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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

ELEVATED TEMPERATURE DIFFUSION BONDING OF TUNGSTEN TO TUNGSTEN UNDER PRESSURE

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by

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ABSTRACT

Solid state diffusion bonding of tungsten to tungsten was investigated at temperatures ranging from 1700 to 2600°C, under surface contact pressures up to 3000 psi, while under high vacuum or hydrogen atmosphere. Various interface coatings were employed to promote diffusion, including graphite, oxide, metal slurries, electroplates, direct surface oxidation, and Mo-W deposits from carbonyl decompositions. Thorough metallurgical bonding was achieved, particularly with the latter two surface coatings, after 2 hours at 2350°C in H_2 under 1400 psi. Corresponding tensile strengths of 30,000 psi were obtained. Powder-compacted tungsten sheet containing 50 v/o UO_2, spray-coated with an outer layer of tungsten, was effectively bonded to itself and to tungsten metal under 2 hour diffusion treatments at 2000°C and moderate pressures of the order of 1000 psi.

ACKNOWLEDGEMENT

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INTRODUCTION

Performance requirements for materials at elevated temperatures have drawn increasing attention to tungsten, which resists melting up to 3410°C, the highest melting point of any of the metal elements. Recent intensive investigations have developed considerable information on the fundamental properties and behavior characteristics of tungsten and tungsten-base alloys (1,2). Included in such studies has been work concerned with the joining of tungsten (3,4). The results reported in the areas of brazing and welding of tungsten show steady advances over formidable metallurgical and environmental difficulties. There are applications, however, in which fusion bonding is impractical and in which solid state diffusion bonding may provide the most appropriate method of effecting a metallurgical joint where tungsten metal parts are involved.

Though the number of investigations concerned with the effects of pressure on diffusion are relatively small, it has been reported that hydrostatic pressure decreases the self-diffusion coefficients of sodium (5), phosphorus (6), and zinc (7). Extensive work has been done on the aluminum-nickel system and the aluminum-uranium system by Castleman and Seigle (8,9). Storchheim (10,11,12) has reported investigations on aluminum-nickel, aluminum-copper, aluminum-iron, aluminum-zirconium, and aluminum-thorium. Fugardi and Zambrow (13) have used isostatic pressing at elevated temperautres to study the bonding characteristics of alloys involving Zircalloy, uranium, zirconium, titanium, niobium, nichrome, and stainless steel. In some cases, pressure increased the growth rates of intermetallic phases, while in others there was a decrease. Though much remains to be learned and understood concerning the operation of the diffusion process under pressure, at least one applicable conclusion has been suggested. A purely mechanical effect is recognized (8) in which pressure enhances the formation of the bonded region between two interfaces by repressing the presence of macroscopic defects and voids and effectively increasing the cross-sectional area available for interdiffusion. This effect has been observed in the present investigation involving tungsten.

CHAPTER 1

EXPERIMENTAL PROCEDURE

1.1. General

The procedures and results reported upon have been concerned with the development of a method for bonding tungsten to tungsten in the solid state with the transmission of an acceptable level of tensile stress across the junction. A number of methods were tried which involved variations in temperature, time, pressure, and interfacial additions between the tungsten surfaces to be bonded. A summary of the various combinations which were investigated is given in Table I.

The method employed in each individual trial consisted of applying to the opposing surfaces of tungsten specimens a thin layer of a material which could be expected to promote a bond between them. Table II lists the coatings which were tried and the method used to deposit them.

1.2. Specimens and Coating Procedure

In the course of trial runs several different kinds of specimens were employed. For most of the trials, a pair of tungsten discs 3/8 inch in diameter by 1/8 inch in thickness were used. The discs were cut

TABLE I

BONDING CONDITIONS AND CHARACTERISTICS

Conditions for Bonding							Character of Bond Formed		
Coating	Test No.	Temp. (°C)	Time (hr)		Press. (psi)	Type of Specimen	Extent of Diffusion	Grain Growth Across Interface	Other Observations
a. OXIDE COATINGS									
WO_3 Slurry	4079 (3)	450 800 1700	1/2 2 2	H_2 H_2 H_2	1400 1400 1400	3/8 in. D discs	Slight; discontinuous toward circumference	None	Much unreduced oxide
	4134 (R-1)	830 2000 2000	1/4 1/2 1/2	Vac. Vac. H_2	1400 1400 1400	3/8 in. D discs	None	None	Much unreduced oxide
	4178 (R-16)	2350 2350	1/2 1-1/2	Vac. H_2	1400 1400	3/8 in. D discs	Sporadic	None	Much unreduced oxide
	4184 (R-18)	2350 2350	1 2	Vac. H_2	1400 1400	3/8 in. D discs	In initial stage	In initial stage	Some unreduced oxide
WO_3-90% MoO_3-10% Slurry	4188 (R-20)	2350	2	H_2	1400	3/8 in. D discs	Very slight	None; voids	Poor contact at interface
	4195 (R-25)	2350	2	H_2	1400	3/8 in. D discs	75%	75%	Some voids and unreduced oxide
	4207 (R-34)	2350 2350 2600	1/2 1 1	Vac. H_2 Vac.	1400	3/8 in. D discs	Moderate at one end	Partly	Limited contact
Oxide from Torch	4211 (R-38)	2350	2	H_2	1400	3/8 in. D discs	Sporadic	Partly	Limited contact
Oxide from 2/3 He+ 1/3 O_2 @ 1000°C	4362 (RB-7)	2350	2	H_2	1400	3/8 in. D rods	Moderate; very porous	Moderate	Many voids
	4287 (R-49)	2350	2	H_2	1400	3/8 in. D discs	Complete	Columnar grains across interface	Small voids near interface
2/3 He+ 1/3 O_2	4596 (R-75)	2350	2	H_2	1400	3/8 in. D discs	80%	Center area	Poor contact at edges

Conditions for Bonding						Character of Bond Formed		
Coating	Test No.	Temp. (°C)	Time (hr)	Press. (psi)	Type of Specimen	Extent of Diffusion	Grain Growth Across Interface	Other Observations
				b. METAL SLURRY COATINGS				
Mo Slurry	3963 (W-8)	1700	1-1/2 H_2	100	1/32 in. flat wire 1/16 in. sheet	Limited; Mo layer remained	In initial stage	
	3898 (W-2)	1700	16 H_2	27	1/32 in. flat wire 1/16 in. sheet	None	None	High porosity at interface
	4091	800 800 2500 2500	1/2 Vac. 2 H_2 1 Vac. 2/3 H_2	600	3/8 in. D discs	Very sporadic; diffusion incomplete	Partial	High porosity at interface
	4151 (R-4)	2000	1-1/2 H_2	600	3/8 in. D discs	Good; but high conc. of Mo at interface	Complete; interface grains very small	Densely speckled oxide particles in interface
	4161 (R-5)	2300	1-1/2 H_2	600	3/8 in. D discs	Good	Considerable, but columnar	Densely speckled oxide particles in interface
W Slurry	4391 (R-61)	2000	2 H_2	2700	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated, sintered, re-coated)	Good at ends; poor in middle	Good where bonded	Voids
	4495 (R-65)	2000	2 H_2	2700	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated, sintered, re-coated)	99%	99%	Thorough bonding
	4497 (R-68)	2350	2 H_2	5300	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated, sintered, re-coated)	None	None	
	4296 (R-51)	2350	2 H_2	2700	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated, sintered, W-coated)	100%	100%	No voids

Conditions for Bonding						Character of Bond Formed		
Coating	Test No.	Temp. (°C)	Time (hr)	Press. (psi)	Type of Specimen	Extent of Diffusion	Grain Growth Across Interface	Other Observations
b. METAL SLURRY COATINGS (Continued)								
W Slurry	4298 (R-53)	2000	2 H_2	2700	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated, sintered, & W-coated)	Intermittent	Good, where bonded	Many cracks in sheet
	4306 (R-55)	2000	2 H_2	0	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated, sintered, & W-coated)	100%	100%	One sheet cracked
	4580 (R-72)	2000	2 H_2	2700	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated, sintered, & W-coated). 3/8 in. disc coated with WO_3 from He + O_2 mixtures.	Very little	2%	Peeling of W-coating from UO_2-W sheet
	4564	2350	2 H_2	2700	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated, sintered, & W-coated). 3/8 in. disc coated with WO_3 from He + O_2 mixture.	Limited	Limited	Peeling of W-coating from UO_2-W sheet

Conditions for Bonding						Character of Bond Formed		
Coating	Test No.	Temp. (°C)	Time (hr)	Press (psi)	Type of Specimen	Extent of Diffusion	Grain Growth Across Interface	Other Observations
c. GRAPHITE COATINGS								
Graphite Slurry (commercial)	4210 (R-36)	2000	1/2 H_2	1400	3/8 in. D discs	Good at one end	Very limited	Non-uniform contact; extensive voids, cracks
		2600	2 Vac.	1400				
		2000	1/2 Vac.	1400				
		1700	1/2 Vac.	1400				
	4212 (R-37)	2000	1/2 H_2	2400	1/16 in. sheets loaded with 50 v/o UO_2	Good; but numerous voids and impurities	Considerable, but not uniform	Bond not uniform
		2600	2 Vac.	2400				
		2000	1/2 Vac.	2400				
		1700	1/2 Vac.	2400				
Graphite Slurry (Spectrographic)	4280 (R-43)	2350	2 H_2	1400	3/8 in. D discs	Good at one end	Good at one end; none at other end	Contact uniform; carbide inclusions at interface
	4281 (R-47)	2000	3 H_2	1400	3/8 in. D discs	None; coarse undiffused layer	None	Non-uniform contact
	4286 (R-48)	2000	3 H_2	1400	3/8 in. D discs	Very slight; undiffused layer remained	None	
	4307	2000	3 H_2	0	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated, & sintered)	Limited	Very limited; but growth within W-coat	
W + 1.0% C	4295 (R-50)	2350	2 H_2	2700	1/16 in. sheets loaded with 50 v/o UO_2	Intermittent	Some; highly porous	Contact intermittent
	4297 (R-52)	2000	2 H_2	2700	1/16 in. sheets loaded with 50 v/o UO_2	Complete	Complete	Excellent bond
	4305 (R-54)	2350	2 H_2	0	1/16 in. sheets loaded with 50 v/o UO_2	None	None	Sheets completely deteriorated

Conditions for Bonding						Character of Bond Formed		
Coating	Test No.	Temp. (°C)	Time (hr)	Press. (psi)	Type of Specimen	Extent of Diffusion	Grain Growth Across Interface	Other Observations
				c. GRAPHITE COATINGS (Continued)				
W + 1.0% C	4332 (R-58)	2000	2 H_2	2200	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated & sintered)	Intermittent, but good at contact points	Good, but with small voids present	40% of interface void
W + 0.5% C	4447 (R-64)	2000	2 H_2	2700	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated & sintered)	99%	99%	Excellent bond
	4496 (R-66)	2350	2 H_2	5300	1/16 in. sheet loaded with 50 v/o UO_2 (W-coated & sintered) 3/8 in. disc (coated)	None	None	
	4570 (R-71)	2000	2 H_2	2700	1/16 in. sheet loaded with 50 v/o UO_2 (W-coated, sintered, coated with W + .5%C). 3/8 in. disc coated with WO_3 from He + O_2 Mixture.	15%	Little	Bonding at one end
	4581	2000	2 H_2	2700	1/16 in. sheet loaded with 50 v/o UO_2 (W-coated, sintered, coated with W + .5%C). 3/8 in. disc coated with WO_3 from He + O_2 Mixture.	None	None	Peeling of W-coating from W-UO_2 sheet

