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RHENIUM AND RHENIUM–TUNGSTEN DEPOSITION BY THERMOCHEMICAL REDUCTION OF THE HEXAFLUORIDES—A PRELIMINARY STUDY

F. W. HOERTEL* and J. G. DONALDSON

Rolla Metallurgy Research Center, Bureau of Mines, U.S. Department of the Interior, Rolla, Mo. 65401 (U.S.A.)

Summary

Near-optimum parameters were determined by the Bureau of Mines for vapor deposition of rhenium on heated copper substrates by hydrogen reduction of rhenium hexafluoride (ReF_6). High-purity deposits of nearly 90% theoretical density were obtained with the reaction chamber at 250 °C, with a H_2 to ReF_6 volume ratio of 25 to 1, and with a ReF_6 flow rate of 5 grams per hour. Some rhenium deposited as a loose, black powder. When the established near-optimum parameters were carefully followed, this could be minimized but never completely avoided. Varying the reaction chamber pressure, both above and below atmospheric, yielded excessive quantities of rhenium powder. Deposition efficiencies, based on only the coherent metal, ranged between 70 and 75%. Massive deposits contained only spectrographic traces of impurities. The average microhardness (Knoop, 100-gram load) of vapor-deposited rhenium was 907.

Limited research on the deposition of rhenium–tungsten alloys by reduction of the mixed hexafluorides produced deposits in which linear composition gradients were pronounced; this nonhomogeneity was attributed to the wide variation in optimum hydrogen-reduction temperatures of the two hexafluorides (250 °C for ReF_6 and 550 °C for WF_6). Using deposition temperatures between 250 ° and 550 °C did not eliminate the composition variations.

Introduction

Rhenium, one of the less-plentiful elements and classified, along with manganese and technetium, in Group VII B of the Periodic Table, has become important as a refractory metal. During the past 10 years, much effort has been expended toward recovery of larger quantities of this metal and toward development of procedures for its fabrication.

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*Now retired.

In 1925 rhenium was discovered in Germany by Noddack, Tacke and Berg [1]. Rhenium sources and recovery methods were investigated by Churchward and Rosenbaum [2], in 1963, to delineate potential reserves of this metal. In 1959 the Committee on Refractory Metals of the National Research Council [3] estimated that 12,000 pounds of rhenium could be produced annually from the current production of molybdenite from porphyry copper operations in the United States. Also in 1959, the Rhenium Panel of the Committee on Refractory Metals of the Materials Advisory Board [3] estimated the potential rhenium output of the free world at approximately 20,000 to 30,000 pounds annually.

Because of its properties, choice of rhenium for an increasing number of refractory metal applications is promising. Rhenium's high melting point (3,167 °C) is second only to that of tungsten (3,370 °C) among the metals; it has a low vapor pressure near its melting point; it has good strength and ductility at elevated temperatures; it does not exhibit a ductile to brittle transition; and recrystallized rhenium retains its ductility even at cryogenic temperatures. In addition, rhenium has a high resistance to the detrimental reaction between electronic or electrical filaments in vacuum or inert gas and small amounts of residual water vapor present as an impurity.

Sims [4] states that rhenium is unique among refractory metals in that it does not form a stable carbide. He states further that although rhenium absorbs enough carbon in solution to become rather brittle, it retains structural shape and does not crumble to powder like other refractory metals that form carbides (tungsten, molybdenum, tantalum, columbium) when exposed to a carbonaceous atmosphere. Rhenium does not tarnish at room temperature; it does, however, oxidize severely in air in a manner reminiscent of molybdenum. This oxidation reaction starts at about 600 °C, and the rate increases rapidly with increasing temperature. Rhenium reacts readily with nitric acid, but its resistance to sulfuric acid is good, and it has a high resistance to hydrochloric acid. Alkalies, particularly fused alkalies, readily attack rhenium.

Rhenium may be electrodeposited from aqueous solutions. Port [5] states that thin-walled tubing and shapes can be produced by vapor deposition accomplished by the thermal dissociation of rhenium pentachloride or rhenium hexafluoride vapors. However, the most common production practice is the hydrogen reduction of ammonium perrhenate.

