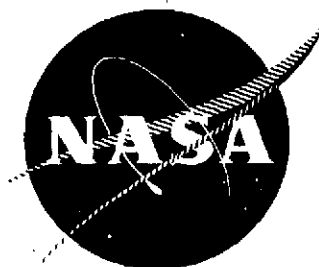


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INVESTIGATION TO DEVELOP A METHOD TO APPLY DIFFUSION BARRIERS TO HIGH STRENGTH FIBERS

by R.D. Veltri, E.L. Paradis, and F.C. Douglas

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16. Abstract A radio frequency powered ion plating process was used to apply the diffusion barriers of aluminum oxide, yttrium oxide, hafnium oxide and titanium carbide to a substrate tungsten fiber. The plating parameters for each of the coatings were chosen so that the best compromise between rate of deposition and adherence to the substrate was obtained. Each of the coatings was examined as to its effect on both room temperature strength and tensile strength at 1093°C of the base tungsten fiber. The coated fibers were then overcoated with a nickel alloy (IN600) to become single cell diffusion couples. These diffusion couples were then exposed to 1093°C for 24 hours, cycled between room temperature and 1093°C, and given a thermal anneal for 100 hours at 1200°C. Tensile testing and metallographic examinations were used to determine that the hafnium oxide coating produced the best high temperature diffusion barrier for tungsten of the four coatings chosen to evaluate. Hafnium oxide was then used to coat a production lot of 15 mil tungsten filament for NASA to evaluate in a composite. These last coated filaments were tested before delivery and the elevated temperature properties of the as received tungsten fiber substrate were found to not have been degraded.					
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INTRODUCTION

Composites containing high strength fibers are being extensively investigated because their mechanical properties can be tailored to satisfy the requirements of particular applications. Dual problem areas in the fabrication and use of metal matrix composites are those of fiber-matrix reaction during fabrication and unwanted interface diffusion during the use of the composite for extended times at elevated temperatures. In particular, tungsten fibers in a nickel alloy matrix composite cannot withstand temperatures above 1000°C for long times such as 1000 hours. The objective of this program was to develop a method of applying a diffusion barrier to high strength tungsten fibers which would result in non-reactive coated fiber with sufficient strength for incorporation into a nickel alloy matrix.

In a previous program (Ref. 1) the ion plating technique was successfully demonstrated as a unique means of applying a diffusion barrier coating to the refractory fibers of tungsten, columbium, carbon and aluminum oxide. The rf approach used for ion plating at United Aircraft Research Laboratories showed the feasibility for the coating of very stable oxides such as aluminum oxide, yttrium oxide and hafnium oxide. These could be deposited in a dense adhering layer up to three microns thick.

This program was concerned with screening four barrier coating combinations for high strength tungsten fiber which then would be incorporated in a high nickel alloy. The candidate coating materials were: aluminum oxide, yttrium oxide, titanium carbide, and hafnium oxide.

The screening process proceeded from the four to two coatings until finally, as a result of an evaluation process, the most favorable diffusion coating was chosen. The evaluation process included room temperature and 1093°C tensile tests performed on the coated and uncoated fiber. The better coating fiber combinations were given an overcoat of IN600 nickel alloy. These diffusion couples besides being tested at room temperature and 1093°C were given thermal cycling tests for 24 hours and were also thermally annealed at 1200°C for 100 hours. Metallographic examination, scanning electron microscopy and electron microprobe analysis were used to evaluate fracture surfaces, determine fiber coating degradation, and determine any diffusion across the fiber interface region in the zone of the diffusion barrier.

EXPERIMENTAL PROCEDURE

Ion Plating: Apparatus and Operation

The description of the ion plating apparatus designed and developed at the United Aircraft Research Laboratories used in this program was given in detail in Ref. 1. For completeness, part of that description is included in Appendix 1. Briefly, the ion plating of fibers was accomplished by suspending the substrate fibers along the inside vertical axis of a cylindrical source tube. The entire cylindrical tube was made of the material of that particular barrier being deposited.

Target Discussion

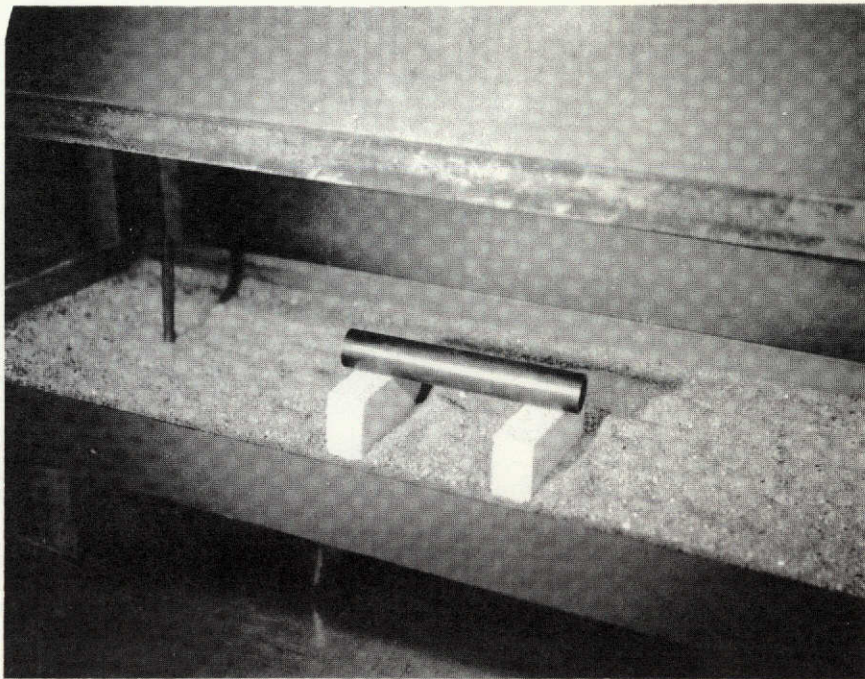
Each oxide candidate barrier was hot pressed into right circular cylinders 38.1 cm long, with a 6.35 cm outside diameter and a 0.3175 to 0.635 cm thick wall by outside vendors. The hafnium oxide and yttrium oxide targets had a graphite-type coating on the inner cylindrical surface. This coating was encountered previously (Ref. 1) and proved troublesome in that attempts to mechanically remove or sputter off the coatings were only partially successful. The vendor was also not able to produce a clean inner surface on these targets or remove the coatings.

Attempts were made to determine a heating cycle in air which would literally burn the coating off. Temperatures of 575°C to 600°C were found to be sufficient to remove the coating and yield a clean inner surface on test pieces which were broken from old targets. Rectangular muffle furnaces although satisfactory for thermal cycling presented uneven heating and support problems which initiated thermal shock cracks. A stress relief glassware oven 60.9 cm high by 60.9 cm wide by 183 cm long was found to present a fairly soft thermal gradient with enough volume to eliminate the thermal shock conduction problem associated with end supports of the cylindrical tubes.

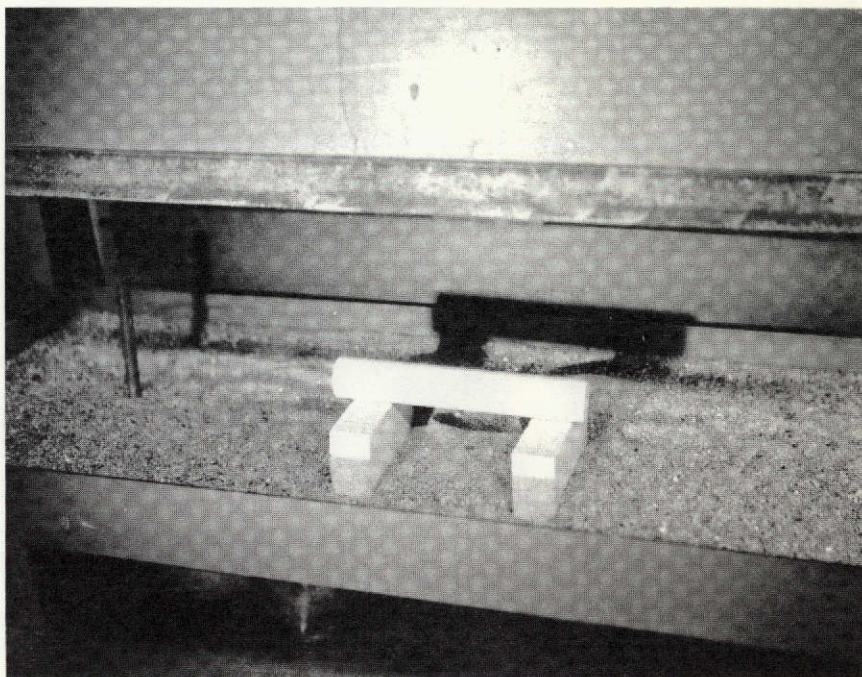
The new yttrium oxide cylindrical target was placed in the center of the floor of the cool oven and supported on two standard firebricks. The oven was then heated at 100°C/hr up to 650°C. This temperature was held for 10 hours then the oven was cooled at the rate of 100°C/hr. The target came out of the oven pure white. Photographs of this target before and after thermal cycling can be seen in Figs. 1 and 2. The hafnium oxide target was then given the same thermal treatment. Upon removal this target still had a slight shade of gray on the inner surface.

The targets were then prepared using the procedure described in Appendix 1.

YTTRIUM OXIDE TARGET BEFORE CLEANING



YTTRIUM OXIDE TARGET AFTER CLEANING



Deposition Rates

The duration of a run was directly proportional to the deposition rate and total film thickness required. Deposition rates were determined for all materials deposited in the program and a summary is presented in Table I. Power inputs to the ceramic targets were kept low since it was found that the yttrium oxide would not sustain electrical stresses greater than 1.58 watts per cm^2 without failure for the wall thickness that was available in this program.

Although deposition rates with these materials could be increased in principle, the cost was prohibitive for this program because higher deposition rates caused target fractures. To extend target life, the system was run at a low power level where the targets could survive. This low power level resulted in a low deposition rate necessitating a correspondingly low substrate bias voltage during deposition. This mode of ion-plating may be referred to as bias sputtering. However, the process still incorporates all the elements of ion-plating and will be referred to as such throughout this report.

Testing Procedure

Tensile Testing

Room temperature tensile tests were made using an Instron table model tensile testing machine. A hot tensile tester for fibers was designed and built at UARL. A small resistance wound furnace was used for operation at 1093°C which was required in this program. The furnace produced a reasonable hot zone as compared to the furnace described in Ref. 1. and also exhibited marked durability for daily recycling to test temperature. A photograph of the entire hot tensile testing apparatus is shown in Fig. 3. In this figure can be seen the controls for heating and water cooling of the wax used to grip the fibers outside the hot zone. A small quartz tube insert was used within the furnace core to provide a jacket for an argon bath around the fiber being tested for oxidation protection at 1093°C . Before this equipment was used for testing ion plated fibers, hot tensile test data were taken on tungsten and boron fibers at 500°C , 700°C and 1000°C . These tests were made to compare results with those previously published (Refs. 2,3) for tungsten and boron fibers. Since the comparison of new hot tensile strength results was within acceptable limits, it was felt that when the temperature level of 1093°C was used, the equipment would not have to be considered a problem in interpreting the hot ultimate tensile strength of ion plated fibers.

For the testing of 15 mil tungsten fiber the load cells used in this apparatus did not have the capacity to produce tensile breaks. For these larger filaments the resistance wound furnace was mounted vertically between the jaws of the Instron table model machine and is shown in Fig. 4.

Thermal Cycling Apparatus

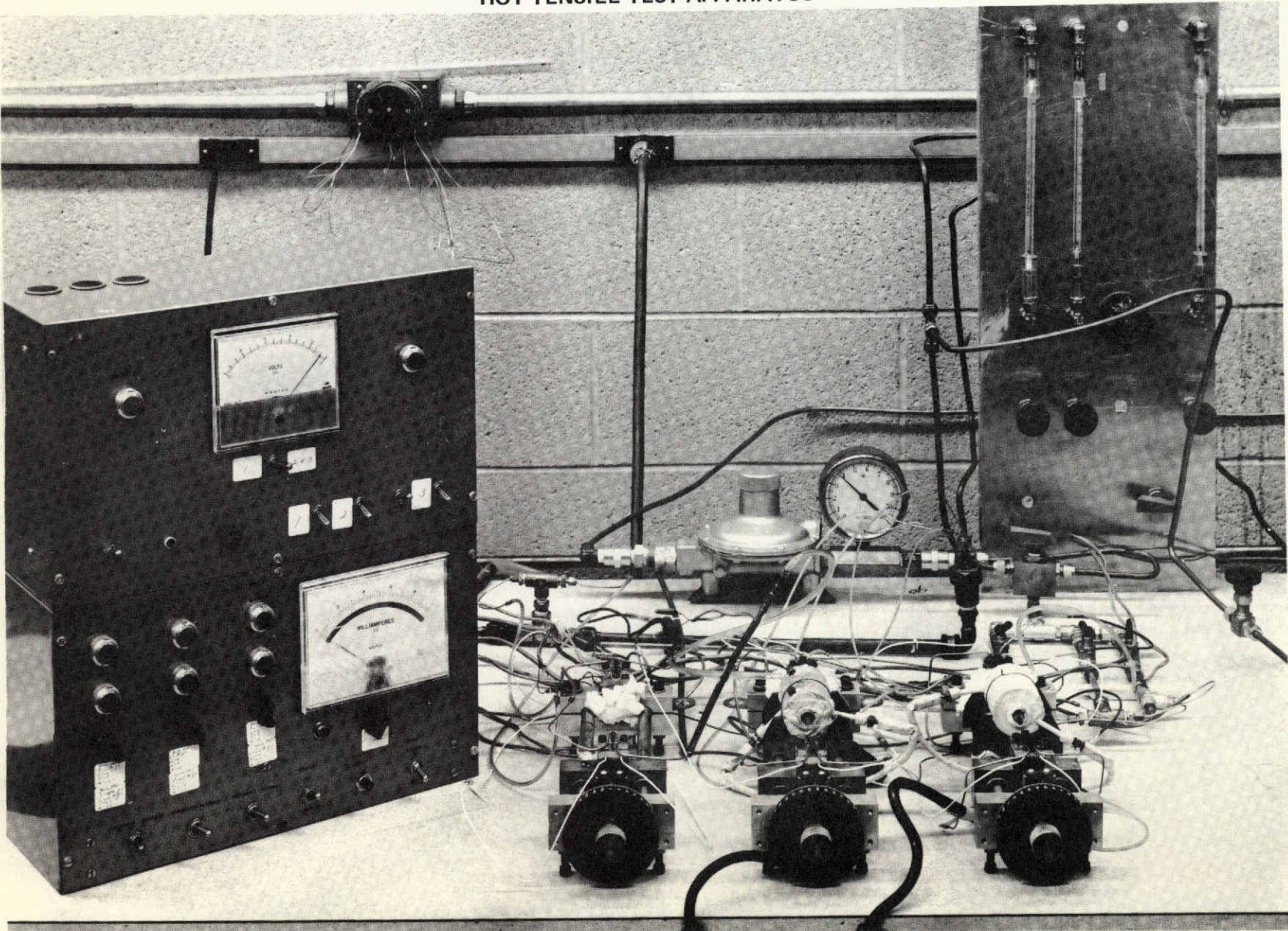
The thermal cycling and exposure tests were done in a vertical Kanthal wound tube furnace. A cinch and drum assembly was used to raise and lower a closed end quartz tube within the cylindrical furnace. Each coated and uncoated fiber exposed to high temperature was encapsulated in quartz tubes. The fiber was placed in a small diameter quartz tube and evacuated. Clean argon was backfilled into the tube and then evacuated again and sealed at the end to maintain the vacuum. All thermally treated fibers, overcoats, and diffusion couples were thus exposed only to vacuum at the elevated temperatures.

TABLE I

DEPOSITION RATES IN CYLINDRICAL CATHODE

<u>Material</u>	<u>Rate</u> <u>Å/Min</u>	<u>Sputtering</u> <u>Atmosphere</u>	<u>Power</u> <u>Watts/cm²</u>
Al ₂ O ₃	128	Argon	2.37
HfO ₂	90	Argon	1.58
HfO ₂	65	50% Argon 50% O ₂	1.58
HfO ₂	20	O ₂	1.58
Y ₂ O ₃	30	Argon	1.58
Y ₂ O ₃	20	80% Argon 20% O ₂	1.58
TiC	250	Argon	1.58
IN600 Ni	1500	Argon	3.16

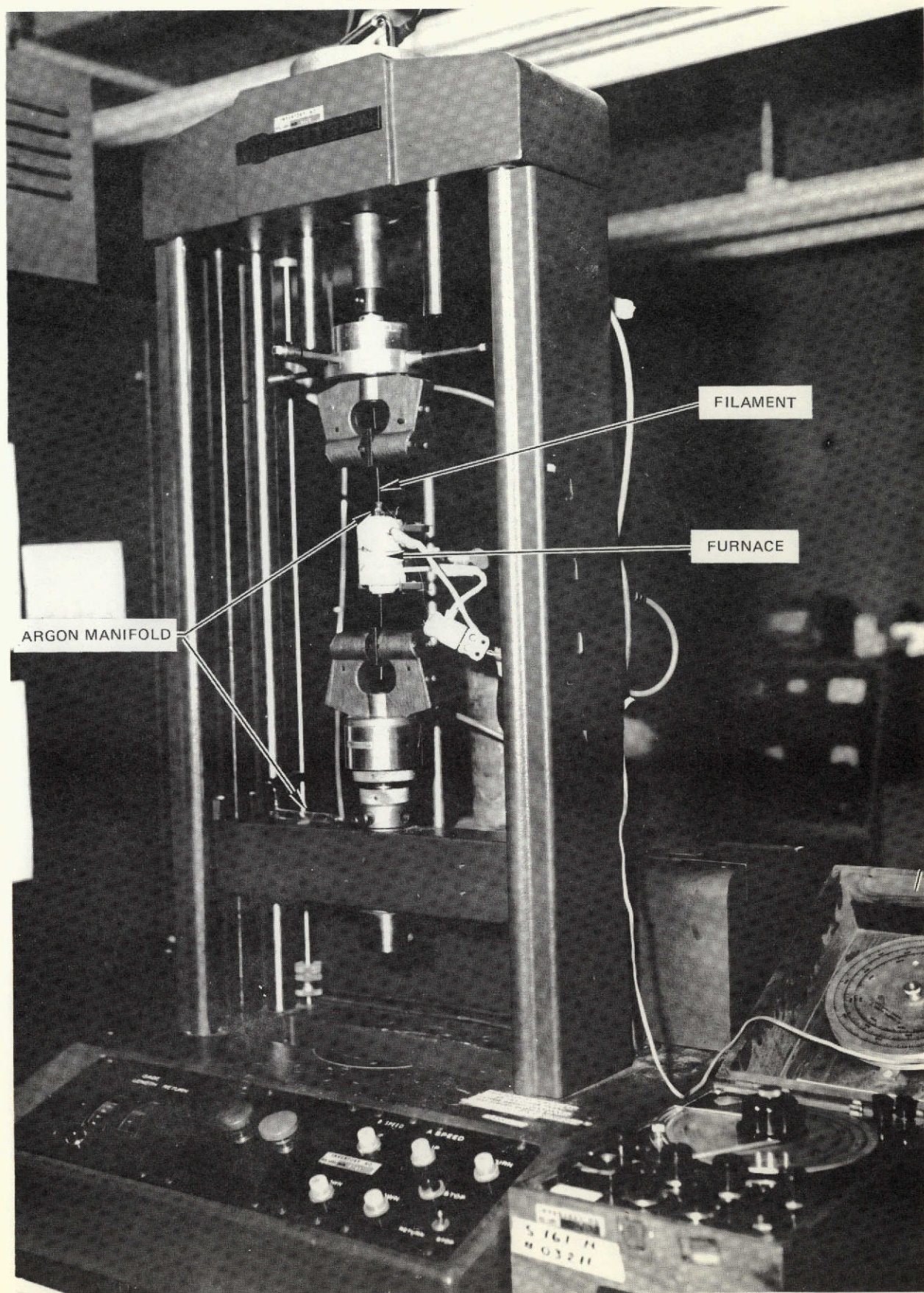
HOT TENSILE TEST APPARATUS



RL-73-351-A

FIG. 3

HOT TENSILE TESTING APPARATUS



RESULTS

Ion Plating Fiber Experiments

Ion Plating Fibers

The aluminum oxide diffusion barriers were ion plated onto the five mil tungsten substrate using previously obtained parameters. The parameters used for hafnium oxide, yttrium oxide, and titanium carbide are listed in Table II.

When the hafnium oxide target was used, the coated fibers of run 8 had a grayish tinge and the inside of the hafnium oxide target was noticeably darker than before the ion plating process. Previous ion plating experience with zirconium oxide at reduced pressures had shown that zirconium oxide goes slightly off stoichiometry and turns gray. When heated in the presence of oxygen the gray zirconia again takes on its characteristic yellow color. It was therefore felt that possibly the hafnium oxide target was behaving in a similar manner. Experimental runs 11, 13, and 14 were then made in which the amount of oxygen present in the ion plating chamber was varied to 20, 50 and 100% of the total reduced pressure atmosphere present during the ion plating process.

The yttrium oxide target behaved in a similar manner in that a slight discoloration of the target was noted after operation in 100% argon. Coatings were then also made with various amounts of oxygen mixed with the argon. The partial pressure of oxygen resulted in smoother coatings. These parameters are also listed in Table II.

The titanium carbide parameters listed in Table II are similar to those previously described except that no oxygen was used in the plating atmosphere and the time of plating was noticeably shorter due to the almost metallic conductivity of the target.

Ion Plating Diffusion Couples

The nickel alloy overcoat that was used in this program was IN600. The target was machined from a forged bar to the same cylindrical dimensions that were described for the oxide targets. In Table III are listed the runs used to obtain a (25-50) micron thick overcoat onto the fibers that had previously been coated with a barrier layer.

Mechanical Properties Due to Ion Plating

Effects of Ion Plating on 25°C Tensile Properties of Tungsten Fiber Substrate

A benefit of the ion plating process as a method of coating substrates is that the thermal exposure experienced by the substrate is relatively cool compared

TABLE II

ION PLATING EXPERIMENTAL RUNS

<u>Run Number</u>	<u>Power Watts</u>	<u>Bias</u>	<u>Substrate</u>	<u>Hafnium Oxide</u>		
				<u>Time Minutes</u>	<u>Pressure Microns</u>	<u>% Atmosphere O₂</u>
8	1000	550	W	240	15	0
11	1000	550	W	240	15	20
13	1000	550	W	240	15	50
14	1000	550	W	360	15	100
<u>Yttrium Oxide</u>						
16	1000		Rate Determination	422	15	0
17	1000	550	W	800	15	0
18	1000		Rate Determination	453	15	20
19	1000	550	W	1015	15	20
20	1000	550	W	1015	15	20
<u>Titanium Carbide</u>						
24	1000	550	Rate Determination	60	15	0
25	1000	550	W	100	15	0
26	1000	550	W	100	15	0
27	1000	550	W	100	15	0
28	1000	550	W	100	15	0

TABLE III

NICKEL ION PLATING RUNS

<u>Run Number</u>	<u>Power Watts</u>	<u>Substrate</u>	<u>Time Minutes</u>
32	2000	4 W 2 W/HfO ₂ 2 W/TiC 2 W/Y ₂ O ₃ 2 W/Al ₂ O ₃	392
33	2000	10 W/TiC 2 SiC	392
34	2000	4 W/HfO ₂ 3 W/Al ₂ O ₃	392
35	1000	10 W/Y ₂ O ₃	392
36	2000-1000	12 W/HfO ₂	380

All runs were made with the same bias and in 15 microns of argon

to temperatures required for chemical vapor deposition (see Fig. A-4). To assure that no degradation of the basic tungsten fiber had occurred due to the application of the various diffusion barriers, uniaxial tensile tests were made at room temperature to compare the as received tensile strength of the tungsten to that of the coated fibers. The results of these tests are listed in Table IV.