Conditions for Bonding						Character of Bond Formed		
Coating	Test No.	Temp. (°C)	Time (hr)	Press. (psi)	Type of Specimen	Extent of Diffusion	Grain Growth Across Interface	Other Observations
d. ELECTROPLATED COATINGS								
Ni	4240 (T3, T4)	1700	2 H_2	5000	1/16 in. sheets loaded with 50 v/o UO_2 (W-coated & sintered) 1/32 in. flat wire	Extensive	Extensive; larger grains at interface	Tensile shear specimen; fractured before test
	4190 (R-23)	2350	1-1/2 H_2	600	3/8 in. D discs (uncoated) 1/32 in. flat wires (plated)	Complete; some porosity	Complete; wires small-grained; disc large-grained	Abnormal large grain in discs
	4401 (RB-2)	2000	2 H_2	1400	3/8 in. D discs	Complete	Complete; interface small-grained	Very slight porosity
Alloy: 85% Re 15% Ni	3948 (W-6)	1700	2 H_2		1/32 in. flat wire 1/16 in. sheet	Partial	None	Incomplete contact
	4189	2350	1-1/2 H_2	1000	1/16 in. sheets loaded with 50 v/o UO_2 (plated) 1/32 in. flat wire (Ni-flash)	Limited; voids and impurities present	Partial	Incomplete surface contact
	4239 (T1, T2)	1700	2 H_2	5000	1/16 in. sheets loaded with 50 v/o UO_2 (uncoated) 1/32 in. flat wires	In initial state: undiffused layer remained	Partial	Tensile shear specimen; fractured before test
	4241 (T5, T6)	1700	2 H_2	5000	1/16 in. sheets loaded with 50 v/o UO_2 (uncoated) 1/32 in. flat wires (plated)	Intermittent	Only where Ni-Re coat was bonded	Tensile shear specimen; failed at 3100, 2400 psi
Pt	4203 (R-31)	2350	2 H_2	1400	3/8 in. D discs	Complete at one end; voids at other end	Complete where contact existed	Non-uniform contact
					1/32 in. flat wire 1/16 in. sheet	Intermittent: layer remained	None	Partial contact

Conditions for Bonding						Character of Bond Formed		
Coating	Test No.	Temp. (°C)	Time (hr)	Press (psi)	Type of Specimen	Extent of Diffusion	Grain Growth Across Interface	Other Observations
e. CARBONYL COATINGS								
$Mo(CO)_6$	4135 (R-2)	2000	1 H_2	1400	3/8 in. D discs	In initial stage	None	Coherent Mo layer at interface
	4150 (R-3)	2400 2350	1/2 H_2 1 H_2	1400	3/8 in. D discs	Complete	Complete	Trace of small particles at interface
	4173 (R-14)	2350	1-1/2 H_2	600	3/8 in. D disc 1/32 in. flat wire	Complete	Complete	Much porosity throughout
	4191 (R-24)	2350	1-1/2 H_2	600	3/8 in. D disc 1/32 in. flat wire	Very limited	Very limited	Voids present
	4196 (R-26)	1700	6 H_2	600	3/8 in. D disc (uncoated) 1/32 in. flat wire (coated)	Very limited	None	Very poor contact
	4198 (R-28)	1700	6 H_2	600	3/8 in. D disc (uncoated 1/32 in. flat wire (coated)	Very limited	Very slight	Poor contact
	4200 (R-30)	1700	12 H_2	600	3/8 in. D disc (uncoated) 1/32 in. flat wire (coated)	Very limited	Very slight	Poor contact
	4206 (R-33)	1700	6 H_2	600	3/8 in. D disc (uncoated) 1/32 in. flat wire (coated)	Partial	Fair	Undiffused Mo layer present; voids
	4162 (R-6)	2350	1-1/2 H_2	600	1/32 in. flat wire (coated)0.025 in. sheet loaded with 50 v/o UO_2 (coated)	Partial	Moderate	Wires imbedded in sheet; voids

Conditions for Bonding						Character of Bond Formed		
Coating	Test No.	Temp. (°C)	Time (hr)	Press. (psi)	Type of Specimen	Extent of Diffusion	Grain Growth Across Interface	Other Observations
e. CARBONYL COATINGS (Continued)								
$Mo(CO)_6$	4165 (R-11)	2350	1-1/2 H_2	4000	1/16 in. sheets loaded with 50 v/o UO_2 (coated)	Complete	Complete	Sheets cracked
	4166 (R-13)	2350	1-1/2 H_2	800	1/32 in. flat wire (coated)0.025 in. sheet loaded with 50 v/o UO_2(coated)	Complete; but intergranular voids in wire	Complete	Sheets bent
	4177 (R-15)	2350	1-1/2 H_2	800	1/32 in. flat wire (coated)0.025 in. sheet loaded with 50 v/o UO_2 (coated)	Complete; small impurities present	Complete	Sheets bent
	4242 (T-7, 8,9)	1700 2350	2 H_2 1 Vac.	4450	1/32 in. flat wire (coated)0.025 in. sheet loaded with 50 v/o UO_2(coated)	Intermittent; slight	None; but grain growth within sheet	Tensile shear specimens failed at 1675,3450 psi
$Mo(CO)_6$-50%	4366 (R-58A)	2350	2 H_2	1400	3/8 in. D discs	Limited	Slight	Impurities and voids at interface
$W(CO)_6$-50%	4446 (R-63)	2000	2 H_2	1400	3/8 in. D discs	Good	Fair; Mo layer incompletely diffused	Impurities at interface
$W(CO)_6$	4163 (R-8)	2350	1-1/2 H_2	1400	3/8 in. D discs	In initial stage	None	Contact on one end only
	4164 (R-9)	2300	6 H_2	1400	3/8 in. D discs	None	None	Coatings diffused into discs; no other bond
	4183 (R-17)	2300	6 H_2	1400	3/8 in. D discs	None	None	Coatings diffused into discs; no other bond
	4197 (R-27)	2350	6 H_2	1400	3/8 in. D discs	95%	95%	Some small voids
	4199 (R-29)	2350	1 H_2 2 Vac	1400	3/8 in. D discs	95%	95% in initial stage	Some small voids
	4205 (R-32)	2350 2600	1 H_2 4 Vac	1400	3/8 in. D discs	90%	Limited; a few voids	One large grain present
	4208 (R-35)	2350 2600	1 H_2 12 Vac	1400	3/8 in. D discs	Good, except large grains	25%; 75% large grains	Voids at interface

TABLE II

COATINGS APPLIED TO TUNGSTEN SPECIMENS

Surface Coat	Method of Application
Electroplated	
Ni	Ni plate ~.00006 in. thick from electrolytic bath
Ni-Re	Ni and Re plates ~.00005 in. thick from electrolytic bath
Graphite	
Commercial	C coating resulted from dipping into graphite slurry
Spectrographic	C coating resulted from dipping into graphite slurry
Metal Slurry	
Mo	Mo powder suspension sprayed on
W	W powder suspension sprayed on
W + 0.5% C	Suspension of W and C powder mixture sprayed on
W + 1.0% C	Suspension of W and C powder mixture sprayed on
Oxide Slurry	
WO_3	WO_3 powder suspension sprayed on
WO_3-90%, MoO_3-10%	WO_3-MoO_3 powder suspension sprayed on
Direct Oxidation	
From Oxyacetylene Torch	WO_3 formed on W surface from torch heat, in air
From 1/3 O_2 + 2/3 He Mix	WO_3 formed on W surface from furnace heat, under He-O_2
Carbonyl	
$Mo(CO)_6$ $W(CO)_6$ $Mo(CO)_6$-50%, $W(CO)_6$-50%	Mo, W, and Mo + W deposited upon contact of outgassed heated specimens with respective carbonyls at thermal decomposition temperature of 250°C under 30 mm pressure.

from swaged tungsten rod from a commercial source. For tensile specimens, the discs were readily replaced by rod from the same source, 3 inches in length. In some cases, 1/16 inch diameter tungsten wire flattened to 0.040 inch across flats was used between 3/8 inch diameter discs or between tungsten sheet 1/16 inch in thickness. The sheet form was particularly adaptable for powder-compacted mixtures of tungsten and uranium dioxide. The particulars of individual coating procedures are described in the following sub-sections.

1.2.1. Electroplating

Coatings 6×10^{-5} inch thick of nickel and of an alloy of 85% Re-15% Ni were deposited on ground and lapped surfaces of tungsten specimens by electroplating.

Nickel was plated from a Watts type (14) nickel bath following a standard plating procedure of degreasing, alkali cleaning and acid pickling.

Ni-Re plating was applied following standard plating procedure utilizing the bath of Netherton and Holt (15).

1.2.2. Graphite Slurry Coating

A surface layer of carbon was deposited by repeated dipping and air-drying of specimens in a commercial mixture of colloidal graphite in naptha. Satisfactory coatings by this method were improved in quality by the use of a spectrographic grade of graphite in vythene. A suspension of 50% graphite and 50% vythene by volume was used for successive dippings until a thorough coat of graphite adhered to the tungsten surface.

1.2.3. Metal Slurry Coating

Surface layers of molybdenum and tungsten were deposited on ground surfaces of 3/8 inch diameter tungsten disc specimens by the spray method. Powder of 2 micron particle size was mixed with water to which 1.5 w/o of a thickening agent had been added to promote suspension. The proportions were adjusted to spraying consistency and the slurry coatings were deposited and dried to a thickness of about 0.002 inch.

1.2.4. Oxide Slurry Coating

Oxide slurries were prepared from very fine powders, of the order of a few microns or less in particle size. These powders were obtained by a precipitation process from chemical solution.

A precipitate of tungstyl oxinate was produced from the addition of an acetic acid solution of oxine to an aqueous solution of ammonium meta tungstate. The oxinate was then calcinated at 800°C until only the oxide of tungsten remained.

A simultaneous precipitate of tungstyl and molybdenyl oxinates was produced from a similar process which included ammonium hepta molybdate in the aqueous solution. Calcination at 600°C resulted in oxides of tungsten and molybdenum in the form of very fine powders.

Surface layers of WO_3 powder and of a mixture of 90% WO_3 and 10% MoO_3 powders were deposited on ground surfaces of 3/8 inch diameter tungsten disc specimens by the spray method. A liquid vehicle solution was prepared from 20 g of ethyl cellulose binder in 400 cc of n-butyl acetate. To 10 cc of this solution was added 15 cc of n-butyl acetate and 20 g of oxide to form a suspension of spraying consistency. The sprayed deposit was dried to a thickness of about 0.002 inch.

1.2.5. Carbonyl Deposition

Coatings of tungsten, molybdenum, and of combinations of the two were applied to specimens by thermal decomposition of the respective carbonyls. Decomposition temperatures of both tungsten and molybdenum carbonyls are similar, both ranging near 250°C, depending upon pressure in the system. It was determined that an intimate mixture of the two carbonyls, when decomposed in a manner applicable for either carbonyl alone, produced a coating of composition near that of the original components.

In practice, a quartz tube, 25 mm I.D. by 18 inches long, sealed at one end, was fitted with a source of water vapor by placing a dampened plug of quartz wool in the sealed end. To this damp plug was added approximately 1 g of the required carbonyl or carbonyl mixture. The specimen to be coated was inserted half-way down the tube. The quartz tube was then connected to a vacuum source, and evacuated. The apparatus was arranged so that the specimen was within the field of an induction heater. After preliminary evacuation, the specimen was heated to 700°C for 2 minutes in an outgas cycle. Upon cooling, the specimen was dropped down to the end of the tube so that the part to be coated was in contact with the carbonyl powder. The specimen was then reheated at reduced power with a pressure regulator in the line to control carbon monoxide pressure. At a controlled pressure of 30 mm, the reaction was evaluated by means of a flowmeter which indicated the rate of CO evolution. When the reaction had proceeded sufficiently to deposit a coating of the order of 0.001 inch in thickness the power was turned off. The specimen was removed after the furnace had been allowed to cool.

1.2.6. Direct Oxidation

An oxide coating was produced on specimen surfaces directly by heating them in the flame of an oxyacetylene torch.

An alternate procedure which provided for better control and proved to be more suitable involved the heating of specimens in a tube furnace under controlled atmosphere. Specimens to be oxidized were placed face up in the horizontal quartz tube of a resistance furnace. At a temperature of 1000°C, a mixture of 1/3 oxygen and 2/3 helium was admitted into one end of the tube. Helium was added when it was found that oxygen alone did not produce an even oxide coating. A baffle was placed at the tube inlet to even out the gas flow and promote heating of the gas mixture before it contacted the specimens. A period of 2 minutes was generally sufficient for the formation of a uniform yellow surface coating of tungsten oxide.

1.3. Diffusion Treatment Apparatus

A preliminary apparatus for diffusion treatment employed a conventional molybdenum-wound, hydrogen atmosphere, resistance furnace which was operable up to 1750°C. A hydraulic ram was used to supply bonding pressure. The need for higher temperatures, quicker response, and improved flexibility in operation led to the construction of the diffusion bonding apparatus used throughout the project. It consisted of a specially designed environmental chamber in which tungsten specimens could be heated to high temperatures while axial pressure was maintained normal to the interface to be bonded. The details of the design are shown schematically in Fig. 1 and photographically in Figs. 2, 3, and 4. A quartz tube 100 mm in diameter by 15 inches in length formed the evacuable chamber. The tube rested on a silicone rubber O-ring which was countersunk in a water-cooled brass base. A water-cooled brass top-flange, likewise containing an O-ring, sealed the chamber and also suspended a longitudinally split, water-cooled copper induction concentrator within the quartz tube. A 25-turn copper induction coil surrounding the concentrator outside the quartz tube, powered by a 25 kw, 450 kc induction generator, induced sufficient heat energy to maintain specimen interfaces at temperatures as high as 2600°C. Axial loading up to 150 lb was provided by the water-cooled end of the piston of an air compression jack actuated by available 50 psi air pressure. The air jack was double-acting, enabling convenient up and down movement of the piston for emplacement of specimens. The environmental chamber was evacuated by an auxiliary vacuum system and filled with hydrogen or inert gas through an inlet in the top flange. Hydrogen was removed through an exit below the bottom flange where the outflow was burned safely in a flame jet.

