HIGH TEMPERATURE PROTECTIVE COATINGS FOR REFRACTORY METALS

PROGRESS REPORT NO. 2

PREPARED UNDER CONTRACT NO. NASw-1405

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

UNION CARBIDE CORPORATION

CARBON PRODUCTS DIVISION

PARMA, OHIO

HIGH TEMPERATURE PROTECTIVE COATINGS FOR REFRACTORY METALS

by

J. Rexer and J. M. Criscione

PROGRESS REPORT NO. 2

Prepared under Contract No. NASw-1405

UNION CARBIDE CORPORATION
CARBON PRODUCTS DIVISION
PARMA, OHIO

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TABLE OF CONTENTS

HIGH TEMPERATURE PROTECTIVE COATINGS FOR REFRACTORY METALS

by

J. Rexer and J. M. Criscione

I. INTRODUCTION

The research performed under Contract NASw-1405 is a continuation of work initiated under NASA Contract NASw-1030.[1] The major objectives of this contract are (1) to develop procedures for applying protective coatings of iridium on refractory metals, with special emphasis directed towards optimizing the fused salt electrodeposition of iridium, and (2) to study the rates of inter-diffusion of iridium with the refractory metals tungsten, molybdenum, and niobium. This report summarizes the research effort for the period 21 April to 21 October, 1966.

II. SUMMARY

The electrolytic cell design used under Contract NASw-1030[1] has been modified in an attempt to provide an effective method for electrodepositing iridium on refractory metals. Two modifications were made: (1) an inert gas chamber was juxtaposed but separated from the fused salt chamber by a gate valve to allow the admission of the refractory metal to the electrolyte without admitting air and (2) the previously-used alumina crucible was replaced by a graphite crucible to eliminate contamination due to the presence of aluminum oxide. Thus far, ten tungsten, ten molybdenum, and six niobium specimens have been coated with iridium. Acid testing and visual examination revealed that all of the coatings were dense and coherent.

An automatic temperature controlled, induction heated diffusion annealing system has been constructed and calibrated. Various hot pressed tungsten-iridium diffusion couples were annealed at 1300°, 1530°, 1710°, 1900°, and 2125°C. The sectioned specimens are being subjected to metallographic examination.

III. EXPERIMENTAL

A. Materials

High purity iridium sheet was obtained from Engelhard Industries, Incorporated. Sheet iridium, 0.005-inch thick, was used for the diffusion experiments and 0.040-inch thick sheet iridium was used for electroplating.

The niobium (0.020-inch thick sheet) was purchased from the Stellite Division of Union Carbide Corporation. Molybdenum and tungsten sheets (0.020-inch thick) were purchased from the Fansteel Metallurgical Corporation.

The sodium and potassium cyanide are high purity analytical reagent grades.

B. Sample Preparation

Iridium-coated samples were prepared by electrodeposition from a fused salt electrolyte and by pressure bonding. The latter plating method is being used to prepare samples for the diffusion studies.

1. Fused Salt Electroplating

The refractory metal substrates are being electroplated with iridium using the fused salt system reported previously.[1] A schematic diagram of the apparatus is shown in Figure 1. The molten salt, 70 w/o sodium cyanide and 30 w/o potassium cyanide, is contained in an ATJ graphite crucible. This crucible is contained in another graphite crucible, and the entire assembly is housed in a steel container. The apparatus consists of two chambers separated by a gate valve. The lower chamber contains the molten salt, the temperature of which is determined by means of a chromel-alumel thermocouple positioned between the two graphite crucibles. The upper chamber extends from the gate valve to the plexiglass lid; its function is to minimize oxidation and moisture pickup in the lower chamber while electrodes are removed or inserted into the cell. While the cell is in operation, both chambers

contain argon which has been bubbled through concentrated sulfuric acid, at greater than ambient pressure. With the gate valve closed, the upper chamber is flushed with argon.