The ion plating of aluminum oxide appeared to be the only coating that had a deleterious effect upon the strength of the base tungsten fiber.

Effects of Ion Plating on the 1093°C Tensile Strength of the Tungsten Fiber Substrate

To observe the effects of the ion plated diffusion barriers on the properties of the base tungsten fiber, each of the coatings combinations were tensile tested at 1093°C after a nine minute soak in an argon atmosphere. The results of these tests are listed in Table V.

After the testing of the hafnium oxide coated filaments of run 14 the testing furnace failed. Although the thermocouples in the new furnace indicated 1093°C the results of the base line uncoated tungsten fiber was 14% higher than that previously obtained. The testing of the yttrium and titanium carbide coated tungsten in this new furnace were also 14% higher but the information extracted from all these tests at 1093°C was the same. The ion plating process does not degrade the elevated temperature strength of the base tungsten fiber up to 1093°C. It also appears that even the coatings ion plated in the presence of a partial pressure of oxygen yielded similar test results at 1093°C.

In Figures 5, 6, and 7 are shown scanning electron photomicrographs of the fracture zones of the hafnium oxide coated fibers broken at room temperature and 1093°C. An uncoated tungsten fiber was heated in air to 1093°C as shown in Fig. 8.

In Figure 9 are shown the scanning electron photomicrographs of the fracture surfaces of yttrium oxide coated tungsten broken at room temperature and 1093°C in argon. These same pieces were then moved slightly in the field of the SEM to observe the behavior of the yttrium oxide coating in the fracture zone. This view for the two fibers is shown in Fig. 10. The coating appears to be separating from the base tungsten fiber in the tensile break zone. This could be due to either a lack of good adhesion or just too thick a coating for this particular fiber combination.

In Figure 11 are shown the room temperature and 1093°C fracture areas of the titanium carbide coated tungsten fibers. The 1093°C fracture in this figure shows

TABLE IV

ROOM TEMPERATURE TENSILE TESTS OF COATED FIBER

<u>Run Number</u>	<u>Sample</u>	<u>UTS</u> <u>(KN/CM²)</u>	<u>Average UTS</u> <u>(KN/CM²)</u>
	W	289 289 289 289 289	289
5	W/Al ₂ O ₃	244 291 200 219	238
8	W/HfO ₂	291 289 289 291	290
11	W/HfO ₂ (20% O ₂)	276 285 292 295	287
13	W/HfO ₂ (50% O ₂)	295 293 293 292	294
14	W/HfO ₂ (100% O ₂)	293 292 294 293	293
17	W/Y ₂ O ₃	287 287 289 287 288	288
25	W/TiC	291 289 291 289 287	290

TABLE V

TENSILE TESTS AT 1093°C OF COATED FIBERS

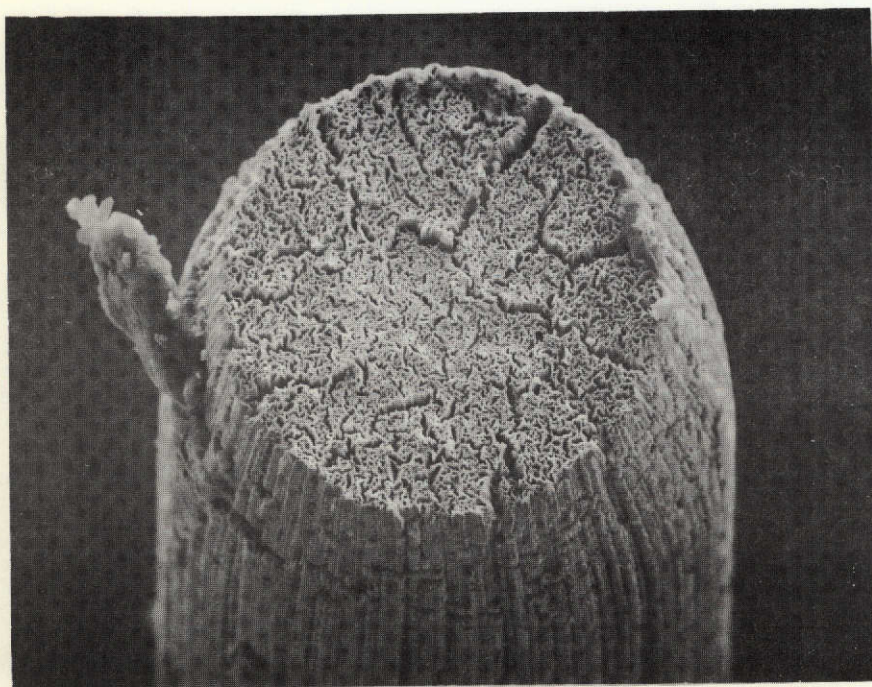
<u>Run Number</u>	<u>Sample</u>	UTS (KN/CM ²)	Average UTS (KN/CM ²)
	W	83 86	84
5	W/Al ₂ O ₃	83 90 91 92 83	88
8	W/HfO ₂	83 85 81 81 88	84
11	W/HfO ₂ (20% O ₂)	86 84 88 96 82	87
13	W/HfO ₂ (50% O ₂)	83 85 86 85 86	85
14	W/HfO ₂ (100% O ₂)	90 86 87 86 90	88
	W	102 100 99	100

TABLE V (Cont'd)

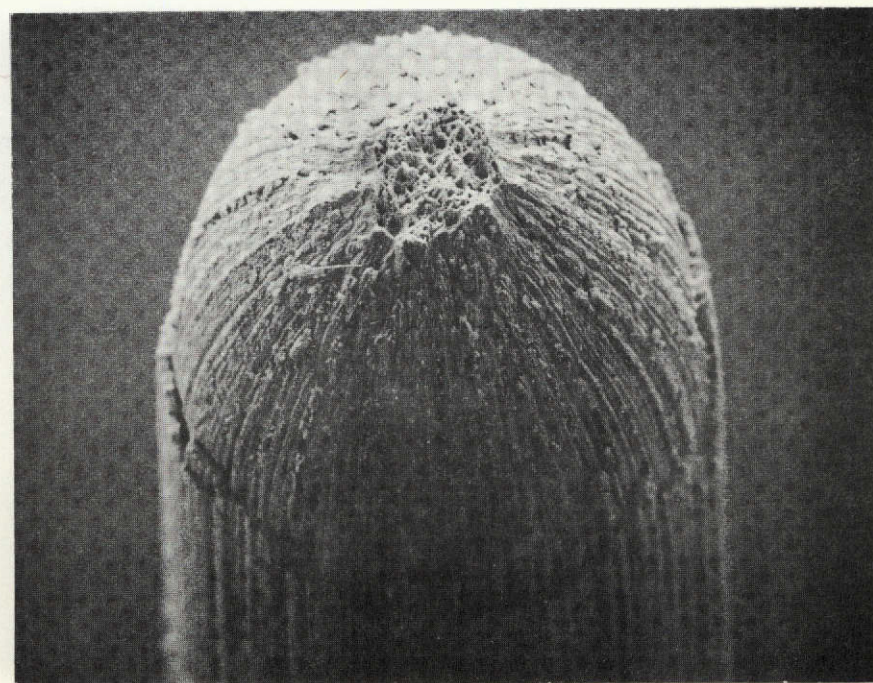
<u>Run Number</u>	<u>Sample</u>	<u>UTS</u> <u>(KN/CM²)</u>	<u>Average UTS</u> <u>(KN/CM²)</u>
17	W/Y ₂ O ₃	95	98
		95	
		96	
		100	
		102	
25	W/TiC	102	99
		99	
		96	
		100	
		96	

SEM OF FRACTURE ZONE TUNGSTEN/HAFNIUM OXIDE

RUN 8



ROOM TEMPERATURE

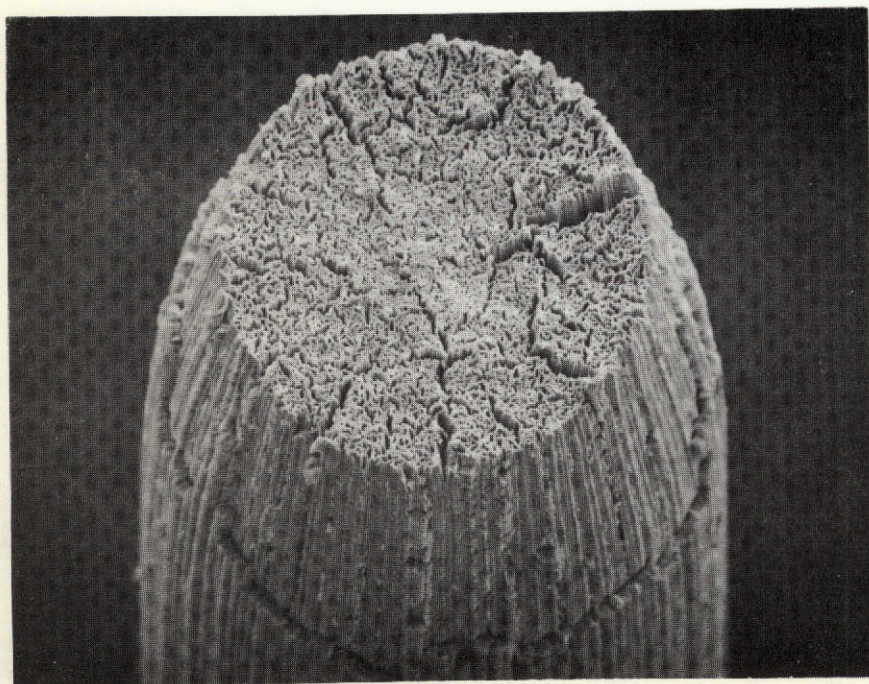


1093°C

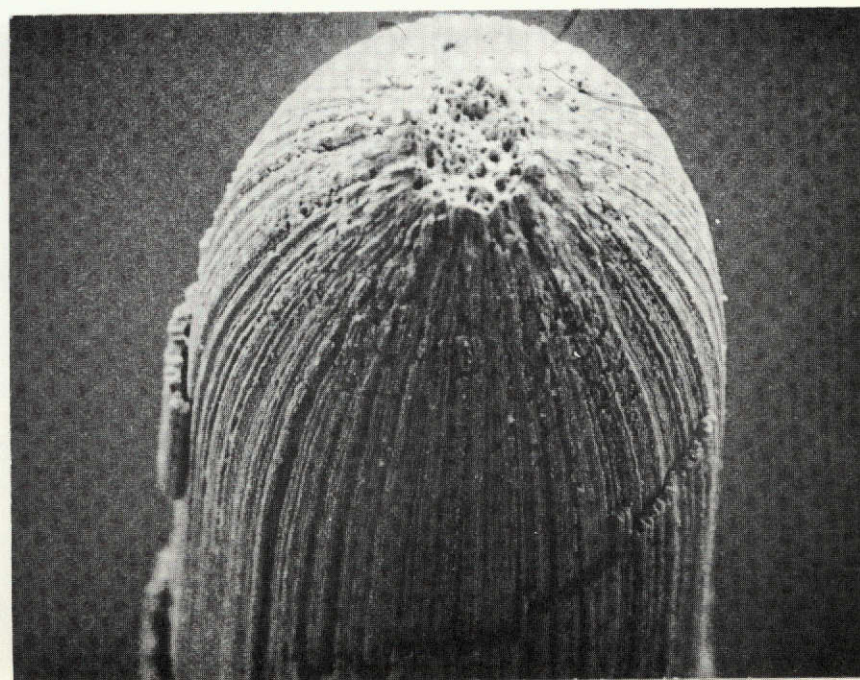
SEM OF FRACTURE ZONE TUNGSTEN/HAFNIUM OXIDE

(20% O₂)

RUN 11



ROOM TEMPERATURE

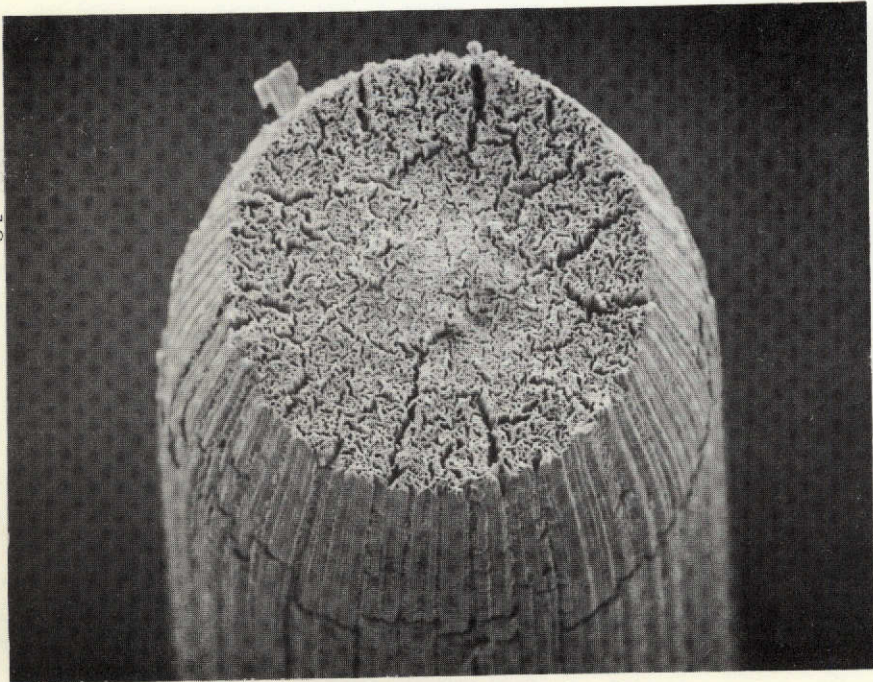


1093°C

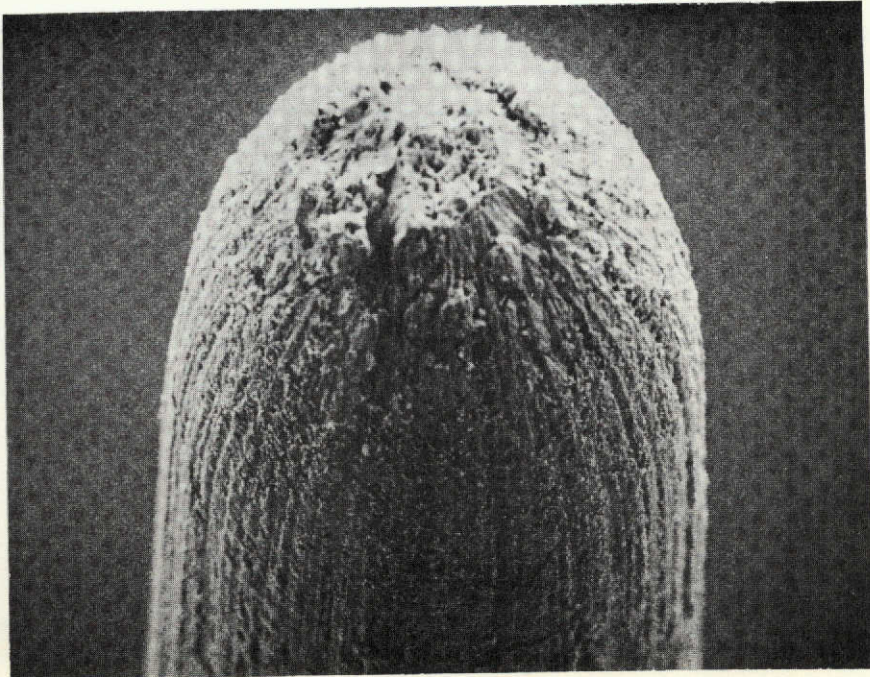
SEM OF FRACTURE ZONE TUNGSTEN/HAFNIUM OXIDE

(100% O₂)