1.3.1. Insertion of Specimens

The procedure for carrying out a particular diffusion treatment involved the raising of the top brass platform (Fig. 1) to permit

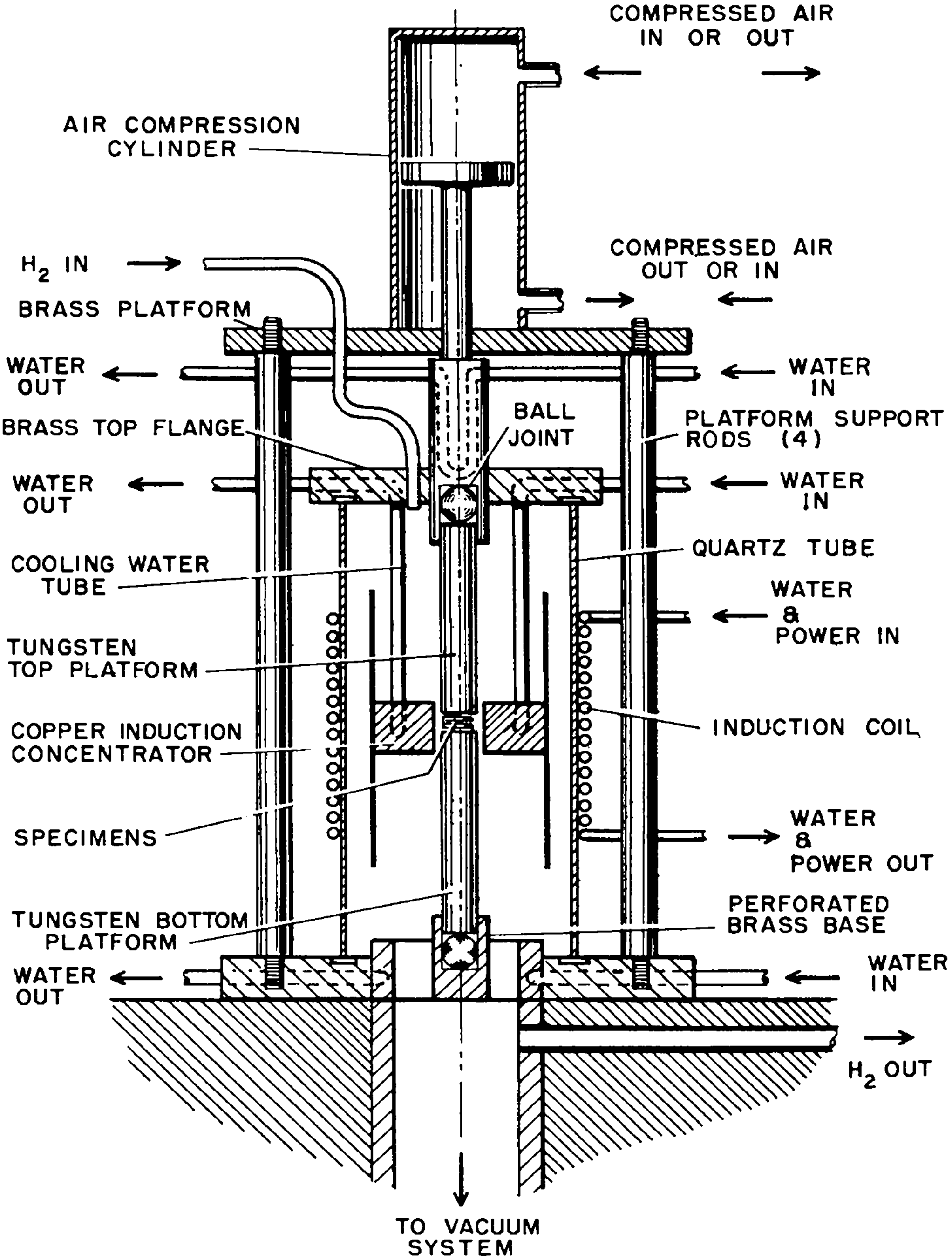


Fig. 1. Schematic drawing of the high temperature induction furnace. Furnace was capable of heating specimens to over 2600°C.

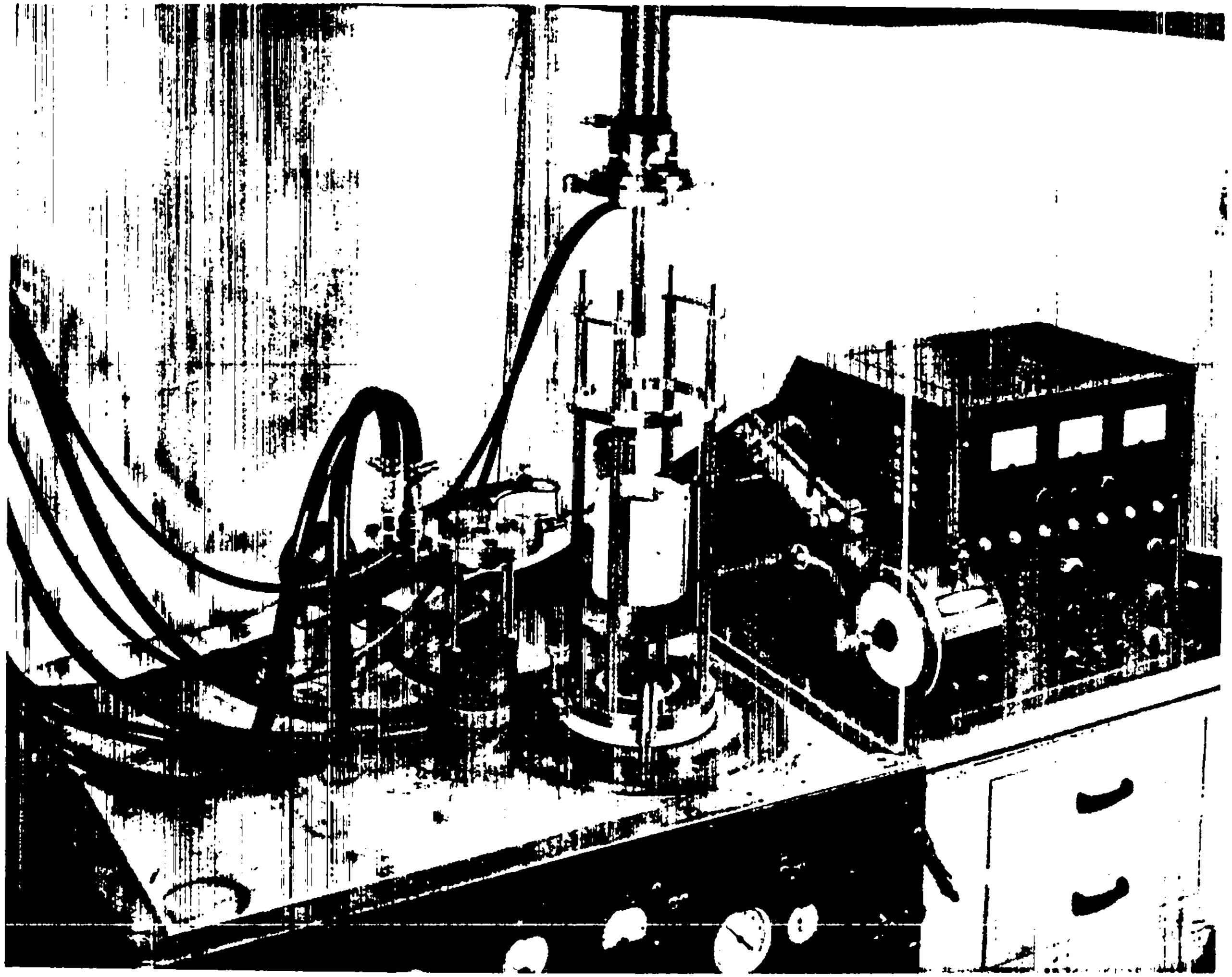


Fig. 2. Induction furnace disassembled. The remote control and tubular buss from the induction power supply are shown in the right hand portion of the figure.

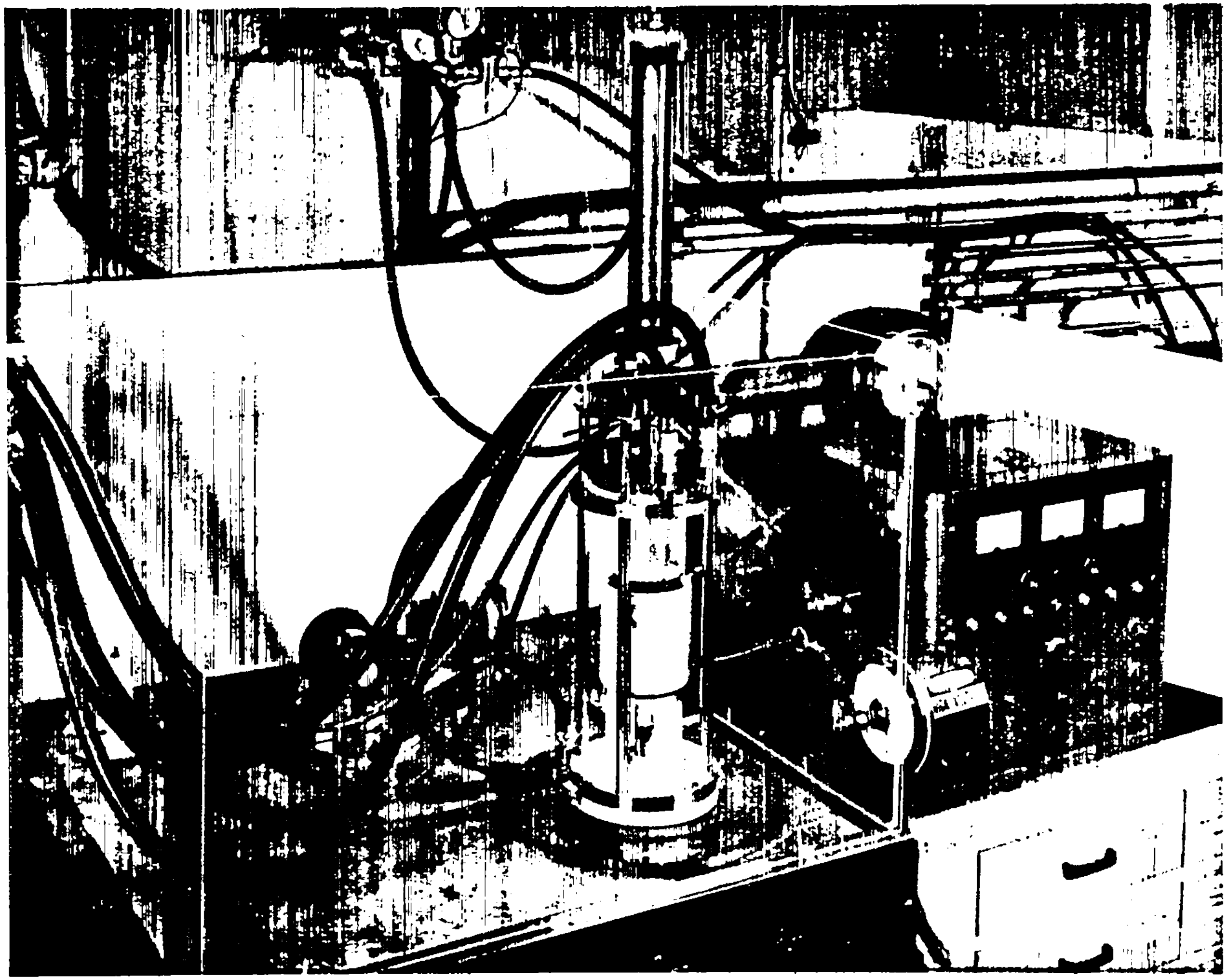


Fig. 3. Induction furnace assembled and in operation at 1200°C. A plastic shield was provided as a safety measure in case of furnace failure.

