measurement of the displacement. A wire-and-spring combination was used to connect the transformer core and stirrup assembly to the load cell of the tensile machine to reduce the rate of loading. The load cell and differential transformer signals were fed to an X-Y recorder. The loading, as recorded on the y-axis, was calibrated with the appropriate weights (100 to 500 g). Displacement, as recorded on the x-axis, was calibrated by moving the differential transformer a distance of 1 mil measured by the micrometer which supported it. Displacement calibrations were made with the stirrup pulled against the anvil with a force of 100 g to insure that the transformer core would remain fixed while the transformer was moved. Care was taken to operate with the relative positions of core and transformer in the region of linear response.

- A. Mosley Autograph x-y recorder (5 mv-100 v).
- B. Leeds and Northrup portable potentiometer.
- C. Ballantine Model 310A electronic voltmeter.
- D. Raytheon voltage regulator, Serial No. G-589, 95-130 v, 60 w.
- E. Model 200CD Hewlett-Packard audiooscillator.
- F. Raytheon voltage regulator, 95-130 v, 120 w, Serial No. 6354.
- G. Schaevitz Type 010M-L differential transformer.

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FIGURE 17. AUXILIARY EQUIPMENT FOR COMPRESSION-TESTING UNIT

FIGURE 18. THREE VIEWS OF COMPRESSION-TESTING EQUIPMENT

FIGURE 19. COMPRESSION TESTS OF INDIVIDUAL NIOBIUM-COATED AND UNCOATED UO₂

After the unit was calibrated, a series of "dry runs" was made to determine the magnitude of deformation of the anvil and stirrup. A typical standardization curve is given in Figure 19. It can be seen that the deformation of the apparatus is small relative to that obtained with a sample of uncoated UO_2 .

For carrying out the compression test, a single particle of coated or uncoated UO_2 was placed on the stirrup. This was accomplished by use of a glass rod having an end pulled down to a tip of about 3 mils in diameter. The tip of the rod was touched to a lightly oiled cloth and then brought in contact with a single particle of UO_2 . A drop of alcohol was placed on the stirrup with an eyedropper, and the oiled tip of the glass rod holding the single particle was brought in contact with the alcohol. This released the particle on the stirrup. A slowly increasing load was then applied to the particle until fracture occurred.

Typical curves obtained for uncoated and coated particles are shown in Figure 19. The plastic deformation of the ductile coating is easily discerned.

The full potentialities of this evaluation procedure had not been realized at the time of writing this report. However, it is expected that the method will prove useful in evaluating the fabricability of individual coating particles as a function of process variables.