RUN 14



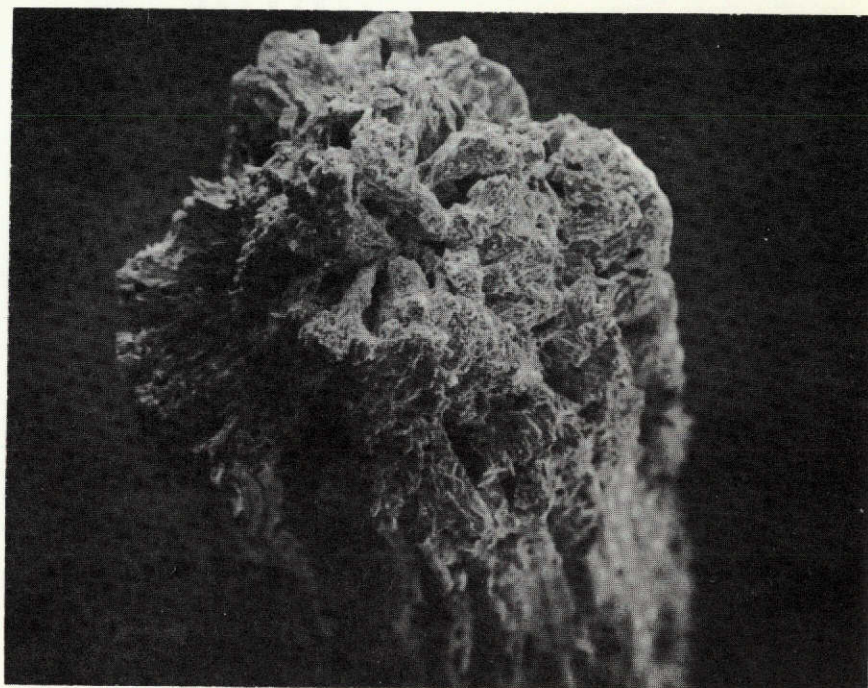
ROOM TEMPERATURE



1093°C

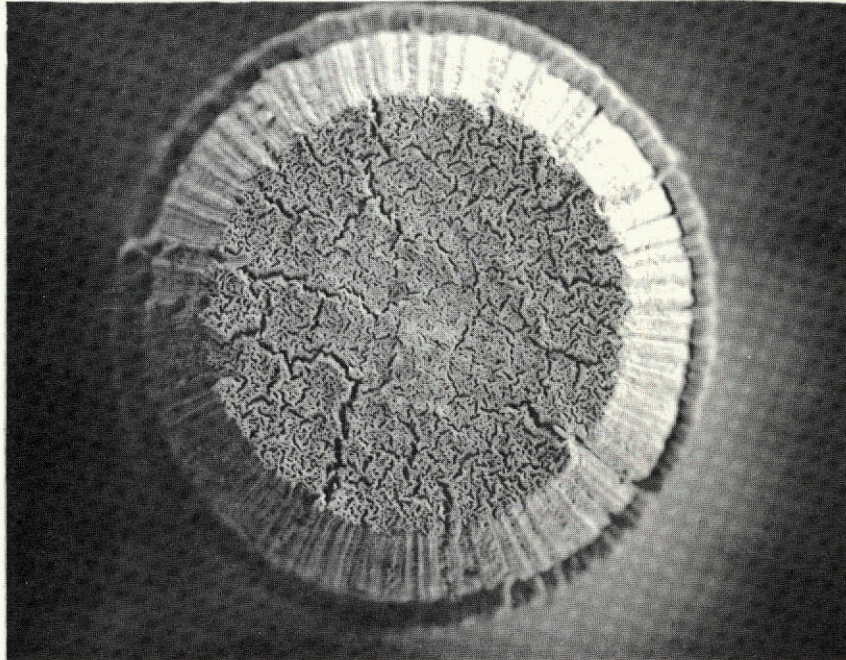
19

SEM OF FRACTURE ZONE TUNGSTEN UNCOATED IN AIR



1093°C

SEM VIEW OF FRACTURE ZONE TUNGSTEN/YTTRIUM OXIDE



ROOM TEMPERATURE

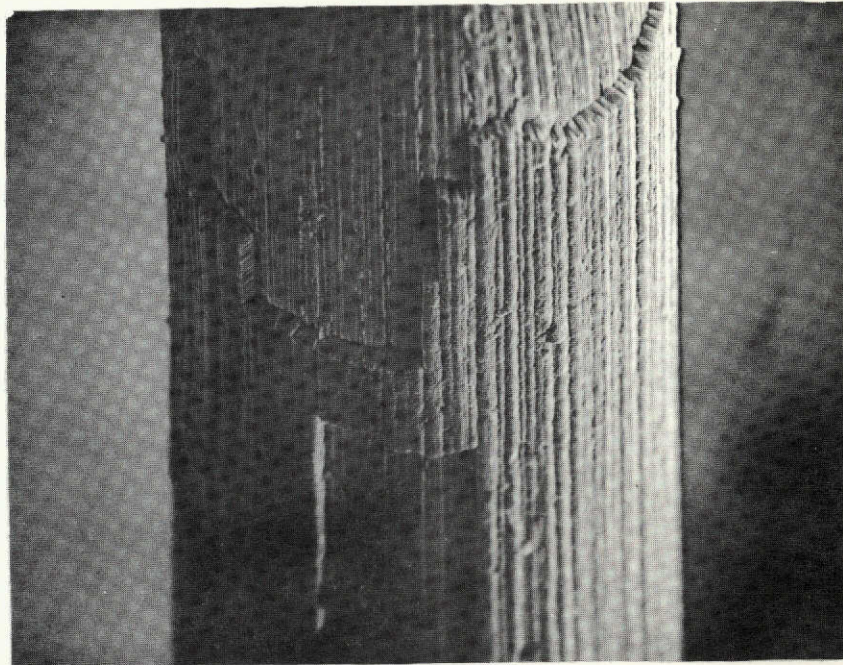
20 μ



1093 $^{\circ}$ C

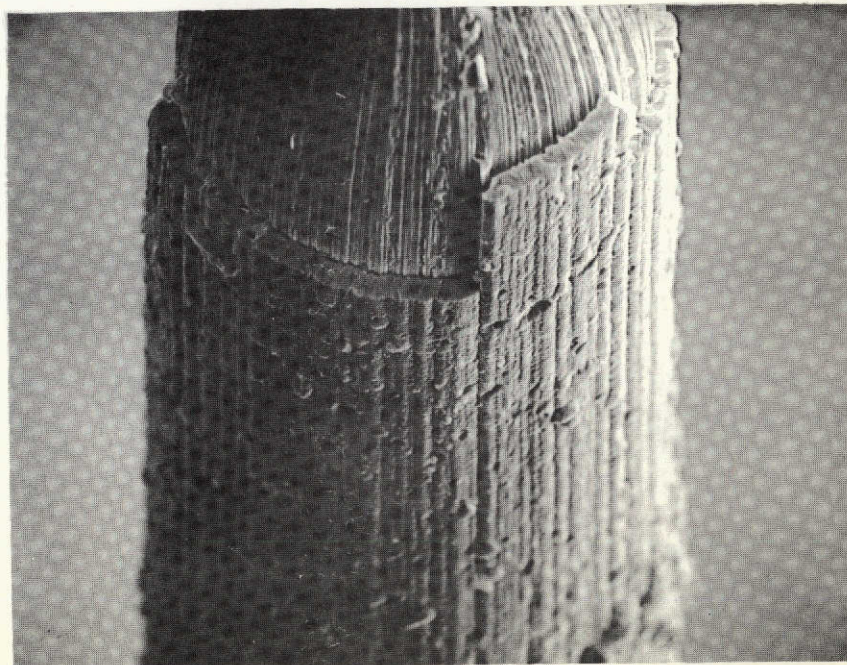
20 μ

SEM VIEW OF SURFACE TUNGSTEN/YTTRIUM OXIDE



ROOM TEMPERATURE

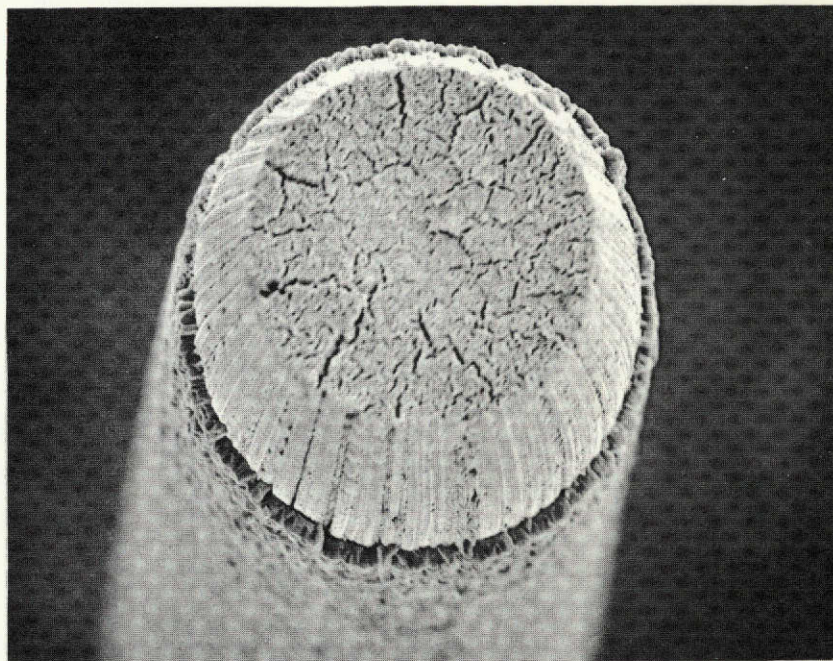
20 μ



1093 $^{\circ}$ C

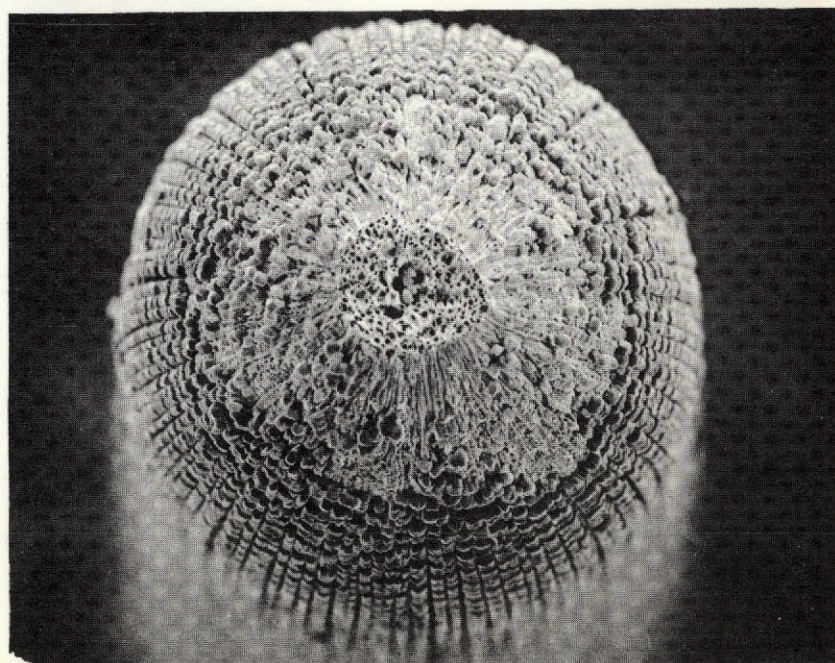
20 μ

SEM VIEW OF FRACTURE ZONE TUNGSTEN/TITANIUM CARBIDE



ROOM TEMPERATURE

20 μ



1093°C

20 μ

the titanium carbide coating yielding with the base tungsten fiber. In Fig. 12 are shown the surfaces of these coatings away from the fracture. The titanium carbide coating appears to be broken into tiny islands adhering to the tungsten surface. It is not certain whether this is the result of thermal exposure or the presence of many minicracks in the coating. In either case, it appears that a nickel overcoat would have a clear path toward the base filament.

Effects of the IN600 Overcoat

The IN600 nickel alloy was ion plated onto all the fiber coating combinations. A problem that did occur during the thermal exposure tests was the occasional lack of uniformity of the barrier coating. In Fig. 13 are shown two photomicrographs of nickel coated onto a tungsten-yttrium oxide filament. These two photographs were made from sections 7.5 cm apart on a 30 cm long filament. The fiber in Fig. 13(A) has the normal appearance of a filament at this stage of processing. It is not certain that the missing section of yttrium oxide seen in Fig. 13(B) was due to the mounting and polishing operation or lack of adherence of the ion plated yttrium oxide coating, or the handling required for the overcoat operation. Examination of these areas, after thermal exposure, thus proved difficult.

Barrier Evaluation

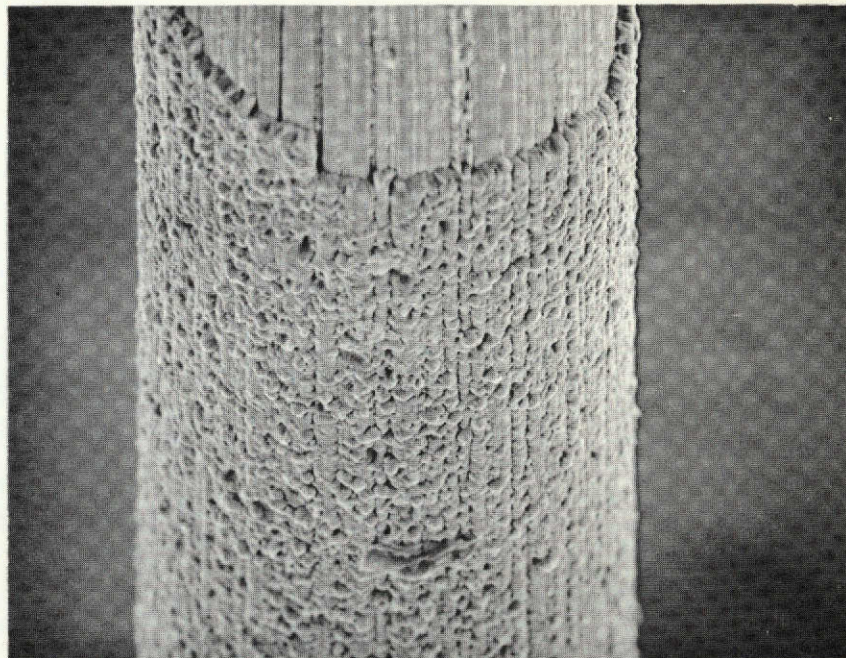
Recrystallization of Tungsten Fiber as Means of Determining Diffusion Protection

The five nickel overcoat combinations (tungsten/nickel, tungsten/aluminum oxide/nickel, tungsten/hafnium oxide/nickel, tungsten/titanium carbide/nickel, and tungsten/yttrium oxide/nickel) were encapsulated in quartz tubes and vacuum sealed. They were then each given a twenty-four hour soak at 1093°C. It was thought that the diffusion barrier would prevent recrystallization of the tungsten fiber core.

In Fig. 14 are shown the unprotected tungsten and a typical diffusion barrier filament. All the barrier coated tungsten filaments appeared similar to the unprotected tungsten fiber in that the fine grain of the base tungsten filament was unchanged after this twenty four hour exposure.

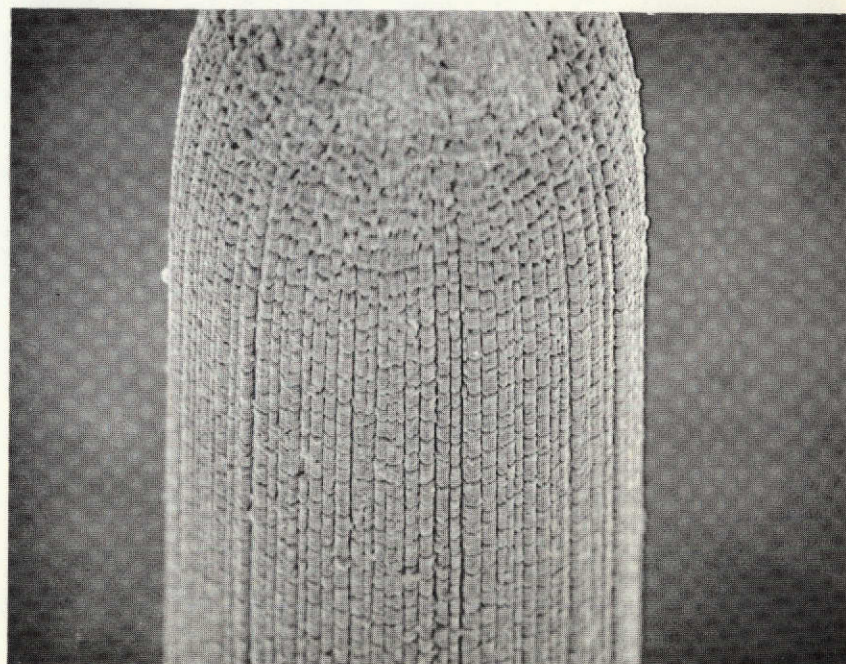
To determine the onset of damage to the base tungsten fiber in a nickel environment, the five nickel overcoated combinations were prepared and exposed for twenty four hours at 1270°C. In Fig. 15 are shown the unprotected tungsten and the titanium carbide barrier tungsten filaments. The unprotected tungsten has undergone a complete change and the advancing line of diffusion can be seen in the titanium carbide barrier protected filament. The remaining three candidate barriers are shown in Fig. 16. All three (aluminum oxide, hafnium oxide, and yttrium oxide) oxide barrier coatings appear to afford tungsten sufficient protection at 1270°C for twenty four hours when surrounded by nickel IN600 alloy.

SEM VIEW OF SURFACE TUNGSTEN/TITANIUM CARBIDE



ROOM TEMPERATURE

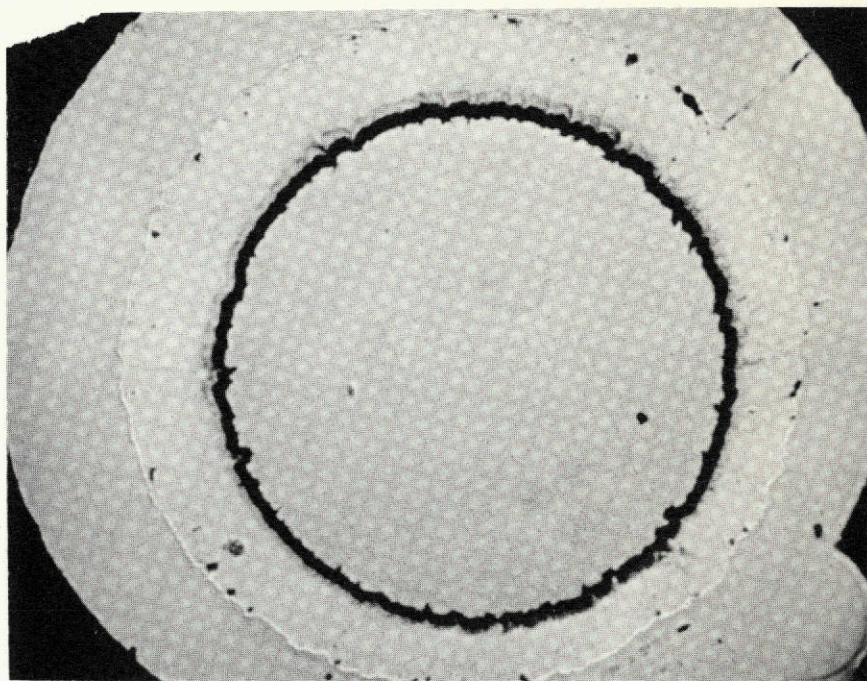
20 μ



1093 $^{\circ}$ C

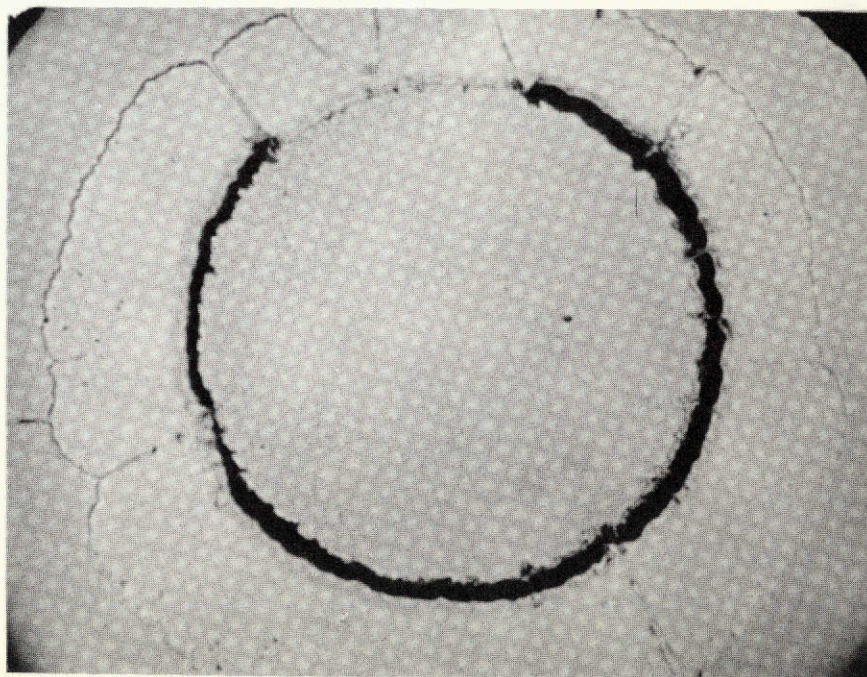
20 μ

TUNGSTEN/YTTRIUM OXIDE OVERCOATED WITH NICKEL



A

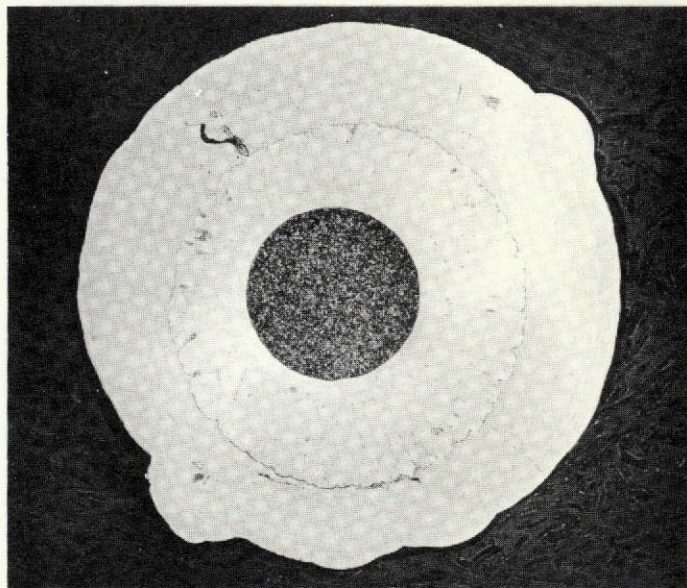
20μ



B

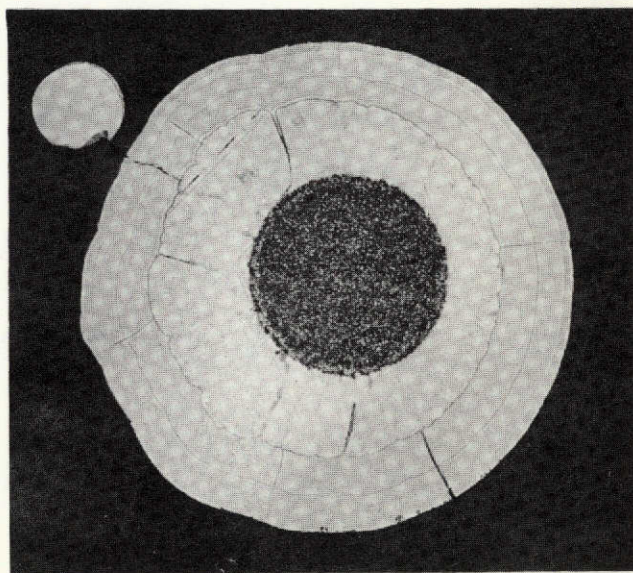
20μ

TWENTY-FOUR HOUR EXPOSURE AT 1093°C



TUNGSTEN/NICKEL

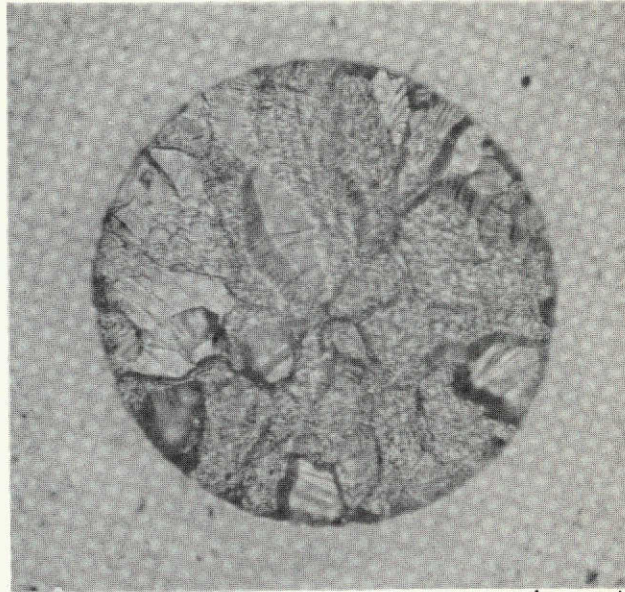
50μ



TUNGSTEN/HAFNIUM OXIDE/NICKEL

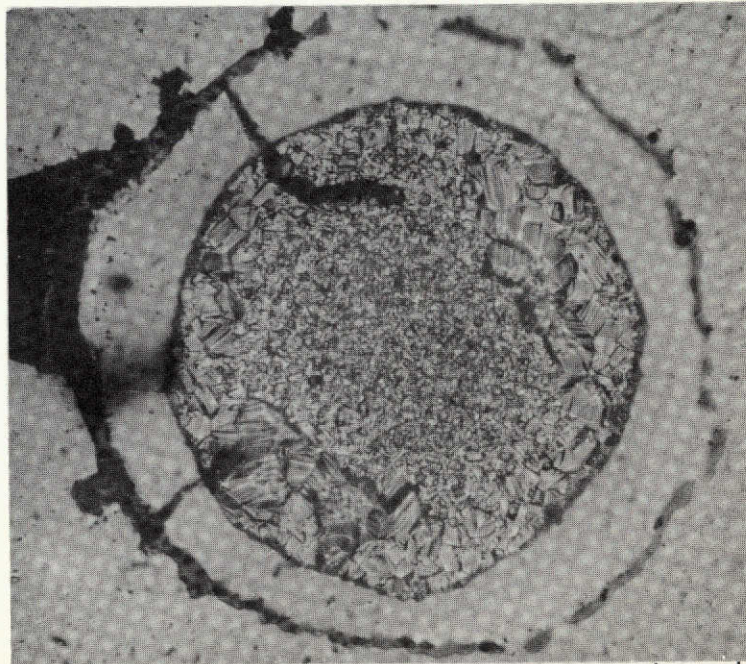
50μ

TWENTY-FOUR HOUR EXPOSURE AT 1270°C



TUNGSTEN/NICKEL

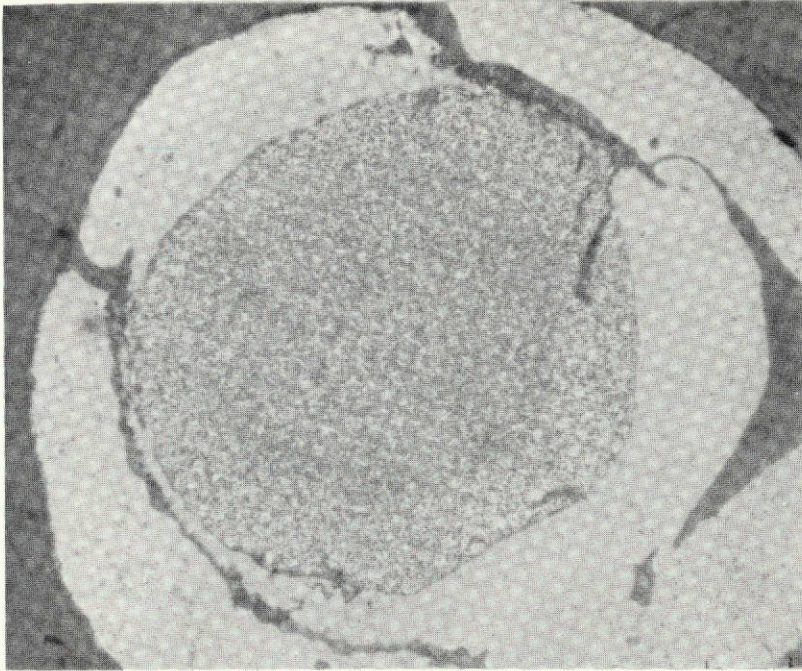
20 μ



TUNGSTEN/TITANIUM CARBIDE/NICKEL

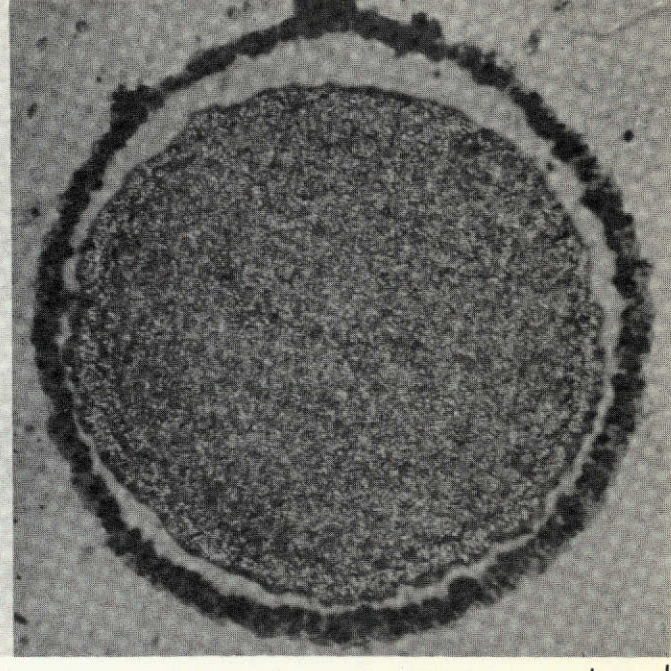
20 μ

TWENTY-FOUR HOUR EXPOSURE AT 1270°C



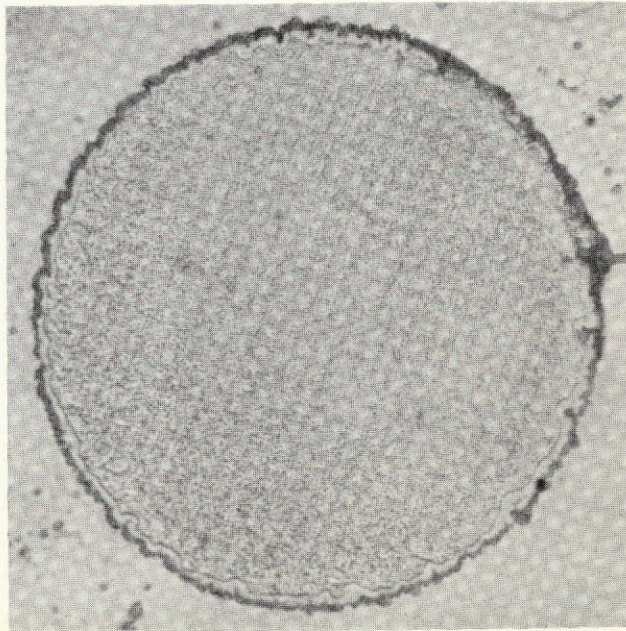
TUNGSTEN/YTTRIUM OXIDE/NICKEL

20μ



TUNGSTEN/HAFNIUM OXIDE/NICKEL

20μ



TUNGSTEN/ALUMINUM OXIDE/NICKEL

20μ

A confirmation of the protection afforded the base tungsten fiber from recrystallization by the ion plated diffusion barriers was received from the NASA program monitor. He took the same five combinations listed above and cast an iron alloy around them. He then exposed these diffusion couples to 1093°C for 90 hours. A photomicrograph of the cross section of an uncoated filament is shown in Fig. 17. In Fig. 18 are shown the titanium carbide coated tungsten and the aluminum oxide coated tungsten. The yttrium oxide coated tungsten and the hafnium oxide coated tungsten fibers are shown in Fig. 19. The protection from recrystallization (see Fig. 17) of the base tungsten fiber by the ion plated barrier coatings was the same as that obtained in the experiments done at UARL that were described above.