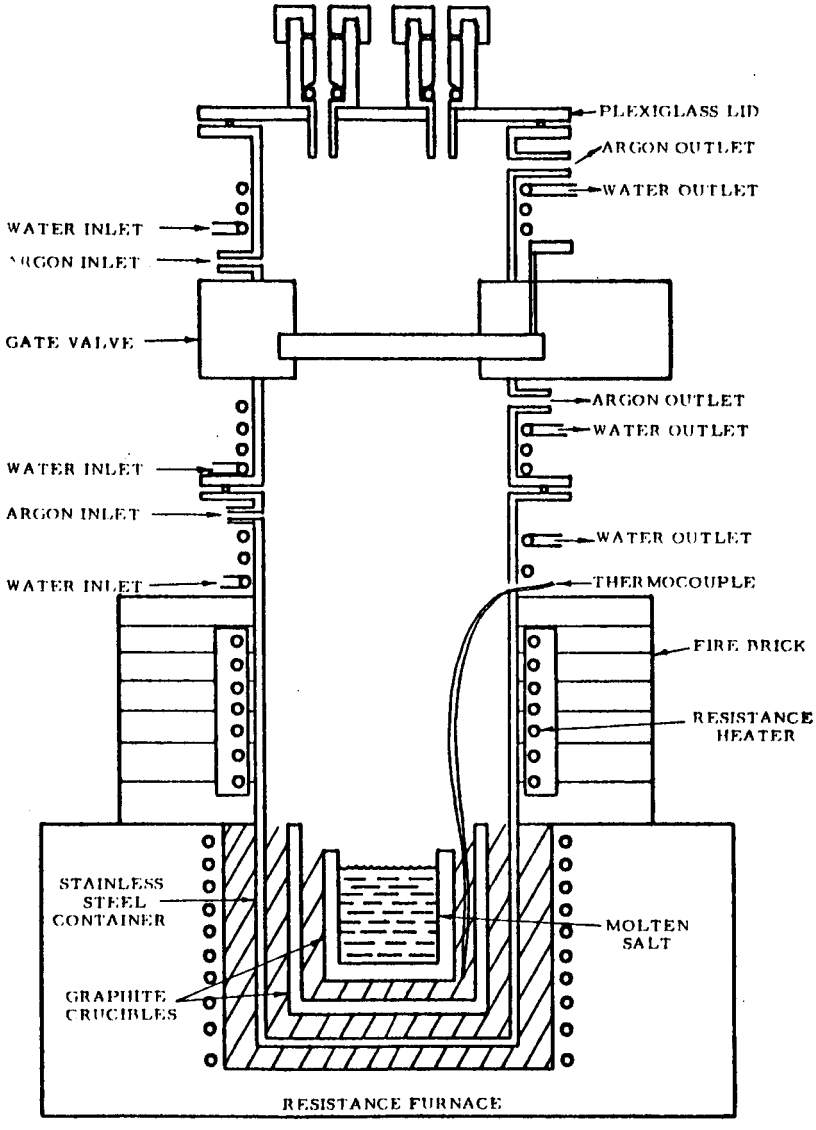

Figure 1. Fused Salt Cell

N-9760

The anodes consist of strips of iridium approximately $^3/_8$-inch wide by 0.040-inch thick. The cathodes are 0.020-inch thick sheets of the refractory metals, approximately one-inch square. Both the anodes and cathodes are held in position in the molten bath by nickel lead-in rods inserted through the plexiglass lid. The iridium anodes are attached to the nickel lead-in rods by

graphite fasteners. Iridium wires (0.020-inch in diameter) spot-welded to the refractory metal cathodes and to small strips of stainless steel are also attached to the nickel lead-in rods by graphite fasteners. Rubber "O" rings are used as air-tight seals between the plexiglass lid and the cell.and between the lid and the nickel lead-in rods.

A solid-state power source capable of supplying a direct current of 10 to 1000 ma was used. The molten bath is charged with iridium by using two iridium electrodes connected to the direct current power supply. The use of alternating current, as recommended by Withers and Ritt,[2] was not necessary, since the anode efficiency always tended to be much higher than the cathode efficiency. After coherent iridium deposits are obtained, refractory metal cathodes and an iridium anode are immersed into the molten salt bath.

Improper substrate preparation prior to electroplating invariably results in coatings that are neither coherent nor adherent. Since adherent iridium coatings on the refractory metals were not obtained with any degree of consistency, during the period covered by Contract NASw-1030[1] a variety of surface preparations were tried. As a result of these investigations, a standard procedure for the surface preparation of substrate metals was devised. It consists of the following steps: (1) polishing the substrate metal surface with wet abrasion papers through 600 grit, (2) scrubbing with hot Alconox solution, (3) rinsing with distilled water, (4) dipping into a dilute sulfuric acid solution (7-8 percent) to insure neutralization of any residual basic solution, (5) washing again with distilled water, and (6) washing with 95 percent ethyl alcohol. The specimens are dried in air before being placed into the fused salt electroplating bath.