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JMB:NDV:JHO:VMS:EER/mmk

APPENDIX

SUMMARY OF DATA ON COATING OF UO_2 POWDER

TABLE A-1. SUMMARY OF DATA

Lot	UO ₂ Mesh Size	Bed Weight, g	Coating Material	Reactor Temperature, C	Hydrogen Flow Rate, g per hr	Excess-Hydrogen Ratio	Reactant Flow Rate, g per hr	Run Time, hr	Performance(a)	Bed(b)
15177-1	-100+140	100.0	Nb	950	66.0	18.7	NbCl ₅ 19 g	6.0	A	--
-2	-100+140	100.0	Nb	950	16.5	17.0	51.4	2.0	A	--
-3	-100+140	102.7	Nb	950	16.7	34	26.4	9.0	B, C	--
-4	-100+140	100.0	Nb	950	21.0	29	39.0	5.0	C, E	--
-5	-100+140	100.0	Nb	950	32.7	67	26.5	4.0	D	--
-6	-100+140	100.0	Nb	850	34.0	153	12.0	2.0	A	--
-7	-140+200	100.0	Nb	850	38.7	190	11.0	2.0	A	--
-8	-100+140	100.0	Nb	850	43.5	60	39.0	3.0	A	--
-9	-100+200	100.0	Nb	850	34.0	92	20.0	1.5	A	--
-10	-100+200	101.0	Nb	850	48.0	78.5	33.0	4.0	D	--
-11	-100+200	100.0	Nb	850	28.5	120	12.8	3.5	C	--
-12	-100+140	100.0	Nb	850	32.1	101	17.1	2.75	B	--
-13	-140+170	100.0	Nb	700	32.0	211	8.3	6.5	B	--
-14	-140+170	100.0	Nb	800	30.5	85.5	19.2	3.75	B	71.9
-15	-140+170	100.0	Nb	900	30.5	104	15.8	4.5	C, E	--
-16	-140+200	100.0	Nb	850	31.3	128	13.7	4.5	D (0.9)	88.6
-17	-140+200	100.0	Nb	850	30.5	97	14.4	5.25	A	77.5
-3Cr	-100+140	64.0	Cr	880	12.8	--	--	4.0	A	--
-18	-140+200	100.0	Nb	850	32.5	123	14.1	5.5	C	83.5
-19	-100+140	100.0	Nb	850	32.7	137	12.9	5.0	D (0.0)	85.9
-20	-100+140	100.0	Nb	850	32.7	128	13.8	5.5	A	78.7
-21	-100+140	100.0	Nb	850	32.7	154	11.3	4.4	C	77.6
-22	-140+170	100.0	Nb	850	34.0	98	17.0	6.0	A	--
-23	-80+100	100.0	Nb	850	40.2	114	18.7	9.7	A	84.9
-24	-80+100	100.0	Nb	850	41.2	116	19.2	8.4	C, E	74.2
-25	-100+150	100.0	Nb	850	34.0	129	14.3	10.0	C, E	88.5
-26	-100+150	100.0	Nb	850	42.5	132	17.3	7.0	D (4.9)	83.2
-27	-100+150	100.0	Nb	850	36.4	79.3	23.0	7.25	A	75.8
-28	-140+270	100.0	Nb	850	32.0	98.0	17.6	14.0	C, D (0.49) E	89.0
-29	-140+270	109.4	Nb	850	40.5	104	21.0	9.0	C, D (10.3)	85.4
-30A	-140+270	100.0	Nb	850	33.1	78	12.5	7.0	A	84.0
-30B	-140+270	68.5	Nb	850	26.6	65.7	21.2	6.75	A	91.4
-30C	-140+270	68.5	Nb	850	25.8	78.8	15.5	5.75	D (1.6)	86.1
-31A	-140+270	50.0	Nb	850	28.7	78.3	19.7	8.0	D (5.9)	79.5
-31B	-140+270	50.0	Nb	850	27.0	107	13.6	9.0	D (13.7)	75.2
-32A	-140+200	50.0	Nb	850	25	88	15.1	6.75	A	84.6
-32B	-140+200	50.0	Nb	850	25.4	72	19.0	6.75	D (22.4)	85.2
-33	-100+140	100.0	Nb	850	31.4	111	15.0	9.0	A	93.5
-34	-80+100	100.0	Nb	850	32.8	89	17.8	6.75	A	84.6
-35	-100+140	100.0	Nb	850	35.3	97	15.9	10.7	A	68.8
-36	-100+140	100.0	Nb	850	27.2	69.4	21.1	7.25	D (0.0)	92.0
-37	-120+140	100.0	Nb	850	25	58.7	23.2	8.5	C, E	92.0
-37A	-120+140	73.2	Nb	850	24.2	71	18.4	11.25	A	88.6
-37B	-120+140	64.0	Nb	850	26.0	58.5	24.0	8.0	D (0.0)	82.0
-37C	-120+140	67.5	Nb	850	28.0	78.6	19.2	12.75	D (8.9)	83.1
-37D	-120+140	73.2	Nb	850	26.0	71.6	19.7	10.25	A	89.6
-37E	-120+140	65.0	Nb	850	26.7	71.3	20.3	11.25	A	--
-37F	-120+140	65.0	Nb	850	27.4	72.6	20.5	10.5	A	85.3
-38	-100+140	47.7	Nb	850	29.5	72.5	18.0	6.0	D (4.6)	69.0
-39	-100+140	44.1	Nb	850	24.7	67.2	19.9	5.8	A	77.2
-40	-100+140	58.5	W	750	29.4	176	WCl ₆ , 11.0	1.0	A	90.4

