HIGH TEMPERATURE PROTECTIVE COATINGS FOR REFRACTORY METALS

by

J. Rexer

FINAL TECHNICAL REPORT

Prepared Under Contract No. NASw-1405

UNION CARBIDE CORPORATION
CARBON PRODUCTS DIVISION
PARMA, OHIO

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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I. INTRODUCTION

Under Contract NASw-1030, [1] a preliminary investigation was conducted on the use of iridium as a high temperature oxidation protective coating for tantalum, niobium, molybdenum, and tungsten. The results of that effort, summarized in the Final Report for that program, emphasized the high potential of iridium as an oxidation protective coating for refractory metals. The research performed under the present program, Contract No. NASw-1405, is a continuation of the work initiated under NASA Contract No. NASw-1030. The objectives of the present program were (1) to develop procedures for applying protective coatings of iridium on refractory metals, with special emphasis directed towards improving the fused salt electrodeposition of iridium, (2) to study the rate of growth of the reaction zones formed between iridium and some of the refractory metals, (3) to study the changes in thickness of iridium coatings on some of the refractory metals due to interdiffusion and intermetallic compound formation, and (4) to examine microscopically with a microbend tester the mechanical behavior of iridium coated and heat treated specimens.

The results of the program conducted under Contract No. NASw-1405 are presented in this report.

II. SUMMARY

An apparatus was designed and constructed to improve the electrodeposition of iridium on some of the refractory metals. Removing electrolyte contaminants originating from the atmosphere and from the alundum crucible permitted the consistent electrodeposition of coherent and adherent iridium deposits of any desired thickness on molybdenum and tungsten. Tantalum and niobium were chemically too reactive with the molten electrolyte to be consistently coated with iridium. A dual coating consisting of a nickel strike on the substrate metals followed by an iridium overlay was developed for these metals.

The amount of the decrease in thickness of an iridium coating on molybdenum, tungsten, and niobium, due to intermetallic compound formations, was determined. From these data, the life expectancy of the coating at elevated temperatures can be estimated. Extrapolation of the data, assuming solid-state diffusion controlled reactions, shows that a 5 mil thick iridium coating at 1700°C will last indefinitely on tungsten, for at least 700 hours on niobium, and for at least 600 hours on molybdenum. Similarly, the same coating at 1900°C will last at least 300 hours, and 130 hours, respectively on tungsten and molybdenum. In contact with niobium, the iridium coating should last at least 200 hours at 1780°C.

Examination with the microbend tester of pressure bonded composites, in both the as-formed and annealed conditions, shows that cracks initiate on the side of maximum tension (the outer iridium surface) and propagate towards the coating-substrate interface. Tungsten-based composites were as brittle as tungsten sheet samples, whereas niobium-based composites were ductile. Molybdenum-based composites failed in a brittle manner at bend angles of approximately 45 degrees, and annealed molybdenum was plastically deformed through a bend angle of 90 degrees. A well-bonded composite will not delaminate easily during deformation, even when a significantly thick reaction zone is present between the coating and the substrate metals.

III. EXPERIMENTAL

A. Materials

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

Tantalum and niobium sheets (0.020-inch-thick) were purchased from the Union Carbide Corporation, Materials Systems Division. Molybdenum and tungsten sheets (0.020-inch-thick) were purchased from the Fansteel Metallurgical Corporation.

The sodium and potassium cyanides were high purity analytical reagent grades.

B. Sample Preparation

Iridium-coated samples were prepared either by electrodeposition from a fused-salt electrolyte or by pressure bonding. Coherent and adherent electroplated iridium deposits could not be obtained in some of the systems under study. To provide assurance that a "representative" coating substrate system would be examined, we prepared all samples used for the diffusion and mechanical behavior studies by pressure bonding techniques.

1. Fused Salt Electroplating

The fused-salt system developed by Withers and Ritt[2], and used under Contract NASw-1030[1], was also used in the present program. The electrolytic cell previously used was modified to overcome plating difficulties attributed to atmospheric contamination of both the hot substrate metals and the molten salts. 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) was contained in an ATJ graphite crucible (2-3/4 inches outside diameter by 5 inches high with 3/8-inch thick walls) rather than in the alumina crucible previously used. Granulated alumina was placed as insulation between the two graphite crucibles and between the steel container and the furnace. The apparatus consisted of three chambers. The lower chamber contained the molten salt, the temperature of which was 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, was heated by a separate power supply; this chamber was used to preheat the anode and cathode before they were inserted into the molten salt. No physical barrier separated the lower and middle chambers which were kept under an argon atmosphere. The argon was bubbled through concentrated sulfuric acid before it was admitted into the cell, and the argon pressure within the cell was kept slightly above ambient by means of a gas exhaust bubbler. The upper chamber extended from the gate valve to the plexiglass lid; its function was to minimize oxidation and moisture pickup in the lower chamber while electrodes were removed from or inserted into the cell. By means of the gate valve, the upper chamber could be flushed with argon while a positive argon pressure was maintained in the isolated lower chambers.

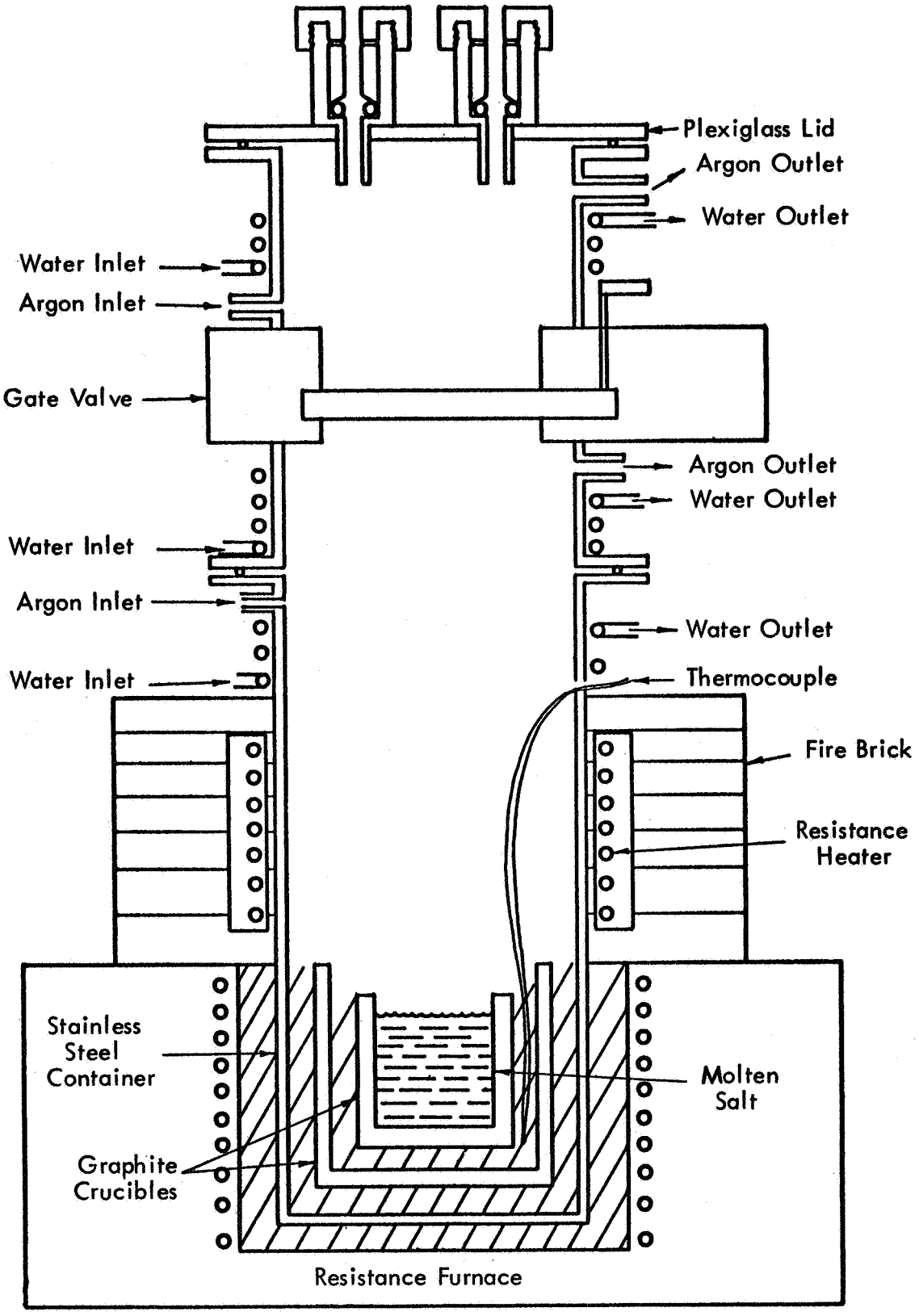

Figure 1. Fused Salt Electroplating Cell

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The anodes consisted of strips of iridium approximately 3/8 inch-wide by 0.040-inch-thick and up to 6 inches in length. The cathodes were sheets (0.020-inch-thick) of the refractory metals approximately one inch square. Both the anodes and cathodes were held in position in the molten salt bath by nickel lead-in rods inserted through the plexiglass lid. The iridium anodes were 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 were also attached to the nickel lead-in rods by graphite fasteners. Rubber "O" rings were used as air-tight seals between the plexiglass lid and the cell and between the lid and the nickel lead-in rods.

Substrate preparation prior to electroplating was found to be a very important factor in obtaining coherent and adherent iridium coatings. A variety of surface preparations were tried (see discussion in the Final Report of Contract No. NASw-1030[1]. As a result of these investigations, a standard procedure for the surface preparation of substrate metals was devised, consisting of the following steps: (1) polish the substrate metal surface with wet abrasion papers through 600 grit, (2) scrub with hot Alconox solution, (3) rinse with distilled water, (4) dip into a dilute sulfuric acid solution (7-8 percent) to insure neutralization of any residual basic solution, (5) wash again with distilled water, and (6) wash with 95 percent ethyl alcohol. The specimens were air dried before being placed into the fused salt electroplating bath.

The procedure for preparing the electrolyte consisted of sealing the powdered cyanide mixture in the electroplating apparatus and thoroughly flushing with argon before heating to approximately 600°C. The salt mixture melts at approximately 500°C. The bath was charged with iridium and some of the cation impurities were removed by passing a direct current (cathode current density between 10 and 20 amp/ft.^{2}) through iridium anodes and spectroscopically pure graphite cathode rods for several days. A solid state power source capable of supplying a direct current of 10 to 1000 ma was used. From time to time, iridium electrodes were used as both anode and cathode to hasten charging of the molten salts with iridium. The use of alternating current to charge the molten salts with iridium, 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 bright metallic iridium electrodeposits were consistently obtained on the graphite rods, the electrolyte was considered sufficiently conditioned for electroplating onto the refractory metals.

2. Pressure Bonding

Samples obtained by pressure bonding sheet iridium (0.005-inch thick) under vacuum to the refractory metals were used for the diffusion ahd mechanical behavior studies. A schematic diagram of the vacuum hot press is given in Figure 2. The die and plungers were machined from Union Carbide Corporation, Grade ATJ stock. The water-cooled steel plunger was made vacuum tight by means of a flexible metal bellows and "O" ring seal attached to the upper plate. Sheet iridium and the refractory metal substrates were each metallographically polished on one side. After the two sheets of metal were carefully washed with 95 percent ethyl alcohol, they were positioned in the die (polished surfaces touching), sandwiched between two thin sheets of "Grafoil".* With the upper graphite plunger inserted, the entire assembly was placed into the vacuum apparatus. The system was evacuated by means of a mechanical pump, and pressure was applied to the specimens before heating. Table I shows the conditions under which diffusion couples for the different systems were prepared; these conditions resulted in good bonding with no observable intermetallic compound formation. The hot-pressed composites were sectioned with a water-cooled abrasive wheel and subsequently used for either the diffusion studies or for examination of the mechanical behavior of the composites.

TABLE I

PRESSURE BONDING CONDITIONS

System	Temperature	Pressure	Time @ Temp.
Mo-Ir	1200°C	1500 psi	1-1/4 hours
W-Ir	1200°C	1700 psi	2-1/4 hours
Nb-Ir	1000°C	1360 psi	1 hour

* "Grafoil" is a registered trademark of Union Carbide Corporation.

