HIGH TEMPERATURE PROTECTIVE COATINGS FOR REFRACTORY METALS

by

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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 interdiffusion of iridium with the refractory metals, tungsten, molybdenum and niobium. This report describes the research effort for the period 21 April to 21 July 1966.

II. SUMMARY

A modification of the previously used electrolytic cell design has been constructed to overcome the difficulties encountered in trying to consistently electrodeposit iridium under Contract NASw-1030(1). The present design includes a sealed unit to eliminate atmospheric contamination of both the hot substrate metal and the molten salts. Preliminary tests indicate that the new cell operates properly and that it may only need minor equipment modifications. Two sheets of molybdenum (each measuring 0.020 inch x 1 inch x 1 inch) were coated with iridium. The coating in one of the samples had a defect which was observed by placing the specimen in concentrated nitric acid solution. The deposition rate was between 0.2 and 0.3 mil per hour. The defective specimen will be sectioned and examined metallographically, while those samples thought to have coherent coatings by virtue of visual examination and acid treatment will be saved, for either oxidation tests or interdiffusion studies.

Preliminary equipment modifications were made in an effort to adapt an induction heating apparatus (previously used for oxidation studies (2)) for the study of the interdiffusion of iridium with tungsten, molybdenum, and niobium, respectively. Using a borrowed controller and recorder and a Honeywell Thermopile, excellent temperature control between 1000° and 2000°C was obtained of a solid bar of tungsten used as the heater-susceptor. A Leeds & Northrup Speedomax AZAR recording controller and a CAT control unit were purchased and are presently being assembled. In addition, an electromagnetic flux concentrator and slip-cast tungsten crucibles are being fabricated.

III. EXPERIMENTAL

A. Materials

High purity iridium sheet was obtained from Engelhard Industries, Incorporated. Sheet iridium, 0.005-inch thick, will be used for the diffusion experiments while 0.040-inch thick sheet iridium will be 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 cyanides are high purity analytical reagent grades.

B. Sample Preparation

Iridium-coated samples will be prepared by electrodeposition from a fused-salt electrolyte and by pressure bonding. Since coherent and adherent electroplated iridium deposits could not be obtained consistently, the samples used for the diffusion studies will be prepared, by pressure bonding techniques.

1. Fused Salt Electroplating Cell

The fused-salt system developed by Withers and Ritt(3), and used under Contract NASw-1030(1), will be used. 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 (2 3/4 inches outside diameter by 5 inches high with 3/8-inch thick walls). Granulated alumina was placed as insulation between the two graphite crucibles and between the steel container and the furnace. The apparatus consists of three chambers: 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 middle chamber, extending from the salt bath up to the gate valve, is heated by a separate power supply; this chamber is used to preheat the anode and cathode prior to their placement into the molten salt. No physical barrier separates these two chambers which are kept under an argon atmosphere. The argon is bubbled through concentrated sulfuric acid. The upper chamber extends from the gate valve to the plexiglass lid; its function is to minimize oxidation and moisture pickup in the lower chambers while electrodes are removed or inserted into the cell. By means of the gate** valve, this chamber can be flushed with argon while isolated from the lower chambers.

The anodes consist of strips of iridium about 3/8-inch wide by 0.040-inch thick. The cathodes are sheets (0.020-inch thick) 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. Between the plexiglass lid and the cell, and between the lid and the nickel lead-in rods; "O" rings are used as air tight seals.

A solid-state power source capable of supplying direct current of 10 to 1000 ma will be used.