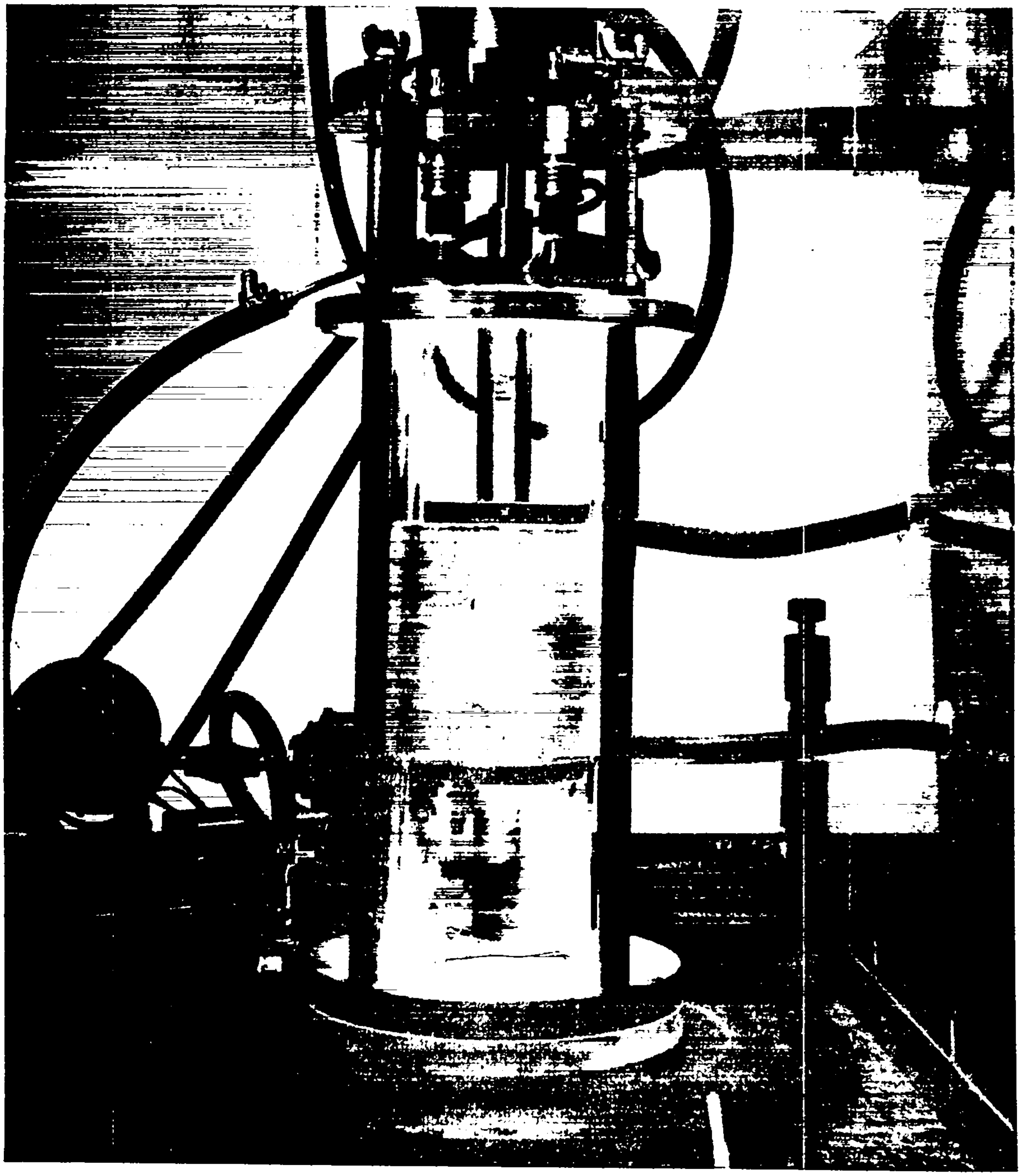


Fig. 4. Induction furnace in operation. Bright spot in center of induction coil is hole used for sighting for temperature control.

removal of the copper induction concentrator and the quartz tube. Disc specimens, tack-cemented at their periphery to prevent misalignment, were then placed on the lower tungsten platform. A light coating of thoria slurry on platform surfaces prevented sticking. For 3 inch long tensile specimens, the platforms were modified to accommodate the longer specimen length. The tensile specimens were taped together to insure alignment during insertion.

1.3.2. The Diffusion Treatment

After careful reassembly to the condition shown in Fig. 1, the chamber was evacuated to 0.1 micron or better for a diffusion treatment under vacuum. For a treatment under hydrogen the chamber was evacuated to 50 microns, purged with helium, re-evacuated to 50 microns and filled with hydrogen. The outflow of hydrogen was burned in a jet flame. Heating to temperature was accomplished by application of power to the induction coil. Temperatures of the order of 2350°C were reached in a matter of a few minutes. After holding for the desired time, the power was turned off, the hydrogen was evacuated, helium was admitted to raise the pressure to atmospheric, the furnace chamber was opened, and the diffusion-bonded specimen was removed. In some instances, an additional diffusion heat treatment was given to groups of such diffusion-bonded specimens, up to six at a time, in a large vacuum-induction furnace. The specimens were placed within a tungsten susceptor inside the induction coil. No further axial pressure was applied to the specimens since they were already in a bonded condition as a result of the previous treatment.

1.4. Metallography

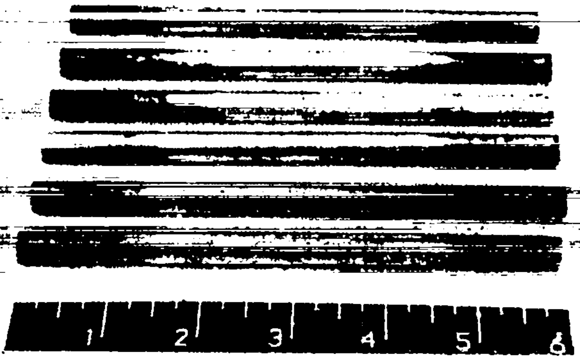
The procedure developed for preparing bonded sections for microexamination followed standard practice, but employed a special transparent epoxy resin mount of good adherency to preserve the character of the bonds produced.

Bonded discs were completely immersed in separately mixed portions of Epon epoxy resin, Shell-828, and its curing agent, diethanolamine. The materials were heated separately at 75°C for 45 to 60 minutes, then mixed together in the proportion of 14 parts curing agent to 100 parts epoxy. The mixture was stirred for 30 minutes prior to pouring into molds to encase the disc specimens. After curing some 16 hours overnight at 75°C, the mounts hardened and permitted diametral sectioning through the bonded interface. Surface preparation included grinding through 600 grit silicone carbide papers, polishing with 0-2 micron diamond paste on metcloth and then microcloth, followed by a 1 minute swab etch with a reagent prepared from 10 g $CuSO_4 \cdot 5\ H_2O$, 40 ml H_2O, and 20 mil NH_4OH.

Photomicrographs were taken at 7.5X and 250X to show the character of the diffusion bonds formed.

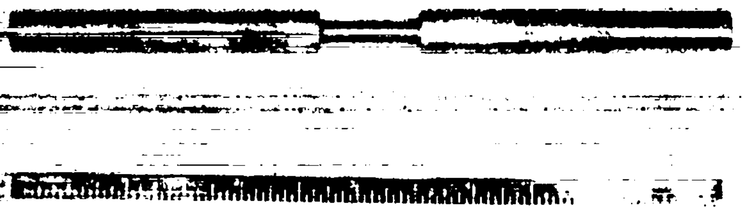
1.5. Tensile Testing

The tungsten rod specimens were 3/8 inch in diameter and 6 inches long in the diffusion-bonded condition (Fig. 5A). They were then ground to a testing diameter of 1/4 inch over a 1 inch gauge length (Fig. 5B). In later tests, however, to minimize time-consuming grinding, the test



A

W butt-joined tensile specimens, 3/8" D, as removed from furnace after diffusion-bonding.



B

W butt-joined tensile specimen, ground to 1/4" D over 1" gauge length, ready for testing.

Fig. 5. Diffusion bonded tensile specimens

diameter was left at slightly less than the original 3/8 inch. Just enough finishing was done to clean up the surface and assure axial alignment.

CHAPTER 2

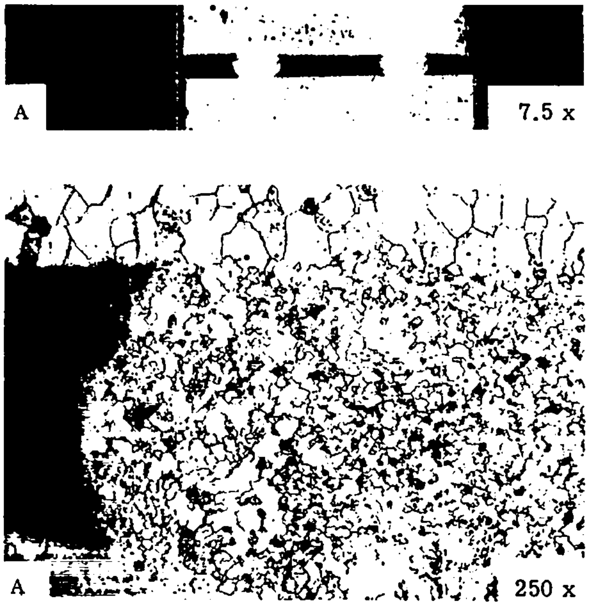
RESULTS AND DISCUSSION

2.1. General

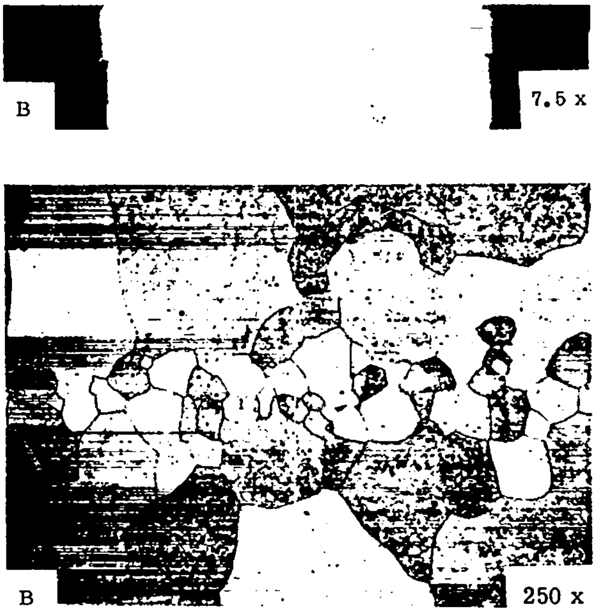
The results of the diffusion bonding investigation have been evaluated primarily by direct microstructural examination of the bonded regions and by tensile testing of bonded specimens.

The photomicrographs in Figs. 6 through 12 show pictorially the nature of the diffusion zones produced between tungsten specimens coated in various ways and subjected to various temperatures, pressures, and environments.

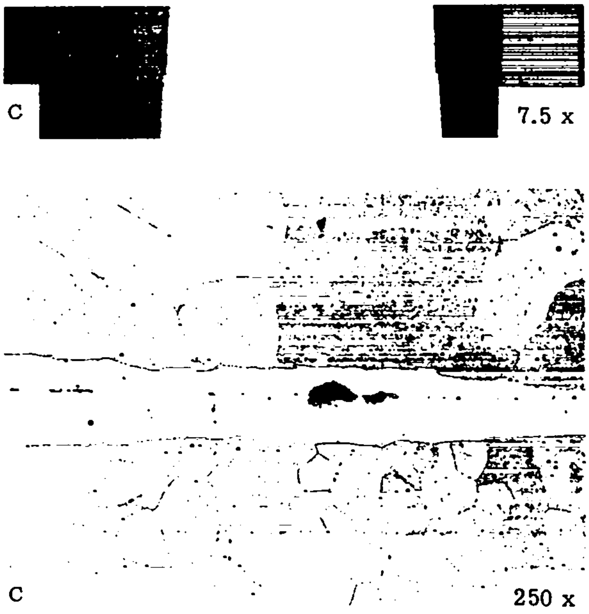
The tensile test results in Table III provide an indication of the strength of diffusion bonds formed. The values obtained show considerable scatter and must be considered to be of a preliminary character at this stage of the tungsten diffusion bonding development. More extensive testing of specific groupings with systematic control of individual variables would be required to establish the optimum procedure for obtaining a tungsten diffusion bond of maximum strength.