Sanderson [6] reports that rhenium hexafluoride (ReF_6) may be reduced with hydrogen at 250 °C. Federer, Heestand, Patterson and Leitten [7] state that rhenium and rhenium–tungsten alloys were vapor deposited by the hydrogen reduction of the metal hexafluorides in the range of 500 ° to 1,000 °C at 5 to 20 Torr. A search of available literature did not produce any other references concerning the reduction of ReF_6 by hydrogen.

The present investigation was undertaken to explore the feasibility of vapor-depositing rhenium and rhenium–tungsten composites by the thermochemical reduction of gaseous hexafluorides with hydrogen and to establish certain near-optimum parameters for these processes. The thermodynamics

of a reaction between ReF_6 and hydrogen are favorable above 25 °C (298 °K).

$ReF_6 + 3H_2 \rightarrow Re + 6HF$
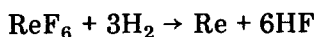
$\Delta F (\quad 298 °K) - 255 \text{ kcal} - 0 \rightarrow 0 + (-388 \text{ kcal})$

$\Delta F (1,000 °K) - 222 \text{ kcal} - 0 \rightarrow 0 + (-393 \text{ kcal})$.

Knowledge of the effects of certain vapor-deposition process variables on some of the properties of the deposited rhenium should provide a basis for the evaluation of the process and should lead to the greater realization of the potential of vapor deposition as a fabrication method. The preliminary nature of the studies limited delineation of all the potentially important variables of this process.

This report describes limited, laboratory-scale, basic experiments by the Bureau of Mines on the following process variables: temperature and pressure in the reaction chamber, the volume ratio of H_2 to the ReF_6 and discontinuous deposition.

Materials and method

Equipment and materials

The equipment, reagents and procedures for this research are, in general, similar to those used earlier at the Bureau's Rolla Metallurgy Research Center for producing high-purity tungsten [8], for coating rocket nozzles with vapor-deposited tungsten [9] and for determining the effects of certain process parameters on vapor-deposited tungsten [10]. Figure 1 is a general view of the laboratory equipment used in the rhenium deposition work.
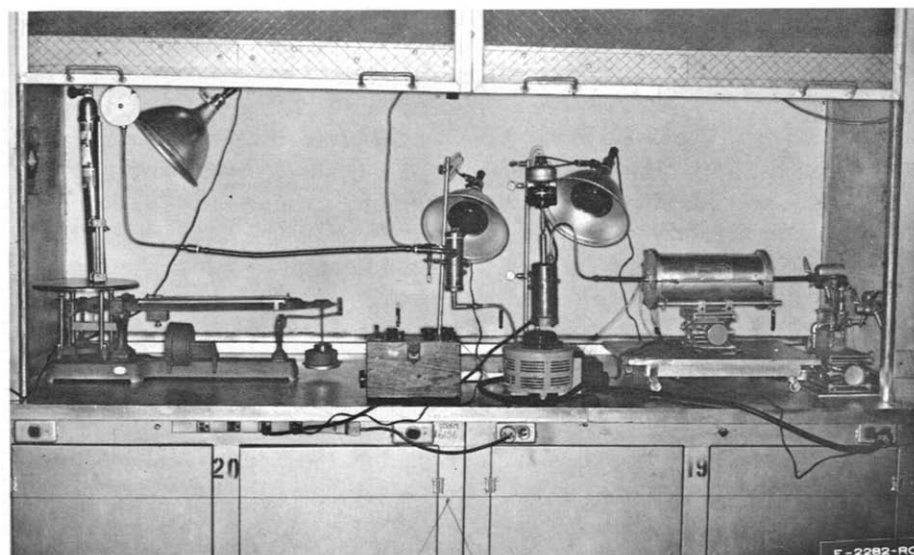