Tensile Strength as a Measure of Diffusion Protection

Ultimate tensile strength was then measured on the same filaments after the twenty four hour exposure at 1093°C. These strengths were measured at room temperature and the results are listed in Table VI. The only coating that seriously appeared to weaken the base fiber was titanium carbide. Photomicrographs of polished cross sections were similar to that of Fig. 14, in that no gross changes in microstructure were noted.

Thermal Cycling of Diffusion Couples

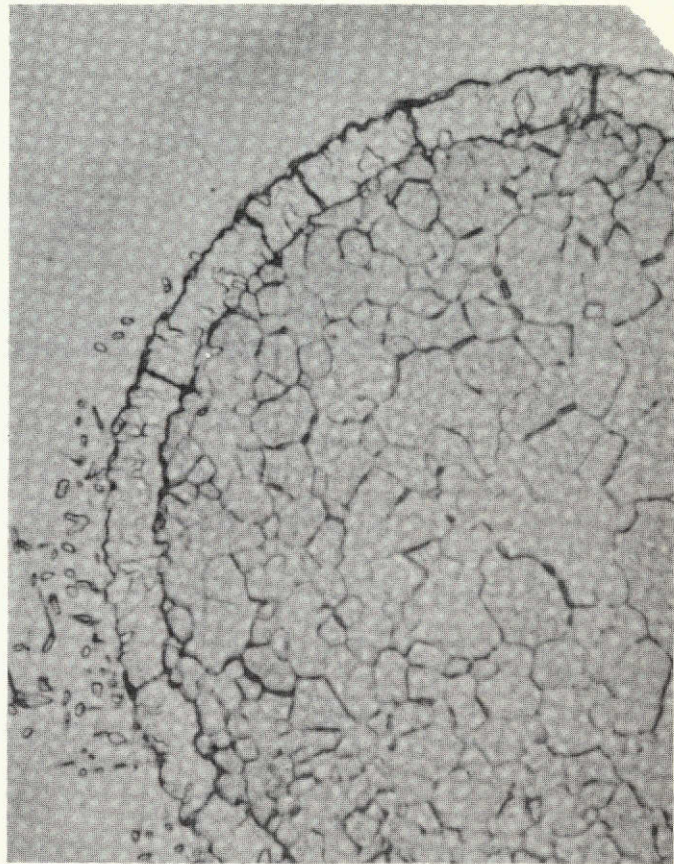
Thermal cycling between room temperature and 1093°C was done with the following four diffusion couples: tungsten-nickel, tungsten-aluminum oxide-nickel, tungsten-hafnium oxide (50% O₂)-nickel, and tungsten-hafnium oxide (100% O₂)-nickel. The elapsed time of a cycle was approximately 15 minutes, yielding 84 to 95 cycles during a twenty four hour period. In Fig. 20 are shown the cross-sections of the tungsten-nickel and tungsten-aluminum oxide-nickel diffusion couples. The two hafnium oxide diffusion couples are shown in Fig. 21. After this number of cycles, some of the filaments have developed kinks and areas where the nickel overcoat had spalled off. Testing of these filaments at room temperature proved difficult due to the handleability feature. Results indicated that the hafnium oxide (50% O₂) couples did retain more tensile strength than the aluminum oxide couples.

These same filaments were then examined in the Scanning Electron Microscope. In Fig. 22 are shown the tungsten-nickel and the tungsten-aluminum oxide-nickel couples. It is not certain whether the pullout of the tungsten was due to poor bonding or embrittlement of the tungsten structure itself that may cause the complete shattering away of the fiber at the moment of fracture. The SEM pictures of the two hafnium oxide barrier couples are shown in Fig. 23. The ion plated coatings in 50% oxygen atmosphere appear to have afforded the base tungsten more protection during the cycle tests.

Thermal Anneal of Diffusion Couples

The coating combinations of aluminum oxide and hafnium oxide were given a 1200°C thermal anneal for 100 hours. Tensile testing of both couples indicated

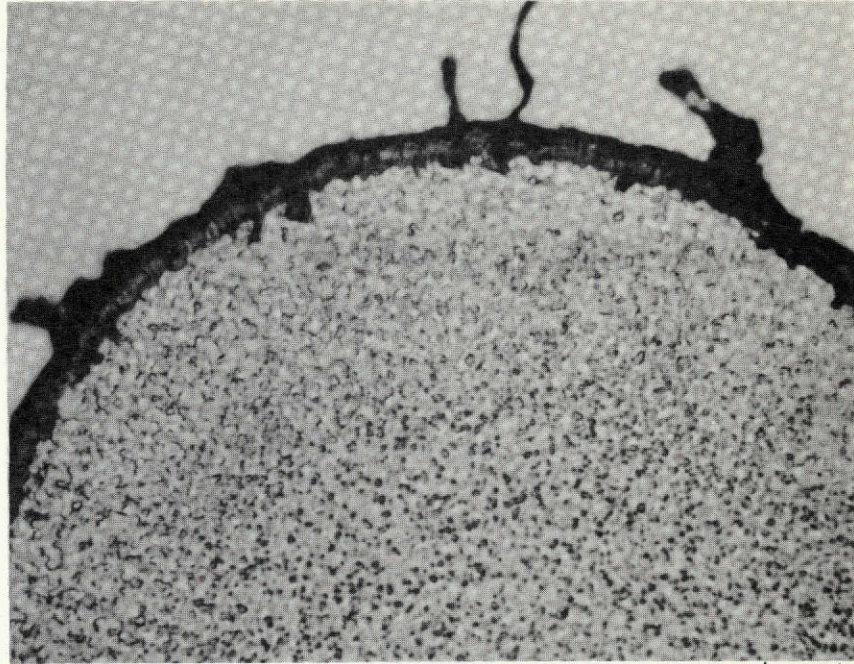
NINETY HOUR EXPOSURE AT 1093°C
IRON ALLOY



UNCOATED TUNGSTEN

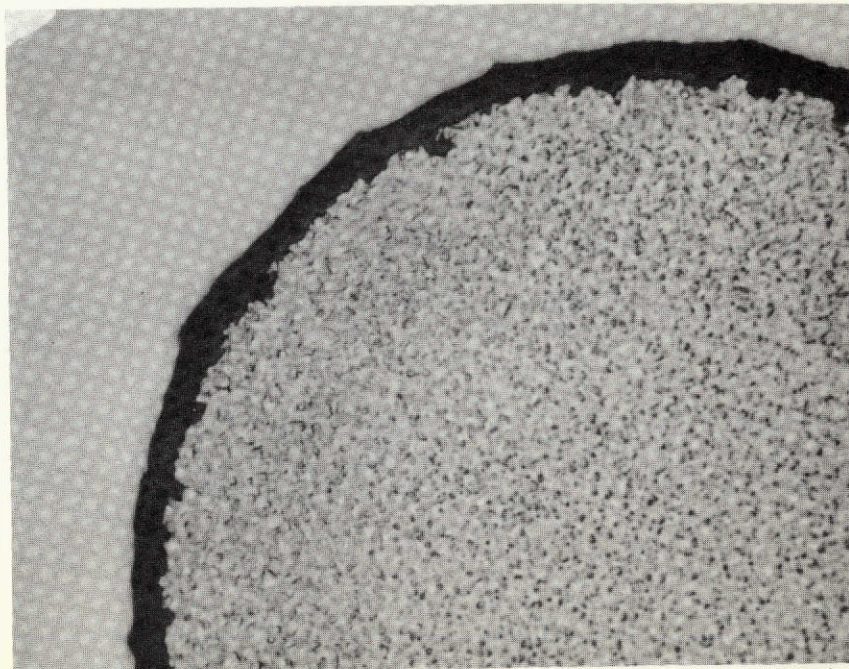
10μ

NINETY HOUR EXPOSURE AT 1093°C
IRON ALLOY



TITANIUM CARBIDE/TUNGSTEN

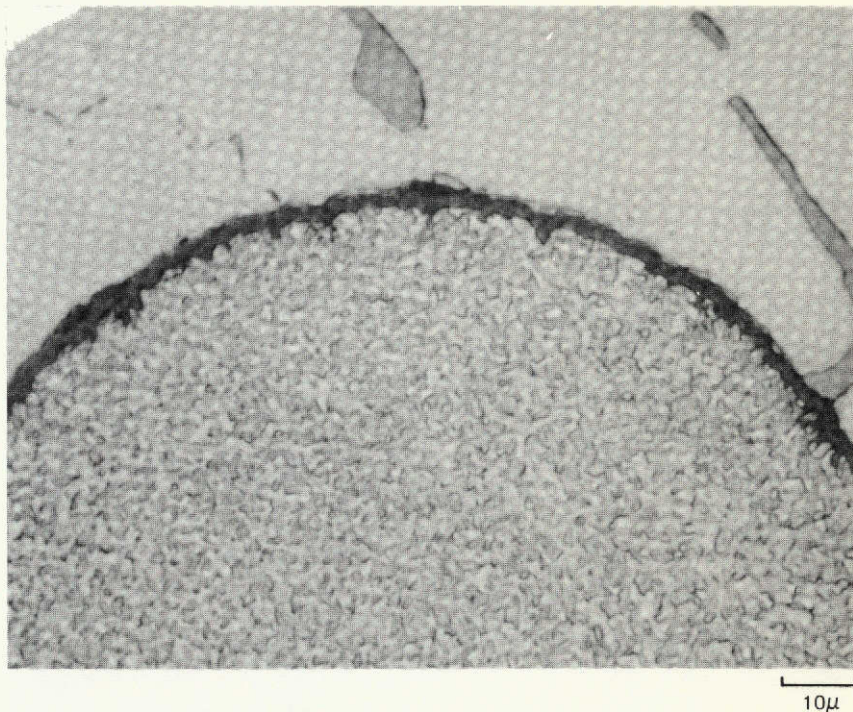
10μ



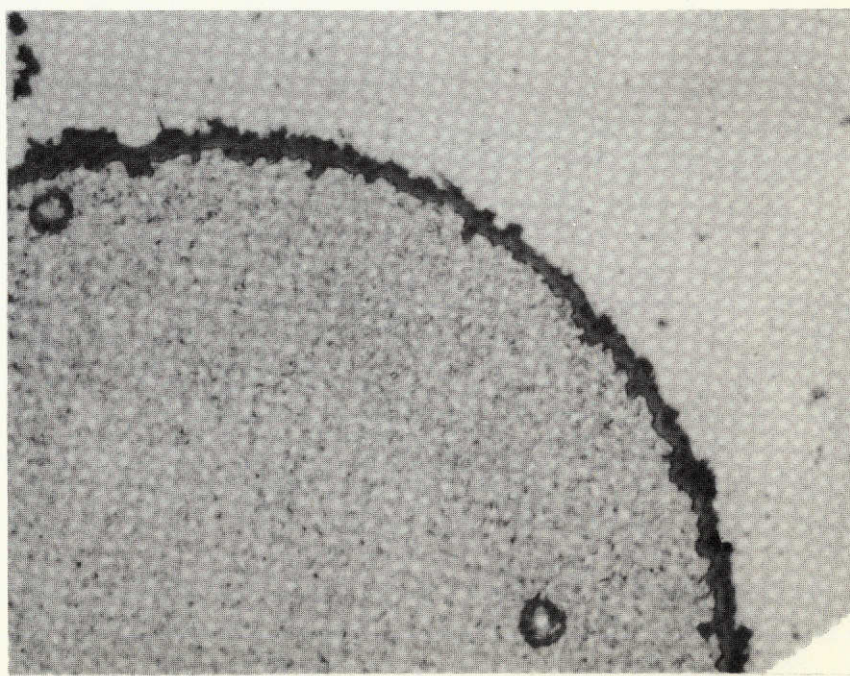
ALUMINIUM OXIDE/TUNGSTEN

10μ

NINETY HOUR EXPOSURE AT 1093°C
IRON ALLOY



YTTRIUM OXIDE/TUNGSTEN



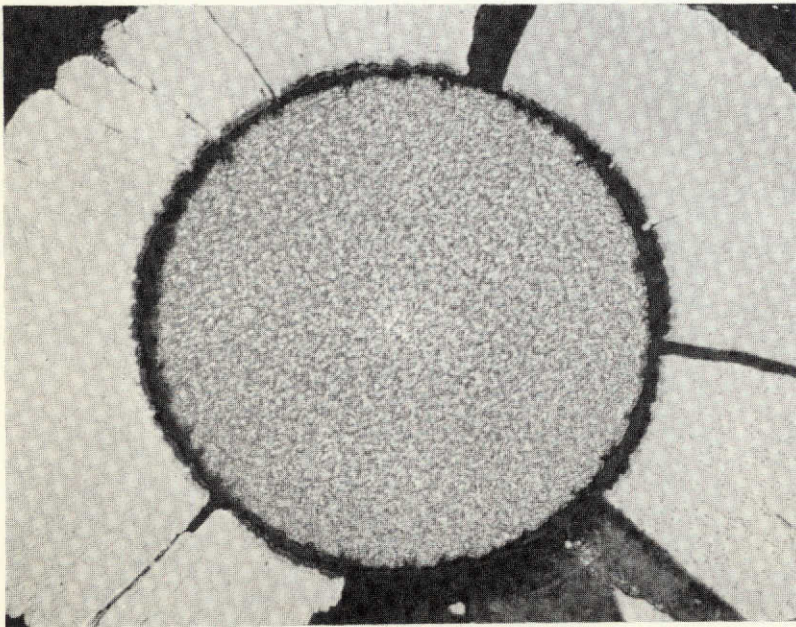
HAFNIUM OXIDE/TUNGSTEN

TABLE VI

ULTIMATE TENSILE STRENGTH AFTER 24 HOURS EXPOSURE AT 1093°C

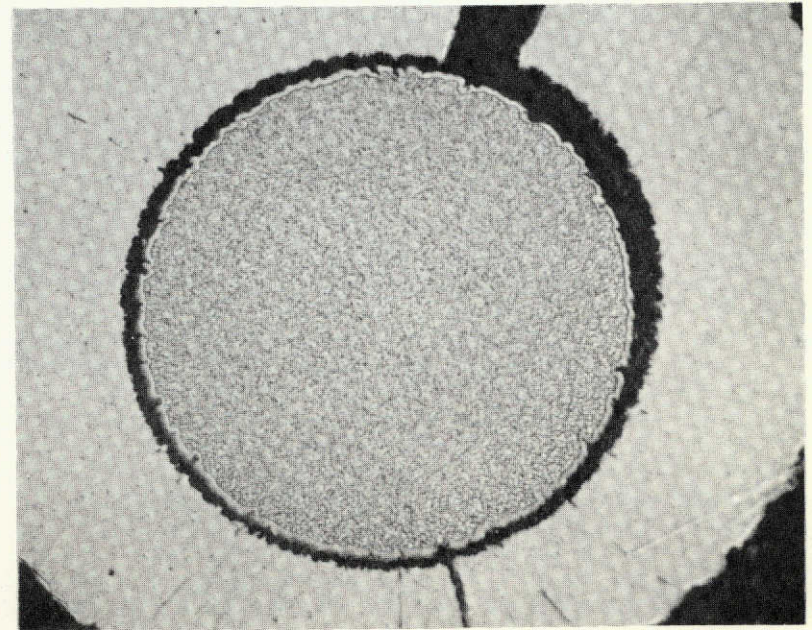
<u>Diffusion Couple</u>	<u>UTS KN/CM²</u>
W/Al ₂ O ₃ /Ni	116
	123
	112
	Average 115
W/Y ₂ O ₃ /Ni	116
	123
	112
	Average 115
W/HfO ₂ (50% O ₂)/Ni	45
	88
	285
	Average 139
W/TiC/Ni	60
	35
	Average 48

DIFFUSION COUPLES
TWENTY FOUR HOUR CYCLIC EXPOSURE



TUNGSTEN-NICKEL

20 μ

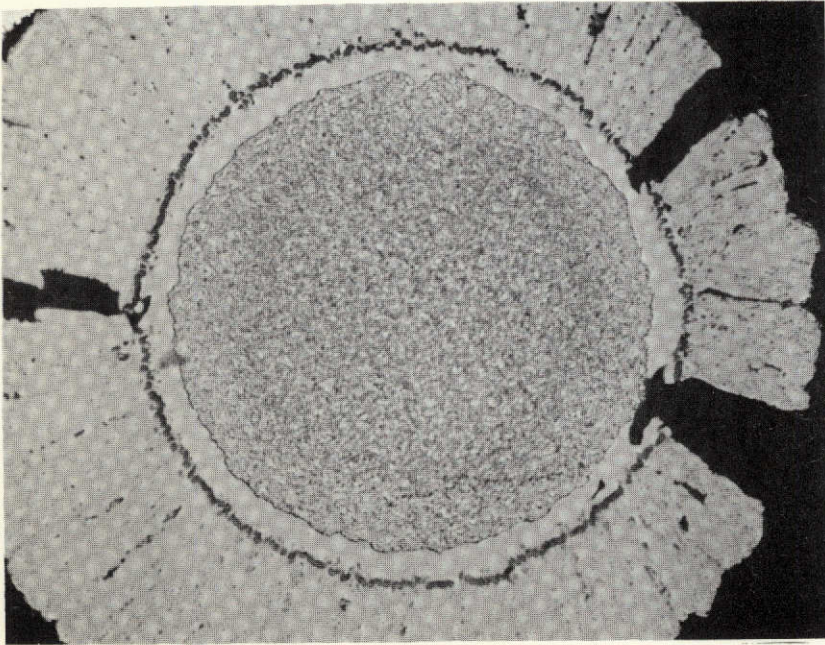


TUNGSTEN-ALUMINUM OXIDE-NICKEL

20 μ

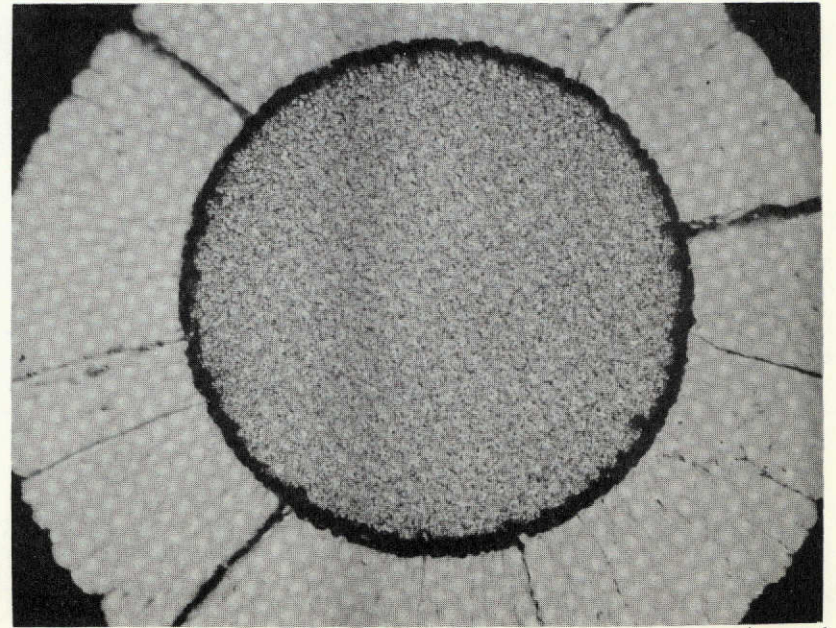
DIFFUSION COUPLES

TWENTY FOUR HOUR CYCLIC EXPOSURE 1093° C



TUNGSTEN-HAFNIUM OXIDE (100% O₂) - NICKEL

20μ

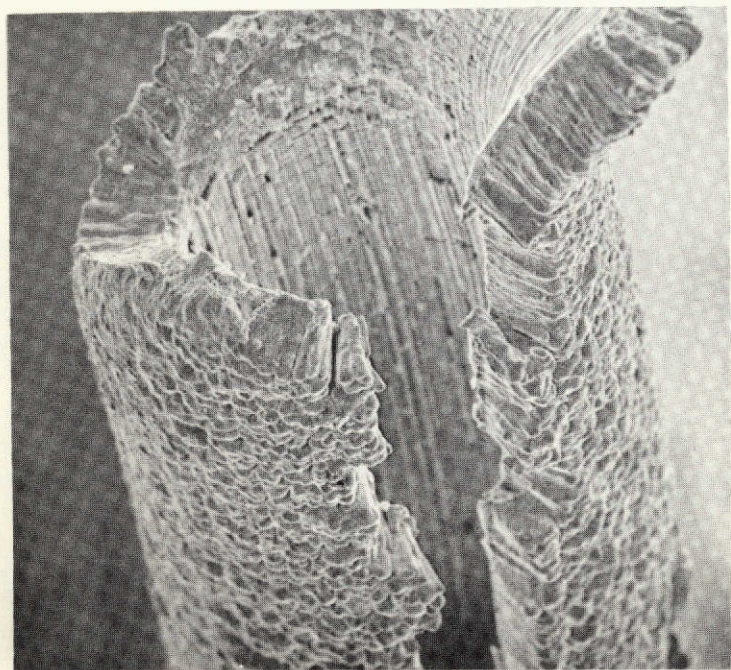


TUNGSTEN-HAFNIUM OXIDE (50% O₂) - NICKEL

20μ

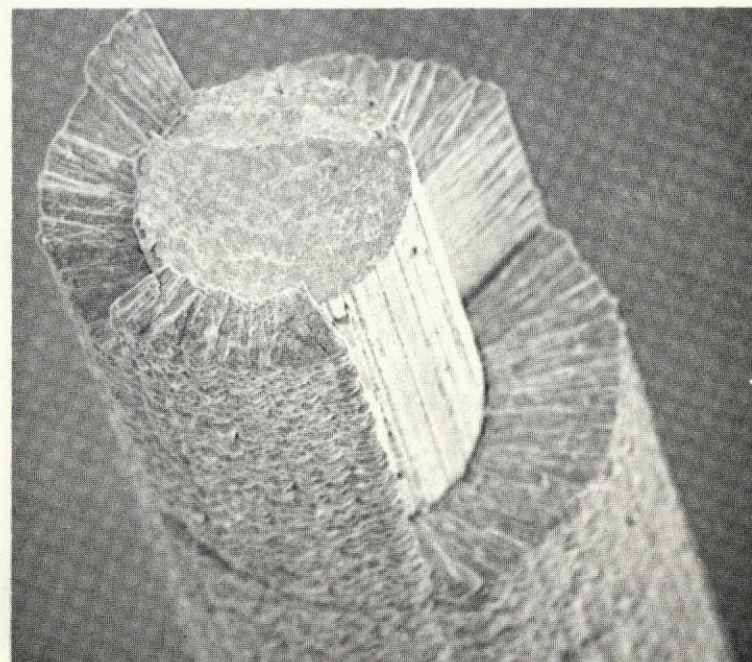
36

SEM OF DIFFUSION COUPLES
AFTER CYCLIC EXPOSURE AT 1093°C



TUNGSTEN- NICKEL

40 μ



TUNGSTEN-ALUMINUM OXIDE - NICKEL

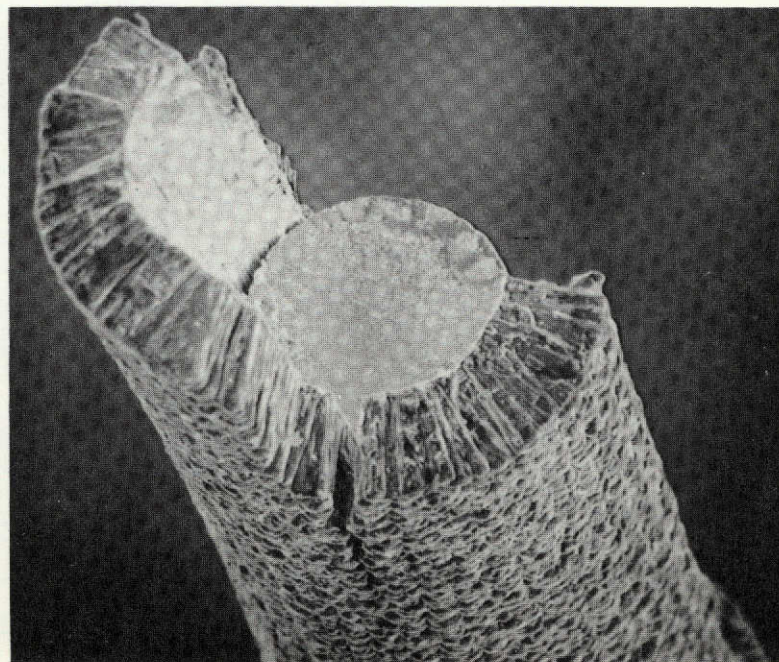
40 μ

SEM OF DIFFUSION COUPLES
AFTER CYCLIC EXPOSURE AT 1093°C



TUNGSTEN-HAFNIUM OXIDE (100% O₂) NICKEL

40 μ



TUNGSTEN-HAFNIUM OXIDE (50% O₂) NICKEL

40 μ

60% loss in tensile strength but were not conclusive enough due to the same handleability problem that was encountered after the cyclic tests. Metallographic examination was then used for determination of possible diffusion damage of the fiber substrate. These examinations included optical photomicrographs, SEM, electron beam probe and line scan analyses of the fiber interface region especially across the ion plated barrier. These will be discussed in the following subparagraphs.