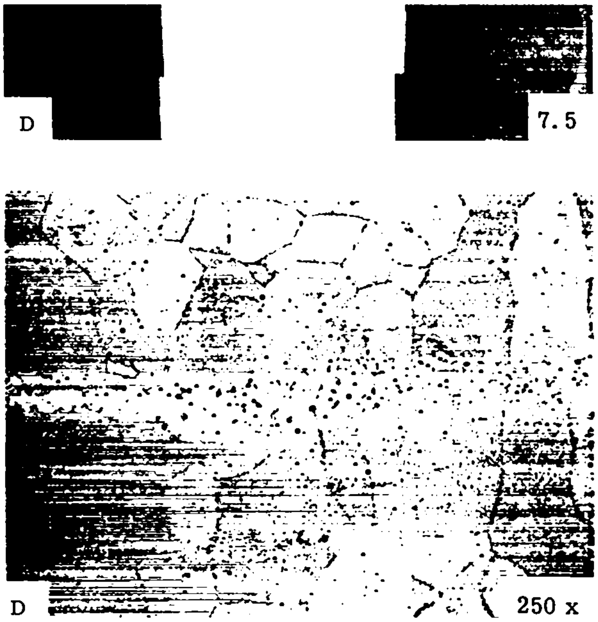
W Discs: (3/8" D). Uncoated.
W Wire: (1/32"). Electroplated with .00006" of Nickel.
Treated at 2350°C for 1 1/2 hours in H_2 under 600 psi pressure. Bonding complete but coarse grains present.



W Discs: (3/8" D). Electroplated with .00006" of Nickel.
Treated at 2000°C for 2 hours in H_2 under 1400 psi pressure. Bonding complete; grain growth across interface.

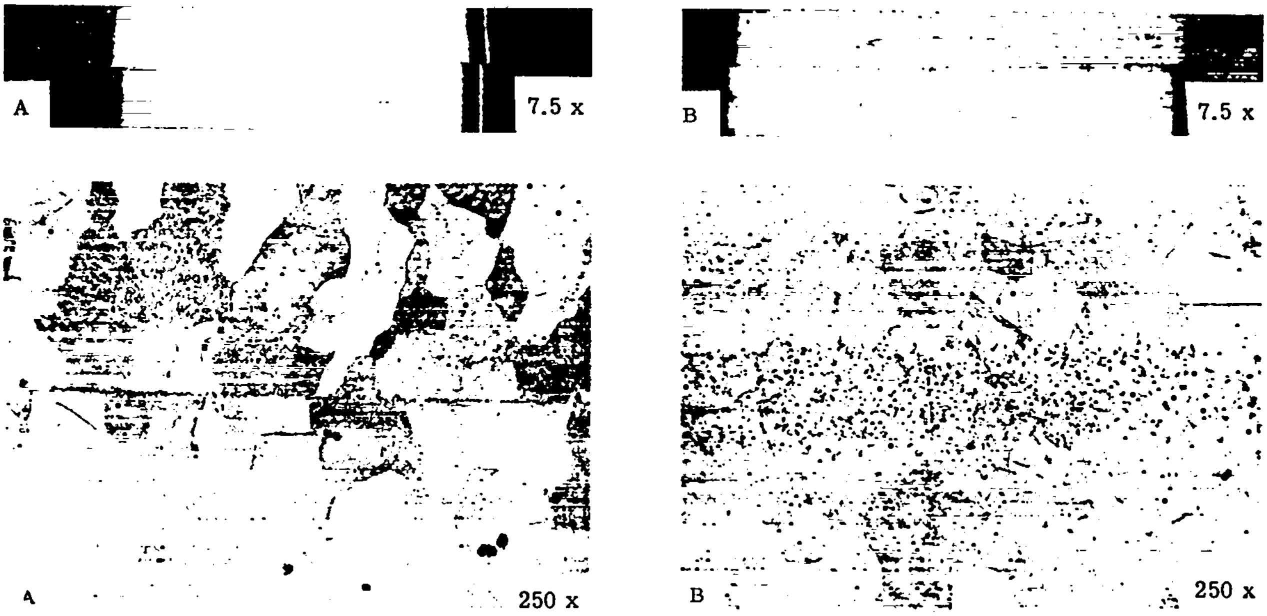


W Discs: (3/8" D). Coated with graphite.
Treated at 2000°C for 3 hours in H_2 under 1400 psi pressure. No diffusion apparent. A coarse undiffused carbide-rich layer remains.



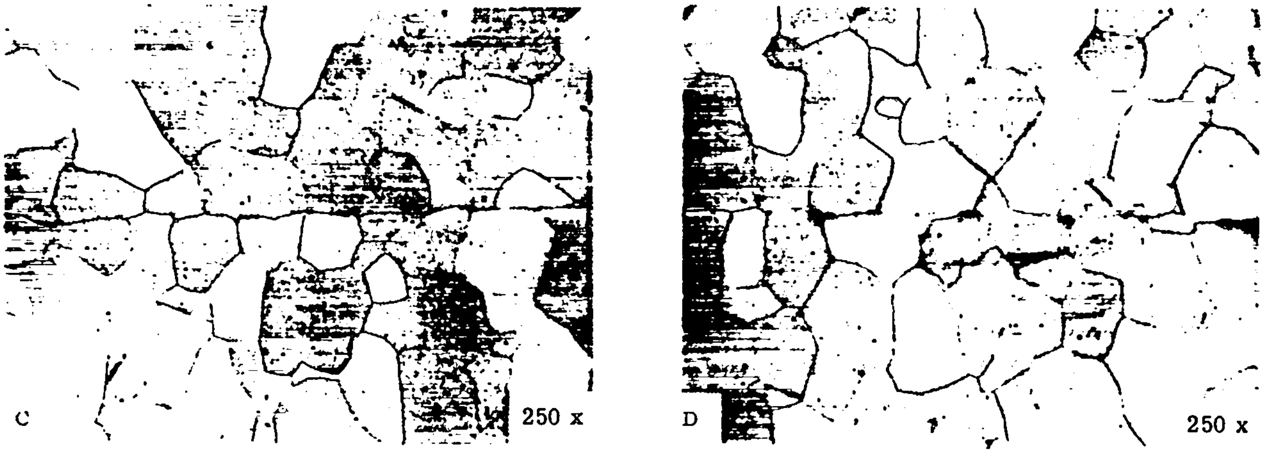
W Discs: (3/8" D). Coated with graphite.
Treated at 2350°C for 2 hours in H_2 under 1400 psi pressure. Partial bonding with diffusion and grain growth across the interface evident, but many inclusions remain.

Fig. 6. Photomicrographs of diffusion bonds produced from electroplated nickel and from graphite coatings.



W Discs: (3/8" D). Spray-coated with WO$_3$ slurry. Treated at 450°C for 1/2 hour and at 800°C for 2 hours in H$_2$ under 1400 psi pressure. Metal bonding evident in central region but diffusion very slight. Unreduced oxide at interface.

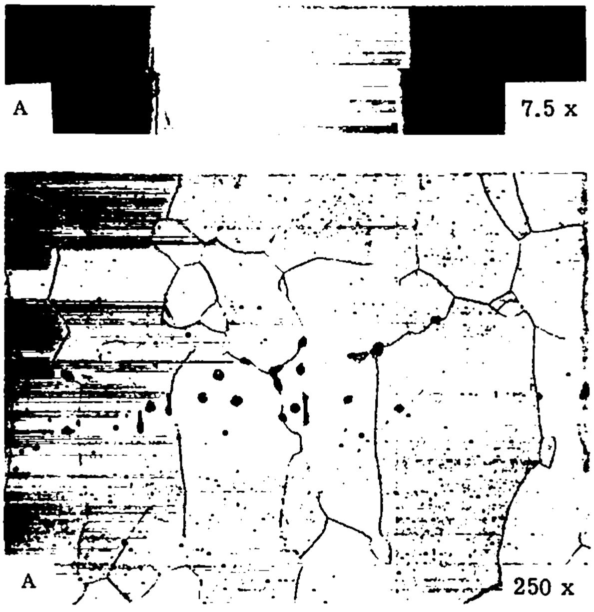
W Discs: (3/8" D). Spray-coated with Mo slurry Treated at 2300°C for 1 1/2 hours in H$_2$ under 600 psi pressure. Diffusion and grain growth have occurred across interface, but considerable inclusions remain.



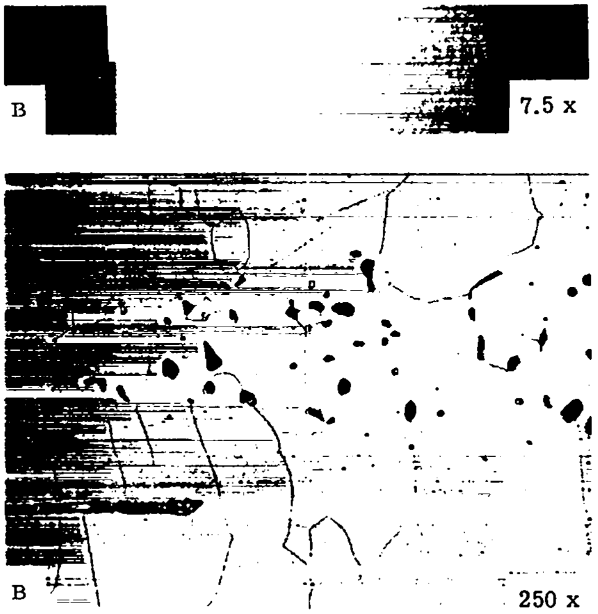
W Discs: (3/8" D). Spray-coated with WO$_3$ slurry. Treated at 2350°C for 1 hour in vacuum and for 2 hours in H$_2$ at 1400 psi pressure. Some diffusion has occurred and grain growth across interface has begun. Very little unreduced oxides remain.

W Discs: (3/8" D). Spray-coated with mixture of 90% WO$_3$ and 10% MoO$_3$ slurry. Treated at 2350°C for 2 hours in H$_2$ under 1400 psi pressure. Diffusion has occurred and grain growth has taken place over 75% of the interface. Voids and unreduced oxides remain.

Fig. 7. Diffusion bonds produced from spray-coated slurries.



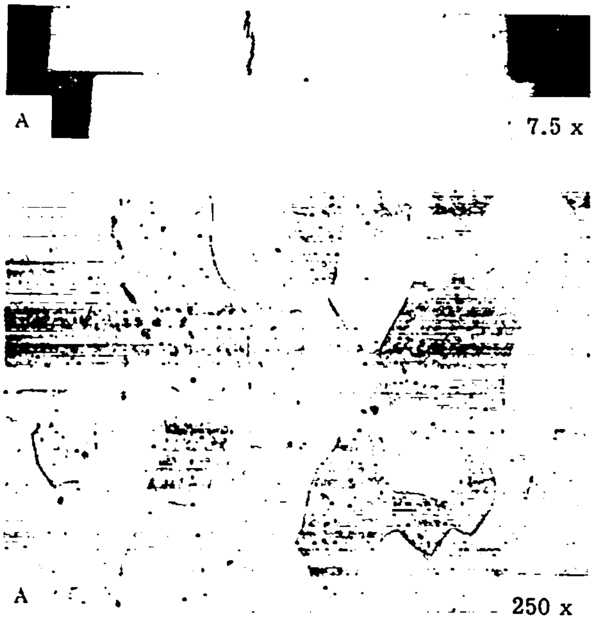
W Discs: (3/8" D). WO_3 coating produced on W surfaces by heating to 1000°C in a mixture of 1/3 O_2 + 2/3 He. Treated at 2350°C for 2 hours in H_2 under 1400 psi pressure. Diffusion complete; original interface entirely obliterated by columnar type grains; voids and unreduced oxides remain.



W Discs: (3/8" D). WO_3 coating produced on W surfaces by heating to 1000°C in a mixture of 1/3 O_2 + 2/3 He. Treated at 2350°C for 2 hours in H_2 under 1400 psi pressure. Diffusion complete. Migration of original interface is to be noted.