2. Pressure Bonding

Sheet-iridium, pressure bonded under vacuum to the refractory **metals, will be the primary source of samples for the diffusion studies.**

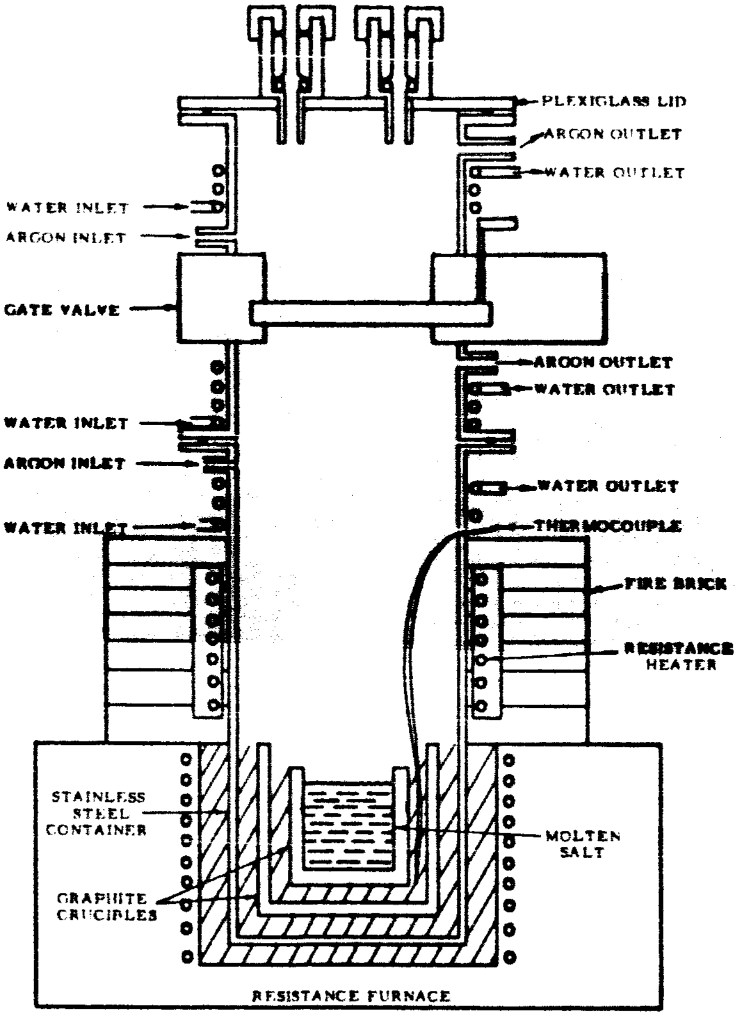

Figure 1. Fused Salt Cell

The die and plunger used for pressure bonding were machined from Union Carbide Corporation, Grade ATJ Stock. Specimens will be heated inductively while under pressure.

C. Diffusion Apparatus

The apparatus to be used for the diffusion studies was formerly used to study the effect of gas velocity on the oxidation of iridium(2). A complete description of the apparatus, which is presently being modified, will be presented in a subsequent report.

Using an electromagnetic flux concentrator, attempts are being made to heat the diffusion couples, which are suspended in a tungsten crucible. The power source used to energize the flux concentrator is a 25 kw output Thermionic Electronic Induction Generator which operates at a frequency of approximately 400 kilocycles. The output of the generator is controlled by means of a saturable core reactor. Specimen temperatures to 2000°C will be automatically controlled using either a Honeywell Thermopile or a thermocouple connected to a Leeds & Northrup Speedomax AZAR recording controller and a CAT control unit.

IV. PROGRESS

A. Fused-Salt Electrodeposition of Iridium

In the latter part of this report period, the new cell was put into operation. Basically, the operation of this cell is similar to the operation of the cells used under Contract NASw-1030 (1). The primary differences in the new cell are that the molten salts are contained in a graphite crucible instead of the alumina crucible used previously, and all electrodes are preheated before thay are immersed into the fused salt bath. The cell was charged with a mixture consisting of 70 w/o sodium cyanide and 30 w/o potassium cyanide, sealed with a solid plexiglass lid, and thoroughly flushed with argon before heating to approximately 600°C. To charge the bath with iridium, and to aid in removing some of the undesirable impurities, a direct current (cathode current density between 10 and 20 amp/ft^2) was passed for several days through iridium anodes and spectroscopically pure graphite cathode rods.