Metallographic Examinations

Electron beam probe analysis of diffusion couples exposed to 1093°C for twenty-four hours

In Fig. 24 is shown the base unprotected tungsten fiber overcoated with the nickel alloy IN600 after the twenty-four hour exposure at 1093°C. In Fig. 25 is the electron scan of a quadrant of this same filament along with the X-ray scans for tungsten and the three major components (Ni, Fe, Cr) of the IN600 alloy. The IN600 components do not appear to have diffused into the tungsten fiber (see Fig. 25 (b,c,e)), but the tungsten from the core does appear to have started to move outward through the nickel alloy (see Fig. 25d).

In Fig. 26 is shown the photomicrograph of the tungsten-aluminum oxide-nickel diffusion couple after exposure for twenty-four hours at 1093°C. In Fig. 27 is the electron scan together with the X-ray scans of components in this diffusion couple. The aluminum oxide coating (Fig. 27c) has kept the tungsten from moving outward (Fig. 27e). The components of the IN600 alloy (Fig. 27 (b,d,f)) have not crossed the aluminum oxide barrier to penetrate the tungsten core.

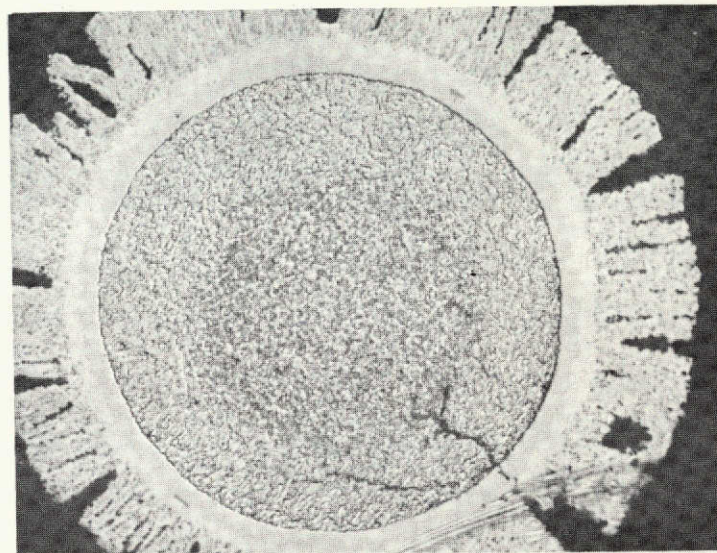
The tensile test results of the hafnium oxide barrier diffusion couple had yielded one low result. The photomicrograph of this weak couple is shown in Fig. 28. The scans for this diffusion couple are shown in Fig. 29. In Fig. 29e the tungsten has again moved outward from the core into the IN600 coating. The components of the IN600 alloy (Fig. 29 (b,d,f)) again appear not to have diffused significantly. The absence of the hafnium oxide layer (Fig. 29c) confirms the low tensile test result. In Fig. 30, is shown the photomicrograph of a tungsten-hafnium oxide-nickel diffusion couple whose tensile strength was what has come to be expected after this type of exposure. The scans for this diffusion couple are shown in Fig. 31. In Fig. 31 (b,d,f) the IN600 components again show no gross movement. The tungsten from the core (Fig. 31e) has not crossed the uniform hafnium oxide barrier (Fig. 31c) to enter the IN600 area.

Electron beam probe analysis of diffusion couples after twenty-four hour cycling between room temperature and 1093°C

The hafnium oxide barrier layer had been ion plated onto the tungsten fiber in two environments. These were 50% oxygen partial pressure in the plasma and 100% oxygen partial pressure in the ion plating plasma. Although in the 100% oxygen partial pressure ion plating was extremely slow, the thin layer deposited

TUNGSTEN/NICKEL DIFFUSION COUPLE

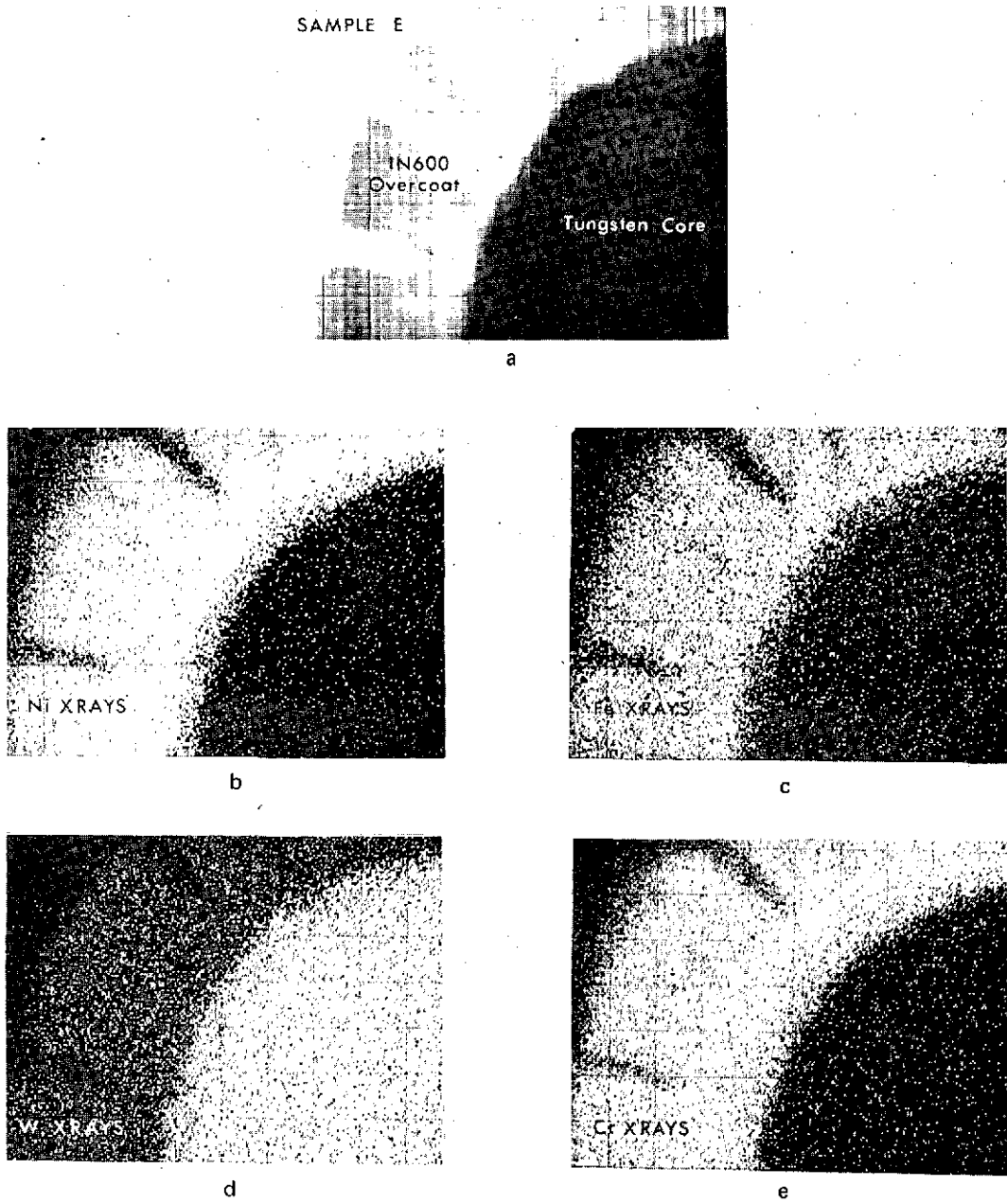
AFTER 24 HOUR EXPOSURE AT 1093°C



SAMPLE E

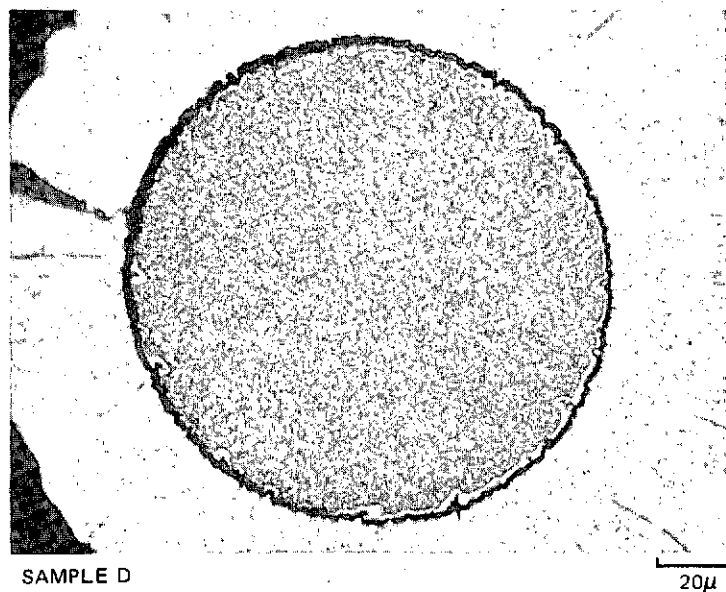
20μ

ELECTRON AND X-RAY SCANS OF W/Ni DIFFUSION COUPLE

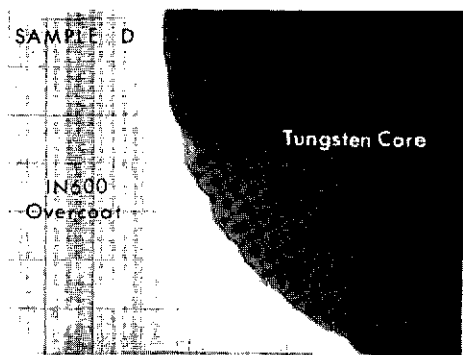


TUNGSTEN/ALUMINUM OXIDE/NICKEL DIFFUSION COUPLE

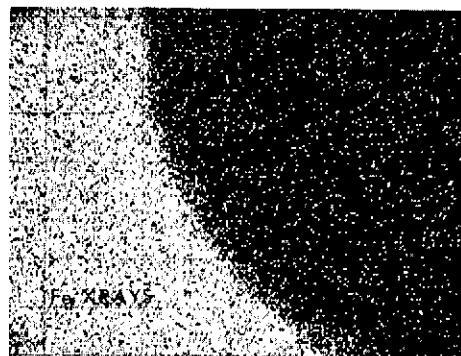
AFTER 24 HOUR EXPOSURE AT 1093°C



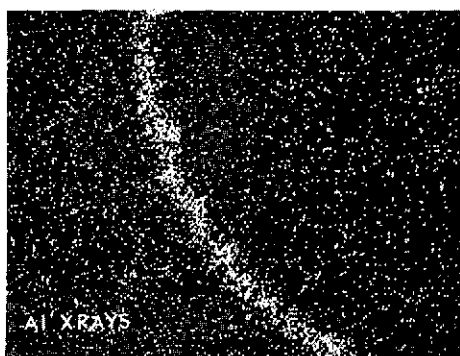
ELECTRON AND X-RAY SCANS OF W/Al₂O₃/Ni DIFFUSION COUPLE



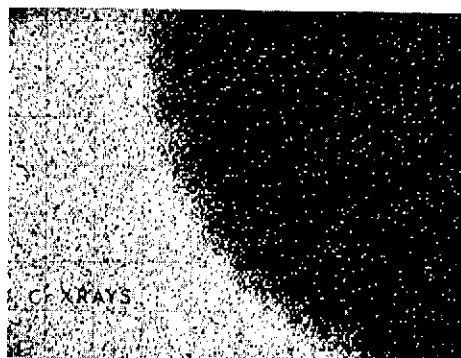
a



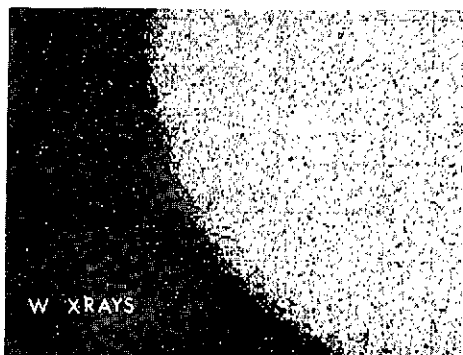
b



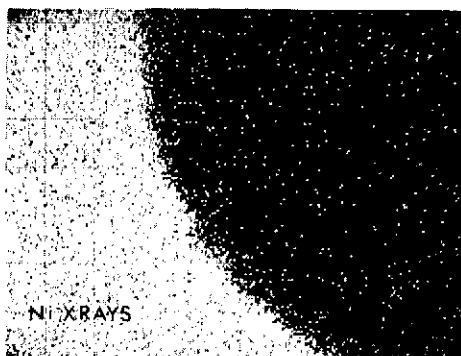
c



d



e

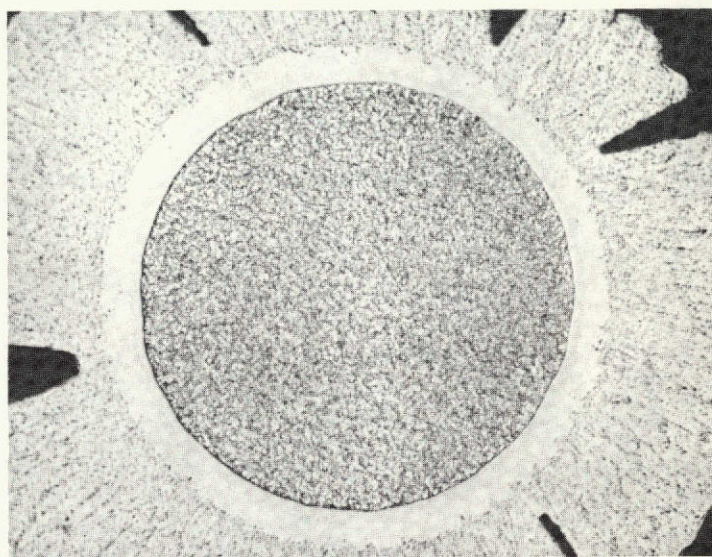


f

TUNGSTEN/HAFNIUM OXIDE/NICKEL DIFFUSION COUPLE

AFTER 24 HOUR EXPOSURE AT 1093°C

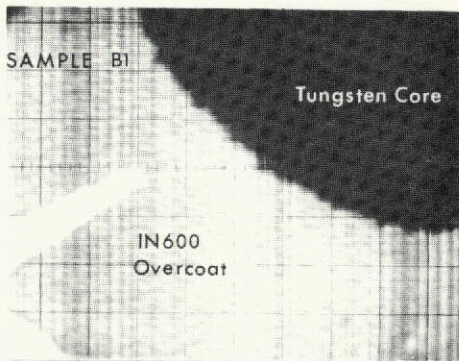
(LOW TENSILE STRENGTH)



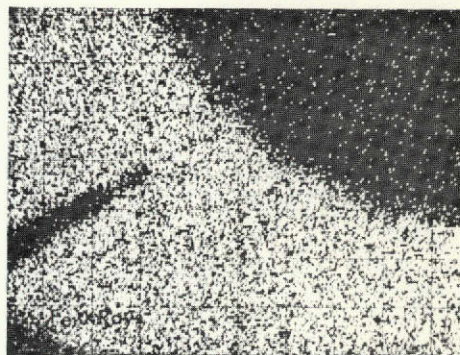
SAMPLE B1

20μ

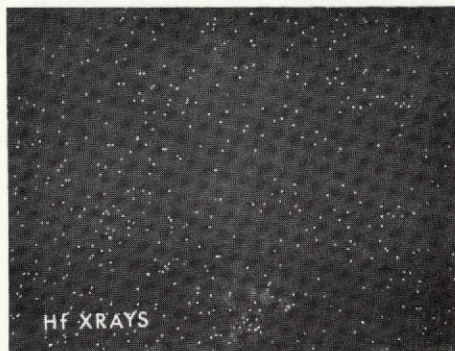
ELECTRON AND X-RAY SCANS OF W/HfO₂/Ni DIFFUSION COUPLE
 (LOW TENSILE STRENGTH)



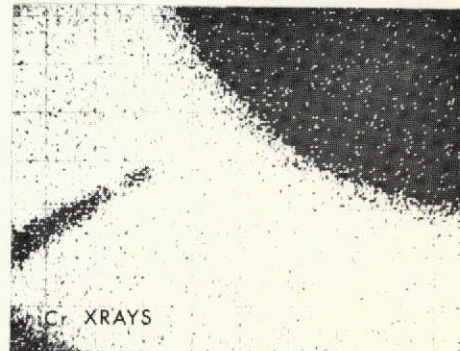
a



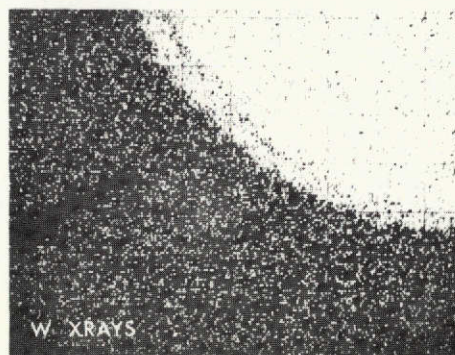
b



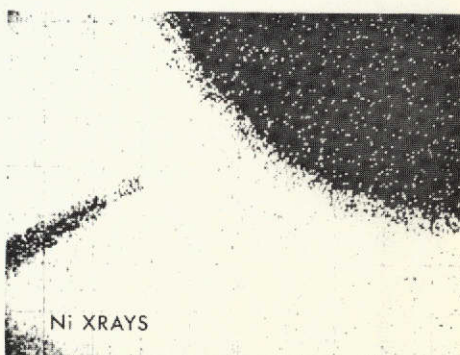
c



d



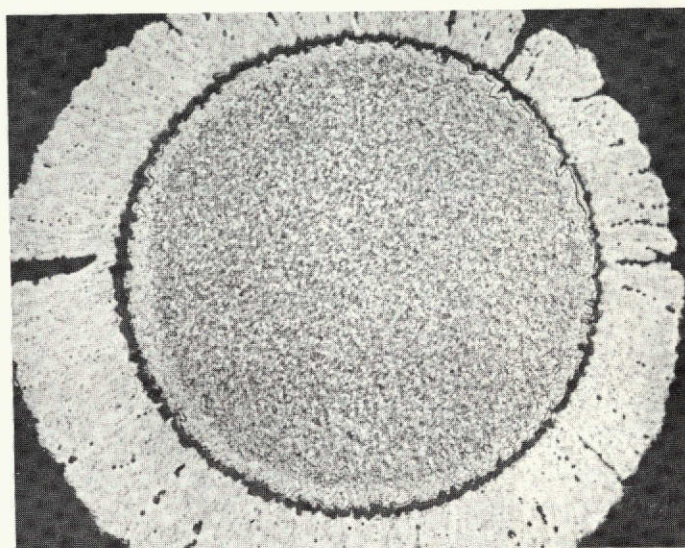
e



f

TUNGSTEN/HAFNIUM OXIDE/NICKEL DIFFUSION COUPLE

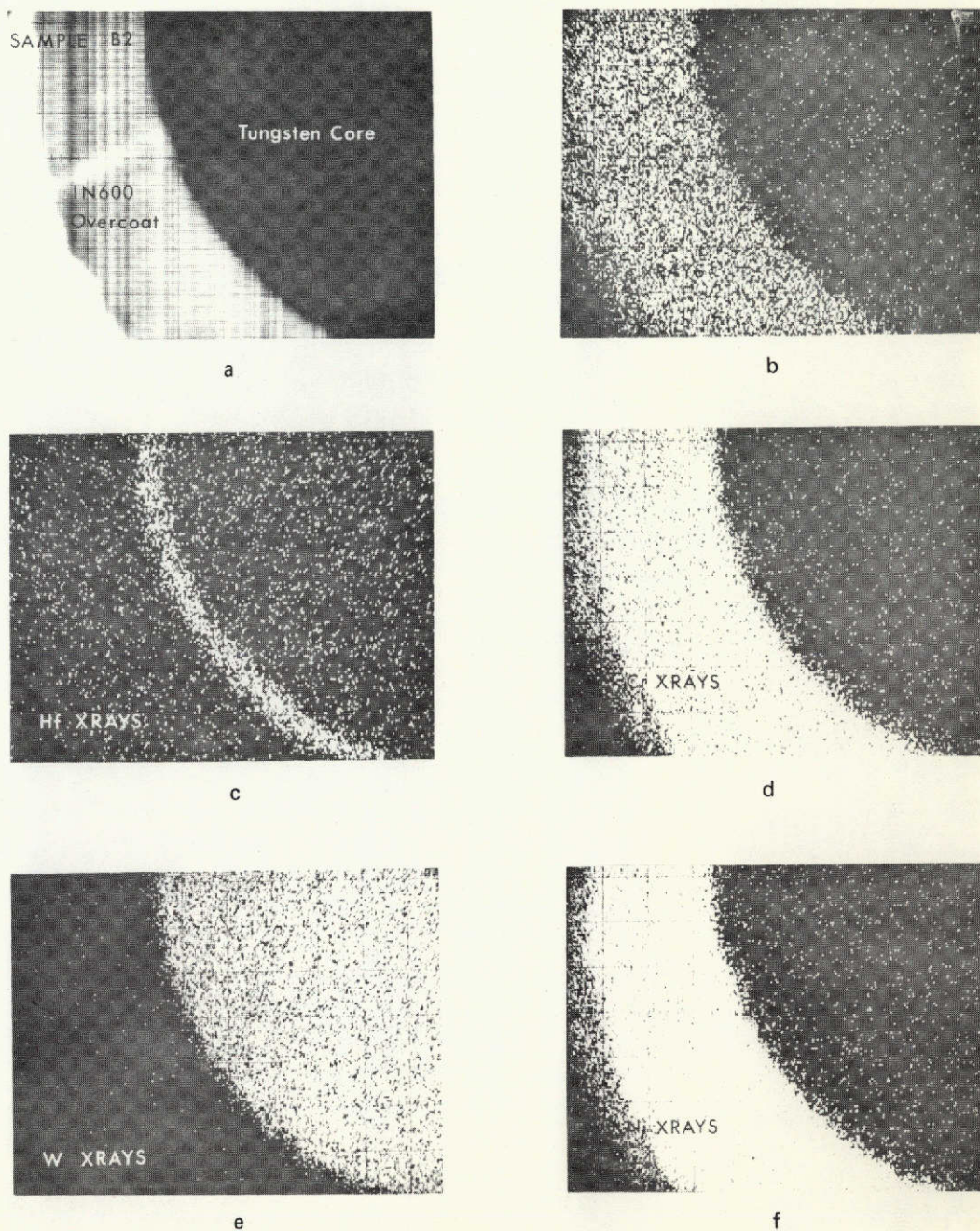
AFTER 24 HOUR EXPOSURE AT 1093°C



SAMPLE B2

20μ

ELECTRON AND X-RAY SCANS OF W/HfO₂/Ni DIFFUSION COUPLE



adhered well. A photomicrograph of the tungsten-hafnium oxide 100% O₂-nickel diffusion couple is shown in Fig. 32. In Fig. 33 are shown the scans for this diffusion couple. The hafnium oxide layer (Fig. 33d) is not as thick as previously shown due to the low rates, but the tungsten (Fig. 33e) was still reasonably prevented from moving outward into the IN600 alloy.