ON COATING OF UO_2 POWDER

Efficiency, per cent Over-All(c)	UO_2 Recovery(d), per cent	Coating Thickness, μ	Coating Hardness (5-Kg Load)(e), VHN	Porosity(f), per cent UO_2 in second leach	Surface Roughness(g)	Remarks
--	--	5-6	218	0.41	B	
--	--	1	310	--	D	
--	--	12	128	<0.001	C	Bed from -2
--	99.8	10	111	0.09	C	
--	101.8	6.5	165	0.002	C	
--	100.0	1.2	--	--	C	
--	100.1	0.8	--	1.68	--	
--	100.1	2.1	121	0.19	C	
--	--	0.8	--	3.62	--	
--	100.7	3.2	130	0.002	C	Bed from -9
--	100.2	1.3	--	0.013	B	
--	--	1.7	150	--	C	
--	--	2.4	149	0.027	D	
72.0	--	2.9	97	0.136	--	
--	--	4.8	179	0.089	C	
74.4	95.5	3.6	90	--	C	
66.5	--	3.0	103	0.083	C	
--	--	1.9	--	--	--	Hydrogen reduction of CrI_2 on bed from Run -3 (Nb)
68.2	--	3.2	152	1.60	C	
73.8	--	4.7	163	--	C	
67.0	--	4.9	114	0.33	B	
--	--	5.2	132	0.59	B	
--	--	2.8	90	<0.001	C	
69.0	--	11.0	115	0.0011	B	
55.9	79.5	9.0	114	--	B	
97.9	92.0	9-10	--	0.038	--	
94.7	94.7	3 and 8	122	<0.001 (8μ)	B	
80.7	98.6	8-9	125	0.001, 0.112	B	
81.0	102.1	9.0	118	0.027	B	
89.7	89.1	8.5	118	0.004	B	
--	--	--	146	0.01, 0.06	D	
66.4	100.9	11.0	--	--	--	Bed from -30A
79.0	98.9	9.5	124	--	C	Bed from -30A
81.1	100.0	9.5	110	--	C	
75.1	--	3 and 24	169	1.38	B	
(100)	101.2	7.6	132	--	C	
79.8	101.6	8.4	119	0.111	C	
88.0	98.2	8	133	--	C	
80.0	100.0	8.5	90	<0.001	C	
76.0	95.2	9	131	--	C	
81.7	98.6	9	112	<0.001	C	
79.9	--	--	--	--	--	
88.6	--	--	--	--	--	Bed from -37
79.2	102.0	47	123	0.0016	C	Bed from -37A
82.1	96.4	52	175	0.0036	C	Bed from -37A
91.6	--	--	--	--	--	Bed from -37
--	99.7	46.	131	0.008	D	Bed from -37D
80.9	101.0	46.	175	<0.001	D	Bed from -37F
61.8	--	8	--	0.0014	--	
75.0	--	11	119	0.0018	B	
76.7	99.4	1.0	--	--	--	Bed from -39

TABLE A-1.