2. Pressure Bonding

Samples obtained by pressure bonding sheet iridum (0.005-inch thick) under vacuum to the refractory metals represent the primary source of specimens for the diffusion studies. The die and plunger used for pressure bonding were machined from Union Carbide Corporation, Grade ATJ stock. Sheet iridium and the refractory metal substrates are each metallographically polished on one side. After the two sheets of metal are carefully washed with 95 percent ethyl alcohol, they are placed into the hot pressing die (polished surfaces touching), the plunger inserted, and the entire assembly placed into the vacuum apparatus. The system is evacuated by means of a mechanical pump and the pressure is

applied before the specimens are heated. Several tungsten-iridium composites were hot pressed at 1600°C for thirty minutes at a pressure of 2700 lb/in^2. Each hot pressed samples was sectioned into pieces measuring approximately $^3/_8$-inch x $^1/_4$-inch. One such section was examined metallographically; the others were heat treated in the diffusion apparatus.

C. Diffusion Apparatus

A schematic diagram of the apparatus used for the diffusion studies is shown in Figure 2. The diffusion couples contained in a tungsten crucible are heated inductively using an electromagnetic flux concentrator. The electromagnetic flux concentrator performs the task of efficiently linking the field, or energy of the induction coil, to the sample. The concentrator, fabricated from copper, contains a slot that eliminates circumferential electrical continuity. The central portion of the concentrator is cooled by water admitted through stainless steel leads which serve the additional role of supporting the assembly. A Pyrex glass mantle is close-fitted over the concentrator and serves both to insulate electrically the induction coil from the concentrator and, at the same time, to provide a controlled atmosphere or, if desired, a vacuum. Associated vacuum facilities are attached to the bottom of the glass mantle and pressures of 2×10^{-6} torr can be achieved consistently with the equipment. The top of the glass mantle is sealed by a cap which is provided with a sight glass.

The diffusion couples (measuring approximately $^1/_4$-inch x $^3/_8$-inch x 0.025-inch) are contained within a tungsten crucible. Bonding of the samples to the crucible is prevented by standing the specimens in a small pellet of Lucalox or thoria containing a slot 0.027-inches wide. The temperature-sensing thermocouple is positioned inside of the tungsten crucible. The crucible is enclosed in an insulating jacket of carbon felt. Temperature readings are made with a disappearing filament Pyro-Micro-Optical pyrometer (Serial No. M-5232) by sighting through a prism and sight glass into a $^1/_8$-inch hole in the lid of the one-inch deep tungsten crucible.