Photomicrograph study of 1200°C thermal anneal diffusion couples

The hafnium oxide and aluminum oxide diffusion couples were given a thermal anneal at 1200°C for 100 hours. The mounted couples were given an acid etch for tungsten. In Fig. 34 is shown the tungsten-aluminum oxide-nickel diffusion couple after the 100 hours at 1200°C. Included for comparison in this figure is the same combination after a twenty-four hour soak at 1093°C. In Fig. 35 is shown the tungsten-hafnium oxide-nickel diffusion couple after the 100 hours at 1200°C. Also included for comparison is the same combination after a twenty-four soak at 1093°C. The recrystallization of both combinations after the thermal anneal could be due to either diffusion attack or simple thermal anneal of the base tungsten fiber. The hafnium oxide layer (Fig. 35) appears to be intact around portions of the tungsten fiber. The protection afforded the base tungsten by this barrier will be discussed under the electron beam probe analysis of these couples.

SEM of 1200°C thermal anneal and twenty-four hour cycled diffusion couples

These same two diffusion couples (aluminum oxide and hafnium oxide) after thermal anneal were broken at 1093°C in argon. Hot tensile tests were also made of these combinations after another set of diffusion couples were cycled for twenty-four hours between room temperature and 1093°C.

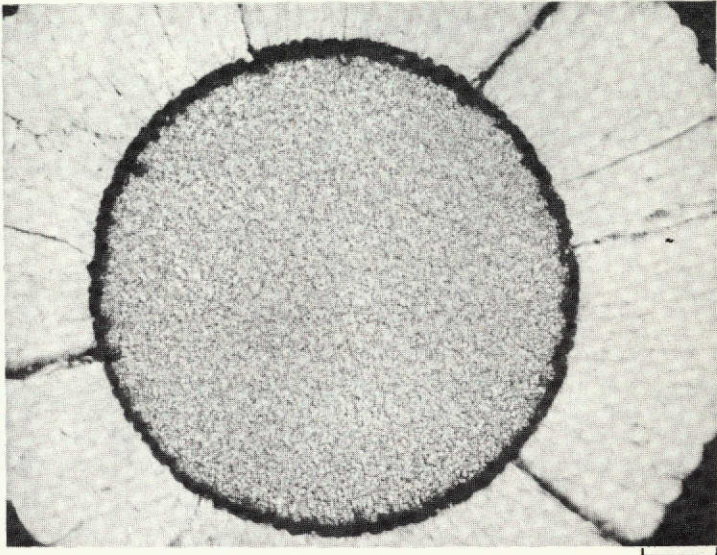
The SEM of the fracture surfaces for both the above thermal conditions for the tungsten-aluminum oxide-nickel diffusion couples are shown in Fig. 36. The fracture surfaces for the tungsten-hafnium oxide-nickel diffusion couples are both shown in Fig. 37. The obvious recrystallization of each type of couple after the 1200°C 100 hour anneal (Fig. 36a, 37a) can be seen.

Electron beam probe analysis of 1200°C thermal anneal diffusion couples

In Fig. 38 is repeated the photomicrograph of the tungsten-aluminum-oxide-nickel diffusion couple after 100 hours at 1200°C, so that the direction of scan can be seen. The electron and X-ray images for this couple are shown in Fig. 39. For this couple the tungsten (Fig. 39e) has moved outward and there is evidence that the IN600 components (Fig. 39 (b,d,f)) have moved inward because the aluminum oxide barrier (Fig. 39c) is no longer intact. In Fig. 40 are shown the line scans for these same elements. In Fig. 40a, a considerable amount of tungsten can be seen to have left the core area. The unevenness of the aluminum oxide coating (Fig. 39c, 38) can also be ascertained by the lines of intensity in Fig. 40b.

TUNGSTEN/HAFNIUM OXIDE (100% O₂)/NICKEL DIFFUSION COUPLE

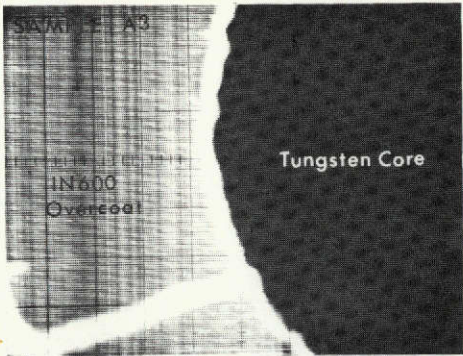
AFTER CYCLIC 24 HOUR EXPOSURE AT 1093°C



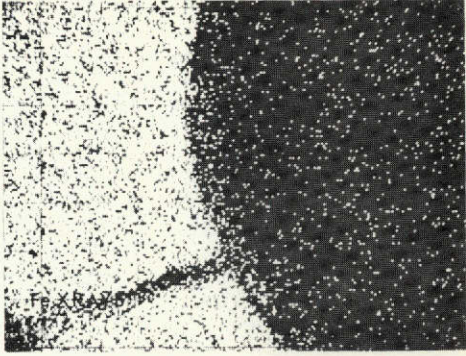
SAMPLE A3

20μ

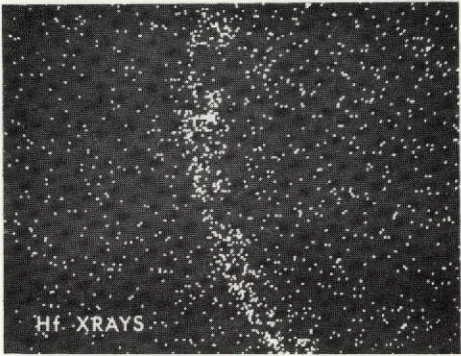
ELECTRON AND X-RAY SCANS OF W/HfO₂ (100% O₂)/Ni DIFFUSION COUPLE



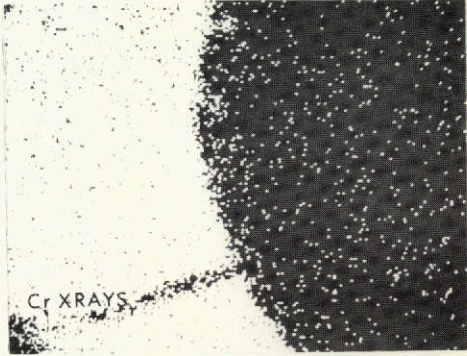
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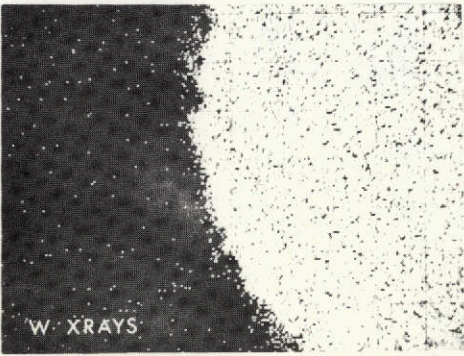
b



c



d

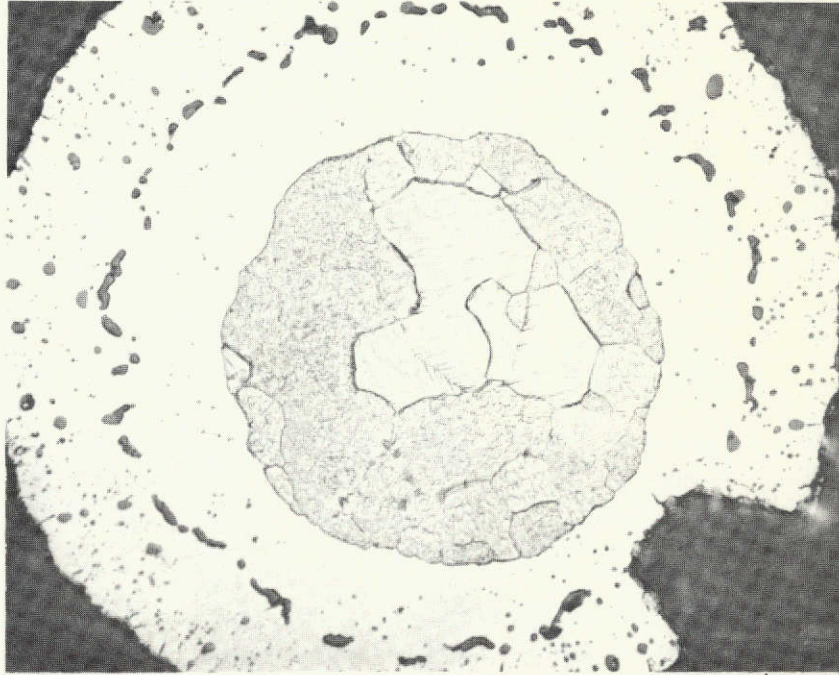


e



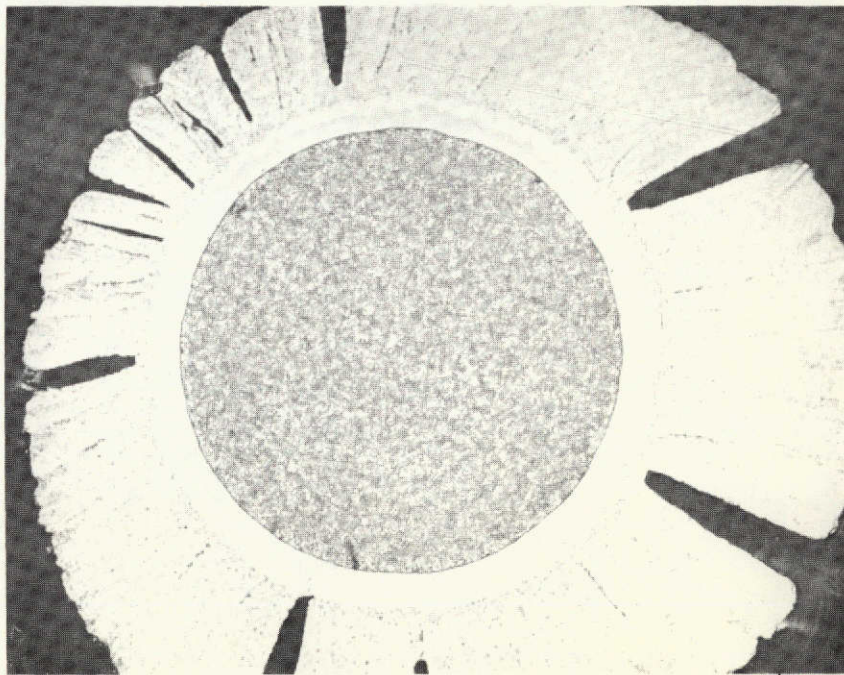
f

TUNGSTEN/ALUMINUM OXIDE/NICKEL DIFFUSION COUPLE
(TUNGSTEN ETCH)



AFTER 100 HOURS AT 1200°C

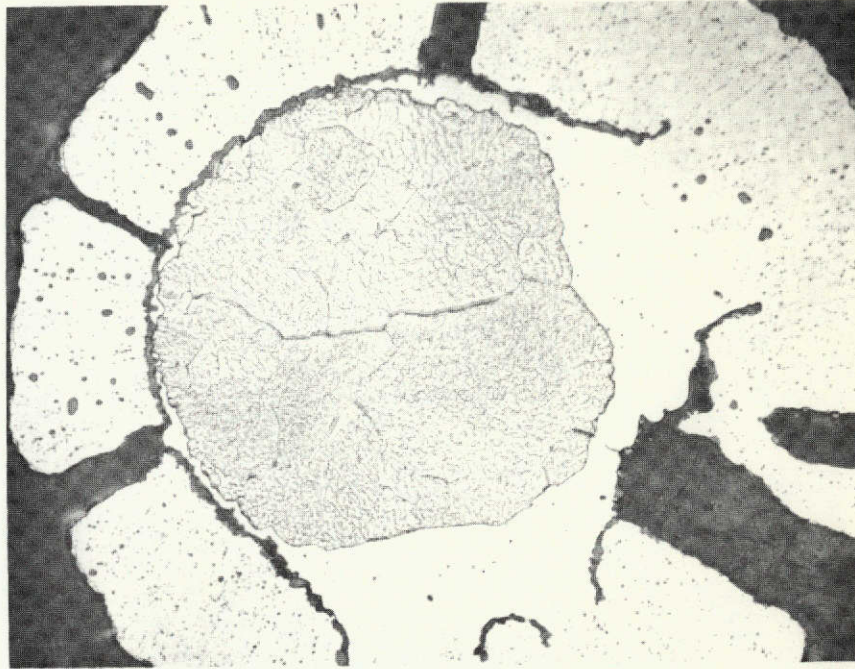
20μ



AFTER 24 HOURS AT 1093°C

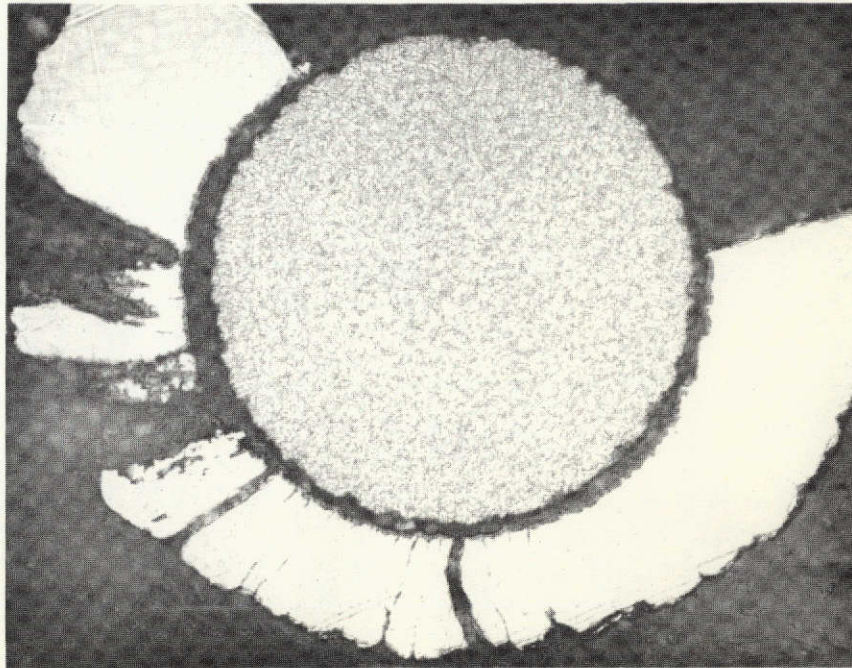
20μ

TUNGSTEN-HAFNIUM OXIDE - NICKEL DIFFUSION COUPLE
(TUNGSTEN ETCH)