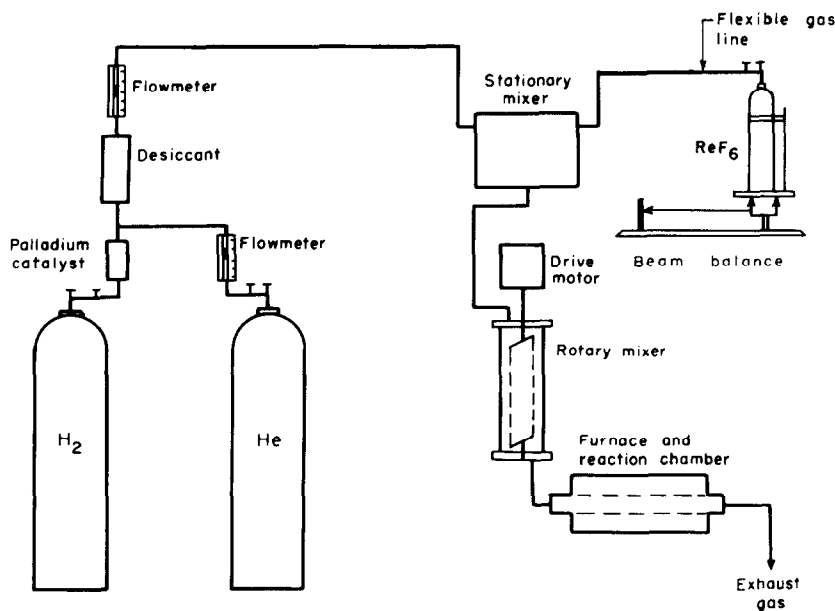Fig. 1. Equipment for vapor-deposition.

Fig. 2. Apparatus assembly used in vapor-deposition work.

The apparatus assembly consisted essentially of a reaction chamber in a tube furnace, a stationary and a rotating gas-mixer, gas flowmeters and a modified solution balance. These components and accessories are shown in Fig. 2.

The reaction chambers were sections of copper tubing of diameter and length selected to best serve the needs of each experiment. The majority of the deposition test work was done with chambers of 1/2-inch-o.d. copper tubing, although 1-inch-o.d. copper tubing was used in some of the work. The temperature of the reaction chamber was controlled by regulating the electrical current input to the heating furnace with a variable autotransformer. Temperature measurement equipment included a thermocouple, thermometers and a potentiometer.

Commercially produced ReF_6 in small steel cylinders was the source of rhenium in the deposition work. A Monel* needle valve was attached to the cylinder outlet to permit more precise flow control than was possible with the cylinder valve alone.

Teflon tubing, previously found suitable to transfer tungsten hexafluoride (WF_6), reacts with ReF_6; therefore, a flexible Monel tube was used between the ReF_6 cylinder and the first mixing chamber inlet to make the balance beam operative and permit continuous weighing of the cylinder during an experimental run.

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*Use of brand names is to facilitate understanding and does not imply endorsement by the Bureau of Mines.

Malm and Selig [11] give the boiling point of ReF_6 as 33.68 °C. According to their data the pressure in the ReF_6 cylinder would be approximately 25.5 p.s.i.g. when the cylinder and its contents are at 50 °C. Tests showed that a steady flow of the fluoride gas could be maintained when the cylinder was at this temperature and, therefore, all tests were made with the gas distributing equipment at 50 °C. No effort was made to purify the commercial ReF_6, and no analysis of this material was available from the producer.

Prepurified-grade hydrogen, 99.9% minimum purity, was used as the reducing agent. Grade A helium, having total impurities of about 20 parts per million, was used as the purge gas and was used to provide an inert atmosphere.

The flow rate of the ReF_6, in grams per hour, was determined continuously by weighing the cylinder. Calibrated glass-bodied flowmeters were used to measure the flow rates of the hydrogen and the helium.

Two types of gas-mixing units were used in the test work. One, a simple stationary-mixing unit (shown assembled in Fig. 1, and disassembled in Fig. 3 of the preceding paper) was constructed from an Inconel tube 2-1/2 inches in diameter and about 7 inches in length. Inconel inlets for the ReF_6 and hydrogen were attached to the tube near the upper end; this end was closed with a solid Inconel cap. The bottom end incorporated the mixed-gas outlet tube. The rotary mixer, which was placed in series with the stationary mixer, had a body constructed from a short section of copper pipe 2-1/2 inches in diameter and 6 inches in length. A copper cap was permanently attached to the top of the unit, and a threaded, removable closure constituted the bottom. A four-vaned copper stirrer attached to a 1/4-inch diameter Monel shaft was positioned inside the mixer. The lower end of the shaft rested in a Teflon end-thrust bearing, mounted in the removable closure. The upper end of the shaft passed through a 3-inch-long Teflon combination seal and bearing that was mounted on the outside of the top of the unit. A copper sleeve about 3 inches in length and 1 inch in diameter was fastened to the shaft by setscrews and was slip-fitted over the Teflon bearing. A silicone lubricant was placed between the inner surface of the copper sleeve and the outside of the Teflon bearing. This lubricant also acted as a second gas seal. A gas inlet was placed at the top of the mixer, and a gas outlet was provided at the bottom of the unit. The stirrer was rotated at approximately 1,700 r.p.m. The mixer is shown in the preceding paper; assembled (Fig. 4) and disassembled (Fig. 5).