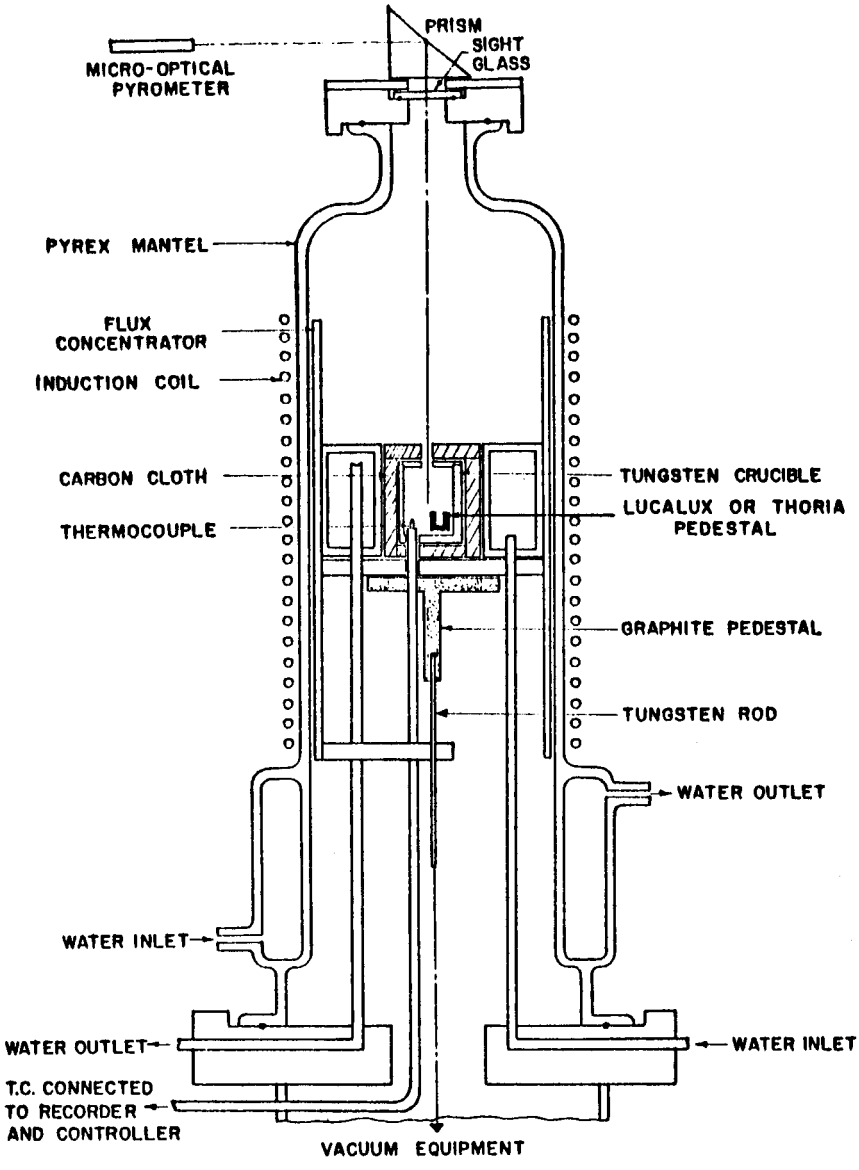

Figure 2. Diffusion Annealing System

N-10299

IV. PROGRESS

A. Fused Salt Electrodeposition of Iridium

In the latter part of the first quarterly report period, the new electroplating apparatus was put into operation. The basic components of the new apparatus are similar to those used under Contract NASw-1030.[1] The major differences in the new apparatus are: (1) the molten salts are contained in a graphite crucible instead of in the alumina crucible previously used, (2) the

heat-affected zone has been extended to about eight inches above the pot furnace, (3) the plexiglass electrode holder is sealed to the top of the apparatus by means of an "O" ring, a technique which permits the maintenance of an argon atmosphere at greater than ambient pressure within the system, and (4) a gate valve is used to isolate the lower portion of the apparatus while electrodes are inserted into or removed from the system.

The data obtained, under Contract NASw-1030, were insufficient to distinguish between electrolyte deterioration due to (1) gradual build-up of impurities to a critical level that prohibited the electrodeposition of coherent iridium deposits, or (2) the thermodynamic instability (i.e., too large a dissociation constant) of the iridium complex anion giving rise to the noncoherent deposits. Thermodynamic instability may not be a major problem, since it can sometimes be overcome by continuous electrolysis. However, contamination of the molten salt with impurities such as oxygen or moisture can have several deleterious effects. If iridium must be maintained in a low valency state, contaminants that may readily oxidize the iridium anion to a higher valency state must be eliminated. Insufficient anode area may also lead to oxidation of the complex iridium anion. In addition, the presence of moisture or oxygen in the hot electrolyte can oxidize the substrate metal surface and prevent a coherent iridium deposit from being adherent. The first molten electrolyte used in the new apparatus was in operation from 26 July, 1966, to 24 August, 1966; ten coherent iridium coated molybdenum and six tungsten specimens were produced. This bath was not in continuous operation (electroplating was never continued over a weekend and rarely overnight) and did not noticeably deteriorate. This fact may indicate that the complex iridium anion responsible for producing a coherent deposit is thermodynamically stable. Failure to produce coherent iridium coatings previously appears to have been primarily caused by oxidation and atmospheric contamination of the molten salts. Although not verified because air and/or moisture were not intentionally introduced into the system, the detrimental effect of atmospheric contaminants was partially substantiated when an argon inlet line broke over a weekend admitting air to the enclosed system. Repeated attempts at rejuvenating the contaminanted bath failed, and the bath was discarded. Another fused salt bath which was in operation for less than one week provided two coherently coated tungsten samples. Unfortunately, the iridium support wires of a tungsten sample broke while the sample was being

placed into the bath, and bath number two was discarded. A similar incident occurred with bath number three. However, the bath did produce coherent iridium coatings on two tungsten and six niobium samples. Thus, this work has demonstrated that tungsten and molybdenum can now be coated fairly consistently with coherent iridium deposits; niobium is quite reactive and still poses some problems.