AFTER 100 HOURS AT 1200°C

20μ

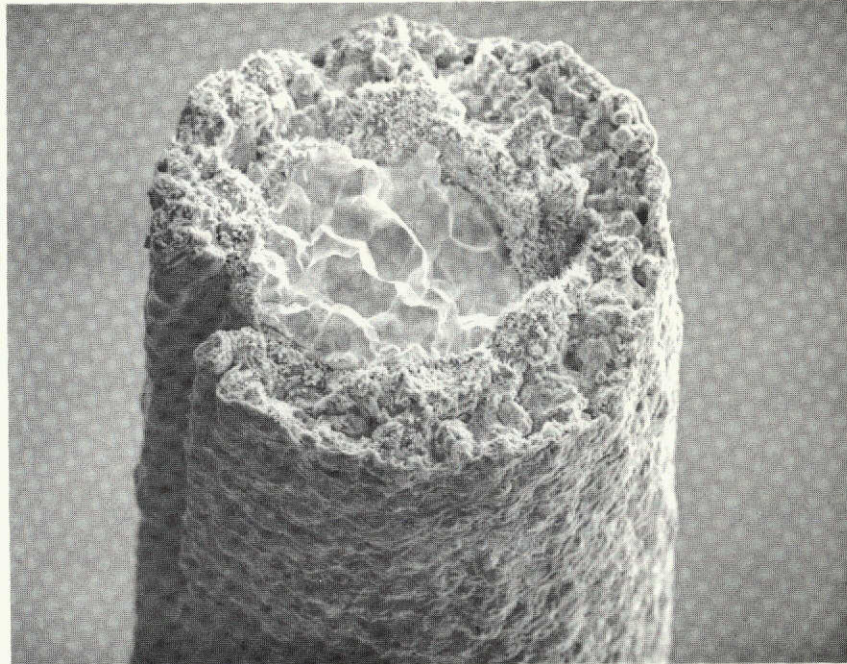


AFTER 24 HOURS AT 1093°C

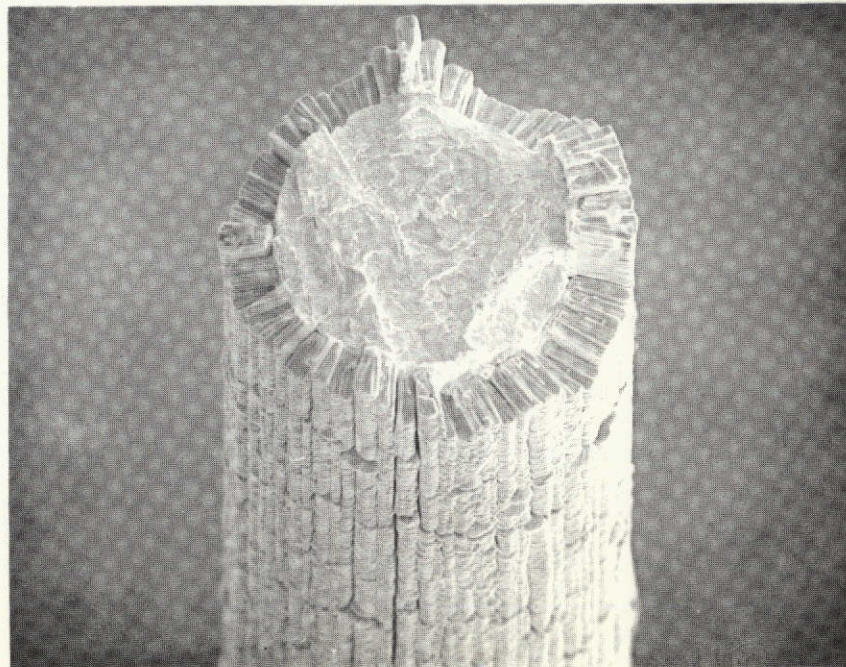
20μ

SEM OF FRACTURE SURFACE OF TUNGSTEN/ALUMINUM OXIDE/NICKEL

BROKEN AT 1093°C IN ARGON



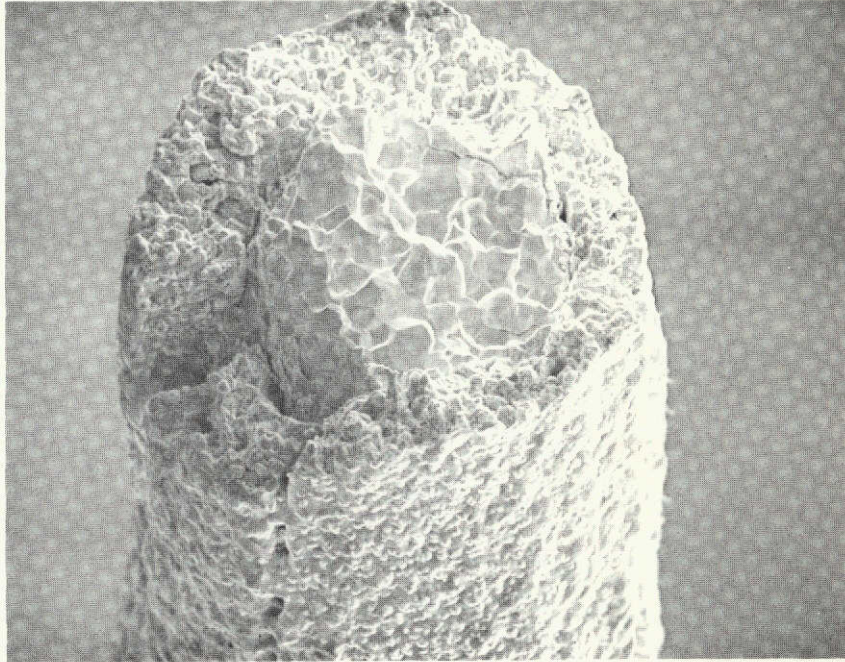
a) 100 HOURS 1200°C ANNEAL



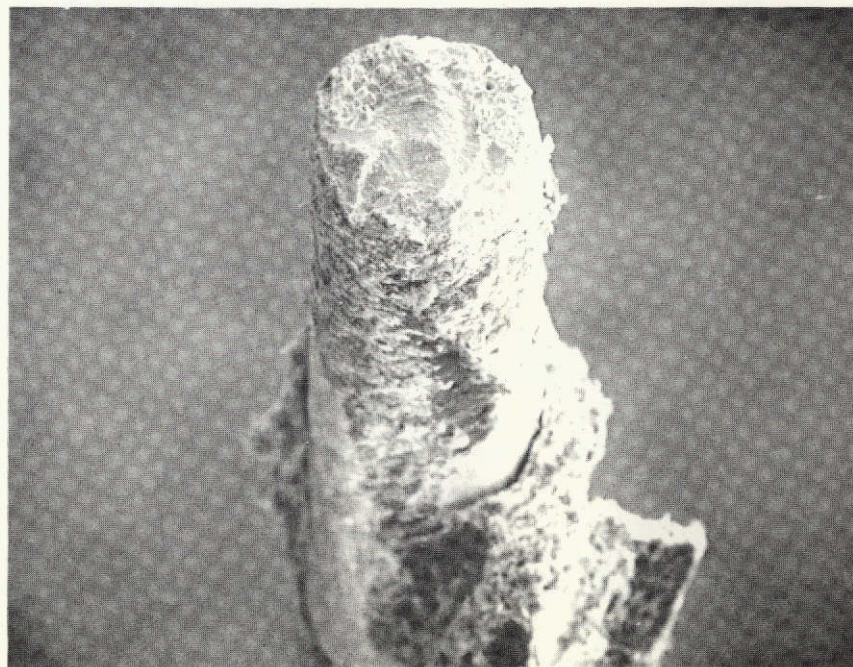
b) 24 HOURS CYCLED 1093°C

SEM OF FRACTURE SURFACE OF TUNGSTEN/HAFIUM OXIDE/NICKEL

BROKEN AT 1093°C IN ARGON

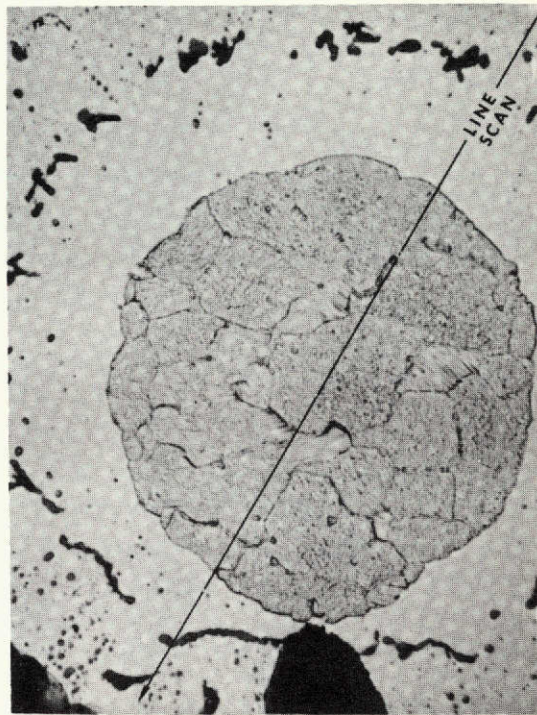


a) 100 HOURS 1200°C ANNEAL



b) 24 HOURS CYCLED 1093°C

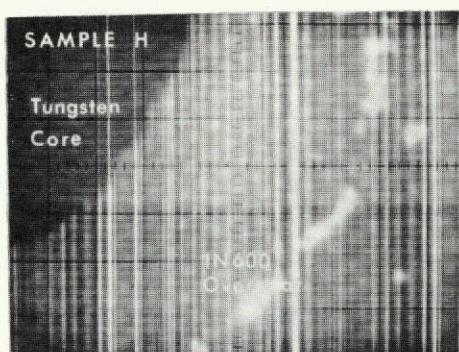
TUNGSTEN/ALUMINUM OXIDE/NICKEL DIFFUSION COUPLE 100 HOURS AT 1200°C



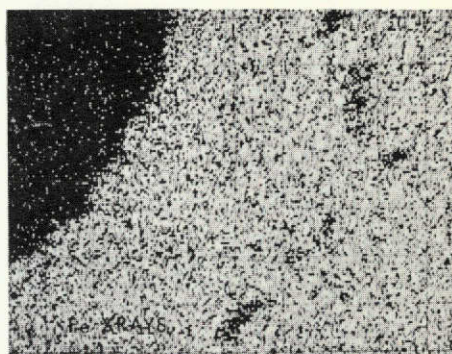
SAMPLE H

20μ

ELECTRON AND X-RAY IMAGES OF W/Al₂O₃/Ni DIFFUSION COUPLE



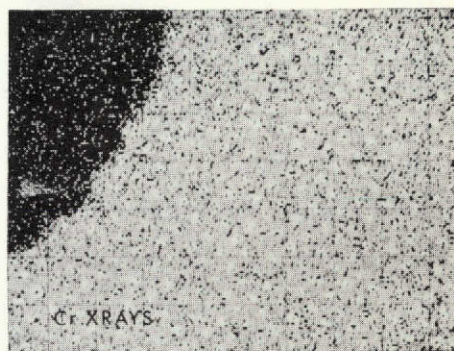
a



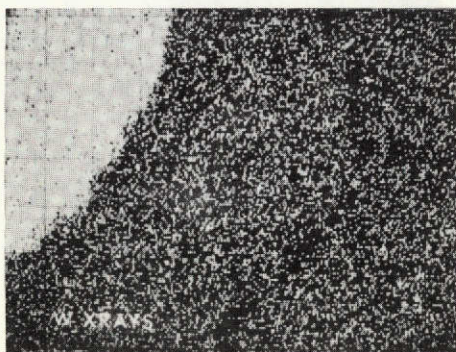
b



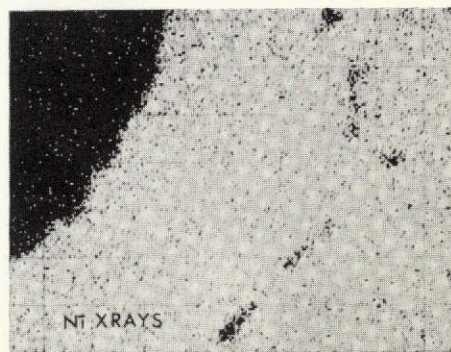
c



d

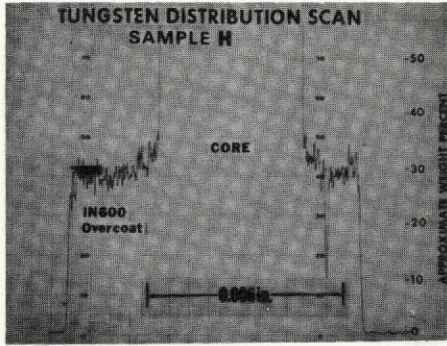


e

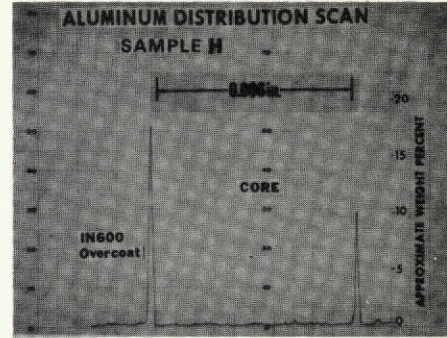


f

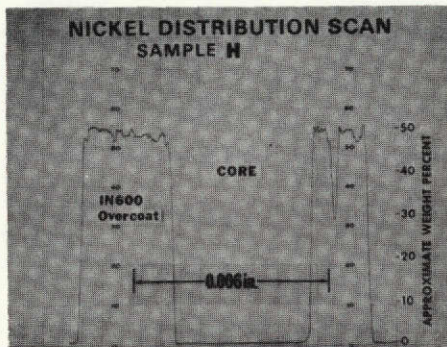
X-RAY LINE SCANS OF W/Al₂O₃/Ni DIFFUSION COUPLES



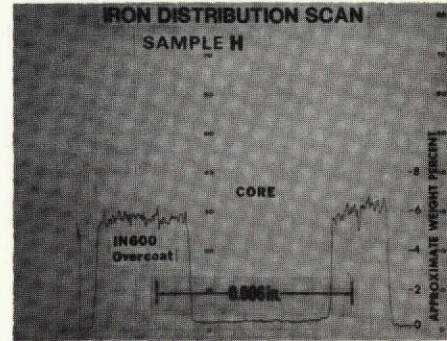
a



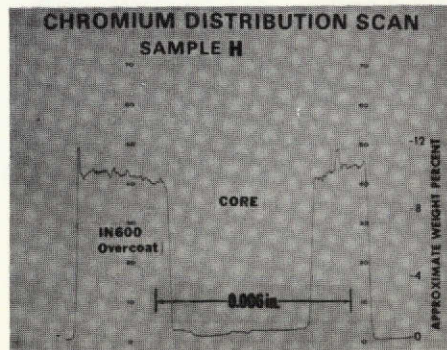
b



c



d



e

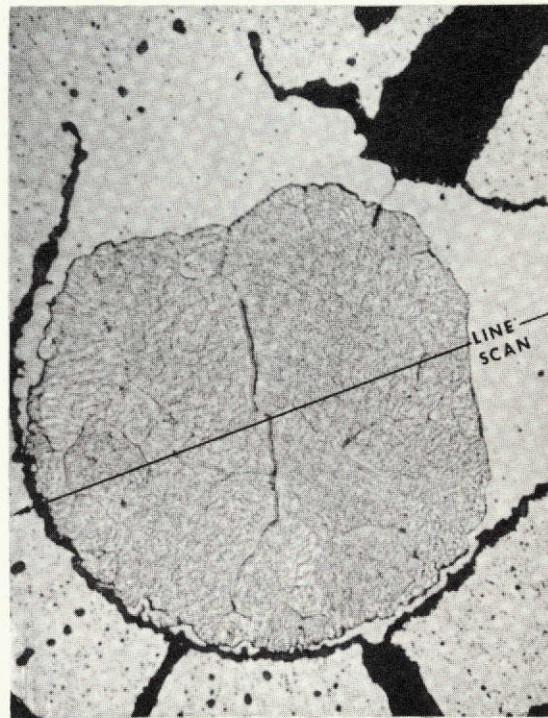
The remaining components appeared to have only slightly penetrated the tungsten core (Fig. 40 (c,d,f)).

In Fig. 41 is repeated a photomicrograph of the hafnium oxide diffusion couple to indicate the direction of the X-ray images and line scans. In Fig. 42 are shown the electron and X-ray images of this diffusion couple. A slight amount of tungsten appears to have moved outward (Fig. 42e) in the areas where the hafnium oxide coating was not around the principle core diameter (Fig. 42c). The line scans of this same couple are shown in Fig. 43. Again, only the tungsten (Fig. 43a) has moved due to the lack of the adhering hafnium oxide coating (Fig. 43b).

Selection of Diffusion Barrier Coating for Composite Evaluation

Hafnium oxide (50% O₂) was chosen as the diffusion barrier to apply to 15 mil tungsten fiber for composite evaluation by NASA. In Table VII are listed the final testing results on the production lot of coated tungsten that was delivered at the close of this program.

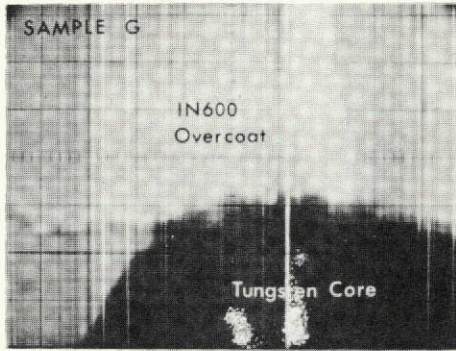
TUNGSTEN/HAFNIUM OXIDE/NICKEL DIFFUSION COUPLE 100 HOURS AT 1200°C



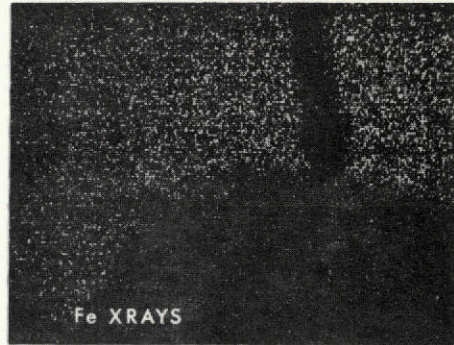
SAMPLE G

20μ

ELECTRON AND X-RAY IMAGES OF W/HFO₂/Ni DIFFUSION COUPLE



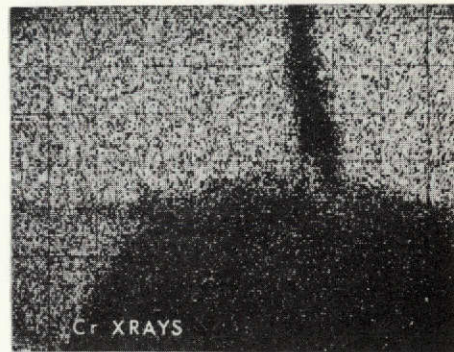
a



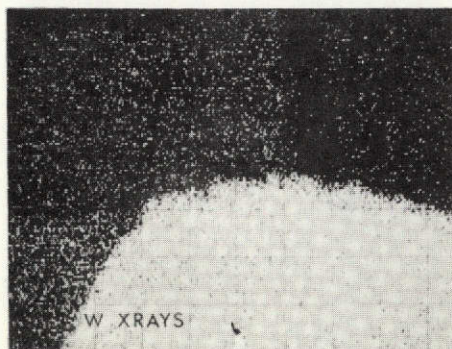
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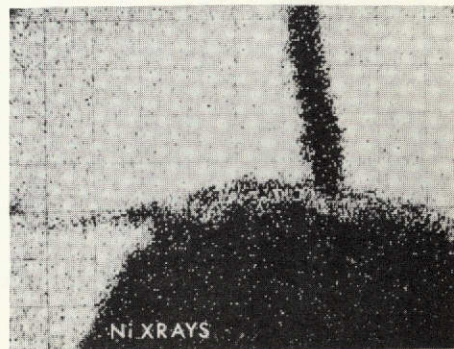
c



d



e



f

X-RAY LINE SCANS OF W/HFO₂/Ni DIFFUSION COUPLES

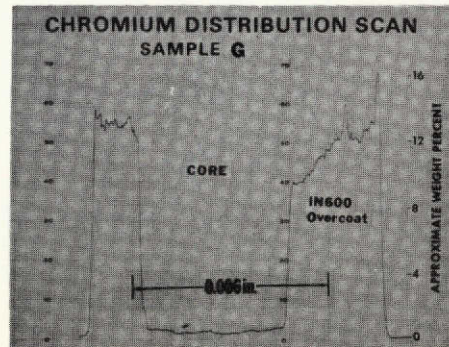
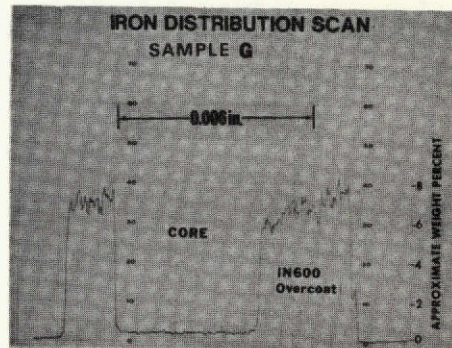
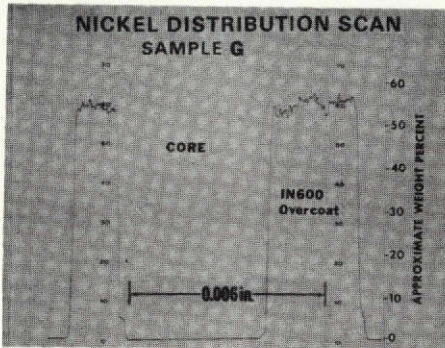
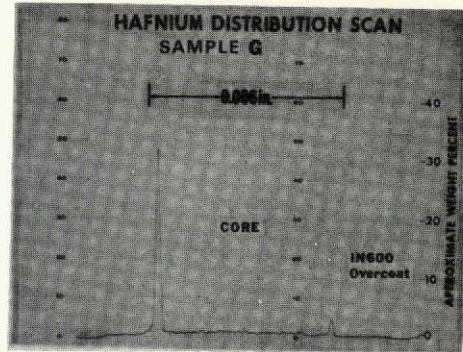
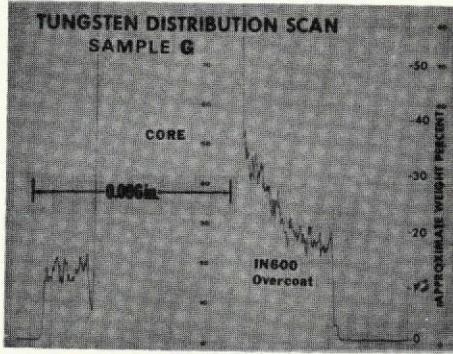


TABLE VII

TEST RESULTS FOR COATED FIBER (FINAL EVALUATION)

<u>Sample</u>	<u>Temperature of Test °C</u>	<u>Tensile Strength KN/CM</u>
As Received 15 mil Tungsten Fiber	Room Temp.	245,241 245
Hafnium Oxide Ion Plated Onto 15 mil Tungsten	Room Temp.	234,238 238
As Received 15 mil Tungsten Fiber	1093°C	79,80 82,76
Hafnium Oxide Ion Plated Onto 15 mil Tungsten	1093°C	76,80,79
Hafnium Oxide Ion Plated Onto 15 mil Tungsten Fiber	Room Temp.	204,206
After 24 Hours Cycling to 1100°C	1093°C	79,82,80
As Received 5 mil Tungsten Fiber this apparatus	1093°C	90,90,91
As Received 5 mil Tungsten Fiber on Old Apparatus	1093°C	83,86

CONCLUSIONS AND RECOMMENDATIONS

The radio frequency ion plating process can successfully deposit a stable oxide coating onto a tungsten fiber. Each of three oxides performed better than the carbide (titanium carbide) coating initially chosen for barrier evaluations. Of the three oxides examined in this program, (aluminum oxide, yttrium oxide, and hafnium oxide) hafnium oxide provided the best protection for the tungsten substrate. The performance of these coatings was evaluated through a series of room temperature and 1093°C tensile tests, thermal cycling tests, and thermal annealing exposures.

As a result of these evaluations the hafnium oxide coating was chosen to apply onto a production lot of 15 mil tungsten filament. These coated filaments were forwarded to NASA for incorporation into high temperature composites. Samples from this production lot were tested before delivery and the elevated temperature properties of the as received tungsten fiber substrate were found to not have been degraded by the ion plating process.

It is recommended that although the hafnium oxide coating was shown to be superior in this program the other two oxides may have potential as high temperature barriers. Future programs should involve in-depth parameter studies for each particular oxide chosen. For example, the crystal structure of the aluminum oxide coating evaluated in this program was the gamma phase since this was the crystal structure of the first material produced under the conditions chosen for operation. If the alpha phase was desired, the following parameters could be varied with this particular crystal structure as the only goal: absolute pressure of the plasma, rate of deposition of the oxide, temperature of the substrate, additions of oxygen to the ion plating plasma, and strength and location of the external magnetic field. Adherence which was a minor problem with yttrium oxide could be examined by studying the effect of the following parameters: rate, duration, and strength of the sputter cleaning procedure and substrate temperature during the cleaning process.

In order to achieve higher deposition rates, targets of the selected materials will have to be found which can sustain appreciably higher voltages and thermal stresses than those used in this program. For example, the HfO₂ target could be made by flame spraying HfO inside of an Al₂O₃ target. In this way Al₂O₃ substrate could support the high electrical and thermal stresses necessary for this system to work at high deposition rates, while the surface HfO₂ would act as the source.

It is also recommended that, if the composites containing the filaments produced in this program being evaluated by NASA exhibit the superior properties intended, a program be conducted in which the present batch process ion plating apparatus is converted to a continuous coating procedure. Another program could be directed toward significantly increasing the rates of deposition in an enlarged batch process apparatus.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the specific contributions of the following colleagues: D. Mankee, managing the ion plating runs; L. Jackman, scanning electron microscope fracture photographs; J. Knecht and A. Manzione, the electron microprobe analyses; Mrs. A. P. Elkins and D. Norton the thermal exposures and tensile tests and Mrs. L. A. Jenkins for the manuscript preparation.

APPENDIX 1

Ion Plating: Apparatus and Operation

The ion plating apparatus used in the present work was designed and developed at the United Aircraft Research Laboratories as a research tool for the deposition of a variety of materials in thin film form. For the present work, right circular cylindrical targets were used. The required material was removed from the inner wall of the cylinder and deposited onto fiber substrates, which were suspended along the axis of the target.

The mechanisms and benefits of the deposition of thin films by ion plating have been discussed in detail by several authors (Refs. 4, 5, 6). To produce good quality films, a chamber is required which can be evacuated to about 10^{-6} torr, then partially backfilled with an inert gas. The plating source must be capable of supplying the plating material in a vapor form such as an evaporated source or a sputtering target. There must be a means of initiating a glow discharge in the low pressure gas in the region of the substrate. Finally there must be an electrical circuit which can maintain a negative bias on the substrate.

Before the plating source is energized, the gas discharge (plasma) is struck and the bias is applied to the substrate. In this way the substrate is sputtered clean prior to film deposition. The plating source is then energized with the bias still applied to the substrate, and deposition takes place on the atomically clean substrate surface. The fact that the substrate can be so well cleaned just prior to deposition is the aspect of ion plating which is principally responsible for producing outstandingly adherent films.

The negative bias is maintained throughout the deposition process, although generally at a reduced potential. During deposition this bias aids in promoting good film adherence by sputtering away loosely bound contaminants and repelling negatively charged contaminants. The added energy imparted to the deposited species by the bombarding ions of the plasma serves to enhance surface migration of the deposited atoms resulting in further improvement of film quality.

Because the deposition takes place at gas pressures in the millitorr range, considerable scattering of the depositing source atoms takes place with the gas molecules. This scattering accounts primarily for the plating of surfaces out of the line of sight of the source.

For the coating of fibers, a cylindrical geometry capable of inward sputtering was used. This arrangement has the advantage that it promotes uniform deposition because of the similar geometry of source and substrate. Furthermore, enhanced deposition rates result because of the concentration effect as the deposit travels inward toward the axis. Finally, this geometry conserves source material because, except for small losses at the ends of the cylinder, the source material that is not intercepted by the substrate and holder is returned to another part of the target to be resputtered.

Several versions of cylindrical cathodes have been developed at the UARL for rf sputtering. The modification that was used to coat fibers is illustrated in Fig. A-1. A photograph of the completely assembled cathode is shown in Fig. A-2. The targets used were right circular cylindrical shells 38.1 cm (15 inches) long, with a 6.35 cm (2.5 inches) outside diameter and a 0.3175 to 0.635 cm (.125 to .250 inches) thick wall.

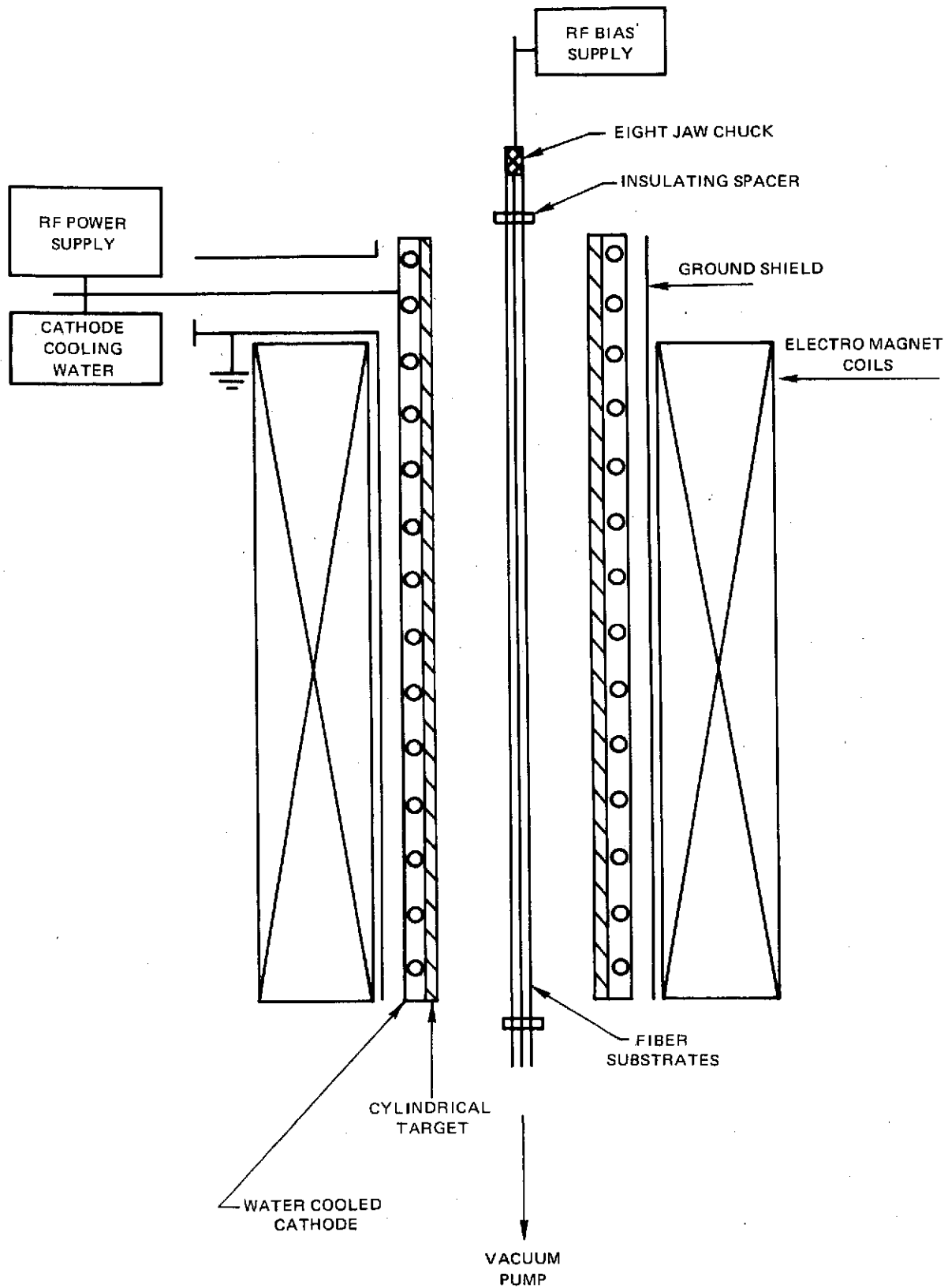
The metal matrix material was IN600 nickel and was obtained as a hot-forged round bar. The nickel was machined to the cylindrical target shape.