The gas distributing lines, with the exception of the flexible line attached to the ReF_6 cylinder, were made of 1/4-inch copper tubing. Monel valves and copper-coated fittings were used throughout the system. Heat lamps were used during each run to maintain the temperature of the gas distribution system at 50 °C, to prevent ReF_6 condensation.

Description of deposition technique

After the laboratory apparatus was assembled for a vapor-deposition experiment, the system was purged with helium. A small amount of this gas

was kept flowing through the assembly while the reaction tube was brought to the desired temperature, which was then kept constant by regulating the electrical current to the tube furnace. Hydrogen was then introduced into the system, the flow of helium was discontinued and the ReF_6 was introduced. When the experiment was completed, the ReF_6 flow was discontinued, the power to the heating furnace was shut off and the deposit was allowed to cool to room temperature in hydrogen.

When the deposit had cooled, the hydrogen flow was discontinued, the system was purged with helium, the reaction chamber was taken from the furnace, the copper tube was slit and mechanically stripped from the deposit, and the deposit was weighed. The appearance of several deposits indicated the presence of byproduct material on the surface. These deposits were washed and dried before weighing.

Data on the weight of the deposits and the amount of ReF_6 used to produce each deposit were used for calculating process efficiencies. Samples of some of the deposits were submitted for metallographic study and Knoop microhardness tests. The microhardness tests were made on a Tukon hardness tester with a Knoop diamond indentor under a 100-gram load. Analysis showed representative deposits to contain spectrographically detectable traces of calcium, copper, iron, magnesium, manganese, nickel and silicon. The presence of most of these impurities may be attributed to a slight attack by ReF_6 on the heated metal section of the gas transport line and the reaction tube.

Description of typical deposits

The duration of most deposition experiments was limited, for economic reasons, so that the thickness of the rhenium ranged from 10 to 20 mils. After some of the near-optimum deposition parameters had been established, the thickness of several deposits was increased to approximately 100 mils (2.5 millimeters).

Reduction of the gas mixture always produced some black metal powder, which deposited near the consolidated rhenium. When the near-optimum temperature and H_2 to ReF_6 volume ratio were used, the amount of black, uncompacted metal was usually small and was concentrated near the exit end of the reaction chamber. This powder was not occluded by the dense metal. The metal was usually smooth and bright, varying in color from light to dark gray.

Figure 3 shows a microstructure typical of depositions made at near-optimum parameters; the black spots in the micrograph are voids in the structure. Specific gravity values of three bright, compact, rhenium deposits were determined by water displacement; these values, 18.44, 18.37 and 18.79, are 88, 88 and 89% respectively of the theoretical specific gravity value of 21.0. Voids in the deposits (see Fig. 3) are probably entirely responsible for the low specific gravity values. The average microhardness of these deposits was 907 (Knoop, 100-gram load).
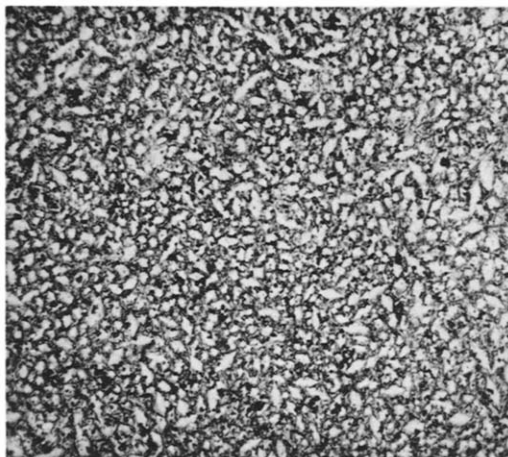
Fig. 3. Rhenium deposited at near-optimum deposition parameters. Black areas are voids. (× 450)

Environmental experiments

Effect of deposition temperature

A series of experiments at ascending reaction-chamber temperatures, ranging from 200 ° to 800 °C, was made to investigate the effect of temperature on the physical properties of the deposits. All runs were made with an ReF_6 flow rate of 5 grams per hour. As rough preliminary tests showed that a high hydrogen volume ratio was essential for efficient ReF_6 reduction, a H_2 to ReF_6 volume ratio of 25 to 1 was chosen for this study.