Lot	UO ₂ Mesh Size	Bed Weight, g	Coating Material	Reactor Temperature, C	Hydrogen Flow Rate, g per hr	Excess-Hydrogen Ratio	Reactant Flow Rate, g per hr	Run Time, hr	Performance ^(a)	Bed ^(b)
15177-40A	-100+140	50.8	Cr	880	12.8	--	--	2.0	D (10.2)	--
-41A	-100+150	49.5	W	750	25.1	152	WCl ₆ , 11.7	5.3	A	--
-41B	-100+150	75.0	W	750	26.1	158	WCl ₆ , 10.9	3.3	A	--
-42	-100+150	49.5	W	750	25	140	WCl ₆ , 11.4	6.0	A	--
-43	-100+140	100.0	Nb	850	30.6	104	NbCl ₅ , 15.9	10.0	A	--
15176-44	-100+140	100.0	Nb	850	30.4	80.3	20.4	7.25	A	89.2
-45A	-140+200	50.0	Nb	850	15.5	43.6	19.2	7.5	A	83.2
-45B	-140+200	50.0	Nb	850	15.4	37.4	22.2	7.25	A	71.4
-46	-80+100	100.0	Nb	850	28.8	77.8	20.0	6.25	A	84.6
-47A	-140+200	50.0	Nb	850	27.0	73.4	19.9	8.0	A	85.8
-47B	-140+200	50.0	Nb	850	27.3	65.2	22.6	8.25	A	81.5
-48A	-140+200	50.0	Nb	850	27.0	63.2	23.1	8.75	A	80.5
-48B	-140+200	50.0	Nb	850	26.9	75.4	22.6	8.25	D (6.2)	78.9
-49	-140+200	50.0	Mo	800	18.0	156	MoCl ₅ , 6.3	3.5	A	--
-50	-140+200	50.0	Mo	800	22.2	166	MoCl ₅ , 7.3	2.25	A	--
-51	-100+140	100.0	Nb	850	30.1	89.9	NbCl ₅ , 18.1	9.0	A	88.7
-52	-80+100	100.0	Nb	850	25.9	73.0	19.2	7.25	A	88.0
-53	-140+170	50.0	W	850	13.4	34.3	WCl ₆ , 2.6	0.75	A	--
-54	-80+100	98.5	Nb	850	31.7	93.1	NbCl ₅ , 18.4	7.75	A	91.1
-55	-100+140	100.0	Mo	800	29.7	211	MoCl ₅ , 7.7	3.0	A	--
-56	-100+140	100.0	Nb	850	28.0	85	NbCl ₅ , 17.8	3.5	C	90.3
-57	-100+140	133.2	W	800	32.0	454	WCl ₆ , 4.66	3.0	A	--
-58	-100+140	100.4	Nb	850	32.0	102.2	NbCl ₅ , 16.9	9.0	D (0.0)	87.9
-59	-100+140	133.8	W	800	32.0	406	WCl ₆ , 5.2	2.5	A	--
-60	-140+170	50.0	NbC	960	--	--	CH ₄ , 39.4 He, 22.7	7.5	A	--
-61	-140+170	50.0	NbC	975	--	--	CH ₄ , 85 He, 21.4	5.0	A	--
-62	-140+170	50.0	NbC	1000	--	--	CH ₄ , 94	1.0	A	--
-63	-140+170	50.0	NbC	850	21.4	81.4	NbCl ₅ , 14.2 CH ₄ , 0.475	5.0	A	--
-64	-140+170	50.0	NbC	850	22.9	78.6	NbCl ₅ , 15.2 CH ₄ , 1.0	4.75	A	--
-65	-140+170	50.0	NbC	850	22.9	101	NbCl ₅ , 12.2 CH ₄ , 30.3	4.0	A	--
-66A	-140+170	50.0	NbC	970	--	--	C ₆ H ₆ , 8.2 He, 15.2	1.0	A	--
-66B	-140+170	49.8	NbC	980	--	--	C ₆ H ₆ , 30.1 He, 15.2	0.75	A	--
-66C	-140+170	50.0	NbC	960	--	--	C ₆ H ₆ , 90.4 He, 15.2	0.25	A	--
-67	-140+270	45.6	NbC	850	9.1	46.4	NbCl ₅ , 10.6 C ₆ H ₆ , 19.6 He, 12.8	3.5	A	--
-67A	-140+270	53.7	NbC	850	5.82	18.6	NbCl ₅ , 16.9 C ₆ H ₆ , 14.6 He, 4.82	2.25	A	--
-68	-100+140	50.0	NbC	700	9.1	30.5	NbCl ₅ , 16.1 C ₆ H ₆ , 20.0 He, 7.5	4.17	A	--

(Continued)