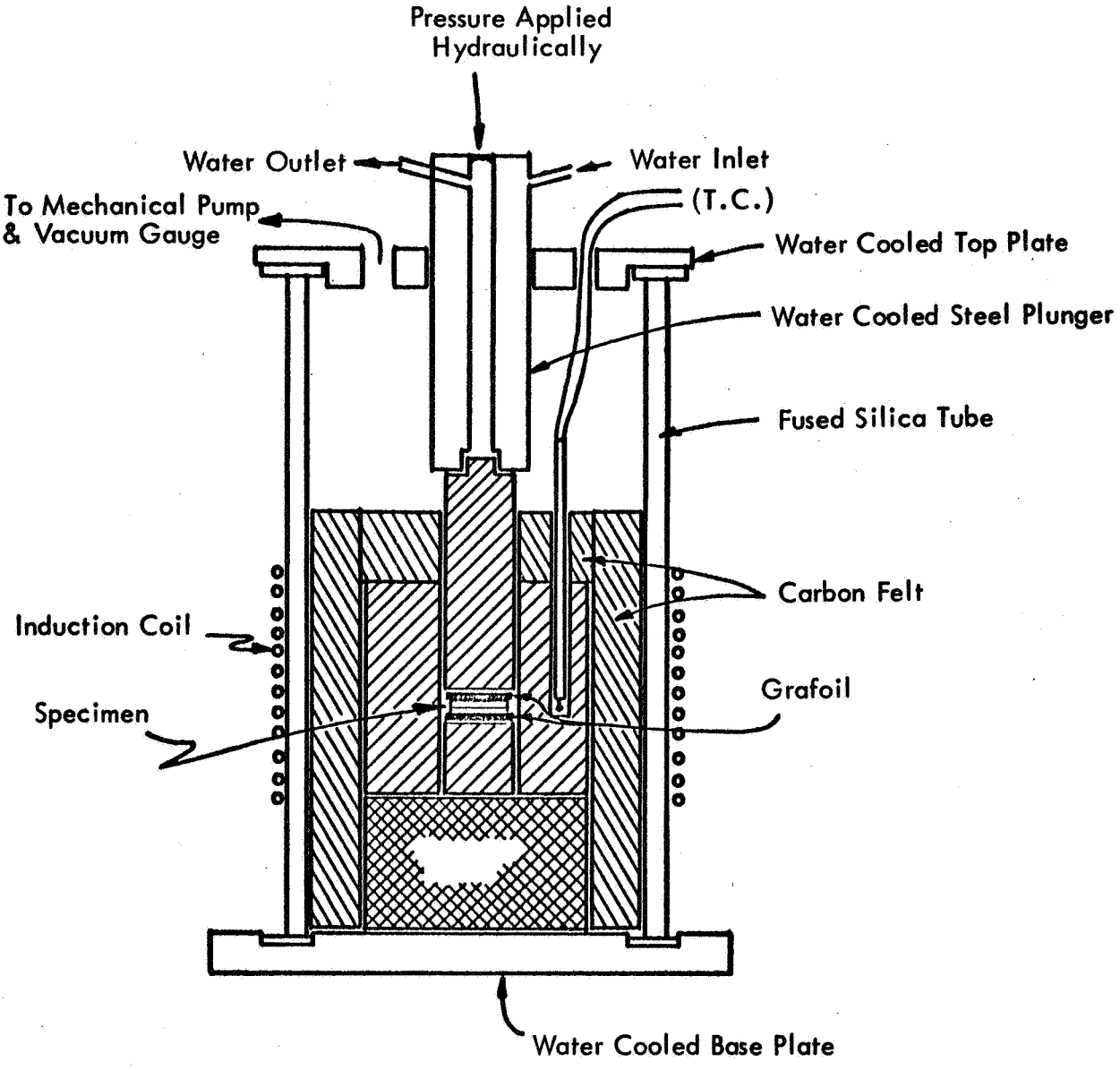

Figure 2. Schematic Diagram of Vacuum Hot Press

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C. Sample Evaluation

1. Heat-Treating Apparatus

A schematic diagram of the apparatus used for annealing samples for the diffusion and mechanical behavior studies is shown in Figure 3. The specimens, consisting of sectioned pieces of the pressure bonded composites, were contained in a tungsten crucible and heated inductively by means of an electromagnetic flux concentrator which efficiently links the field, or energy, of a large induction coil to small samples. The concentrator, fabricated from copper, contains a slot which eliminates circumferential electrical continuity. The central portion of the concentrator is water cooled. The water enters through stainless steel leads which also serve to support the assembly. The power source used to energize the concentrator is a 25 kw output Thermonic Electronic Induction Generator operating at a frequency of approximately 400 kilocycles. The output of the generator is controlled by means of a saturable core reactor.

A Pyrex glass mantle fits closely over the concentrator and serves both to insulate electrically the induction coil from the concentrator and to provide a controlled atmosphere or, if desired, a vacuum. Associated vacuum facilities were attached to the bottom of the glass mantle and pressures of 2×10^{-6} torr could be achieved consistently with the equipment. The top of the glass mantle is sealed by rubber "O" rings in a cap which is provided with a sight glass.

The temperature of the tungsten crucible is automatically controlled from the output of a W-5% Re/W-26% Re thermocouple by a Leeds & Northrup Speedomax AZAR recording controller and a CAT control unit. Automatic temperature control was initially attempted using a Honeywell thermopile connected to the recorder and controller. Attempts were not successful in calibrating the output of the thermopile as a function of black body temperature since the thermopile had to be displaced while samples were loaded and unloaded from the tungsten crucible. Replacing the thermopile with a thermocouple located inside of the tungsten crucible simplified loading and unloading samples in the heating chamber, made the obtaining of preselected temperatures

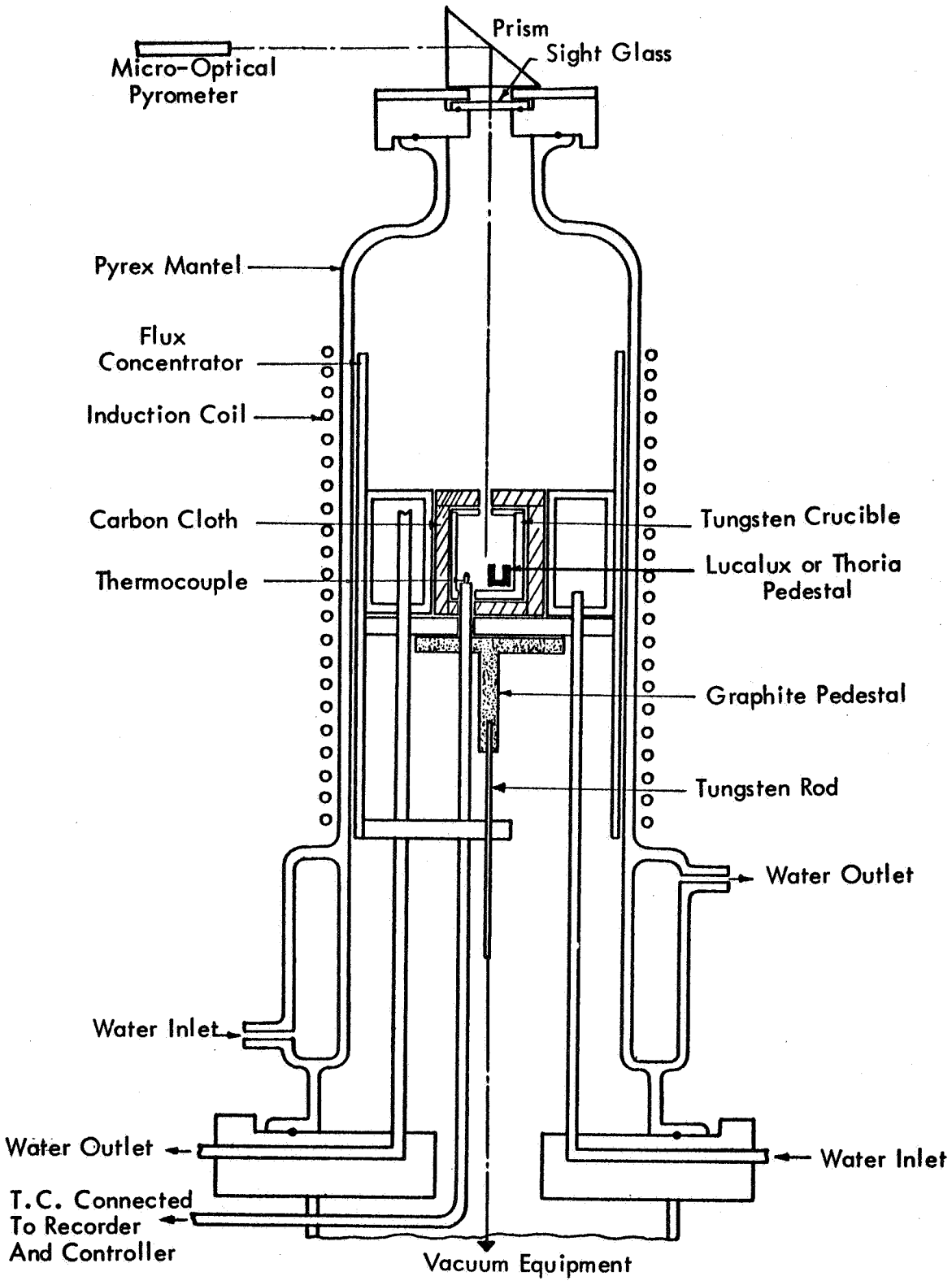

Figure 3. Schematic Diagram of Heat-Treating Apparatus

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easier,and permitted continuous monitoring of the sample temperature with a Pyro-Micro-Optical Pyrometer without disturbing the automatic temperature control system. The first thermocouple used for temperature control was a Pt/Pt-10% Rh thermocouple. The emf of this thermocouple was determined as a function of black body temperature. However, the characteristics of this thermocouple changed with time, possibly due to contamination, and it was removed.

The calibration curves of the W-5% Re/W-26% Re thermocouples, positioned inside of the tungsten crucible, did not change with usage. Several thermocouples were used throughout the project, and each was calibrated against a Pyro-Micro-Optical pyrometer. The pyrometer was calibrated by means of a National Bureau of Standards calibrated tungsten ribbon lamp and a standard arc with sectored disks as radiation sources. Corrections were made for glass absorption. The calibration curves for all thermocouples were similar to the one shown in Figure 4. The temperature plotted is the average of five determinations at each thermocouple output setting.

Initial attempts were unsuccessful at automatically controlling the temperature of a graphite crucible. Deviations from a temperature setpoint resulted in overcontrol, indicating that the specific heat of the crucible was insufficient. The problems encountered with the graphite crucible were not encountered when tungsten crucibles were used. The tungsten crucibles used throughout the program were prepared at the Parma Technical Center by electroplating tungsten on a copper mandrel. The electroforming of coherent tungsten from molten fluoride electrolytes has been described by Senderoff and Mellors[3]. The tungsten crucibles were 7/8-inch in inside diameter, approximately 1-1/4 inches deep, and had 1/32-inch wall thicknesses. An off-center hole was machined into the bottom to admit the thermocouple, and the lid had a 1/16-inch diameter sight hole in the center. The radial temperature distribution within the tungsten crucible was established at several temperatures through the use of a crucible lid containing five 1/16-inch diameter holes. In the accompanying table (Table II), hole number one was located in the center of the lid and the remaining four holes were uniformly distributed between the inner crucible surface and the center hole. No temperature gradients which could be determined by the optical pyrometer were observed.