Examination of the deposits produced in this series showed that the amount of black, uncompacted rhenium powder increased as the reaction-chamber temperature increased from 250 ° to 800 °C. When the reaction-chamber temperature was 250 °C, the minimum amount of undesired rhenium powder and the maximum amount of rhenium in coherent, shaped form was deposited. Only rhenium powder deposited at 200 °C.

Metallographical examination of deposits from this series showed that the microstructure and the grain size of the rhenium remained approximately the same throughout. The surface finish of the massive rhenium deposited in this series had a metallic luster, was generally smooth and was dark gray. The uncompacted rhenium powder was always black

Effect of H_2 to ReF_6 volume ratio

The near-optimum reactant-gas (H_2 and ReF_6) parameter was determined by vapor-depositing rhenium from gas mixtures having different H_2 to ReF_6 volume ratios. These depositions were made at atmospheric pressure, with the reaction-chamber temperature constant at 250 °C, and with a ReF_6 flow rate of 5 grams per hour. The H_2 to ReF_6 volume ratio was varied between 3 to 1 and 30 to 1.

Some undesired, black rhenium powder always codeposited with the massive rhenium. The minimum amount of this powder and the maximum amount of compact rhenium resulted when the H_2 to ReF_6 volume ratio was 25 to 1. Metallographic examination of specimens from deposits obtained in this series revealed that all deposits had microstructures similar to the typical structure shown in Fig. 3.

Effect of reaction-chamber pressure

A limited number of tests were made in which the reaction-chamber pressure was varied slightly, from atmospheric to a hyperbaric pressure equivalent to that exerted by a 16-inch column of water. The reaction-chamber temperature was kept at 250 °C, a H_2 to ReF_6 volume ratio of 25 to 1 was used, and the flow rate of the ReF_6 was maintained at 5 grams per hour.

Examination of the deposits obtained showed that, in this limited range of pressure, and with the temperature and gas ratio optima determined under atmospheric pressure, deposition under hyperbaric conditions was detrimental to the formation of compact rhenium. The amount of undesired rhenium powder depositing increased as the reaction-chamber pressure increased. Metallographical examination of the deposits showed that there was no correlation between reaction-chamber pressure and the metallographical characteristics of the deposited rhenium.

One reduced-pressure run was completed. Deposition was made with the absolute reaction-chamber pressure equivalent to 600 millimeters of mercury. The amount of rhenium powder was excessive, and the overall deposition efficiency was greatly reduced, probably because of increased gas velocities.

Effect of temperature on deposition efficiency

Experimental runs were made at individual temperatures over the range of 250 ° to 450 °C with a constant initial substrate area and with a constant H_2 to ReF_6 volume ratio of 25 to 1. Overall deposition efficiency, including both massive rhenium and powder, varied from 95 to 100%. Deposition efficiency at 250 °C, considering compact rhenium only, was in the 70 to 75% range. As the temperature was raised to 450 °C, the deposition efficiency, again considering massive rhenium only, decreased to approximately 55%.

Effect of discontinuous deposition

Examination of specimens from runs in which the ReF_6 flow was interrupted long enough for deposition to cease, showed that, when the flow of ReF_6 was re-established and deposition was resumed, a line of demarcation appeared in the grain structure. Figure 4 shows the effect of intermittent deposition.
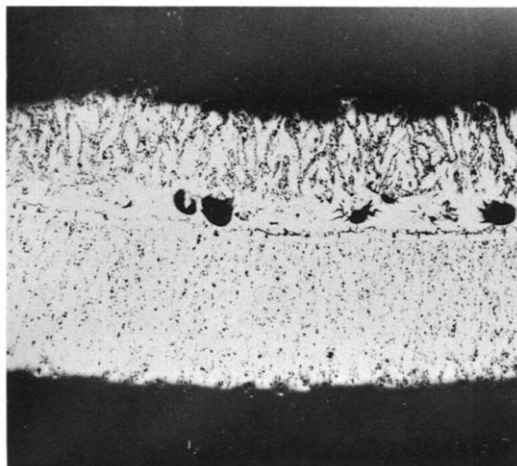
Fig. 4. Deposition from two gas-flow cycles. Deposited progressively from left to right. (× 600)