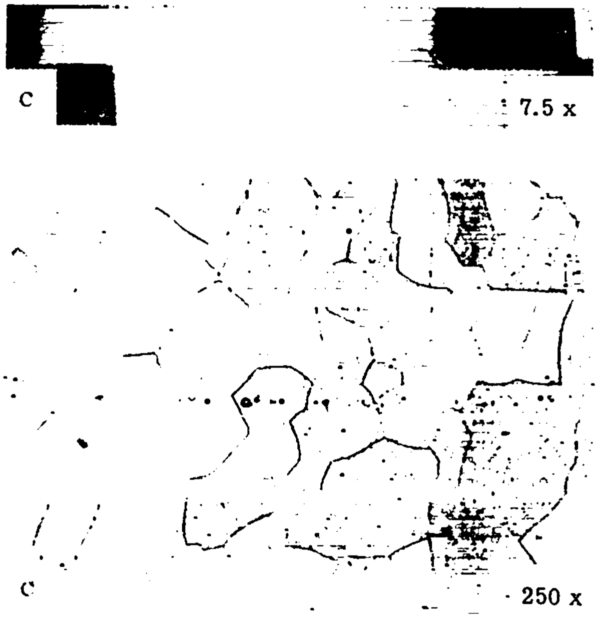
W Discs: (3/8" D). WO_3 coating on W surface produced directly on W surfaces by heating with an oxygen torch. Treated at 2350°C for 2 hours in H_2 under 1400 psi pressure. Some diffusion has occurred with some grain growth across the interface; unreduced oxides remain.

Fig. 8. Diffusion bonds produced from direct oxidation of tungsten surfaces.

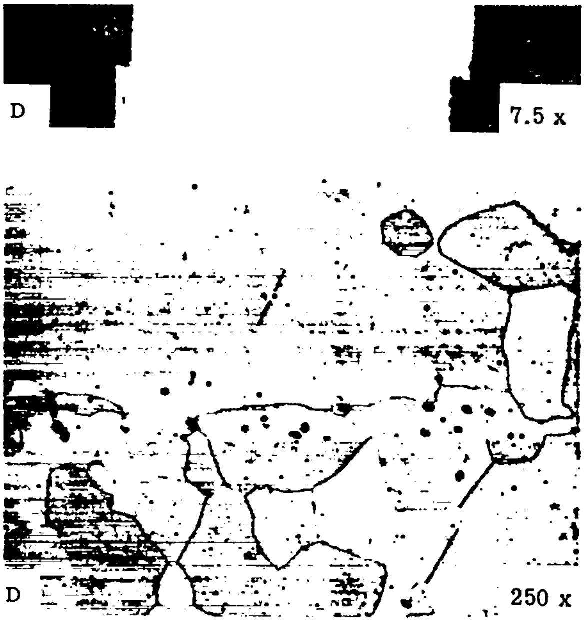


W Discs: (3/8" D). Coated with Mo by thermal decomposition of $Mo(CO)_6$. Treated at 2000°C for 1 hour in H_2 under 1400 psi pressure. Bonding in initial stage; Mo layer not diffused.

W Discs: (3/8" D). Coated with Mo by thermal decomposition of $Mo(CO)_6$.
W Wires: (1/32"). Uncoated.
Treated at 2350°C for 1 1/2 hours in H_2 under 600 psi pressure. Bonding complete but coarse grain and isolated voids present.

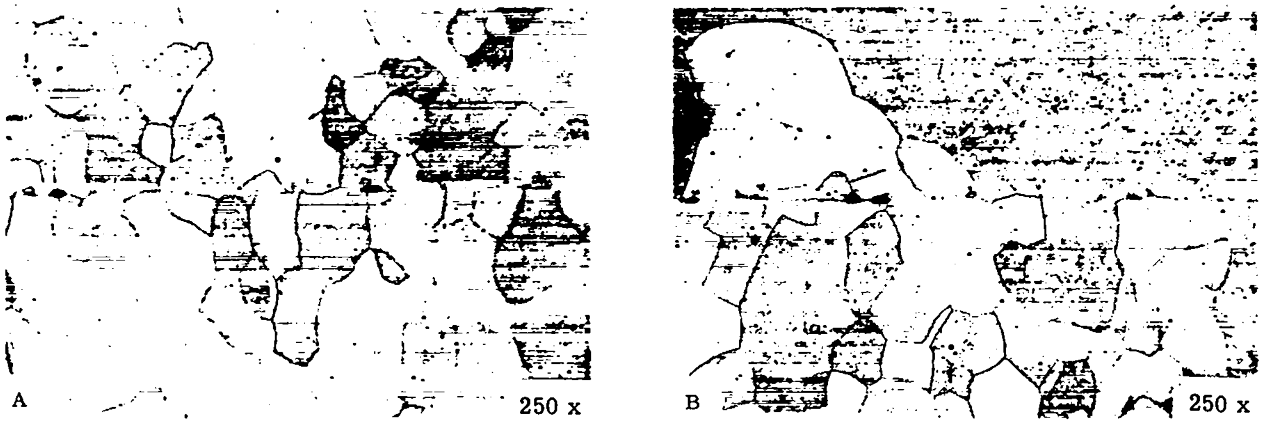


W Discs: (3/8" D). Coated with Mo by thermal decomposition of $Mo(CO)_6$. Treated at 2350°C for 1 1/2 hours in H_2 under 1400 psi pressure. Complete diffusion and grain growth across interface; interface outlined by residual unreduced inclusions.



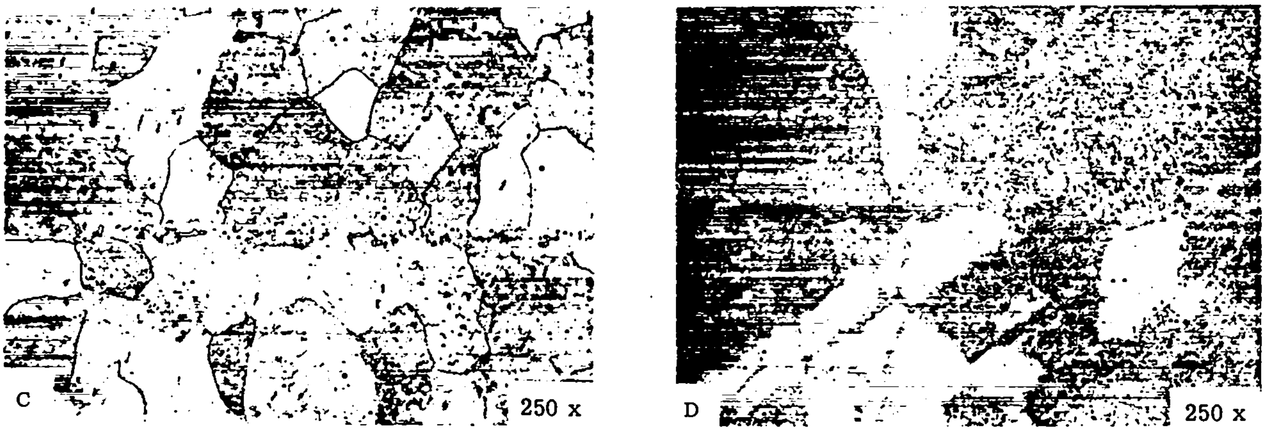
W Discs: (3/8" D). Coated with W by thermal decomposition of $W(CO)_6$. Treated in H_2 for 1 hour at 2350°C and 12 hours at 2600°C under 1400 psi pressure. Bonding complete; inclusions present; large grains produced by high bonding temperature.

Fig. 9. Diffusion bonds produced from carbonyl coatings.



W Discs: (3/8" D). Coated with W by thermal decomposition of $W(CO)_6$. Treated at 2350°C for 6 hours in H_2 under 1400 psi pressure. Bonding complete but isolated voids present.

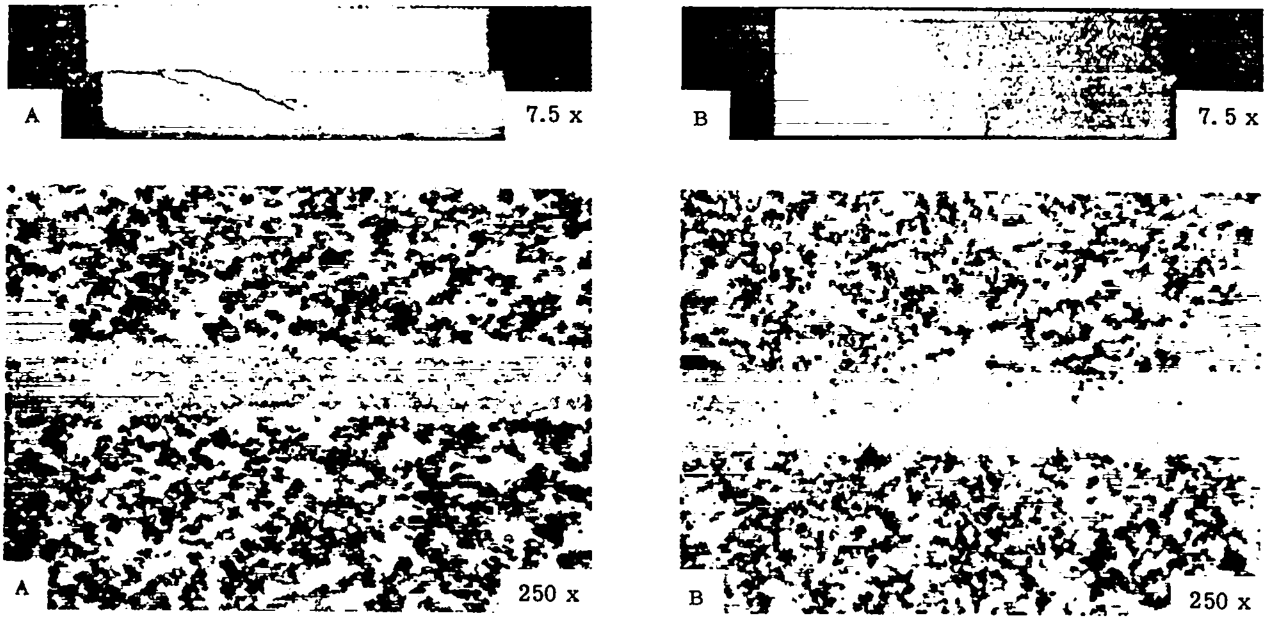
W Discs: (3/8" D). Coated with W by thermal decomposition of $W(CO)_6$. Treated at 2350°C for 2 hours in vacuum under pressure of 1400 psi. Bonding complete but coarse grains and isolated voids present.



W Discs: (3/8" D). Coated with Mo + W from a mixture of 50% $Mo(CO)_6$ + 50% $W(CO)_6$. Treated at 2000°C for 2 hours in H_2 under 1400 psi pressure. Bond formed but diffusion incomplete.

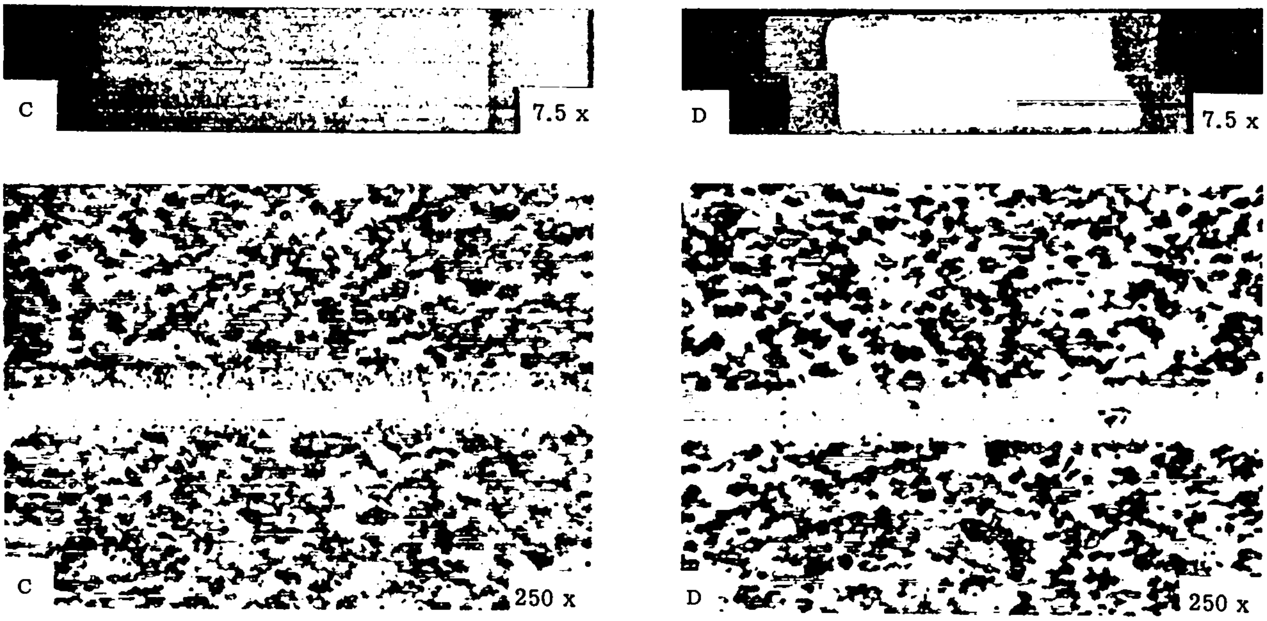
W Discs: (3/8" D). Coated with Mo + W from a mixture of 50% $Mo(CO)_6$ + 50% $W(CO)_6$. Treated at 2350°C for 2 hours in H_2 under 1400 psi pressure complete bond formed.