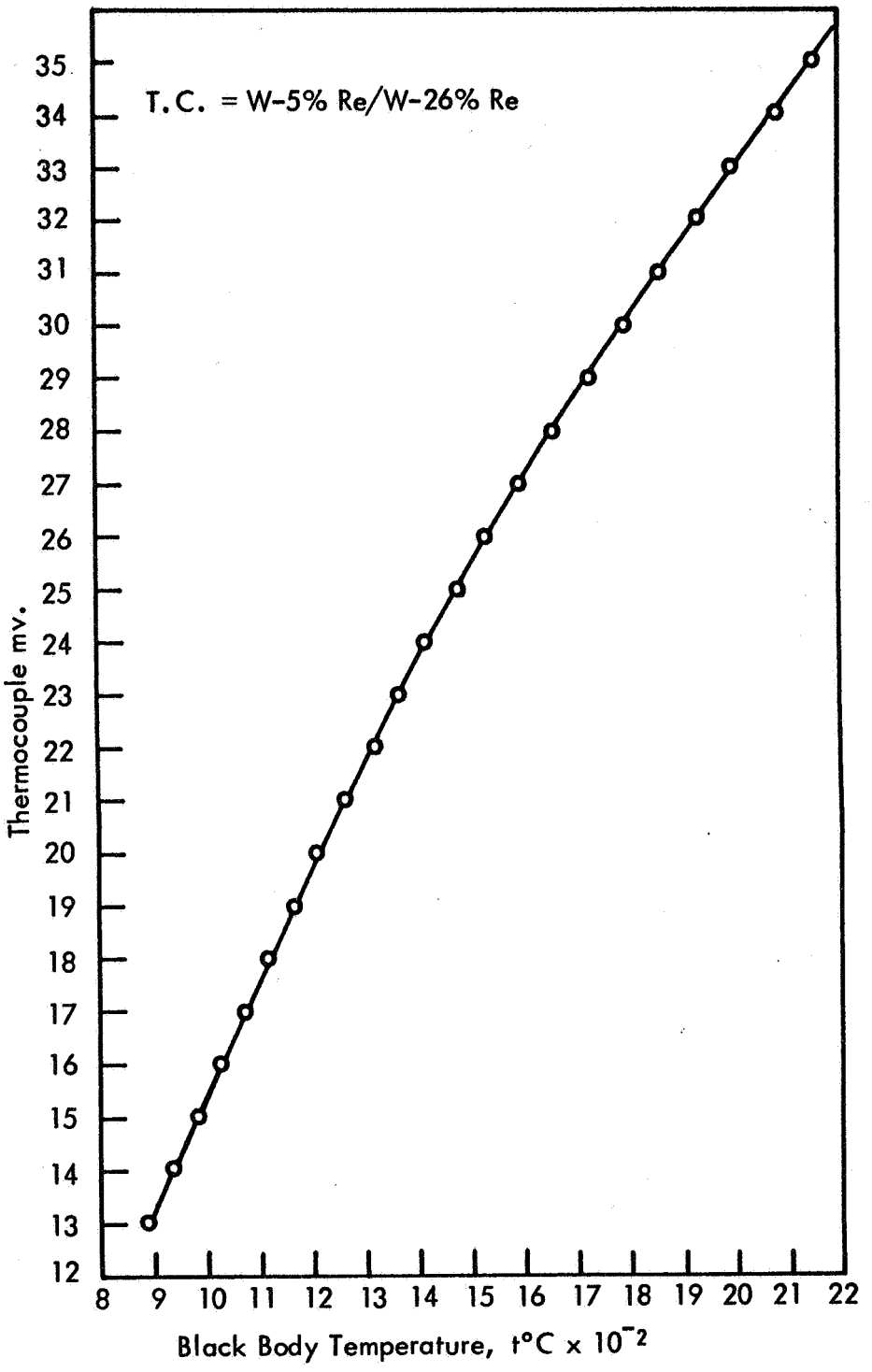

Figure 4. Thermocouple Calibration Curve

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TABLE II

TEMPERATURE GRADIENTS WITHIN THE TUNGSTEN CRUCIBLE

Temp. at* Hole #1, °C	Temp. at Hole #2, °C	Temp. at Hole #3, °C	Temp. at Hole #4, °C	Temp. at Hole #5, °C	Ave. Temp. °C
1288 ± 10	1278 ± 10	1278 ± 10	1288 ± 10	1280 ± 10	1282
1497 ± 10	1491 ± 10	1500 ± 10	1503 ± 10	1497 ± 10	1498
1683 ± 12	1675 ± 12	1700 ± 12	1696 ± 12	1689 ± 12	1689
1900 ± 15	1885 ± 15	1870 ± 15	1900 ± 15	1879 ± 15	1887

* Each recorded temperature is the average of 10 trials.

Specimens were heated from room temperature to any of the desired annealing temperatures within a maximum time of 1-1/2 minutes. After the samples were annealed for the predetermined time at temperature, the induction generator was turned off and the samples were furnace cooled under vacuum. The tungsten crucible cooled from the annealing temperatures to approximately 600°C in less than five minutes. So that the substrate metals would not oxidize, the specimens were kept under a vacuum for at least 1/2-hour after the induction generator was turned off. Argon was admitted into the closed system before the specimen was removed from the heating chamber.

2. Microbend Tester

So that we might obtain a better understanding of failure modes than can be gained from standard bend tests and also to conserve material, we constructed a fixture to allow direct observation of the entire stress gradient as a bending stress was applied to a coating-substrate system. The basic design of the microbend tester follows that proposed by Flinn and Trojan[4]. The microbend tester permitted microscopic observation of the side of the beam while a bending stress was applied to small specimens measuring approximately 1/8 inch x 0.025 inch x 1 inch. Three-point loading was accomplished through two moveable outer loading pins attached by means of a ball joint to the plunger of a spring balance. The spring balance was calibrated to within 1/8 lb. and was equipped with a marker to measure the maximum applied load.

The entire stress gradient, from maximum tension on the outer coating edge to maximum compression on the substrate surface butting against the stationary center loading pin could be observed. Figure 5 shows the microbend tester mounted on a Zeiss microscope and the attached spring balance.

The performance of the microbend tester was evaluated by testing twelve samples of Union Carbide Corporation Grade ATJ graphite on the microbend tester and testing eleven samples, machined from the same large block, by using a standard three-point loading technique. The results are given in Table III. The average flexural strength determined by using the microbend tester, 5500 psi, compared well with the average strength of 6000 psi obtained by the standard test. The maximum deviation from the average strength for samples tested with the microbend tester was ± 1000 psi, whereas on the standard three-point load test it was ± 2200 psi. The difference between the two test values may be caused primarily by differences in instrumentation. In the standard test, the applied load can only be determined to within ± one pound; the spring balance of the microbend tester can be read to within ± 1/8 pound.

The specimens examined with the microbend tester were obtained from the 'as-received' sheet metal and from hot-pressed iridium-coated substrates. Strips, approximately 3/4-inch to one inch long and 1/8-inch wide, of the material to be tested were cut with a water-cooled abrasive wheel. Some of the composites were heat treated to develop a reaction zone. One of the side-of-beam surfaces of each of the sectioned pieces was metallographically polished before testing. Where possible, (such as with some of the 'as-received' substrate metals) one surface was polished and then etched to reveal the grain structure. Iridium-coated specimens were not etched, since etching to reveal the iridium microstructure caused severe chemical attack to both the substrate metal, and the interface between the iridium coating and the substrate metal.

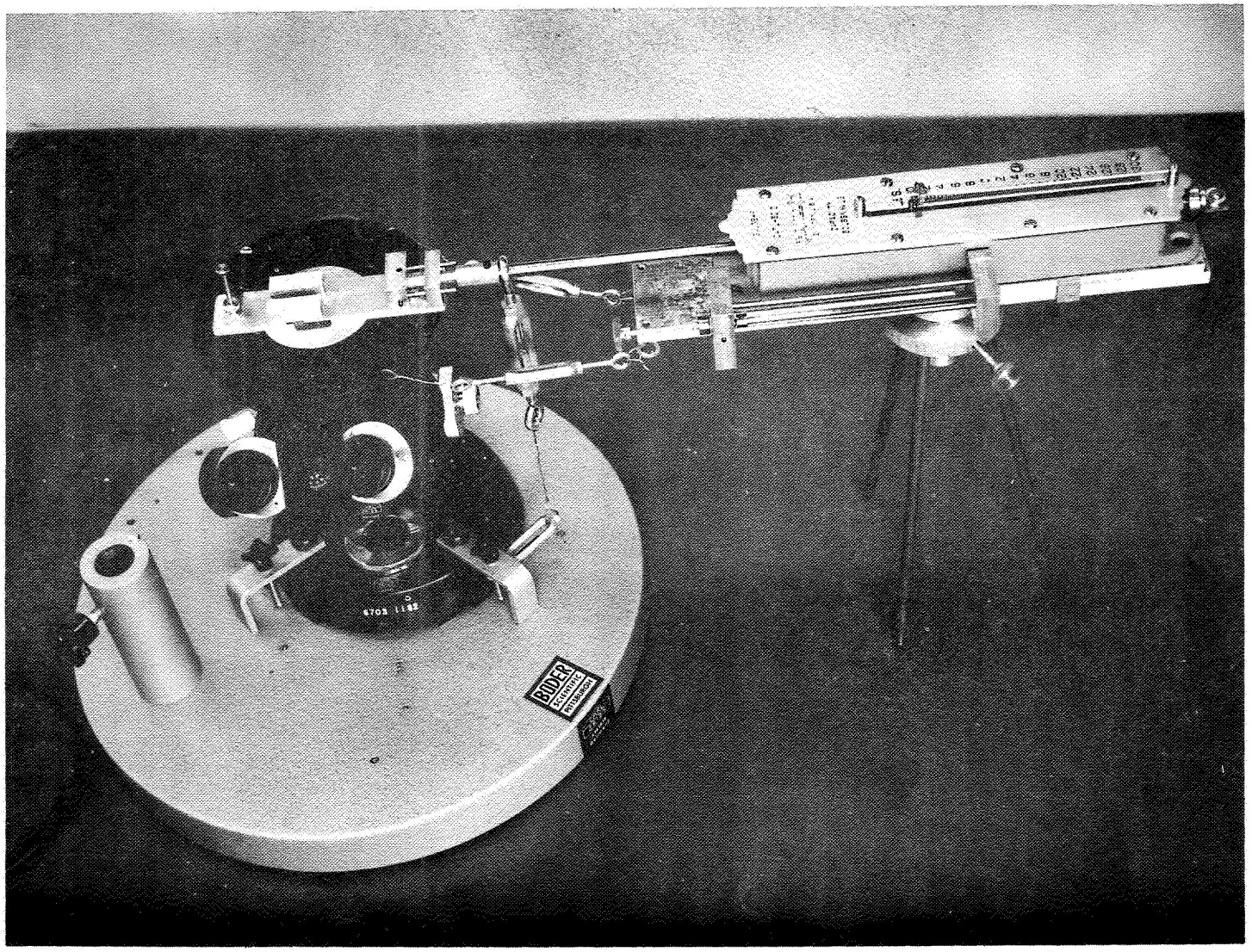

Figure 5. Photograph of Microbend Tester Mounted on Microscope.

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TABLE III

FLEXURAL TEST RESULTS FOR ATJ GRAPHITE

MICROBEND TESTER RESULTS					STANDARD THREE-POINT LOADING TEST RESULTS				
Sample*	Width Inches	Thickness Inches	Maximum Load, lb.	Strength psi x 10^3	Sample*	Width Inches	Thickness Inches	Maximum Load, lb.	Strength psi x 10^3
1	0.0994	0.1005	6-3/4	6.3	1	0.102	0.102	6	5.5
2	0.1009	0.1010	5-1/2	5.2	2	0.100	0.100	6	5.6
3	0.0997	0.1002	6-7/8	6.5	3	0.102	0.099	8	7.3
4	0.1007	0.1012	6-1/4	5.9	4	0.100	0.100	5	4.7
5	0.0955	0.0983	4-1/4	4.5	5	0.101	0.101	9	8.3
6	0.0992	0.1007	5-3/4	5.3	6	0.100	0.100	8	7.5
7	0.1000	0.1000	6	5.6	7	0.099	0.099	6	5.7
8	0.0990	0.0995	5-1/2	5.2	8	0.098	0.100	7	6.7
9	0.0986	0.0990	5-1/2	5.2	9	0.100	0.100	6	5.6
10	0.0996	0.1010	5-3/4	5.3	10	0.100	0.100	7	6.5
11	0.0995	0.1006	5-1/4	4.9	11	0.096	0.100	4	3.9
12	0.0996	0.1003	6-1/2	6.1					
			Average=	$\overline{5.5}$				Average=	$\overline{6.0}$

*Three-point loading with a 0.625 inch span.

3. Visual Examination

All coating substrate composites, regardless of the method of preparation, were examined for external flaws with the unaided eye and with a low-powered microscope. Specimens which could be sectioned, such as those used for the diffusion and mechanical behavior studies and some of the electroplated samples, were metallographically polished and microscopically examined.

Efforts were made to reveal the structural details in molybdenum-iridium and tungsten-iridium composites. Specimens mounted in epoxy resin, polished with 600 grit paper and alundum powder, were given a final polish with one-micron diamond paste on a Texmet polishing cloth. The molybdenum composites were first electrolytically etched for approximately five seconds, anodically, at a DC potential of two volts in a solution containing 300 ml of water and 30 ml of sodium hydroxide. This treatment color tints the molybdenum-rich intermediate phase and preferentially attacks the molybdenum grain boundaries. After the sample was washed in water, it was electrolytically etched for approximately five seconds, anodically, at a DC potential of two volts in a solution of 150 ml of water and 25 ml of phosphoric acid. The second etchant provides some color contrast to the molybdenum grain surface without severely attacking the grain boundaries, neither etchant reacts noticeably with iridium. The tungsten composites were anodically etched for approximately ten seconds at a DC potential of four volts in a solution containing 300 ml of water, 5 ml of ammonium hydroxide, 3 gm of sodium hydroxide, and 2 gm of chromic acid. The etchant color tinted the tungsten-rich intermediate phase blue, and the iridium-rich phase tan to grayish tan.