Preliminary codeposition of rhenium—tungsten alloys

General

Results of the rhenium vapor-deposition work were used as a basis for pioneering experiments with the objective of producing homogeneous rhenium—tungsten alloys of predetermined composition. Although this goal was not attained, some alloys of irregular composition were produced.

The following reduction parameters, which had previously been determined individually for ReF_6 and WF_6, were used for the codepositions:

Deposition temperature:
  Rhenium   250 °C
  Tungsten   550 °C
Mixed gas ratios:
  H_2 to ReF_6 25 to 1
  H_2 to WF_6 4 to 1.

The theoretical volume ratios of ReF_6 to WF_6 required to produce deposits containing nominal 5, 10, 15, 20 and 35 wt. % rhenium were calculated.

Description of techniques and deposits

The apparatus assembly for the codeposition experiments was the same as that used for rhenium deposition except for the mixing chamber, which was modified to allow introduction of WF_6, and for the reaction chamber, which was heated to provide temperatures accommodating both ReF_6 and WF_6 reduction. The temperature profile of the main heat zone showed a gradient between 250 ° and 550 °C. Most of the bimetallic deposits obtained under these conditions were thickest at the inlet side of the reaction chamber

where the temperature was in the 225 ° to 250 °C range. The deposits tapered down to a very thin edge at "downstream" side in the 550 °C zone; this portion of the deposit was reasonably smooth and bright, typical of tungsten deposits. In general, the deposits were dark, rough, nodular and porous.

Chemical analysis of portions of selected deposits indicated that a pronounced rhenium concentration gradient existed in the deposits. Because ReF_6 reduces at a lower temperature than does WF_6, the rhenium concentration was highest in the first portion of the deposit. Adjacent to the exit end the deposits consisted mainly of tungsten.

The longitudinal variation in rhenium content of the deposits was not affected significantly by changes in the deposition temperature or by modifications to the mixing chambers, which were redesigned to more intimately blend the ReF_6, WF_6 and H_2 before this reactant-gas mixture entered the deposition chamber.

In certain experiments the reactant-gas mixture was introduced into the reaction chamber by means of a specially constructed unit that made it possible to impinge the relatively cool gas mixture on the hot reaction chamber walls in an area of uniform temperature, but only slight improvement was noticed in the uniformity of these deposits.

Although the deposition efficiency was high when rhenium was deposited alone, the presence of WF_6 in the reactant-gas mixture appeared to adversely affect the deposition efficiency of the rhenium.

No hardness measurements were made on any of the bimetallic deposits, because of their porosity.

Conclusions

Consolidated rhenium deposits of high purity can be obtained by the hydrogen reduction of ReF_6 from the vapor phase, although some rhenium always deposits as a loose, black powder. The temperature of the reaction zone and the volume ratio of H_2 to ReF_6 significantly influence the amount of massive rhenium deposited. The near-optimum parameters are a temperature of 250 °C and a volume ratio of H_2 to ReF_6 of 25 to 1.

Operating at these gas ratios and temperature, with the equipment described, the best results were obtained with the deposition chamber at atmospheric pressure; both increasing pressure (to 790 millimeters of mercury) and decreasing pressure (to 600 millimeters of mercury) yielded excessive quantities of powdered rhenium. All tests at other than atmospheric pressure were made at the near-optimum parameters.

Rhenium deposition efficiencies, based only on the compact deposits, ranged between 70 and 75%. The average Knoop microhardness of vapor-deposited rhenium was 907, measured under a 100-gram load.

Intermittent deposition causes discontinuities in the metal and is undesirable for forming massive deposits.

No satisfactory codeposits of rhenium and tungsten were obtained,

owing to the wide variance in optimum-reduction temperatures of their hexa-fluorides. Considerably more complex techniques were indicated as necessary to attain homogeneous codeposits.

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