Fig. 10. Diffusion bonds produced from carbonyl coatings.



W - 50 v/o UO_2 Sheets: (1/16"). Spray-coated with W, sintered, and re-spray-coated. Treated at 2000°C for 2 hours in H_2 under 200 psi pressure. Complete diffusion and grain growth across the interface; cracks not related to the bonding problem.

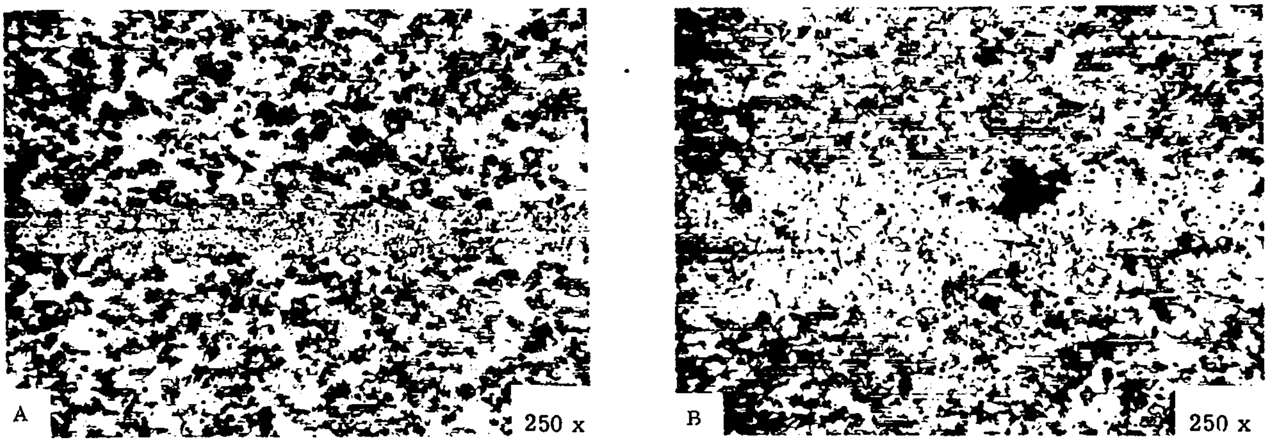
W - 50 v/o UO_2 Sheets: (1/16"). Spray-coated with W, sintered, and re-spray-coated. Treated at 2350°C for 2 hours in H_2 under 800 psi pressure. Complete diffusion and grain growth across interface; some small voids present.



W - 50 v/o UO_2 Sheets: (1/16"). Spray-coated with W, sintered, and then spray-coated with a mixture of W + 1.0 w/o C. Treated at 2000°C for 2 hours in H_2 under 600 psi pressure. Bonding incomplete; some voids pressed at interface.

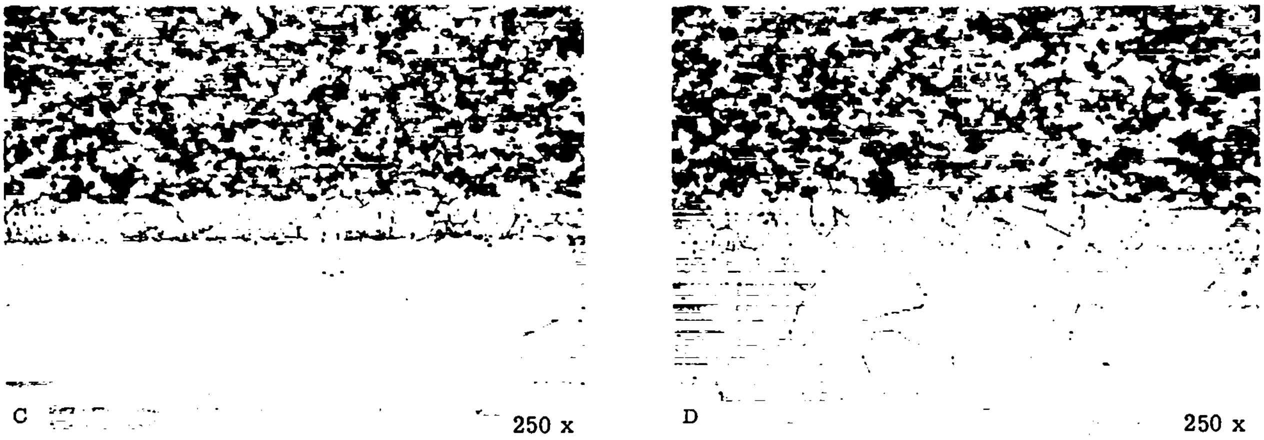
W - 50 v/o UO_2 Sheets: (1/16"). Spray-coated with a mixture of W + 1.0 w/o C and sintered. Treated at 2000°C for 2 hours in H_2 under 1400 psi pressure. Bonding complete; oxide loss at edges not related to the bonding problem.

Fig. 11. Diffusion bonds produced between powder-compacted mixtures of $W\text{-}UO_2$



W - 50 v/o UO_2 Sheets: (1/16"). Spray-coated with graphite. Treated at 2000°C for 3 hours in H_2; no pressure applied. Bonding intermittent; voids present.

W - 50 v/o UO_2 Sheets: (1/16"). Coated with graphite suspension and dried. Treated at 2000°C for 1/2 hour in vacuum and 1/2 hour in H_2, at 2600°C for 2 hours, 2000°C for 1/2 hour and 1700°C for 1/2 hour, all in vacuum under 2400 psi pressure. Considerable diffusion of original interface but many voids present.



W - 50 v/o UO_2 Sheet: (1/16"). Spray-coated with W and sintered.
W - Wire: (1/32"). Electroplated with 85% Re + 15% Ni. Treated at 2350°C for 1 1/2 hours in H_2 under 1000 psi pressure. Bonding poor; very little grain growth across coated interface.

W - 50 v/o UO_2 Sheet: (1/16"). Spray-coated with W and sintered.
W - Wire: (1/32"). Coated with Mo from $Mo(CO)_6$. Treated at 2350°C for 1 1/2 hours in H_2 under 800 psi pressure. Complete diffusion and grain growth across interface; some fine porosity near interface.

Fig. 12. Diffusion bonds produced between powder-compacted mixtures of $W-UO_2$

TABLE III

RESULTS OF TENSILE TESTS

Coating	Diffusion Treatment	Surface Rating*	Tensile Strength (psi)	Average Tensile Strength (psi)
None: Solid W Rod	2 hr @ 2350°C in H_2	5	59700	
" " " "	" " "	5	59000	
" " " "	" " "	5	57000	58570
W-oxide (slurry)	2 hr @ 2350°C in H_2	3.5	9050	
Ni (electroplate)	2 hr @ 2000°C in H_2	2	9000	
15% Ni + 85% Re	2 hr @ 2350°C in H_2	3.5	15125	
" "	" " "	3	23100	
" "	" " "	3	29800	22675
W-oxide (He-O_2)	2 hr @ 2350°C in H_2	4.5	30800	
"	" " "	4	30900	
"	" " "	1	6850	
"	" " "	1	3000	17890
Mo (carbonyl)	2 hr @ 2350°C in H_2	3	12800	
" "	" " "	3	12500	
" "	" " "	4	18900	
" "	" " "	2	17300	
" "	" " "	4	20300	
" "	" " "	3	28800	
" "	" " "	3.5	9000	
" "	" " "	3	18800	
" "	" " "	3	16800	
" "	" " "	3	13600	16880
Mo + W (carbonyls)	2 hr @ 2350°C in H_2	4	27600	
" " "	" " "	4.5	28500	
" " "	" " "	3	26800	
" " "	" " "	3	23900	
" " "	" " "	3	33500	
" " "	" " "	4	6300	
" " "	" " "	3	7800	22060
W-oxide (He-O_2)	2 hr @ 2350°C in H_2 + 7 hr @ 2600°C in Vac	2.5	27100	
"	" " " "	2	7100	17100
Mo (carbonyl)	" " " "	3	11600	
" "	" " " "	3	11200	
" "	" " " "	3	2560	
" "	" " " "	2	3600	7240
Mo + W (carbonyls)	" " " "	5	5430	

*Surface Rating is an arbitrary number assigned to denote relative roughness of fracture surfaces. The number 5 denotes maximum roughness observed and corresponds to thorough bonding. The number 1 denotes minimum roughness and corresponds to inadequate bonding.

2.2. Microstructures of Bonded Regions

The best indication of the nature and extent of solid state diffusion achieved in a particular bonding run was obtained from a microexamination of the cross section of a bonded specimen pair. A number of early failures to obtain adequate bonding resulted from misalignment of the contracting surfaces while under axial pressure. Insertion of 3/8 inch diameter steel balls between the upper and lower ends of the tungsten platforms and their holders (Fig. 1) effectively remedied the difficulty and enabled full surface contact of specimen pairs. Subsequent diametral microexaminations confirmed that good conditions for bonding had been achieved.

The quality of the diffusion bonds formed varied with the conditions imposed. Explorations of suitable coatings for bond promotion (Table II) were carried out. Conditions of pressure, temperature, and environment were sought which would result in the formation of acceptable bonds. Selected photomicrographs have been assembled from among the larger number of bonded specimen pairs listed in Table I.

2.2.1 Bonds Produced by Electroplating

Figure 6 shows two examples of diffusion bonds induced by a preliminary electroplated layer of nickel. In Fig. 6A complete bonding with grain growth across the interface is evident. The much finer grain size of the wire compared to that of the disc is a characteristic of the material. The abnormally coarse grains in one of the discs may be attributed to a deformation nonuniformity during previous fabrication of the rod which became accentuated at the high temperature of the diffusion treatment. Less contrast in grain size is to be noted in Fig. 6B, in which a lower temperature was used. These examples show that a light plating of nickel is capable of promoting a tungsten-tungsten diffusion bond. The relatively low melting point of nickel, however, introduces a disadvantage in the high temperature strength of the tungsten joint unless sufficient treatment is provided to diffuse the nickel layer to a low dilution. In this connection, some platings of 85% Re + 15% Ni were tried but did not produce promising results.

2.2.2. Bonds Produced by Graphite, Oxide and Metal Slurries

Figures 6C and 6D show two results of bonding treatments which employed surface coatings of graphite. In the former, inadequate diffusion of the carbide layer is evident. Increase in temperature in the latter case produced a noticeable improvement, but though substantial grain growth across the interface occurred, considerable inclusions, probably carbides, remained to embrittle the joint.

Three examples of bonds developed from oxide coatings appear in Figs. 7A, 7C, and 7D. In the first, the temperature was obviously too low, diffusion was slight, and unreduced oxides remained at the interface. The higher temperature in the case represented in Fig. 7C promoted greater diffusion and oxide reduction, though grain growth across the interface was limited. A coating of mixed oxides, WO_3 and MoO_3, did not seem to improve the bond. Figure 7D shows voids and unreduced oxides with but slight indications of grain growth across the interface.

The result produced by a metal slurry is shown in Fig. 7B for comparison. Here, grain growth was accomplished but the prevalence of fine inclusions, probably unreduced oxide from the original powder particles in the slurry, detracts from the quality of the bond.

Bonding experiences of this type in which slurry coatings were employed, though not negative, did not appear to offer the promise of other materials. Very likely the low particle density of the coating adhering to the tungsten surface after evaporation of the vehicle was responsible for the marginal nature of the bond.

2.2.3. Bonds Produced by Direct Oxidation

An alternate approach, aimed toward a more natural buildup of an oxide coating on the tungsten surface than that obtained by the more mechanical application by the slurry method, employed the technique of direct oxidation of the specimen itself through exposure to oxygen while at elevated temperature. The simplest approach utilized direct heating of specimen pair surfaces in air with an oxygen torch.

An example of the type of bond obtained between two discs after a typical treatment at 2350°C for 2 hours is shown in Fig. 8C. Although the bond produced is far from optimum quality, it did indicate that this relatively simple and straightforward coating procedure was capable of supporting an interface diffusion.