IV. RESULTS AND DISCUSSION

A. Coating Methods

1. Pressure Bonding

Of the two coating methods used in this investigation, the high temperature pressure bonding method was the only one which consistently produced small sheets of the refractory metals coherently and adherently coated with uniformly thick (approximately 0.005 inch) iridium. In the initial pressure bonding experiments, good adherence was achieved in all systems, partially

because of the formation of a reaction zone between the substrate metal and the iridium coating. Since a reaction zone was not desired for specimens which were later to be annealed for the diffusion experiments, the processing parameters (temperature, pressure, and time-at-temperature) were adjusted so that good adherence was achieved without the formation of an observable reaction zone. The presence or absence of a reaction zone was determined by metallographic examination of sections of the as-formed composites at a magnification of 500X. The processing parameters used to obtain coating adherence without reaction zone formation for each of the systems studied are listed in Table I. Sufficient time-at-temperature to effect a diffusion bond probably causes the good adherence achieved. The photomicrograph in Figure 6 is typical of that obtained for all of the systems studied.

In the previous investigation under Contract No. NASw-1030,[1] several attempts were made to roll bond sheet iridium to sheet tantalum and niobium; during the present program, no specimens were prepared by roll bonding. The method is mentioned briefly here because it is extremely promising for coating large sheets of the refractory metals with iridium. The bond obtained between iridium and the refractory metals is largely dependent upon the kinetics of the reaction occurring. In pressure bonding, the time at which the metal sheets are held at the proper temperature and pressure is an easily controllable variable. Since the contact time of the substrate metal and the iridium coating during roll bonding is very short, greater emphasis must be placed on temperature and pressure to obtain an adherent diffusion bond.

2. Fused-Salt Electrodeposition of Iridium

The previous study[1] showed that improper substrate surface preparation prior to electroplating invariably resulted in an irregular coating which was often nonadherent. This inability to produce adherent iridium coatings on the refractory metals with any degree of consistency necessitated trying a variety of surface preparations. The cleaning processes evaluated were outlined in the final report for Contract No. NASw-1030[1]. A method of surface preparation was developed and standardized for use on all of the substrate metals, and this method, outlined in the experimental section of this report, was used throughout the present program.

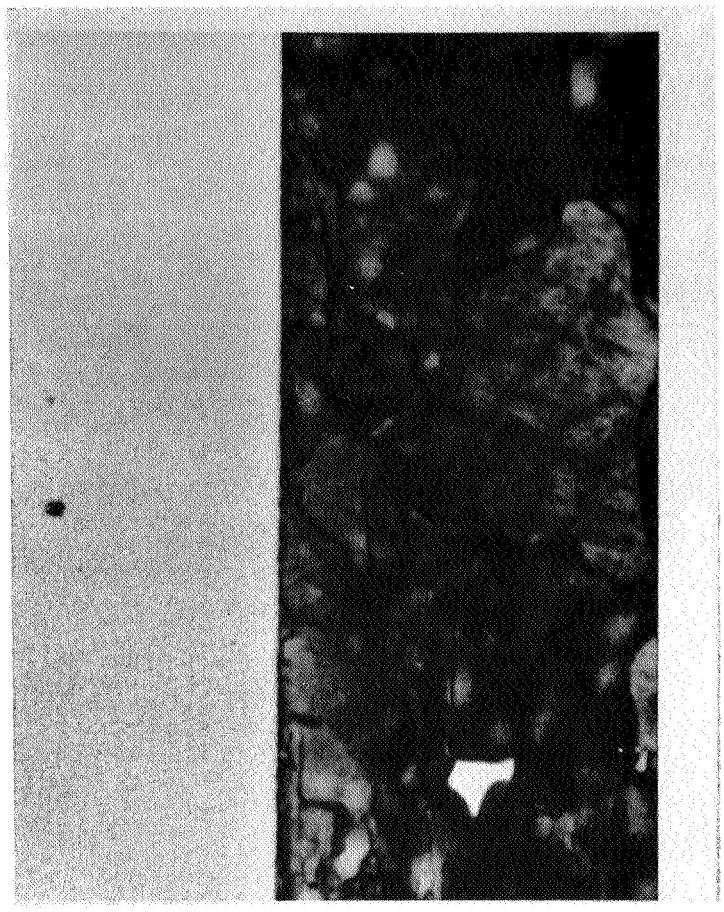

Figure 6. Photomicrograph of Pressure Bonded Sample HP-3M, 1000X.

N-11665

The data obtained under Contract NASw-1030 were insufficient to distinguish between electrolyte deterioration due to (1) a gradual buildup 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. 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. Chemical analysis of portions of the electrolyte during electrolysis [including portions of electrolytes which no longer provided coherent deposits] indicated that iridium must be maintained in a low valency state to produce coherent deposits. Consequently, the new electroplating cell was designed and constructed to minimize atmospheric contamination of the electrolyte. In addition, the previously used alumina crucible was replaced by a graphite crucible to eliminate contamination due to the presence of aluminum oxide. Insufficient anode area may also lead to oxidation of the complex iridium anion. If the anode-to-cathode area is varied, this source of oxidation may readily be eliminated. In addition to directly affecting the valence state of the iridium anion, the presence of moisture or oxygen in the hot electrolyte can oxidize the substrate metal surface and prevent a coherent iridium deposit from adhering. Although the new electroplating cell was designed to minimize atmospheric contamination, the harmful effects of chemical reactions occurring between the hot substrate metals and the hot electrolyte [or impurities in the electrolyte] can further be minimized by depositing a thin strike coat of iridium as rapidly as possible on the substrate surface. Previously, the elctrodes could not be preheated in an inert atmosphere before being immersed into the molten electrolyte. Consequently, the electrolyte could solidify around the cold electrodes, chemically react with the cathode, and then melt as the temperature of the electrodes approached that of the electrolyte. The heat-affected zone of the new cell was extended sufficiently above the molten electrolyte to allow preheating of the electrodes to temperatures near the melting point of the electrolyte.

The first molten electrolyte used in the new apparatus was in operation for one month; ten coherent iridium-coated molybdenum and six tungsten specimens were produced. This electrolyte was not in continuous operation (electroplating was not continued over a weekend and rarely overnight) and did not noticeably deteriorate. This fact suggests that the complex iridium anion responsible for producing the coherent deposits is thermodynamically stable. Previous failures to produce coherent iridium coatings appear to have been caused primarily by oxidation and atmospheric contamination of the molten salts.

This detrimental effect of atmospheric contaminants was demonstrated when an argon inlet line broke over a weekend admitting air to the normally closed system, resulting in electrolyte deterioration and, subsequently, incoherent deposits. If the electrolyte deterioration was caused by an increase in the moisture content, continuous flushing with argon through the enclosed system, and intermittent electroplating in the manner used originally to charge the electrolyte with iridium might eventually lower the moisture content to a level where the electrolyte would once again produce coherent coatings. However, repeated attempts over several weeks at rejuvenating the contaminated electrolyte failed, and the electrolyte was discarded. Apparently, atmospheric contaminants oxidize the iridium anion needed for coherent deposits to a high valency state. The use of an electroplating cell which could be maintained at an argon pressure greater than ambient minimized both the atmospheric contamination of the electrolyte and oxidation of the hot substrate metal.

A second charged electrolyte which was in operation for less than one week provided two coherently coated tungsten samples. Unfortunately, the iridium support wires of a tungsten specimen broke while the sample was being placed into the electrolyte, and this electrolyte was discarded. A similar incident occurred with a third electrolyte after it had produced coherent iridium coatings on two tungsten and six niobium samples. Tungsten and molybdenum could be electroplated consistently with dense, coherent iridium deposits, but efforts to consistently coat niobium and tantalum were not successful. Failure to obtain coherent and adherent iridium deposits on niobium and tantalum cannot be attributed to electrolyte contamination, since the operation of each electrolyte was intermittently checked by electroplating onto a molybdenum substrate. The plating difficulties seem to stem from the ease with which niobium and tantalum react with the molten electrolyte. One method of preventing this chemical reaction was to physically separate the reacting constituents by means of a dense electrically conductive material. After it was determined that a coherent and adherent coating of iridium could readily be plated onto nickel rods, several niobium and tantalum sheet samples were electroplated with less than 0.1 mil-thick nickel from a commercially available nickel sulfamate electrolyte. Iridium was then deposited from the molten

cyanide electrolyte onto the nickel-coated substrate. Microscopic examination of metallographically polished sections of the dual-coated samples showed that both coatings were dense and apparently well bonded.

The successful development of a dual coating for niobium and tantalum made it possible to consistently electroplate all of the substrate metals with dense coherent iridium deposits. The major difficulty that remained was not with the plating itself but with the iridium electrical lead wires which were spot welded to the substrate metals. At times, the welding operation made the lead wires very brittle or a poor bond was obtained, and breakage occurred prior to or during electroplating. In addition, residual impurities around the heat-affected zone of the weld sometimes resulted in pin holes in an otherwise dense and coherent iridium coating.

B. Diffusion Studies

The life expectancy of iridium coatings on refractory metals is principally determined by two factors: loss of iridium through 1) oxidation and 2) intermetallic compound formation. The rate of oxidation of iridium was previously determined under a program [5] designed to evaluate the use of iridium as an oxidation-protective barrier for graphite. The present diffusion studies were carried out to determine the iridium loss due to intermetallic compound formation. Initially, attempts were made to determine chemical diffusivities and the rates of growth of individual reaction zones; however, irregular reaction zone phase boundaries were observed in annealed diffusion couples, and etching the annealed specimens to microscopically reveal these phase boundaries was difficult. The amount of iridium depleted through intermetallic compound formation was, therefore, determined directly from measurements of the thickness of iridium remaining after annealing rather than from measurements of changes in the thickness of the total reaction zone.

1. The Molybdenum-Iridium System

Initially, a great deal of effort was expended in determining precisely the rate of growth of the reaction zone for the molybdenum-iridium system.

Sections of pressure-bonded samples were metallographically polished and etched, and other sections were heat treated. The results are given in Table IV. No evidence of intermetallic compound formation was observed in any of the pressure-bonded specimens, and iridium and molybdenum appeared to be well bonded. Figure 6, a photomicrograph of a section of pressure-bonded sample HP-3M, is typical of the pressure-bonded samples for all of the systems studied; it shows the substrate metal grains, no grain structure in the iridium phase, and no observable reaction zone.

Partial delamination was observed in several samples annealed at temperatures of 1530°C and higher. Particularly noteworthy were samples, HP-4M-1710 and HP-4M-1710-2. After the sample HP-4M-1710-1 was annealed for one hour, a section, HP-4M-1710-2, was annealed for one additional hour at the same temperature. No further increased reaction zone width was observed. There are two possible explanations for this result. Either the process of sectioning HP-4M-1710-1 produced a fracture, or the thermal shock of heating rapidly to the annealing temperature produced a break in the reaction zone.

A double etch method, described in the experimental section of this report, was developed to lightly color-tint the molybdenum grains without severely attacking the grain boundaries. Neither etchant reacted with the iridium-rich intermediate phase sufficiently to reveal clearly the phase boundaries without severely attacking other phases of the composite. Sufficient contrast between phases was obtained so that the interfacial boundaries could be detected under the microscope, but a further increase in contrast would be desirable for photographic purposes. The iridium-rich intermediate phase was bireflectant under polarized light.

Figures 7, 8, and 9 are photomicrographs of samples HP-1M-1300-5, HP-3M-1530-2, and HP-4M-1710-4, respectively, taken at a magnification of 1000X. In these photomicrographs, the molybdenum grains, the molybdenum-rich intermediate phase, and the light (void of structural details) iridium phase can readily be seen. Structural details are not observable in the iridium-rich intermediate phase, and very little contrast is present between this phase and the iridium. In addition, Figures 7 and 8 indicate that iridium may be preferentially diffusing along the molybdenum grain boundaries.