From time-to-time, to hasten charging of the molten bath with iridium, two iridium electrodes were used. As soon as a bright metallic coating was consistently obtained on the graphite rods, attempts were made to coat sheet molybdenum. Two, one-inch square by 0.020-inch thick sheets have been coated with iridium. The coating on one of the samples had a defect which was observed by placing the specimen in concentrated nitric acid solution. The deposition rate was between 0.2 and 0.3 mil per hour.

B. Diffusion Studies

The apparatus to be used for the diffusion studies was formerly used to study the effect of gas velocity on the oxidation of iridium (2). This apparatus was modified and while using a borrowed Leeds & Northrup Speedomax AZAR recording controller and a CAT control unit with a Honeywell Thermopile, efforts were made to control specimen temperatures to 2000°C. Initial attempts at automatically controlling the temperature of a graphite crucible were not successful. Deviations from a temperature-set point resulted in overcontrol indicating that the specific heat of the crucible was insufficient. Results of experiments were excellent using a solid bar of tungsten as the heater-susceptor. Using a crucible with a relatively high specific heat, temperatures to at least 2000°C can be automatically controlled to within a few degrees for prolonged periods of time.

The automatic temperature control equipment discussed above was purchased. In addition, powdered tungsten needed for slip casting crucibles was purchased and a new flux concentrator is being constructed. Presently, the entire apparatus is being assembled.

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Parma, Ohio 44130

August 10, 1966

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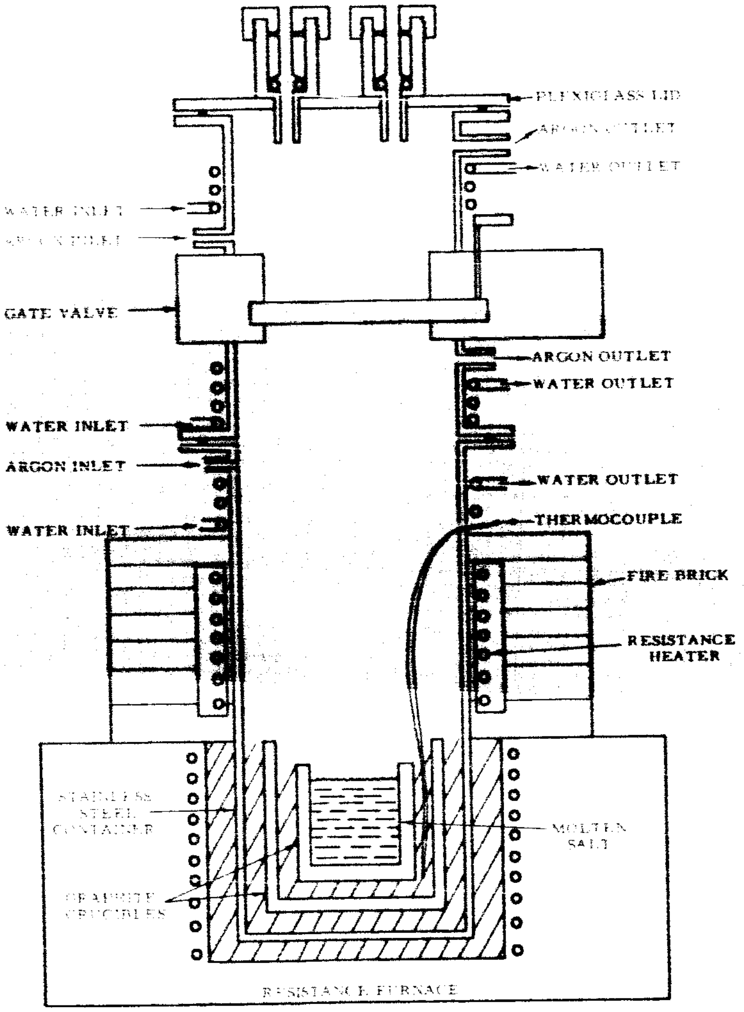
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THERMOCOUPLE
WATER INLET
FIRE BRICK
RESISTANCE HEATER
STAINLESS STEEL CONTAINER
MOLTEN SALT
GRAPHITE CRUCIBLES
RESISTANCE FURNACE