Efficiency, per cent Over-All ^(c)	UO ₂ Recovery ^(d) , per cent	Coating Thickness, μ	Coating Hardness (5-Kg Load) ^(e) , VHN	Porosity ^(f) , per cent UO ₂ in second leach	Surface Roughness ^(g)	Remarks
--	89.9	1-5	--	--	--	Bed from -38
--	--	6-7	--	--	--	
--	--	8-9	--	--	--	Bed from -41A
--	--	6-7	--	--	--	
--	100.9	8	199	<0.001	B	
81.7	98.2	8	126	0.0012	D	
73.5	99.8	8.5	102	<0.001	C	
65.8	97.2	8	110	<0.001	C	
71.0	98.6	8	150	<0.001	C	
77.3	98.8	9-10	118	<0.001	B	
59.1	98.6	8.5	118	<0.001	B	
55.4	--	8-10	110	--	C	
80.5	--	7-8	123	0.009	C	
--	96.5	1.0	--	--	--	Bed from -48A
--	91.3	1.0	--	--	--	Bed from -48B
79.5	--	8-9	109	<0.001	C	
78.9	100.1	8-10	102	0.004	B	
55.8	96.7	0.1	--	--	--	Bed from -15
76.1	99.9	8-10	118	0.0014	B	
94	99.3	1.0	--	--	--	Bed from -51
79	--	9 calculated	114	<0.001	A	
96	101	0.5 calculated	--	--	--	Bed from -56
83.5	--	8-10	132	<0.001	B	
88	99.3	0.5 calculated	--	--	--	Bed from -58
--	--	1.	--	--	--	Bed from -13
--	--	1.	--	--	--	Bed from -14
--	--	<0.1	--	--	--	Bed from -13
--	--	5	--	--	--	
--	--	5	--	--	--	
--	--	4-5	--	--	--	
--	--	<0.1	--	--	--	Bed from -22
--	--	1.	--	--	--	Bed from -66A
--	--	1.	--	--	--	Bed from -22
--	--	1.	--	--	--	Bed from -15
--	--	2-4	--	--	--	Bed from -67
--	--	6	--	--	--	Bed from -6

TABLE A-1.

Lot	UO ₂ Mesh Size	Bed Weight, g	Coating Material	Reactor Temperature, C	Hydrogen Flow Rate, g per hr	Excess-Hydrogen Ratio	Reactant Flow Rate, g per hr	Run Time, hr	Performance(a)	Bed(b)
15176-69	-140+200	50.0	NbC	850	12.7	38.2	NbCl ₅ , 18.0 C ₆ H ₆ , 22.9 He, 7.5	3.0	A	--
-70	-140+170	100.0	C	1000	--	--	CH ₄ , 57.2 Ar, 427	18	A	--
-71	--	99.8	W	800	31.8	248	WCl ₆ , 5.1	5.5	A	--
-72	-100+140	121.5	Cr	850	12.8	165	I ₂ , 9.8 He, 14.8	4.5	B, D (22.6)	--
-73	-100+140	110.2	Cr	895	12.8	159	I ₂ , 10.2 He, 14.8	3.25	C	--
-74	-100+140	102.0	Cr	885	12.8	167	I ₂ , 9.7 He, 58.8	4.75	A	--
-75	-100+140	121.8	Cr	885	12.8	124	I ₂ , 13.1 He, 85.6	2.75	D (1.8)	--
-75A	-100+140	115.9	Cr	890	12.8	135	I ₂ , 12.0 He, 58.8	2.5	A	--
-75B	-100+140	117.0	Cr	890	12.8	176	I ₂ , 9.2 He, 58.8	3.5	A	--
-76	-140+170	100.0	C	1100	--	--	CH ₄ , 55.7 He, 27.8	3.0	F	--
-77	-140+170	100.0	C	1100	--	--	CH ₄ , 55.7 He, 27.8	8.0	A	--
-78	-60+100	64.6	Cr	890	12.8	208	I ₂ , 7.8 He, 14.8	3.0	A	--
-79	-100+140	49.7	Cr	950	12.8	208	I ₂ , 7.8 He, 14.8	2.5	D (0.0)	--
-79A	-100+140	47.5	Cr	895	12.8	129	I ₂ , 12.6 He, 14.8	1.5	D (0.0)	--
-80	-80+100	100.0	Nb	850	51.8	174	NbCl ₅ , 16.1	3.7	B	--
-81	-80+100	72.8	Nb	850	49.2	85	NbCl ₅ , 31.2	2.5	B	--
-82	-80+100	50.0	Nb	850	45.6	143	NbCl ₅ , 17.2	2.5	A	--
-83	-100+140	100.0	Nb	850	32.9	110	NbCl ₅ , 16.1	3.7	A	--
-84	-80+140	59.8	Cr	885	12.8	226	I ₂ , 7.2 He, 69	3.4	D (20.0)	--
-85	-80+140	84.1	Cr	840	4.0	149	CrI ₂ , 4.1 He, 53.5	4.75	D (0.7)	--
-86	-80+100	68.1	C	1200	--	--	CH ₄ , 53.6 He, 21.5	1.0	A	--
16490-1	-100+140	100.0	Nb	850	35.1	125.5	NbCl ₅ , 15.1	9.0	D (6.75)	--
-2	-100+140	126.0	W	800	36.0	149.5	WCl ₆ , 9.54	3.25	A	--
-3	-80+100	100.0	Nb	850	35.5	106	NbCl ₅ , 16.4	7.8	C	--