TABLE IV

DIFFUSION DATA FOR THE MOLYBDENUM-IRIDIUM SYSTEM

Sample No.	Optical Pyrometer Temperature °C	Thermocouple mV	Heat Treat Time, hrs.	Total Reaction Zone Width, μ
HP-1M*				0
HP-2M*				0
HP-3M*				0
HP-4M*				0
HP-5M*				0
HP-1M-1300-1	1292 ± 10	22.65 ± 0.01	1.0	4.2
HP-1M-1300-2	1292 ± 10	22.65 ± 0.01	2.0	---**
HP-1M-1300-3	1292 ± 10	22.65 ± 0.01	4.0	7.0
HP-1M-1300-4	1292 ± 10	22.65 ± 0.01	8.0	9.1
HP-1M-1300-5	1292 ± 10	22.65 ± 0.01	16.0	11.2
HP-3M-1530-1	1527 ± 10	26.58 ± 0.01	1.0	14.0
HP-3M-1530-2	1527 ± 10	26.58 ± 0.01	2.0	19.6
HP-3M-1530-3	1527 ± 10	26.58 ± 0.01	4.0	25.2
HP-3M-1530-4	1527 ± 10	26.58 ± 0.01	8.4	(16.8)**
HP-3M-1530-5	1527 ± 10	26.58 ± 0.01	16.2	(28.0)**
HP-4M-1710-1	1695 ± 10	29.15 ± 0.03	1.0	16.8
HP-4M-1710-2	1695 ± 10	29.15 ± 0.03	2.0	(16.8)**
HP-2M-1710-3	1695 ± 10	29.15 ± 0.03	4.0	(24.0)**
HP-4M-1710-4	1695 ± 10	29.15 ± 0.03	8.0	(30.8)**
HP-5M-1900-1	1895 ± 10	31.94 ± 0.02	0.4	8.4
HP-4M-1900-2	1895 ± 10	31.94 ± 0.02	2.0	(19.6)**

* Sections of the pressure-bonded samples.
** Delamination before or during heating or annealing.

Figure 7. Photomicrograph of Annealed Sample HP-1M-1300-5, 1000X.

N-11666

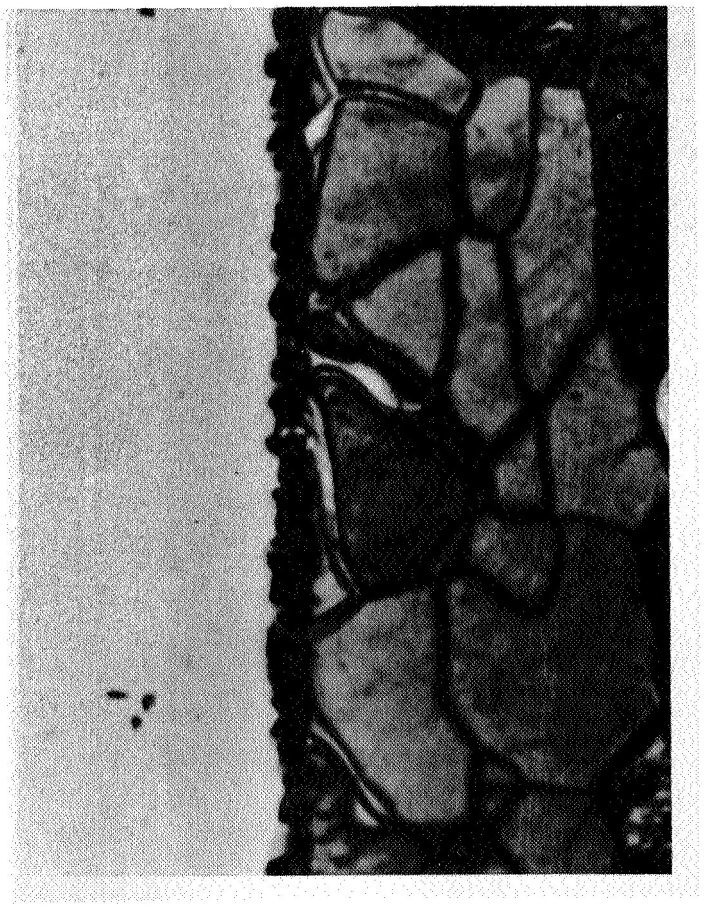

Figure 8. Photomicrograph of Annealed Sample HP-3M-1530-2, 1000X.

N-11667

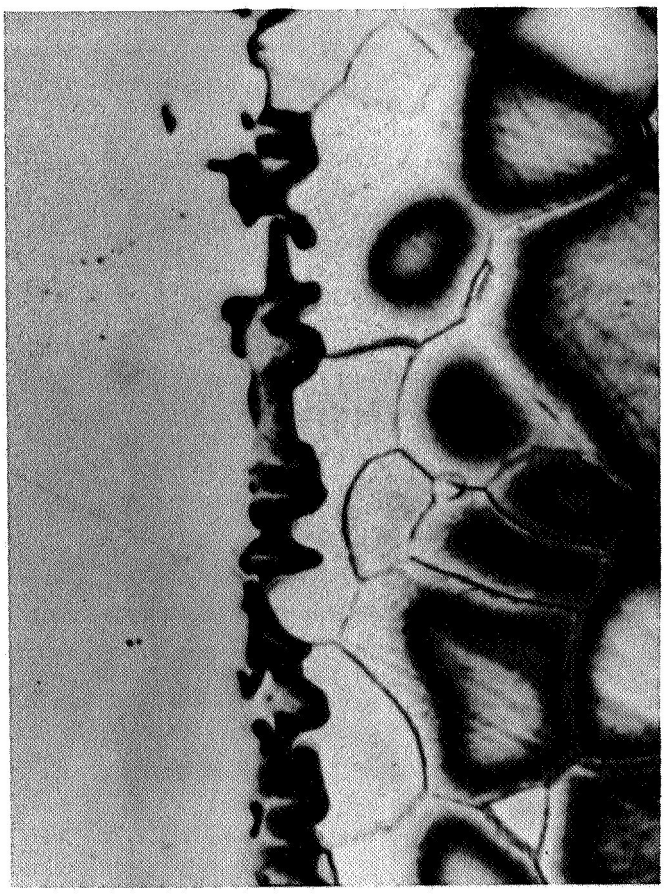

Figure 9. Photomicrograph of Annealed Sample HP-4M-1710-4.

N-11668

In the photomicrograph of Figure 7, two intermetallic phases seem to be present. Giessen, Jaehnigen, and Grant[6] indicated that the three phases Mo_3Ir, MoIr, and $MoIr_3$ exist at 1300°C and that at 1530°C, these phases and an ϵ - phase are present. The ϵ - phase can undergo two eutectoid decomposition reactions on cooling (i.e., $\epsilon \rightarrow Mo_3Ir$ + MoIr and $\epsilon \rightarrow$ MoIr + $MoIr_3$). Similarly, at 1710°C, the phases Mo_3Ir, ϵ, and $\propto MoIr_3$ are present, and the ϵ - phase decomposes on cooling.

In an effort to determine which, if any, of the features of the photomicrographs were artifacts, sections of the above samples were examined with an electron microprobe analyzer. This work was carried out at the Research Laboratory of the Mining and Metals Division of Union Carbide Corporation at Niagara Falls, New York. Figure 10 is an X-ray line scan for iridium in a polished section of Sample HP-3M. The grain structures within the iridium (the dark phase) and molybdenum (light phase) are not discernible. The overall specimen image and the X-ray line scan do not reveal any intermediate compound formation, substantiating the findings of the photomicrograph in Figure 6. The electron microprobe micrographs of Figures 11 through 15 may be compared with the photomicrograph in Figure 8, since they are all of sample HP-3M-1530-2. Figure 11 shows an X-ray scan for iridium. Although this sample has a rather wide band of reaction products, this type of analysis did not detect the different concentrations of iridium in the various intermetallic compounds. The electron scanning image of Figure 12 shows the reaction zone structural details obtainable with the microprobe analyzer. No structural details can be observed in either the iridium or molybdenum (light phase); however, the intermediate phases present in the reaction zone are readily detected, including the iridium rich phases which are difficult to detect in the photomicrograph of Figure 8. The scanning image indicates that there may be as many as five intermediate phases in the reaction zone. Figure 13 shows X-ray line scans for both iridium and molybdenum in which the reaction zone interfaces adjacent to both the iridium and molybdenum are easily located. The intermetallic phases present in the reaction zone could not be identified. Figures 14 and 15 show some structural details in iridium and molybdenum, respectively. In addition, Figure 15 includes an iridium line scan which detected iridium in the molybdenum grain boundaries but not in the grains themselves.

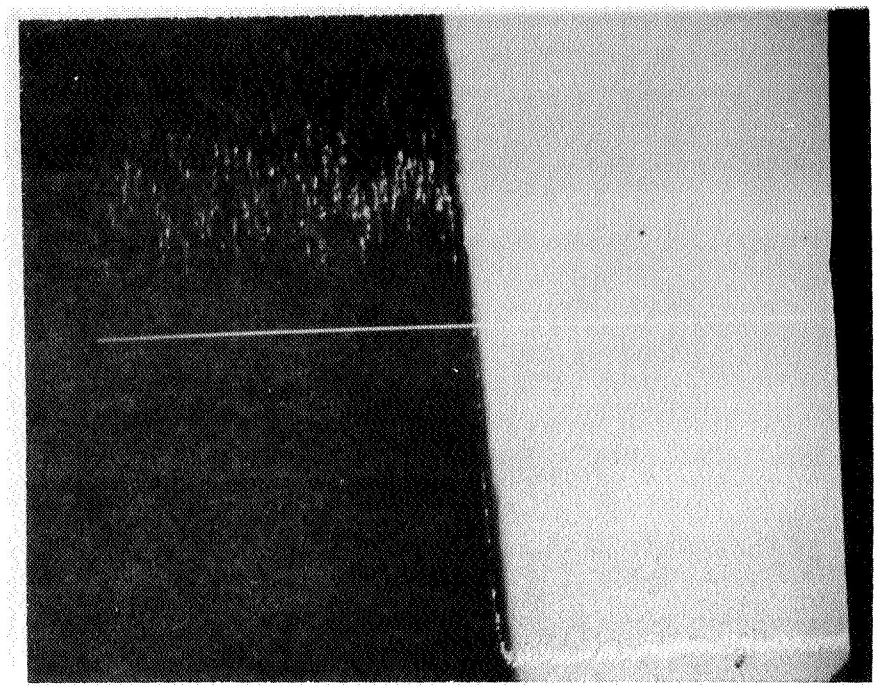

Figure 10. Electron Microprobe X-ray Line Scan for Iridium in Sample HP-3M, 1250X.

N-11669

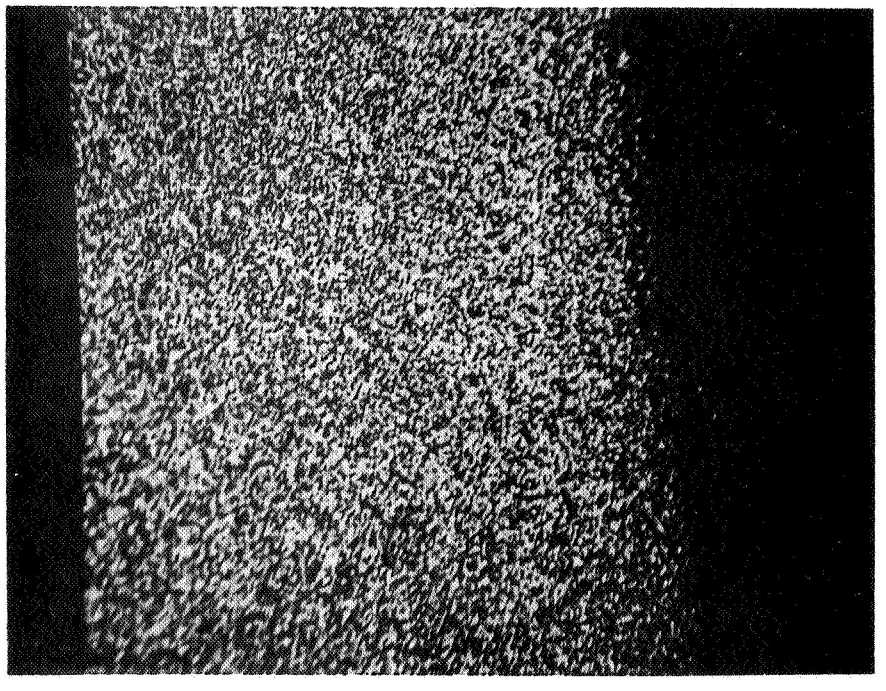

Figure 11, Electron Microprobe X-ray Scan for Iridium in Sample HP-3M-1530-2, 1250X.