B. Diffusion Studies

Construction and calibration of the heat treating apparatus (shown schematically in Figure 2) for the diffusion studies were completed. Automatic temperature control was initially attempted using a Honeywell Thermopile connected to a Leeds and Northrup Speedomax AZAR recording controller and a CAT control unit. Attempts at calibrating the output of the thermopile as a function of black body temperature were not successful, since the thermopile had to be displaced while samples were loaded and unloaded from the tungsten crucible. The thermopile was replaced with a thermocouple which was located inside of the tungsten crucible. This change simplified loading and unloading samples in the heating chamber, made it easier to obtain reproducibly preselected temperatures, and permitted continuous monitoring of the sample temperature with the Pyro-Micro-Optical Pyrometer without disturbing the automatic temperature control system. The first thermocouple used for temperature control was a platinum/platinum-10 percent rhodium thermocouple. The emf of this thermocouple was determined as a function of black body temperature. Unfortunately, the characteristics of this thermocouple changed with time, possibly due to contamination. The temperature of the system is now being controlled from the output of a tungsten-5 percent rhenium/tungsten-26 percent rhenium thermocouple. Thus far, no deviation from the original thermocouple emf-versus-black body temperature characteristic curve has been observed.

After the system was calibrated, sections of several hot pressed tungsten-iridium couples were heat treated. The time-temperature data are listed in Table I. The time interval needed to heat a sample from room temperature to any of the heat treating temperatures was less than 1.5 minutes. Furnace cooling a sample from 2125°C to red heat took approximately five minutes. The temperature variation during an experiment, as determined from the thermocouple emf output, was approximately ±5°C. Sections of the heat treated samples were mounted and polished for metallographic

examination. Difficulties are being encountered in selecting an etchant which will clearly define the reaction zone phase boundaries without destroying the tungsten phase.

TABLE I

ANNEALING DATA FOR TUNGSTEN-IRIDIUM DIFFUSION COUPLE

Sample Number	Temperature °C	Time (hrs) at Temp.
HP 1 - W 1300-1	1300	4
HP 1 - W 1300-2	1300	16
HP 1 - W 1530-1	1530	2
HP 1 - W 1530-2	1530	4
HP 1 - W 1530-3	1530	8
HP 1 - W 1530-4	1530	16
HP 1 - W 1530-5	1530	32
HP 5 - W 1710-1	1710	2
HP 5 - W 1710-2	1710	4
HP 5 - W 1710-3	1710	8
HP 6 - W 1710-4	1710	16
HP 5 - W 1900-1	1900	2
HP 6 - W 1900-2	1900	4
HP 6 - W 1900-3	1900	8
HP 6 - W 1900-4	1900	16
HP 7 - W 2125-3	2125	2

V. FUTURE WORK

Efforts will be made to prepare at least ten samples of each of the refractory metals tungsten, molybdenum, niobium, and tantalum which have been coated with a coherent iridium deposit using the new electroplating apparatus.

The heat treating of diffusion couples will be deferred until a technique has been devised to define the phase boundaries in the tungsten-iridium system.

Union Carbide Corporation
Carbon Products Division
Parma, Ohio 44130

November 28, 1966

REFERENCES

1. Criscione, J.M., Rexer, J., and Fenish, R.G., "High Temperature Protective Coatings for Refractory Metals," under Contract NASw-1030.

2. Withers, J.C., and Ritt, P.E., Proc. Am. Electroplaters Soc., Pp. 124-129, June 17-20, 1957.

DISTRIBUTION

NASA Headquarters (15)
Code RRM
Washington, D.C. 20546

NASA Headquarters
Code RRM
Washington, D.C. 20546
Attn.: Mr. Joseph Maltz

Attn.: NASA Representative (2)
Scientific and Technology Information Facility
P. O. Box 5700
Bethesda, Maryland

Inspector of Naval Materials
Ferguson Building
1793 East 11 Street
Cleveland, Ohio 44114