The ceramic targets were metallized on their outside surfaces. Then they, as well as the metal targets, were indium soldered directly to the inner wall of a copper cathode.

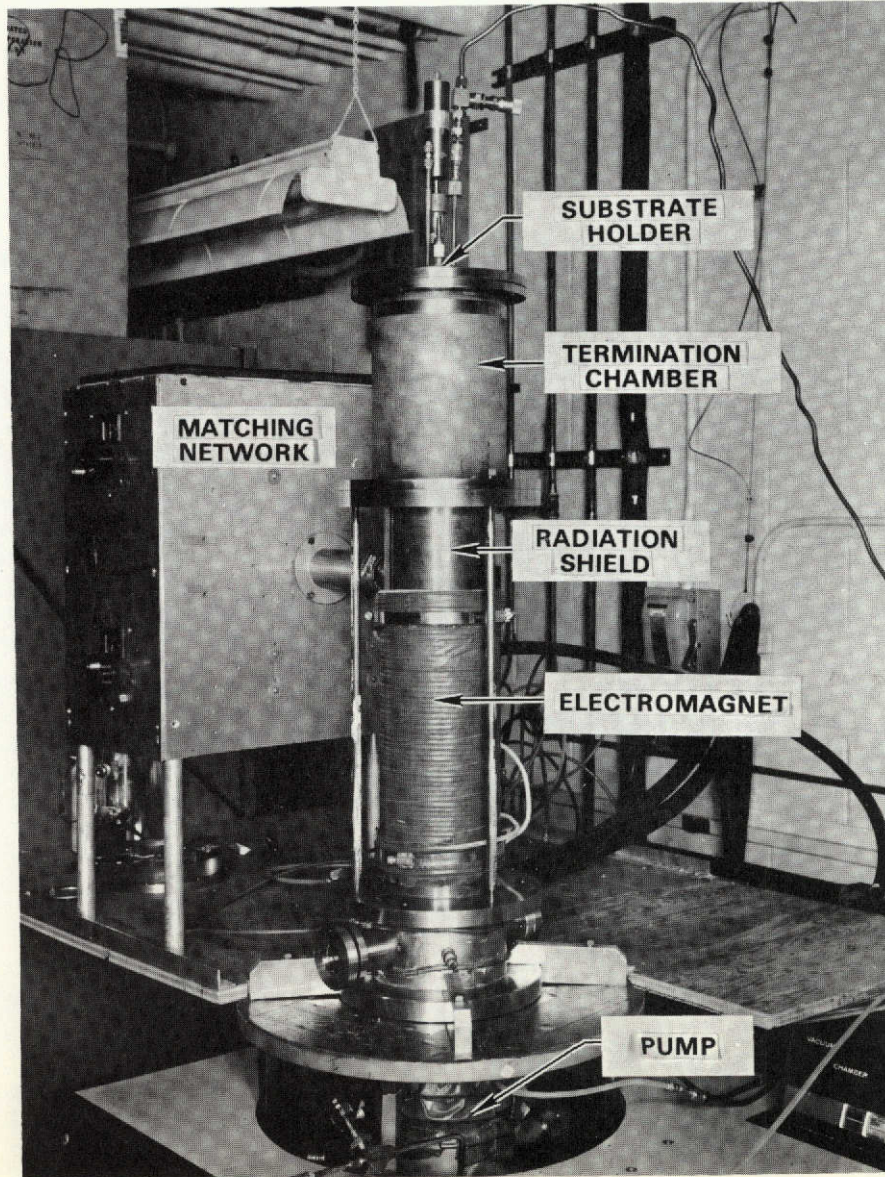
The copper cathode is double walled so that water can be circulated to keep the target cool to avoid thermal stressing. The cooling water, as well as the rf power, is fed in through a coaxial tube threaded to the cathode. The cathode is insulated from ground by a pair of ceramic standoffs at each end. A thin walled copper radiation shield surrounds the cathode and power lead. This shield also serves to support the windings of a cylindrical electromagnet. The electromagnet serves to increase the plasma density in the vicinity of the target by confining the secondary electrons emitted from the target. Up to a point, an increase in plasma density results in an increase in deposition rate. Further, because they are confined to spend more time in the vicinity of the target, the electrons are somewhat thermalized before reaching the fibers. This results in much less heating of the substrate than there would be otherwise.

The fiber substrates are held in a 6 or 8-jaw chuck and suspended parallel to the target axis at a radial distance of 0.635 cm (0.25 inches). A ceramic separator holds them at this radius and prevents the fibers from touching each other. The negative bias is applied to the fibers through an insulated feed-through on the end cap. For the deposition of electrically insulating coatings, the bias must be radio frequency energy. A photograph of the fiber substrate holder is shown in Fig. A-3.

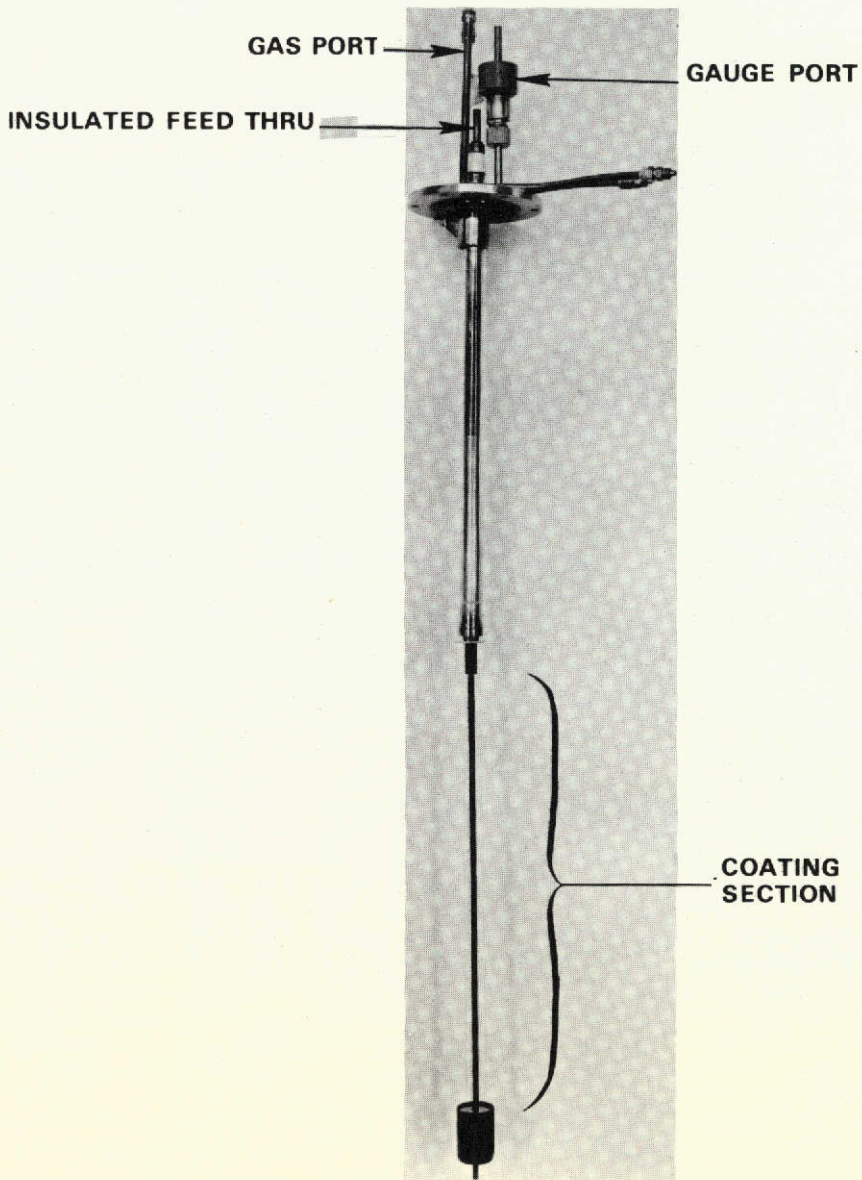
CYLINDRICAL ION PLATING APPARATUS



CYLINDRICAL CATHODE FULLY ASSEMBLED



CYLINDRICAL CATHODE FIBER SUBSTRATE HOLDER



The fiber substrates were prepared by cutting lengths about 45.7 cm (18 inches) from the spools of stock provided by NASA. The lengths were mounted in the substrate holder. The entire assembly was then irrigated with MOS grade trichloroethylene, rinsed with MOS grade methanol, and blown dry in a gentle stream of dry nitrogen.

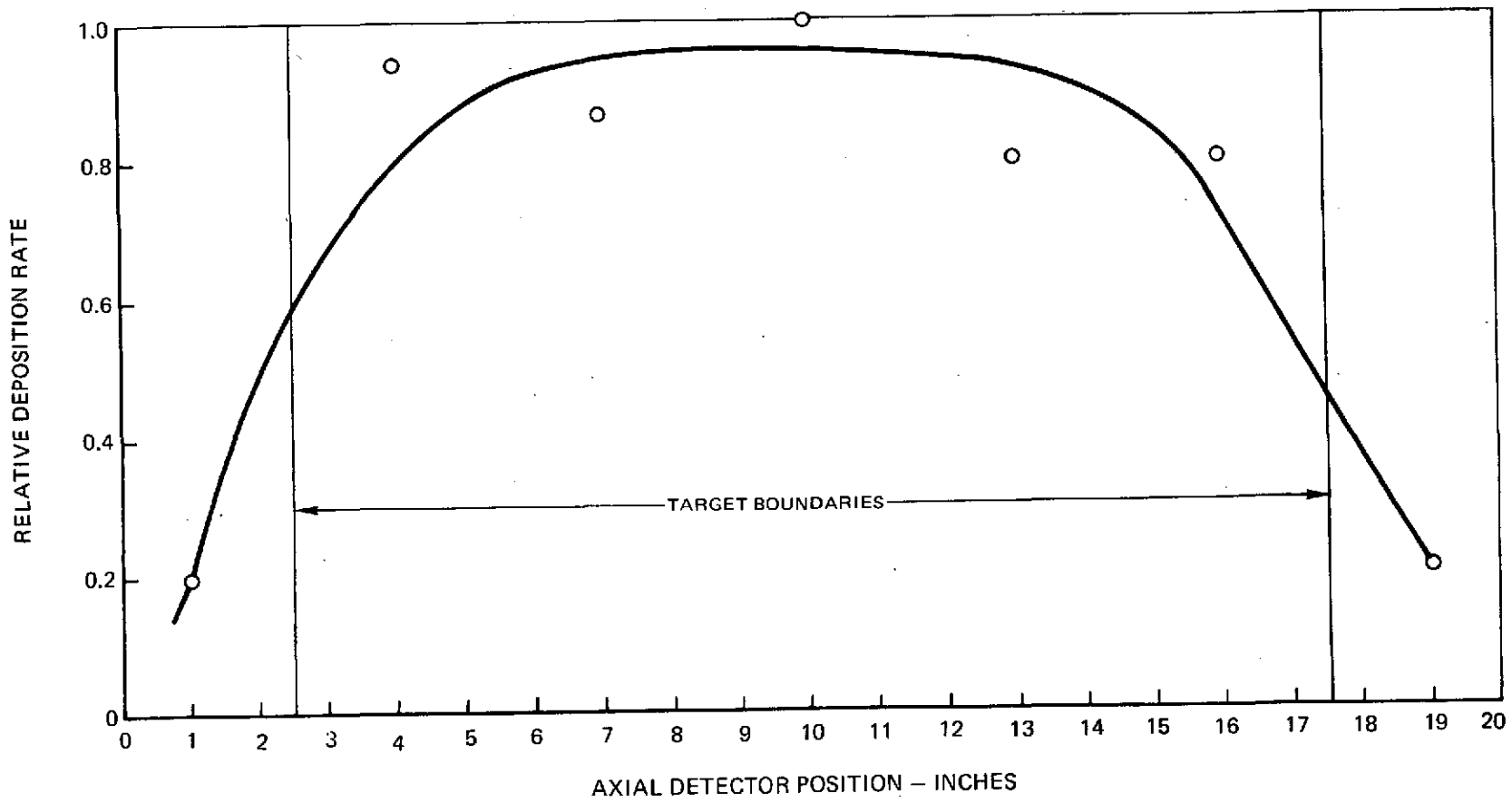
The cylindrical cathode is pumped with a conventional oil diffusion pump backed with a mechanical pump. A liquid-nitrogen-cooled optical baffle is located between the diffusion pump and the cathode. Typically the system is initially pumped down to about 2×10^{-6} torr. The high vacuum valve is then partially closed and 99.999 percent pure argon is admitted through a precision micrometer valve. A dynamic balance is achieved between the inlet gas and the exhaust such that a pressure of 15×10^{-3} torr is maintained in the cathode and 25×10^{-3} torr in the foreline of the diffusion pump.

During a typical run about 100 volts rms rf bias is applied to the fibers and a total of 50 watts is applied to the cathode for the initial 5 minutes. This combination of power inputs allows the tungsten fiber to sputter clean while at the same time the target is sputtering only fast enough to avoid being contaminated by what is being removed from the fibers. The sputterant from the fibers is deposited on the substrate holder fixturing. During the next 5 minutes the power input to the target is gradually raised to one-half of the final operating value. This provides a gradual transition from cleaning to coating, to assure that when coating starts, only clean target material is being deposited. The power is then increased to full value and the bias decreased to about 50 volts rms for the remainder of the run.

The deposition profile as a function of position along the axis was also determined. It is presented in Fig. A-4. Note that for the 30.5 cm (12 inch) long interval between detectors at 10.2 cm (4 inches) and 40.6 cm (16 inches) that the deposition is reasonably uniform. The variation of about ± 10 percent from the average value in this interval is much less than would be expected from other experiments on inwardly sputtering cylindrical cathodes. In their approximately 14 cm (5.5 inch) long cylindrical cathode, Gill and Kay (Ref. 7) measured a variation of about ± 20 percent from the average over the central 80 percent of the cathode.

Depositions were made with an axial magnet field strength of about 40 gauss. The magnetic field profile is shown in Fig. A-5. This flat magnetic field profile was achieved using theory developed by Garrett (Ref. 8). The 40 gauss field was chosen because it produced a reasonable compromise between deposition rate and substrate heating. Lower magnetic fields, while lowering the substrate temperature, would also lower the deposition rate. Higher magnetic fields, while increasing the deposition rate to a point, would also raise the substrate temperature considerably.

TYPICAL DEPOSITION PROFILE IN
CYLINDRICAL ION PLATING APPARATUS



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FIG. A-4

AXIAL MAGNETIC FIELD STRENGTH IN CYLINDRICAL ION PLATING APPARATUS

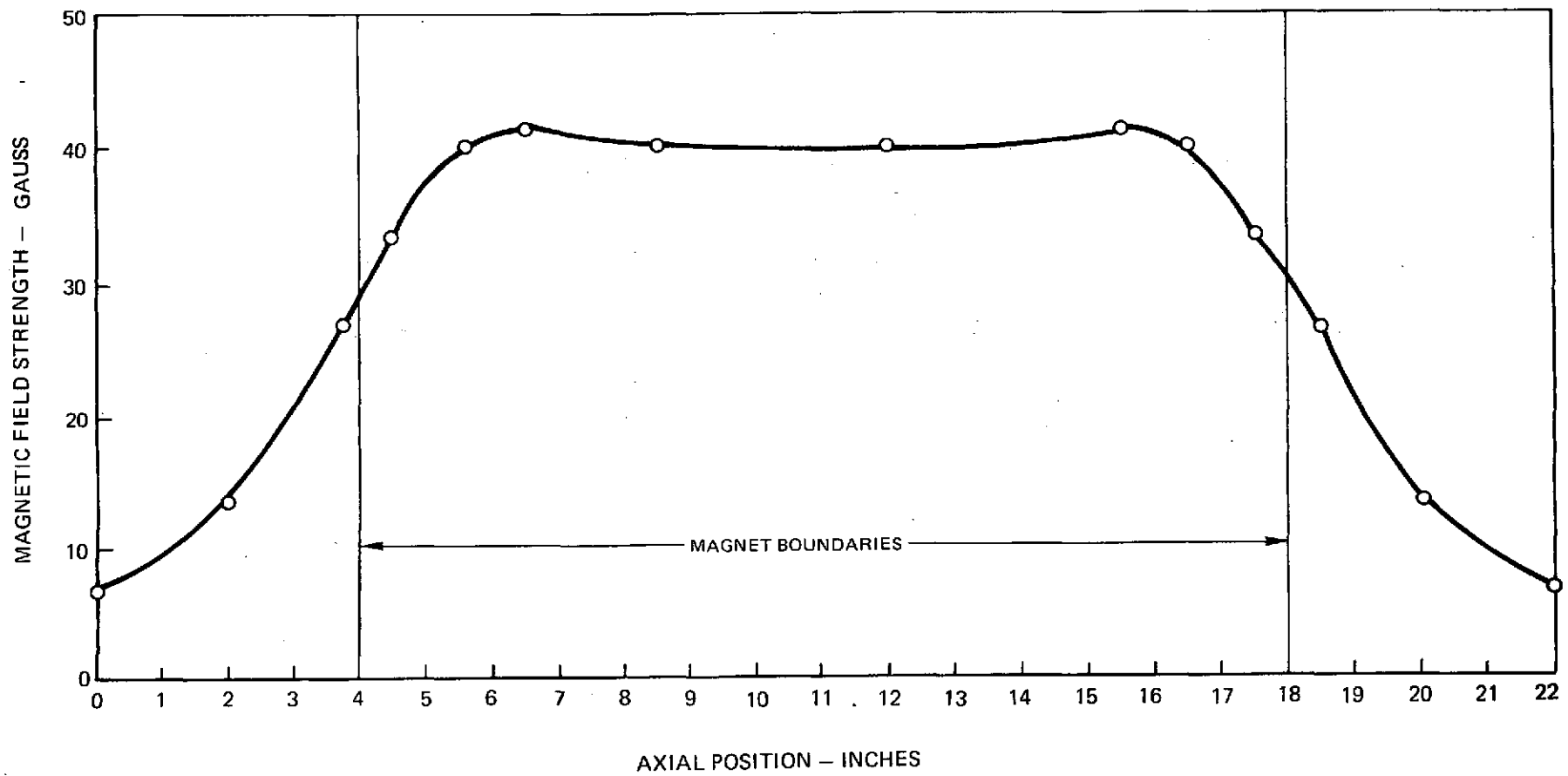
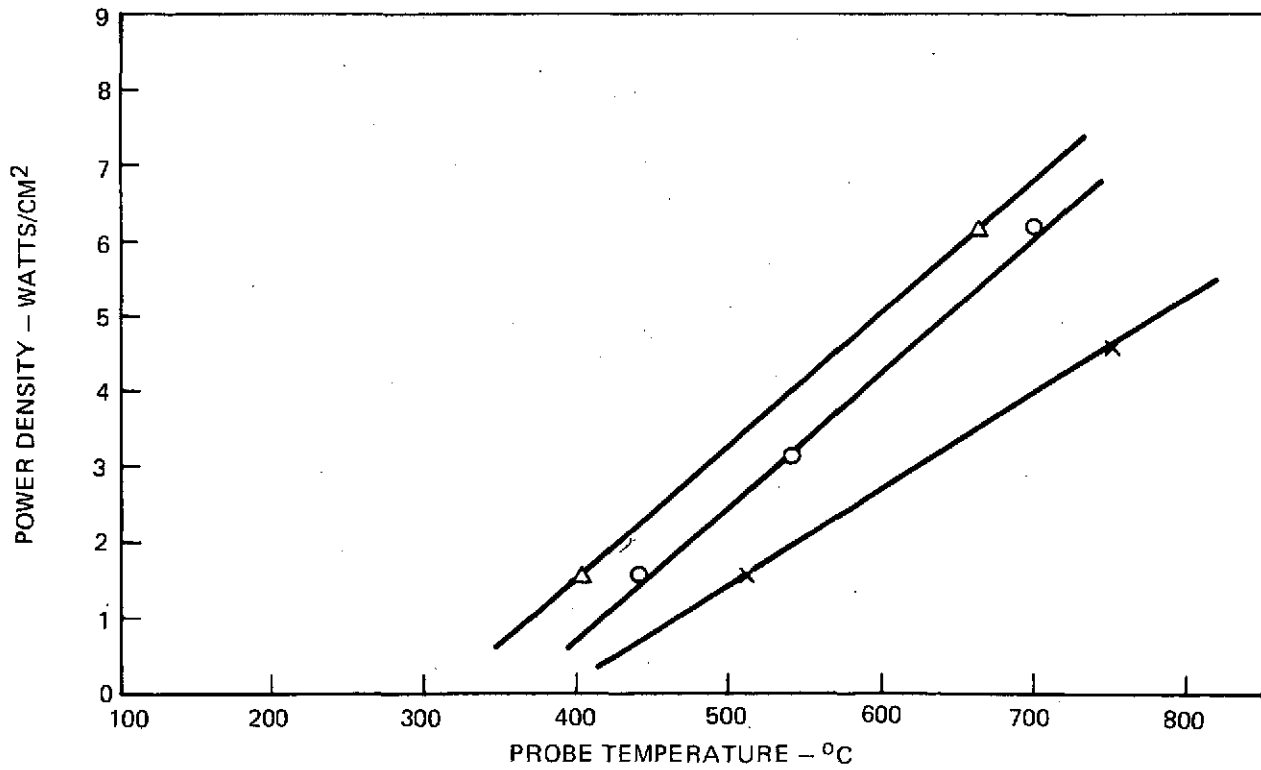


Figure A-6 shows the dependence of the fiber temperature as a function of target input power for several conditions. These temperatures were measured by placing a thin shielded thermocouple at various locations along the target axis at the radial position normally occupied by the fiber substrates. The assumption is made that the fiber reaches essentially the same temperature as the thermocouple did.

PROBE TEMPERATURE AT QUARTER INCH RADIUS
OF CYLINDRICAL ION PLATING APPARATUS

- TEMP AT MID POINT ALONG AXIS - NORMAL BIAS
- △ TEMP AT END - NORMAL BIAS
- × TEMP AT MID POINT - CLEANING BIAS



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