N-11670

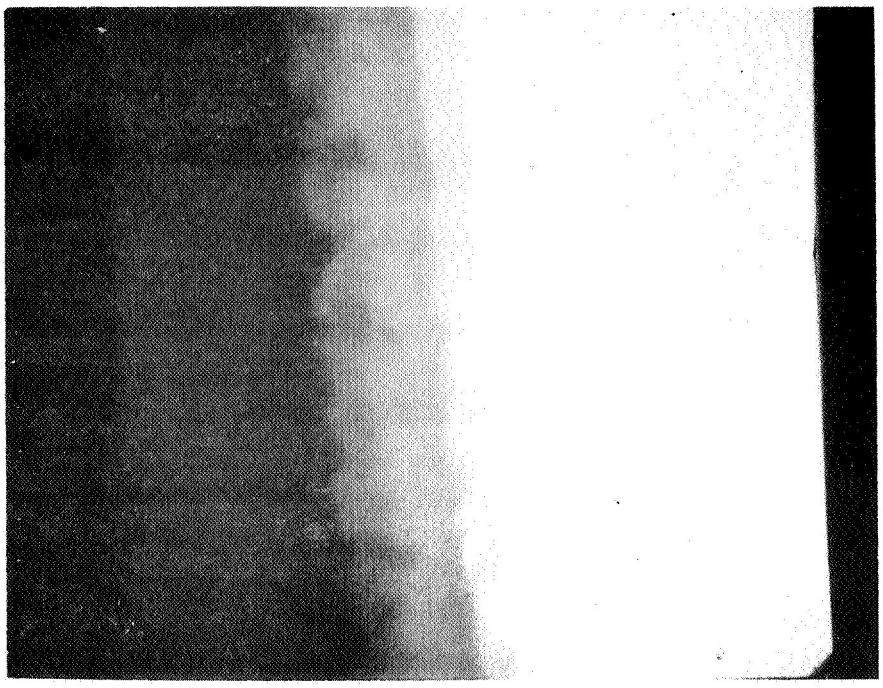

Figure 12. Electron Microprobe Electron Scanning of Sample HP-3M-1530-2, 1250.

N-11671

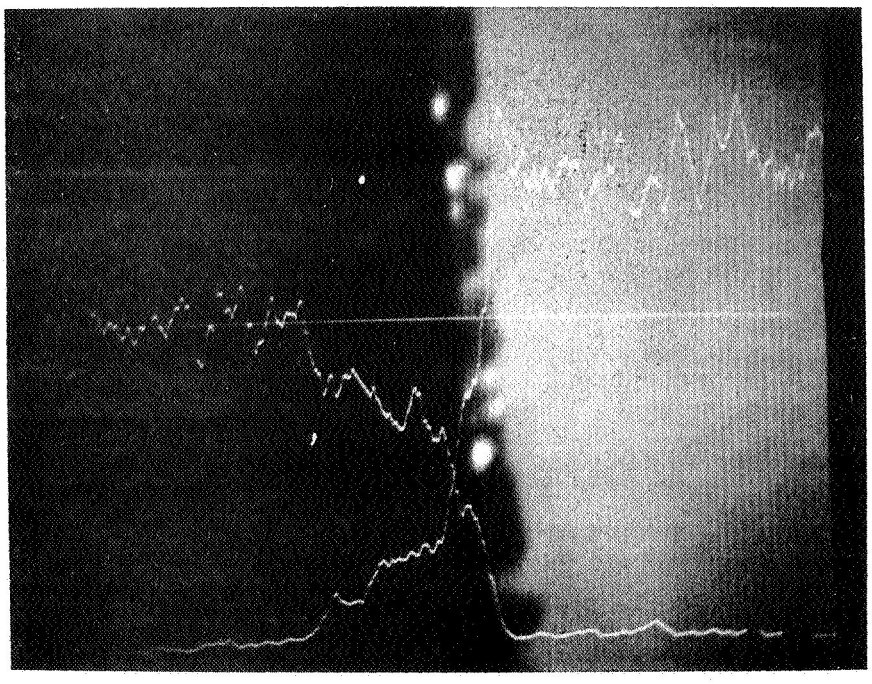

Figure 13. Electron Microprobe Iridium and Molybdenum X-ray Line Scans in Sample HP-3M-1530-2, 1250X.

N-11672

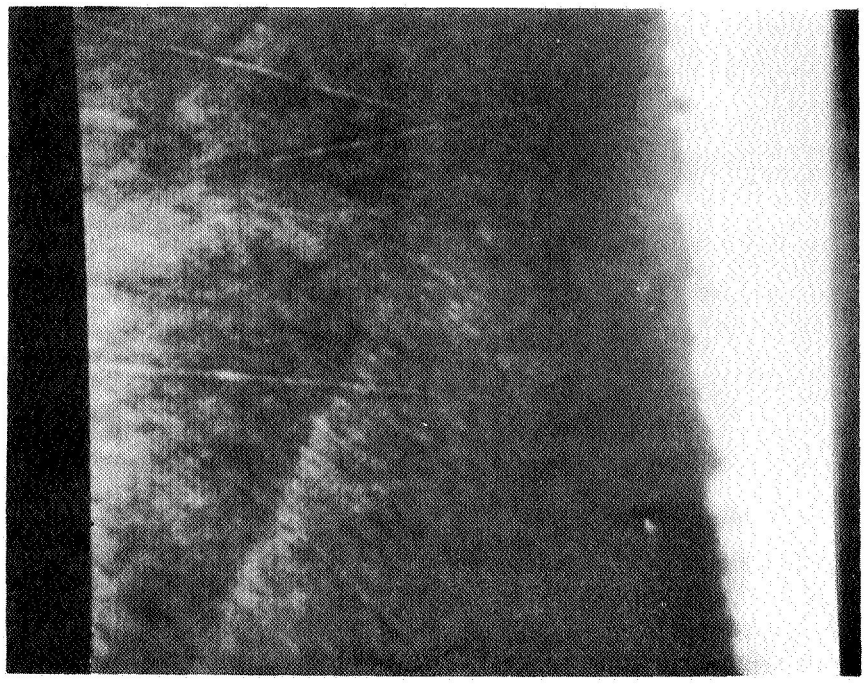

Figure 14. Electron Microprobe Electron Scanning Image for Iridium Structural Details in Sample HP-3M-1530-2, 1250X.

N-11673

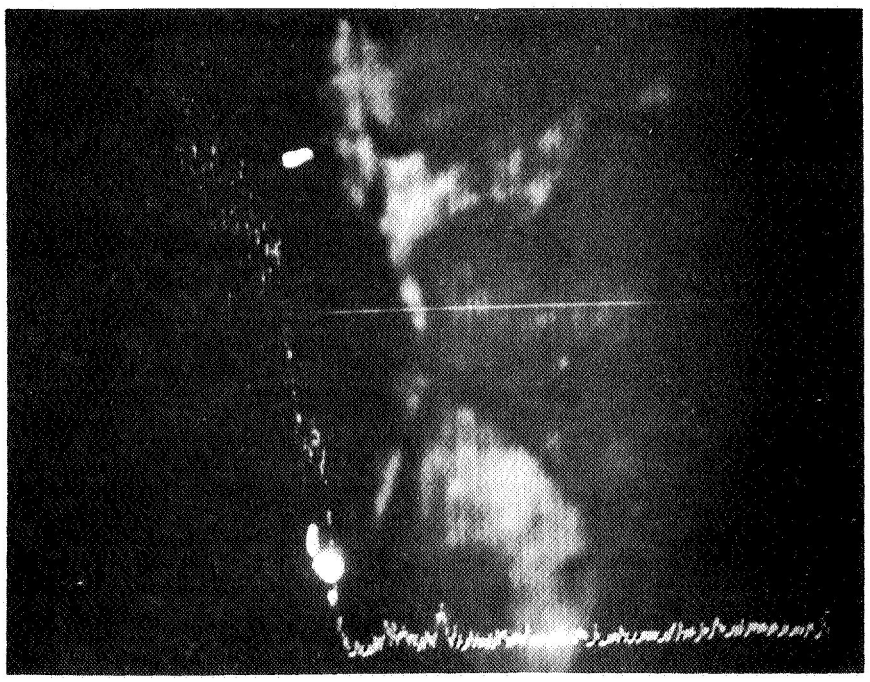

Figure 15. Electron Microprobe Electron Scanning Image for Molybdenum Structural Details and an Iridium X-ray Line Scan of Sample HP-3M-1530-2, 1250X.

N-11674

An iridium point count in the molybdenum grains and in the boundaries separating the grains definitely indicated the presence of iridium within the boundaries but none within the grains.

Similar electron microprobe analyses were conducted on sections of samples HP-3M-1530-3, HP-4M-1900-2, HP-1M-1300-5, and HP-4M-1710-4 which also show some preferential grain boundary diffusion of iridium in molybdenum. Although grain boundary diffusion may not occur appreciably at all annealing temperatures, preferential grain orientation or grain boundary diffusion results in the formation of highly irregular reaction zone interfacial boundaries.

As a consequence of the above findings, efforts to precisely determine the reaction zone growth rate was de-emphasized in favor of direct measurements of the thickness of the iridium layer after annealing. Additional molybdenum-iridium diffusion couples were pressure bonded, and sectioned pieces, measuring approximately 1/8 inch or 1/4 inch square, were metallographically polished on one side exposing both the molybdenum and the iridium. The thickness of iridium was measured by means of a microscope with a calibrated eye piece: the average deviation of the measured iridium thickness for each of the samples was between one and two microns. No reaction zone was observed in the 'as-pressure-bonded composites'. After the specimens were vacuum annealed, they were repolished on the same surface and remeasured, primarily to determine the decrease in thickness of the iridium coating. Although the thickness of the reaction zone formed was also measured, no effort was made to increase the contrast between phases by etching, making this measurement difficult to obtain. The results are listed in Table V.

TABLE V

HEAT TREATMENT OF IRIDIUM COATED MOLYBDENUM

Sample Number	Heat Treatment	Reaction Zone Width, Microns	Decrease in Iridium Thickness, Microns
7M-2	4 hrs. @ 1300°C	6.7	2.4
7M-9	7.8 hrs. @ 1300°C	9.6	0.2
7M-1	16.4 hrs. @ 1300°C	11.7	10.7
6M-3	1 hr. @ 1500°C	14.8	3.0
7M-7	4 hrs. @ 1500°C	21.6	7.8
6M-6	8.4 hrs. @ 1500°C	21.5	12.8
6M-4	12.1 hrs. @ 1500°C	27.7	3.4
6M-8	14.9 hrs. @ 1500°C	27.4	16.1
6M-6	16.3 hrs. @ 1500°C	24.6	13.1
7M-8	1 hr. @ 1700°C	18.0	8.7
7M-4	4 hrs. @ 1700°C	27.7	12.5
7M-5	8.3 hrs. @ 1700°C	33.3	14.5
6M-2	12.0 hrs. @ 1700°C	43.6	14.2
7M-3	16.6 hrs. @ 1700°C	51.2	22.4
7M-13	1 hr. @ 1900°C	20.1	11.4
7M-12	2 hrs. @ 1900°C	29.3	14.0
6M-B-3	3 hrs. @ 1900°C	26.7	13.2
7M-10	4 hrs. @ 1900°C	36.0	15.3
6M-1	5 hrs. @ 1900°C	35.2	20.4
6M-7	5 hrs. @ 1900°C	36.0	7.9
7M-11	6 hrs. @ 1900°C	46.2	27.2

The average deviation in the measurement of the thickness of iridium remaining after annealing varied between one micron and four microns. The magnitude of this average deviation is thought to depend largely upon (1) the amount of irregularity of the interface between the iridium and the iridium-rich intermetallic phase, (2) the difficulty in sharply resolving this interface microscopically due to a lack of contrast between the two adjacent phases, and (3) the fact that surfaces of the sheets of iridium and molybdenum are neither optically flat nor perfectly parallel. Even though extreme care is taken to remove as little material as possible in repolishing the annealed specimens, the as-received iridium varied in thickness sufficiently to introduce errors of a few microns. The samples in Table V heat treated at 1300°C show that the reaction zone increases in width with increasing time and temperature. However, the calculated decrease in thickness of iridium is less for sample 7M-9 than for 7M-2, although 7M-9 was held at 1300°C almost twice as long as 7M-2. The growth of the reaction zone is independent of irregularities in thickness of the as-received sheet iridium and molybdenum. The growth depends upon grain orientation, prior thermal history, and mechanism of growth. The calculated changes in thickness of the iridium coating is related to the same factors controlling the reaction zone growth in addition to irregularities in the thickness of the iridium coating. An estimate of the life expectancy of a five mil iridium coating on molybdenum, by extrapolation of the data, indicates that the coating would last longer than 600 hours at 1700°C and for approximately 130 hours at 1900°C.

2. The Tungsten-Iridium System

The research effort for the tungsten-iridium system was analogous to that for the molybdenum-iridium system. The results are presented in a chronological sequence. Efforts were made to reveal the reaction zone of the tungsten-iridium system by using the polishing and etching techniques of Rapperport and Smith[7]. Their etchant proved to be too severe, resulting in preferential attack of the tungsten and tungsten-rich intermediate phase. A color etch was developed, described in the experimental section, which color tinted the tungsten rich intermediate phase blue and the iridium-rich phase tan to grayish tan. The resuts are given in Table VI. The data show that sample HPI-W was the only pressure-bonded specimen for this series of experiments which was well bonded without developing a reaction zone.