Figures 8A and 8B illustrate creditable results obtained from a variation of the direct oxidation procedure. Here, the specimens were heated to 1000°C in helium which was then displaced by a mixture of

1/3 oxygen and 2/3 helium for 2 minutes. After a similar diffusion treatment complete bonding was obtained. The interface grains are somewhat columnar and some voids and unreduced inclusions are present but on the whole the method produced a promising bond. Figure 8B is of some special interest in that it shows a migration of the interface away from its original position, an example of the Kirkendall effect.

2.2.4. Bonds Produced by Carbonyl Deposition

Some of the most promising bonds were produced by deposition of coatings of molybdenum, or tungsten, or both from the carbonyl compounds of those metals. Figures 9 and 10 show representative examples. The sequence of molybdenum coatings in Figs. 9A, 9B and 9C illustrates the improvement resulting from an increase in temperature and pressure. In Fig. 9A, a lower temperature situation, inadequate diffusion is evident. The case of Fig. 9B involving wire specimens shows extensive diffusion and grain growth but poor uniformity of grain structure attributable to differences between the two parts of the diffusion pair. Figure 9C illustrates a sound bond. Only slight inclusions remain to outline the original interface. The offset between specimens is not significant since this tendency was eliminated in later runs by the modification in the apparatus described under Section 2.2.

Figure 9D shows a case of thorough bonding obtained with a tungsten coating from the thermal decomposition of $W(CO)_6$. However, some inclusions remain even after a lengthy 12 hour diffusion treatment at the high temperature of 2600°C. The undesirable growth of abnormally large grains also occurred. A somewhat similar result appears in Fig. 10A after only 6 hours at 2350°C. Figure 10B shows thorough bonding after only 2 hours at 2350°C, though the growth of grains across the interface appears to be at an initial stage.

Comparison of the bonding results obtained from molybdenum coatings and from tungsten coatings indicates more extensive diffusion and interface grain growth from the former at lower temperatures and shorter times, an effect which may be related to the lower melting point of molybdenum. The thorough nature of the bonding obtained from both coatings suggested an investigation of their behavior as an intimate single-coat mixture deposited from a mixture of their carbonyls. Examples of such results, employing a mixture of 50% $Mo(CO)_6$, are shown in Figs. 10C and 10D. In the former, the relatively low temperature of 2000°C did not support complete diffusion and unreduced inclusions remained at the interface. In the latter, however, quite thorough bonding resulted after 2 hours at 2350°C. Diffusion and grain growth across the interface, a minimum of inclusions, and good uniformity in grain size add to the promise of this type of bond.

2.2.5. Bonds Produced between Tungsten-coated Sheet Specimens of W-50 v/o UO_2 Compacts

Interest in the use of tungsten as a base material for fuel elements in reactor design suggested exploration of the bonding capabilities of sheet specimens compacted from powder mixtures of tungsten and UO_2.

As a standard procedure, all such sheet compacts were coated with tungsten powder and sintered. The puspose of this coating was to prevent loss of the uranium oxide at elevated temperatures.

The diffusion bonds studied in this investigation thus were those between the applied tungsten coatings. However, in the course of the diffusion treatments, adherence of the tungsten coat to the sheet compact received the added benefit of the high temperature diffusion treatment.

Figures 11 and 12 show representative examples of bonding obtained under various diffusion conditions. Figure 11A indicates that a good bond can be formed at the lower temperature of 2000°C and at the lower pressure of 200 psi. No noticeable improvement is evident in Fig. 11B, in which higher temperature and pressure were used. Figures 11C and 11D illustrate the effect of including 1.0 w/o C in the tungsten spray-coat. The structure in Fig. 11D shows fewer voids in the interface, in keeping with the fact that a higher pressure was maintained during bonding. In these two structures no particular improvement ascribable to the carbon addition is to be noted. Figure 12A shows an inadequate bonding condition resulting from a spray-coating of the surfaces with graphite followed by the diffusion treatment with no pressure applied. In a similar case (Fig. 12B), under higher temperature and with the application of pressure, rather extensive diffusion occurred, though the presence of voids detracts from the quality of the bond.

Figure 12C shows the result obtained from the use of an electroplated Ni-Re layer on a tungsten wire specimen of a sheet-wire couple. Diffusion of the tungsten spray-coating into the sheet is evident, but the plated layer appears to act more as a barrier than as a promoter of diffusion under the conditions imposed. More positive bonding was obtained in Fig. 12D which illustrates extensive diffusion achieved in a similar sheet-wire couple. Here, however, the molybdenum coating from a carbonyl deposition has been noticeably more effective.

Usable pressures are limited when bonding tungsten wires to W-UO_2 compacts. Low pressures do not provide adequate surface contact while high pressures distort the geometry of the specimens.

2.3. Tensile Tests

All tensile specimens tested parted at the bond interface. The character of the fracture surfaces varied and appeared to be related to the extent of bonding and to the breaking strength observed. Examination of the fracture surfaces indicated that, in general, specimens which exhibited high tensile strength had a rough surface, while those of low tensile strength had a smooth surface. Surface roughness was an indication of the extent of diffusion, grain growth, and bond establishment across the interface. Table III, which lists the tensile test results of several types of effectively bonded specimens, includes a surface rating for each specimen tested. In most cases, a direct correlation with tensile strength is evident; however, the rating is purely arbitrary and there are instances in which a rough surface is associated with a low strength, due very likely to nonuniform bonding and existence of localized regions of weakness from which early fracture propagated.

Though Table III shows a total of 35 recorded tensile tests, this number represents only 50% of the specimens originally diffusion-treated for testing. The brittle nature of tungsten accounted for considerable mortality during machine grinding of gage lengths and general preparation. Such breakage was not confined to the bonded cross section, a behavior which points up the sensitivity of this material to low values of shock and bending that would be of no consequence in ordinary metals. Another cause of breakage which frequently occurred during insertion in test grips was a misalignment of specimen segments produced by nonaxial bonding. The latter condition was greatly minimized after the ball-joint modification (Section 2.2) was applied.

Although considerable variation exists in the recorded tensile strengths of specimens tested within a similarly coated and treated group, the average strengths nevertheless indicated notable promise for this joining approach as a whole. When low strength values which obviously are related to incomplete bonds are discarded, the average strengths approach 50% of the tensile strength of original tungsten rod, similarly treated.

The value of 22,675 psi for Ni-Re bonded specimens indicates a fair transmission of tensile strength across such a bonded joint which should be suitable for many applications, though possibly not for those at the higher temperatures. The 30,850 psi average of the two well-bonded furnace-oxidized specimens, though based on a smaller number of tests, represents the highest tensile average obtained and warrants further development of this type of coating. The relatively low average of 16,880 psi obtained for molybdenum carbonyl-coated specimens is lower than that of half of the specimens of this type tested. The scatter among individual tests is attributed to a general uneven condition and a tendency toward flaking of this coating, as applied. It is to be noted that this tendency was not observed in tungsten coatings similarly applied. This and other indications suggest that a tungsten coating applied by the carbonyl method would probably promote a more effective bond. However, since the corresponding diffusion treatment would require a longer time at higher temperature, such further development along these lines was deferred in favor of other approaches.

The more uniform and adherent coat resulting from a mixture of molybdenum and tungsten carbonyls is reflected in the tensile results as well as in the appearance of the microstructure, as previously discussed. The 22,060 psi average of all tests of this group may be revised to 28,060 psi if the two very low values are excluded. The remaining tensile strengths are quite uniform and show much less spread than other groups.

Extension of the 2 hour diffusion heat treatment at 2350°C to include an additional 7 hours at the higher temperature of 2600°C (Section 1.3.2) did not result in improvement in tensile strength values. Instead, individual test values were generally lower and their average also was lower for each of the bond types tested (Table III). It appears that the lower strengths are related to the observed coarse grain structure which resulted from the additional high temperature anneal. These observations suggest that a more effective direction for diffusion treatment extensions to promote bond improvement and increase tensile strength lies in the area of long times at lower temperatures, certainly not higher than the original bonding temperature.

CHAPTER 3

CONCLUSIONS

1. A diffusion bond can be developed between separate pieces of solid tungsten under suitable conditions of temperature, pressure, and the contacting surfaces.

2. Various degrees of bonding are promoted by coating the contacting surfaces with an auxiliary material. In order of increasing effectiveness, the following were found to promote bonding: graphite slurry; molybdenum and tungsten oxide slurries; molybdenum and tungsten metal slurries; electroplated nickel; tungsten oxide resulting from direct surface oxidation; molybdenum, tungsten, and Mo-W deposited by thermal decomposition of carbonyl compounds.

3. Temperatures above 2000°C are required to promote thorough W-W bonding; temperatures of the order of 2350°C for 2 hours, when applied with suitable contact pressures, were generally effective in promoting diffusion across an interface and thorough bonding of a couple.

4. The most promising bonds from a microstructural standpoint have been formed from contact surface coatings of (a) tungsten oxide from

direct surface oxidation, and (b) Mo-W mixture deposited from the carbonyls of those metals.

5. Contact pressures materially promote diffusion bonding. The limitation on their magnitude is the retention of structural form. Values of the order of 1400 psi, at temperatures up to 2350°C, have contributed to thorough bonding without shape distortion.

6. Powder-compacted tungsten sheet containing 50 v/o UO_2, spray-coated with an outer layer of tungsten, bonds thoroughly to itself and to tungsten metal under 2 hour diffusion treatments at 2000°C and moderate pressures of the order of 1000 psi.

7. Tungsten-tungsten bonds promoted by effective interface coatings and subsequent diffusion treatments are capable of transmitting stresses as high as 30,000 psi in standard tensile tests.

REFERENCES

1. Barth, V. D., "Physical and Mechanical Properties of Tungsten and Tungsten-Base Alloys," Battelle Memorial Institute, Defense Metals Information Center Report DMIC-127 (March 15, 1960).

2. Barth, V. D., "Review of Recent Developments in the Technology of Tungsten," Battelle Memorial Institute, Defense Metals Information Center Report DMIC-Memo-108 (March 18, 1961).

3. Monroe, R. E., "Joining of Tungsten," Battelle Memorial Institute, Defense Metals Information Center Memorandum DMIC-Memo-74 (Nov. 24, 1960).

4. Albom, M. J., "Joining Tungsten to Tungsten," Mater. Design Eng., 55, No. 6, 12-13 (1962).

5. Nachtrieb, N. H., Weil, J. A., Catalano, E., and Lawson, A. W., "Self-Diffusion in Solid Sodium. II The Effect of Pressure," J. Chem. Phys. 20, 1189-91 (1952).

6. Nachtrieb, N. H. and Lawson, A. W., "Effect of Pressure on Self-Diffusion in White Phosphorous," J. Chem. Phys. 23, 1193-95 (1955).

7. Liu, T. and Drickamer, H. G., "The Effect of Compression and of Hydrostatic Pressure on the Diffusion Anisotropy in Zinc," J. Chem. Phys. 22, 312-19 (1954).

8. Castleman, L. S., and Seigle, L., Research Laboratories, Sylvania Electric Products Inc., "Fundamentals of Diffusion Bonding, I (SEP-227) Aug. 13, 1956; II (SEP-245) Feb. 15, 1958; III (SEP-251) June 30, 1958; IV (SEP-253) June 30, 1959."

9. Castleman, L. S., "An Analytical Approach to the Diffusion Bonding Problem," Nucl. Sci. Eng. 4, 209-226 (1958).

10. Storchheim, S., "Some Studies of Aluminum-Copper and Aluminum-Zirconium Solid State Bonding," Sylvania Electric Products, Inc., Report SEP-164 (June 7, 1954).

11. Storchheim, S., "Solid State Bonding and Canning of Thorium with Aluminum," Nuclear Science and Technology TID-2508 (Del.), Vol. 1A, Issue 3, Dec. 1955, pp 395-407.

12. Storchheim, S., "Hot Pressure Bonding," Metal Progr., July, 1957, p 97.

13. Fugardi, J. and Zambrow, J. L., "Bonding of Various Metals and Alloys by Isostatic Pressing at Elevated Temperatures," Sylvania-Corning Nuclear Corp., Report SCNC-272 (Dec. 1958).

14. Graham, A. K., Electroplating Engineering Handbook, Reinhold Publishing Corporation, New York, 1955, p. 210.

15. Netherton, L. E., and Holt, M. L., "Electrodeposition of Rhenium-Nickel Alloys," J. Electrochem. Soc. 98, 106-109 (1951); Electrodeposition of Rhenium-Cobalt and Rhenium-Iron Alloys," J. Electrochem. Soc. 99, 44 (1952).