Footnotes appear on the following page.

(Continued)

Efficiency, per cent Over-All(c)	UO ₂ Recovery(d), per cent	Coating Thickness, μ	Coating Hardness (5-Kg Load)(e), VHN	Porosity(f), per cent UO ₂ in second leach	Surface Roughness(g)	Remarks
--	--	4.5	--	--	--	Bed from -7
--	--	3-4	--	--	--	
99	--	1-2	--	--	--	Nb coating applied outside BMI
--	--	1	--	--	--	Ditto
--	--	Discontinuous coating	--	--	--	Bed from -4, -5, -6, -7
--	--	Discontinuous coating	--	--	--	Bed from -73
--	--	Discontinuous coating	--	--	--	Nb coating applied outside BMI
--	--	Discontinuous coating	--	--	--	Bed from -75
--	--	Discontinuous coating	--	--	--	Bed from -75A
--	--	Bed oxidized	--	--	--	
--	--	1-2	--	96.1	--	
--	--	Discontinuous coating	--	--	--	Cr crystals (2.39 Cr) were mixed in the bed to check possible transfer of Cr to UO ₂
--	--	Discontinuous coating	--	--	--	Bed from -74 with 4.5 g Cr crystals mixed with the bed
--	--	Discontinuous coating	--	--	--	Bed from -74, pickled in HCl to remove Cr
--	--	4	1207 (KHN, 25-g load)	0.60	B	NbCl ₅ contaminated with car- bonaceous material
--	--	8	1845 (KHN, 25-g load)	--	C	Bed from -80, NbCl ₅ contami- nated with carbonaceous material
--	--	12	550 (KHN, 25-g load)	<0.001	A	Bed from -81
--	100.3	4-5	133	<0.001	A	
--	--	Discontinuous and con- tinuous coating	--	--	--	Bed from -3 (10.1 g), -80 (15 g), -81 (15 g), -82 (15 g), and outside BMI (4.7 g)
46	--	Discontinuous and con- tinuous coating	--	--	--	Bed from -3 (40.75 g), -81 (14.1 g), and -82 (29.25 g)
--	--	2	--	Rapid reaction with 6 N HNO ₃	--	
--	104	8-10	120	0.020	B	
90.5	--	2	--	--	--	Nb coating applied outside BMI
--	87.6	8-10	137	0.0039	B	

Footnotes for Table A-1

(a) Performance:

- A. Good fluidization (boiling bed); no difficulty during entire run.
- B. Poor fluidization (slugging bed), required constant attention.
- C. Bed sintered during shutdown; no agglomeration after cooling in helium.
- D. Bed partially or totally sintered during run; percentage of material remaining agglomerated after cooling in helium and after screening is given in parentheses; where the weight of permanent sinter was not recorded, no parenthetical figure is given.
- E. Reactor broke on cooling; coating slightly oxidized.
- F. Reactor broke during run; bed oxidized.

(b) Fraction of product on bed, based on weight gain.

(c) Fraction of feed as product on bed and foil.

(d) Based on analysis of product, see p 31 in text.

(e) Converted from light-load KHN, see "Hardness Measurements and Metallography of Niobium-Coated UO_2 " in text.

(f) See "Coating Porosity" in text.

(g) Surface roughness code, see Figure A-1.

A-33817

FIGURE A-1. SURFACE-ROUGHNESS CLASSIFICATION