TABLE VI

DIFFUSION DATA FOR THE TUNGSTEN-IRIDIUM SYSTEM

Sample No.	Optical Pyrometer Temperature °C	Thermocouple mV	Heat Treat Time, hrs.	Total Reaction Zone, Width, μ
HP1-W*				0
HP5-W*				5.6
HP6-W*				5.6
HP7-W*				7.0
HP1-W1300-1	1295 ± 10	22.65 ± 0.01	4.0	4.2
HP1-W1300-2	1295 ± 10	22.65 ± 0.01	16.0	5.6
HP1-W1530-1	1538 ± 10	26.58 ± 0.02	2.0	7.0
HP1-W1530-2	1538 ± 10	26.58 ± 0.02	4.0	9.8
HP1-W1530-3	1538 ± 10	26.58 ± 0.02	8.4	12.6
HP1-W1530-4	1538 ± 10	26.58 ± 0.02	15.8	14.0
HP1-W1530-5	1538 ± 10	26.58 ± 0.02	32.2	21.0
HP5-W1710-1	1705 ± 10	29.15 ± 0.03	2.0	11.2
HP5-W1710-2	1705 ± 10	29.15 ± 0.03	4.0	14.0
HP5-W1710-3	1705 ± 10	29.15 ± 0.03	8.27	18.2
HP5-W1710-4	1705 ± 10	29.15 ± 0.03	16.1	23.8
HP5-W1900-1	1905 ± 10	31.94 ± 0.03	2.1	16.8
HP6-W1900-2	1905 ± 10	31.94 ± 0.03	4.0	19.6
HP6-W1900-3	1905 ± 10	31.94 ± 0.03	7.9	28.0
HP6-W1900-4	1905 ± 10	31.94 ± 0.03	16.3	33.6
HP7-W2125-3	2127 ± 10	34.40 ± 0.02	2.0	16.8

* Sections of the pressure-bonded samples.

When determining reaction rates for systems limited by diffusion, one should start with a sample which is well bonded and which does not contain reaction products. Since the metallographic preparation and microscopic examination of samples were extremely time consuming, sections of the pressure-bonded samples were annealed before the information was obtained that several of the pressure-bonded samples already contained measurable reaction zones. Consequently, the total reaction time for those samples is the heat-treat time listed in Table VI plus the time at temperature needed to develop the reaction zone of the pressure-bonded specimen. At the higher temperatures, where the reaction zone develops very rapidly and/or at very long reaction times, the difference between the listed time and the actual time needed to develop the zone width becomes negligibly small.

The data in Table VII are for the series of experiments in which the decrease in thickness of iridium was determined as a function of time at specific temperatures. As with the molybdenum-iridium system, sections of pressure-bonded samples were metallographically polished on one side and the thickness of the iridium coating measured using a microscope with a calibrated eyepiece. The samples were not etched or color tinted. No reaction zone was observed in the samples before they were annealed. The reaction zone grows very slowly, and, consequently, iridium decreases in thickness very slowly in this system. Several attempts were made to obtain data at 1300°C. Specimens were annealed at that temperature for 1.5, 5.2, and 11.0 hours. No decrease in thickness of the iridium was observed in any of the samples. The maximum reaction zone growth was approximately six microns. At 1500°C, the iridium loss was less than five microns in 16.2 hours, and the reaction zone width was 10.8 microns. Since samples annealed at 1700°C for approximately seventy hours lost less than 10 microns of iridium, the life of a five-mil-thick coating at this temperature would be over 1000 hours. The data at 1900°C indicate that a five-mil-thick iridium coating would last at least 300 hours.

TABLE VII

HEAT TREATMENT OF IRIDIUM
COATED TUNGSTEN

Sample Number	Heat Treatment	Reaction Zone Width, Microns	Decrease in Iridium Thickness, Microns
10 W-3	1.5 hrs @ 1300°C	~ 3	No Change
10 W-6	5.2 hrs @ 1300°C	---	No Change
10 W-5	11.0 hrs @ 1300°C	6.3	No Change
10 W-8	16.2 hrs @ 1500°C	10.8	4.4
11 W-1	9.2 hrs @ 1700°C	17.1	10.4
11 W-5	11.0 hrs @ 1700°C	19.6	5.7
10 W-10	17.0 hrs @ 1700°C	19.3	1.6
11 W-4	46.0 hrs @ 1700°C	27.5	2.7
11 W-3	67.5 hrs @ 1700°C	32.4	7.8
10 W-2	1.0 hrs @ 1900°C	12.0	8.5
10 W-1	4.0 hrs @ 1900°C	17.6	7.9
10 W-9	5.0 hrs @ 1900°C	19.7	7.8
10 W-7	6.0 hrs @ 1900°C	23.3	10.2
11 W-B-7	7.0 hrs @ 1900°C	22.0	11.6
11 W-2	8.4 hrs @ 1900°C	22.2	14.2
10 W-11	10.2 hrs @ 1900°C	26.5	14.5

3. The Niobium-Iridium System

In the niobium-iridium system, no reaction zone was observed during microscopic examination of metallographically polished, (but not etched) sections of the pressure-bonded composites. No effort was made to develop an etchant capable of delineating the reaction zone interfacial boundaries for this system. Sections of the pressure-bonded composites were metallographically polished on one side and the thickness of the iridium coating measured by using a microscope. After the samples were annealed, they were remeasured to determine both the decrease in thickness of the iridium and the width of the reaction zone formed. The data obtained are presented in Table VIII. At 1300°C, no decrease in thickness of the iridium could be measured until a sample was annealed for 65.7 hours. Since an eutetic reaction occurs in this system at 1840 ± 20°C[8], the maximum annealing temperature was 1780°C. The data indicate that a five-mil-thick iridium coating will last at least 200 hours at this temperature.

4. Comparison of Systems Behavior

The results of the experiments designed to determine the decrease in thickness of an iridium coating on the refractory metals show that the most rapid decrease occurs in the molybdenum-iridium system and the slowest in the tungsten-iridium system. Although the data are insufficient for a detailed analysis of reaction mechanisms, estimates of the life expectancy of an iridium coating can be obtained by assuming solid-state diffusion controlled reactions. Extrapolation of the present data (the decrease in thickness of iridium proportional to the time to the one-half power) indicates that a five-mil-thick iridium coating on molybdenum would last over 600 hours at 1700°C and for approximately 130 hours at 1900°C. In contact with tungsten, the iridium coating would last over 1000 hours at 1700°C and at least 300 hours at 1900°C. In contact with niobium, the iridium coating should last over 700 hours at 1700°C and at least 200 hours at 1780°C. Iridium coated molybdenum[9] and tungsten[10] composites may be used at temperatures over 2000°C. However, the iridium-niobium[8] composites are limited to a maximum temperature of 1840 ± 20°C because of a eutectic reaction at that temperature.

TABLE VIII

HEAT TREATMENT OF IRIDIUM COATED NIOBIUM

Sample Number	Heat Treatment	Reaction Zone Width, Microns	Decrease in Iridium Thickness, Microns
1 Nb-8	4 hrs. @ 1300°C	3.4	No Change
1 Nb-11	30 hrs. @ 1300°C	13.4	No Change
1 Nb-10	65.7 hrs. @ 1300°C	19.3	5.6
1 Nb-5	2 hrs. @ 1500°C	12.2	4.2
1 Nb-6	4 hrs. @ 1500°C	16.7	5.9
1 Nb-7	8 hrs. @ 1500°C	17.7	3.6
1 Nb-13	8.2 hrs. @ 1500°C	19.0	6.3
1 Nb-12	12.2 hrs. @ 1500°C	23.7	5.6
1 Nb-9	16.4 hrs. @ 1500°C	23.5	6.1
1 Nb-2	1 hr. @ 1700°C	17.2	4.0
1 Nb-1	2 hrs. @ 1700°C	24.9	3.1
1 Nb-3	3 hrs. @ 1700°C	38.5	3.5
4 Nb-B-6	6 hrs. @ 1700°C	51.8	7.8
1 Nb-4	8.2 hrs. @ 1700°C	56.2	5.5
3 Nb-1	1 hr. @ 1780°C	27.7	10.9
3 Nb-2	2 hrs. @ 1780°C	37.8	6.9
3 Nb-3	5 hrs. @ 1780°C	55.5	11.9
3 Nb-6	6 hrs. @ 1780°C	68.9	19.3

It had previously been determined[5] that iridium will oxidize in air flowing at high velocities at approximately 0.1 mil per hour at 1700°C and at 0.2 mil per hour at 1900°C. Since this work indicates that the iridium loss due to internal reactions is very much less than that due to oxidation, for all practical purposes, the life of the coating will be determined by the oxidation rate. However, at low air flow rates and/or low partial pressures of oxygen, where the oxidation rate may be more than an order of magnitude lower, both oxidation and intermetallic compound formation must be considered in determining coating life.

C. Mechanical Compatibility

The microbend-tester was described in the experimental section of this report together with data obtained in evaluating the performance of this apparatus. Subsize specimens of the base metals, molybdenum, tungsten, niobium, and iridium were examined with the microbend tester. The results are given in Table IX. Strips of these metals, approximately one inch long, were cut from the as-received sheet with a water-cooled abrasive wheel. The iridium strips were sectioned from 0.040 inch thick sheet and machined to a thickness of approximately 0.020 inch. The surface which was to be observed with the microscope during bending was metallographically polished but not etched. The four molybdenum specimens which were not heat treated prior to testing did not fracture. However, with all of these samples, the applied loads reached maximum values corresponding to strengths between 172,000 and 201,000 psi and then decreased as bending was continued. The molybdenum specimen heat treated at 1550°C for one hour was bent to 90 degrees with a maximum applied load of four pounds (representing a maximum strength of 104,000 psi). Two of the tungsten samples failed in shear (delaminated) at strengths of 379,000 and 340,000 psi; in a third sample, the load reached a maximum value of 11.25 lbs (corresponding to a flexural strength of 267,000 psi) and then decreased with no observable indication of either a shear or tensile break. One tungsten specimen was heated at 1500°C for 1-1/2hours under vacuum, furnace cooled, and tested. This sample fractured at a breaking strength of 182,000 psi.

TABLE IX

FLEXURAL TEST RESULTS FOR THE BASE METALS

Sample* Number	Width, B Inches	Thickness, D Inches	Maximum Applied Load, P lbs.	Flexural** Strength psi x 10^5	Comments
Mo-1	0.1188	0.0215	9 1/2	1.95	Load dropped off. No break.
Mo-2	0.0982	0.0210	4	1.04	Heat treated at 1550°C for 1 hr. No break, 90° bend.
Mo-3	0.1128	0.0222	8 1/2	1.72	Load dropped off. No break.
Mo-4	0.1046	0.0212	8 1/8	1.94	" " " " "
Mo-5	0.1014	0.0210	8	2.01	" " " " "
W-1	0.1081	0.0216	17	3.79	Failed in shear.
W-2	0.1092	0.0222	16 1/4	3.40	" " "
W-3	0.0981	0.0220	11 1/4	2.67	Load dropped off. No break.
W-4	0.0832	0.0220	6 1/2	1.82	Heat treated at 1550°C for 1 1/2 hrs. Clean break.
Nb-1	0.1196	0.0215	3 3/4	0.64	Load dropped off. No break.
Nb-2	0.1264	0.0211	3 5/8	0.61	Heat treated at 1000°C for 1 hr. Load dropped off. No break.
Ir-1	0.1208	0.0213	7 3/4	1.33	Clean break.
Ir-2	0.1269	0.0196	3 3/8	0.65	Heat treated at 1700°C for 1 hr. Load dropped off. Sample bent to ~90° before failure.

*The molybdenum and tungsten samples were tested with a fixture having a 0.750 inch span, L, while the remainder were tested with a fixture having a 0.625 inch span.

**Calculated using the expression $S = \frac{3/2\ PL}{BD^2}$

The as-received niobium and the sample annealed at 1000°C for one hour did not fracture; the applied loads reached maximum values corresponding to strengths of 64,000 and 61,000 psi, respectively, and then decreased as bending was continued. In the iridium sample that was not annealed, observable cracks initiated on the tension side of the sample at a load of 7-1/2 lbs. The load increased to a maximum value of 7-3/4 lbs (corresponding to a strength of 133,000 psi) when brittle failure occurred with very little bending (less than ten degrees). Cracks started on the tension edge of the annealed iridium sample at a load of 1-3/4 lbs and on the compression side at 2 lbs. Slip lines were observed when the applied load reached 3-1/4 lbs. The applied load reached a maximum value of 3-3/8 lbs (corresponding to a strength of 65,000 psi) and then decreased as the sample was bent to approximately 90 degrees. At this angle, failure did occur; however, unlike the previous unannealed sample that virtually exploded into two parts, failure was of a more ductile nature as the grains were slowly torn apart.

Strips, approximately 1/8 inch wide, were sectioned from the pressure-bonded composites with a water-cooled abrasive cut-off wheel. The strips were metallographically polished on a side showing both the substrate metal and the coating. Microscopic examination of the coating substrate interfaces did not reveal intermetallic compound formation. Iridium coated samples of molybdenum, tungsten, and niobium were tested with the microbend tester in both the 'as pressure bonded' condition and after annealing. The outer iridium surface was at maximum tension, and the outer substrate metal surfaces were under a compressive force. The results are given in Table X. In both of the 'as pressure bonded' molybdenum substrate samples, cracks started at the outer iridium edge and propagated in an irregular path towards the molybdenum-iridium interface. No observations could be made as to whether the cracks propagated along the iridium grain boundaries or across the grain, since the samples were not etched. The initial cracks were observed at an applied load of 8-1/2 lbs for sample 6M-B and nine lbs for sample 7M-B. These loads correspond to strengths of 1.01×10^5 psi and 1.04×10^5 psi, respectively.

TABLE X

FLEXURAL TEST RESULTS FOR IRIDIUM COATED SAMPLES

Sample* Number	Substrate	Width, B, Inches	Thickness, D, Inches	Maximum Applied Load, P, lbs.	Flexural Strength psi x 10^5	Comments
6M-B	Molybdenum	0.1207	0.0256	12	1.42	As pressure-bonded
7M-B	"	0.1161	0.0264	13	1.51	" " "
6M-B-3	"	0.1218	0.0260	6-7/8	0.78	Annealed at 1900°C for 3 hours.
10W-B	Tungsten	0.1192	0.0257	15	1.79	As pressure-bonded
11W-B	"	0.1187	0.0257	22-1/4	2.66	" " "
11W-B-7	"	0.1224	0.0256	11-1/4	1.31	Annealed at 1900°C for 7 hours.
1Nb-B	Niobium	0.1259	0.0244	11-1/2	1.44	As pressure-bonded
2Nb-B	"	0.1231	0.0273	6-3/4	0.69	" " "
4Nb-B	"	0.1225	0.0271	13-1/2	1.41	" " "
4Nb-B-6	"	0.1203	0.0271	6-1/2	0.69	Annealed at 1700°C for 6 hours.

* All samples were tested with a fixture having a 0.625 inch span, L, and three point loading.

Both samples, bent to approximately 45 degrees, failed suddenly when a crack reached the molybdenum-iridium interface. No delamination of the coating from the substrate was observed until one or more cracks reached the interface. Then, in a very rapid sequence, a crack widened, the leading crack tip propagated a very short distance along the interface and the molybdenum failed. Figure 16 is a macrophotograph of sample 7M-B after testing. The annealed molybdenum composite behaved similarly. No cracks were observed in the reaction zone and the specimen did not delaminate.

Bending tungsten-iridium samples produced cracks that started at the outer iridium edge and propagated towards the tungsten-iridium interface. In the 'as pressure bonded' sample (10W-B) and the annealed sample (11W-B-7), the primary cracks went straight through the entire sample, resulting in destruction with very little bending. In sample 11W-B, the tungsten delaminated after the primary crack had progressed through the iridium and most of the tungsten. In all iridium coated tungsten samples, no cracks developed at the iridium-tungsten interface nor in the interaction zone of the annealed sample.

In the niobium-iridium system, each sample behaved slightly differently during testing. The iridium-coating of sample 1 Nb-B failed at an applied load of 11-1/2 lbs (strength of 1.44×10^5 psi) and then delaminated. Sample 2 Nb-B was bent more than 90 degrees with no indication of failure other than the formation of some very small cracks on the outer edge of the iridium. When the applied load was released to remove the specimen from the bend tester, the iridium and niobium separated. Iridium work hardens very rapidly compared with niobium and, therefore, has a greater tendency to spring back when the applied load is released. The severe bend may have weakened the iridium-niobium bond sufficiently so that differences in spring-back could result in delamination. Sample 4 NB-B was also bent through an angle greater than 90 degrees. However, no delamination occurred. At the magnifications used to observe the sample during bending (30X and 70X), no cracks could be seen. After the sample was removed from the bend tester, microscopic examination at 200X revealed shallow cracks along the outer iridium edge.

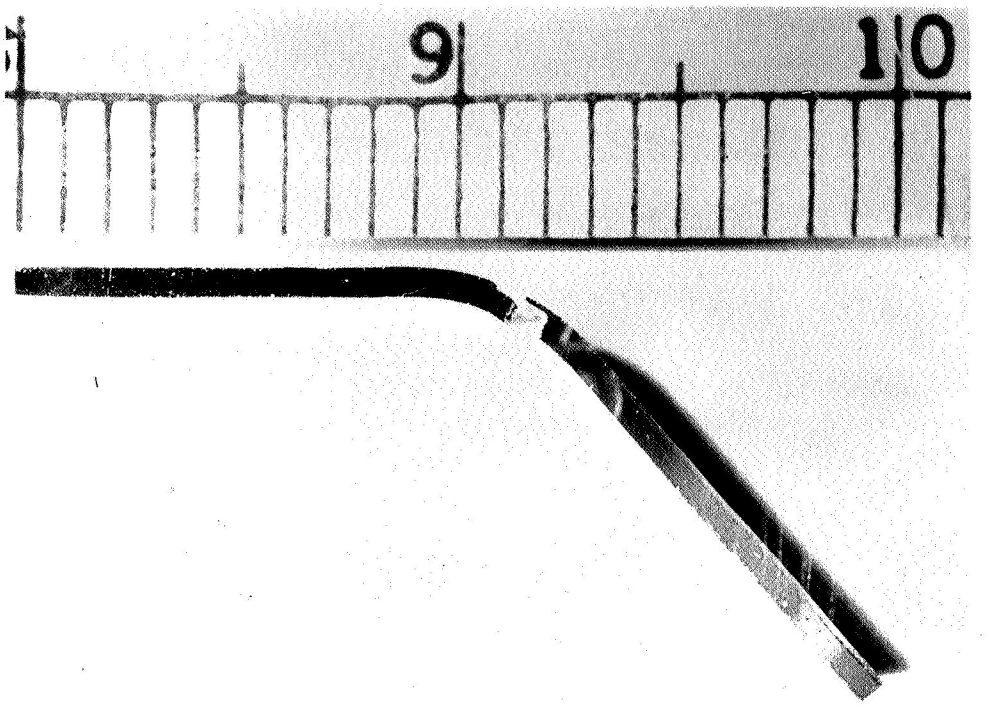

Figure 16. Macrophotograph of Bend Test Sample 7M-B.

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The annealed niobium-iridium sample 4 Nb-B-6) was the only sample tested in which cracks started during bending at the internal iridium interface as well as at the outer iridium edge. When the sample was bent further, the internal cracks traveled towards the outer iridium edge (towards the side of maximum tension). At an applied load of 5-1/2 lbs (representing a strength of 58,000 psi), cracks were observed in the reaction zone; and, at 5-3/4 lbs, the iridium started to separate from the reaction zone. The applied load reached a maximum value of 6-1/2 lbs, corresponding to a strength of 69,000 psi, and then decreased as bending continued. The sample was bent to an angle greater than 90 degrees without completely delaminating and without complete destruction of either the coating or the substrate metals. Examination of this sample after testing revealed that some of the iridium had separated from the substrate. However, the separation was local and did not cause complete failure. In addition, at the position of the bend, part of the iridium coating contained a crack which extended completely through the iridium and the remainder of the iridium was bent in a ductile manner.

The unusual ductile behavior of iridium pressure-bonded to niobium (and also to tantalum) was also observed in the previous investigation[1]. Sheet iridium is fabricated by plastically deforming the metal at elevated temperatures. At ambient temperatures, iridium normally exhibits a high degree of work hardening which is unusual for a metal having a face-centered cubic structure. Cracks which appear after deformation have been observed to propagate along grain boundaries. This behavior is usually indicative of an impurity which agglomerates at the grain boundaries. Iridium annealed in contact with niobium or tantalum seems to work harden less than iridium annealed under vacuum alone. One may speculate that niobium and tantalum act as getters for the particular impurities which contribute to the brittle behavior of iridium. It would be of practical and theoretical value to pursue a research program leading to the development of a ductile iridium at ambient temperatures.

A comparison of the mechanical behavior of the composites with that of the substrate metals indicates that pressure-bonded molybdenum composites have a flexural strength 20 percent below that of the 'as-received' sheet molybdenum and 40 percent higher than annealed sheet molybdenum. The annealed composite, containing a 26.7 mil thick reaction zone, had a flexural strength 20 percent lower than that of annealed sheet molybdenum. The 'as-received' and the annealed molybdenum were plastically deformed (through a bend angle of 90 degrees). The composites developed cracks on the side of maximum tension (the outer iridium surface) and failed in a brittle manner at a bend angle of approximately 45 degrees. The tungsten composites were as brittle as the tungsten sheet samples, and the breaking strengths were lower than those of the base metal. Niobium can be extensively deformed plastically. The niobium composites were also the most ductile composites having flexural strengths greater than that of the substrate metal. Iridium-coated refractory metals can be deformed plastically if the uncoated substrate metal deforms plastically. In addition, a well-bonded composite will not delaminate easily during deformation, even when a substantial reaction zone is present between the coating and the substrate metal.

V. CONCLUSIONS AND RECOMMENDATIONS

Iridium is a very promising oxidation-resistant coating for the refractory metals. The studies showed that iridium can be pressure bonded to molybdenum, tungsten, niobium, and tantalum. Intricately shaped objects of molybdenum and tungsten can be coated with coherent and adherent iridium of any desired thickness by electrochemical means. Tantalum and niobium are chemically too reactive with the molten electrolyte to be consistently coated with iridium. However, a dual coating was developed for these metals which consisted of a nickel strike on the substrate metals followed by an iridium overlay. Roll bonding would be an ideal way of cladding large sheets of the refractory metals; however, additional effort will be needed to determine the best processing parameters. Although plasma spraying was not attempted during this investigation, it may be an alternate method of applying the coating to both sheet and intricately shaped items.

At elevated temperatures, iridium reacts with the refractory metals to form intermetallic compounds which consume iridium and which may form a continuous network, constituting a brittle reaction zone between the coating and the substrate. The amount of the decrease in thickness of an iridium coating on molybdenum, tungsten, and niobium due to intermetallic compound formations was determined. From these data, the life expectancy of the coating can be estimated. Extrapolation of the data, assuming solid-state diffusion controlled reactions, shows that a five-mil-thick iridium coating will last almost indefinitely on tungsten, for at least 700 hours on niobium, and for at least 600 hours on molybdenum at 1700°C. Similarly, the same coating will last at least 300 hours, and 130 hours, respectively, on tungsten and molyybdenum at 1900°C. In contact with niobium, the iridium coating should last at least 200 hours at 1780°C. The loss of iridium due to internal reactions is very much less than that due to oxidation in air at ambient pressure when the air is flowing at high velocities. Consequently, for all practical purposes, the life of the coating will be determined by its oxidation rate. At low air flow rates and/or partial pressures of oxygen, the oxidation rate may be more than an order of magnitude lower than under the severe conditions. Under these circumstances both oxidation and intermetallic compound formation must be

considered in determining the coating life. Tests that simulate the conditions under which the iridium coated refractory metals will be used are recommended to complete the evaluation test.

The evaluation of the mechanical behavior of the composite materials has shown that: (1) well bonded composites did not delaminate easily during deformation, even when a substantially thick reaction zone was present between the coating and the substrate metal; and (2) cracks initiate on the side of maximum tension (the outer iridium surface) during bending and propagate towards the coating-substrate interface. Tungsten bend composites were as brittle as plain tungsten sheet samples, and niobium bend composites were ductile. Molybdenum-based composites failed in a brittle manner at bend angles of approximately 45 degrees, whereas annealed molybdenum was plastically deformed through a bend angle of 90 degrees.

The results of this investigation and of the previous one[1] showed that the mechanical behavior of iridium varied depending upon prior thermal and environmental history. Sheet iridium normally exhibits a high degree of work hardening, a behavior which is unusual for a metal having a face-centered cubic structure. The brittle behavior of iridium was also observed during this investigation. However, of greater significance was the fact that many of the iridium coatings which were electrodeposited on copper were very ductile and that iridium roll bonded or pressure bonded to tantalum or niobium also deformed in a ductile manner. This evidence emphasizes the need for a research program to determine the effect of specific impurities on the deformation characteristics of iridium. It would be of practical and theoretical value to pursue a research program which would (1) give a clear understanding of the deformation characteristics of iridium, and (2) lead to the development of a ductile iridium at ambient temperatures.

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