SIX MONTH PROGRESS REPORT

DEVELOPMENT OF FABRICATION PROCESS FOR METALLIC FIBERS OF REFRACTORY METAL ALLOYS

by

L. H. Amra, L. F. Chamberlain, F. R. Adams, J. F. Tavernelli, and G. J. Polanka

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

January 20, 1966

CONTRACT NAS3-7906

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ABSTRACT

One objective of this contract is the development of the fabrication processes for producing 5 mil diameter wire. The six refractory metal alloy systems under study are: TZC, AS-30, W-Re-ThO_2, W-Hf-C, FS-85, and T-222. The strength goal for these wires is a stress-to-density ratio of 125,000 inches for a rupture life of 3,000 hours in a temperature range of 2000°F to 2200°F.

A small amount of TZC alloy wire at 5 mils diameter has been produced by working down vacuum cast ingots. The AS-30 alloy has been melted. Considerable difficulty has occurred in attempts to produce workable tungsten alloy bars from pressed and sintered powders, in both tungsten systems. However, recent efforts with the tungsten-rhenium-thoria system are very encouraging.

The other part of the task contracted for, the designing and building of a six station creep, stress-rupture test equipment, has progressed to the building stage. Frequent communications through meetings, phone calls, or letters between contractor and vendor have resolved the basic design concept.

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INTRODUCTION

As a result of the recent work being done on fiber reinforced materials, there is a logical extrapolation that can be drawn wherein superalloy metal bodies reinforced with strong, high temperature wires imbedded in the parent metal matrix should have more useful properties than those of either component alone. The specific application for such composites may be in advanced turbo-jet engines. To test this extrapolation, the present contract seeks to provide six alloy fibers or wires from which three will be selected for more intensive study.

One objective of this contract is the development of the fabrication processes for producing wire smaller than 10 mils diameter with a target size of 5 mils. The strength goal for these wires is a stress-to-density ratio of 125,000 inches for a rupture life of 3,000 hours in a temperature range of 2000°F to 2200°F.

The second objective of this contract requires the contractor to design, fabricate, and test a multi-station, creep and stress-rupture apparatus for the testing of these alloys.

The refractory metal systems that were agreed upon as meriting this attention are:

TZC	(Mo-1.25Ti-0.25Zr-.12C)
AS-30	(Cb-20W-1.1Zr-0.09C)
FS-85	(Cb-28Ta-10W-0.9Zr)
T-222	(Ta-9.6W-2.4Hf)
W-5Re-3ThO_2	
W-2Hf-0.02C	

The first four materials have been commercially available in rod or sheet form for some time and their properties in these forms have been published in various reports and articles. The last two material systems listed have been investigated by others to some extent, although in modified compositions, but they are not commercially available in the normal sense.

The overall contract can be divided into two tasks. Task I includes the designing and building of the multi-station creep, stress-rupture machine; the acquisition or production of the refractory metal ingots or rods; the development of fabrication processes for conversion of the ingots into wire; and the production of 6,000 feet of wire in each alloy system in excess of the amount needed for chemical and metallographic tests and for various wire tests for each composition.

Two tensile tests are to be run at room temperature, and at 1800°, 2000°, 2100°, 2200°, 2400°, and 2600°F in vacuum of 10^{-6} Torr. or better.

Stress rupture tests will be undertaken in the multi-station tester at 2000°, 2200°, and 2400°F to define a 100 hour rupture life curve with at least two data points at each of five stress levels. The tests will be performed in vacuum.

The extent of increase or decrease in the levels of oxygen, nitrogen and hydrogen in alloy wires during extended exposure to high temperature in the atmosphere within the stress and creep rupture apparatus shall be determined by subjecting a sample of 5 mil wire, coiled and weighing one gram, to the environment in the apparatus at 2200°F for a period of 50 to 100 hours, analyzing this sample for oxygen, nitrogen and hydrogen by vacuum fusion gas analysis, and comparing such analyses with analyses of similar samples of the same material that have not been exposed to such conditions.

Task II involves the production of 300,000 feet of each of the three most promising compositions produced and tested in Task I on the recommendation of the contractor and subject to the approval of the NASA Project Manager. As in Task I, suitable chemical and metallographic analyses are to be made to assure more complete knowledge of the materials in question. However, Task II requires appreciably more wire evaluation tests, including creep and stress rupture tests which are to be conducted in the multi-station test equipment.

Two tensile tests are required for each composition at room temperature in air, and at 1800°, 2000°, 2100°, 2200°, 2400° and 2600°F in a vacuum of 10^{-6} Torr. or better.

Definition of a log stress versus log time curve is expected to determine the stress for 1,000 hour life at two temperatures in the range of 2000°F to 2400°F. The program shall have these minimum number of tests: Two tests for each composition at five stress levels for each temperature. Data points which appear to be in error will be checked with repeat tests under the same conditions.

The contractor shall define the creep curves for at least two tests at each stress that causes rupture in 10, 100 and 1,000 hours at the two temperatures used to establish the 1,000 hour stress rupture life. Data points which appear to be in error will be checked with repeat tests under the same conditions.

Tests will be conducted in vacuum or neutral atmospheres to limit contamination. The tests seeking to compare gain or loss of oxygen, nitrogen and hydrogen mentioned in the Task I description are to be used here also.

Section I - Materials and Fabrication Processes

A. Molybdenum Base Alloys (TZC)
Mo+(1.2-1.5)Ti+(.15-.21)Zr+(.11-.14)C

Electrode Preparation

Molybdenum powder containing 1734 ppm carbon was used in preparing the four electrodes for arc melting. The electrodes were hydropressed at 35,400 psi to 2.27 inches O.D. x 25 inches long, having a .74 inch concentric hole running through the entire length. The electrodes were sintered at 1850°C for six hours in a hydrogen atmosphere. Table IAI is a description of the sintered electrodes and analysis of molybdenum powder. The overall average density of the sintered material was 96% of theoretical, having a carbon content of about 1100 ppm. Physically, the electrodes were fairly uniform in size without noticeable distortion lengthwise. The electrodes were then threaded and joined to form a single electrode, 88.25 inches long, weighing 111.0 pounds. Metallic alloying additions were made by inserting, in the center hole, the proper amounts of Ti and Zr rods. Two sizes of Zr (.1" and .085") from the same lot of material plus a .370" Ti rod were inserted to make the required composition. Table IAII is a complete vendor analysis of the Zr and Ti additions.

Arc Melting

Two ingots, TZC-1 and TZC-2, were melted into a four inch diameter copper crucible. The diameter of the cast ingot was 3.908 inches. Melting conditions are shown in Table IAIII. It should be noted that the melting parameters are almost identical for both castings with TZC-2 having only a somewhat slower melting rate.

The two ingots were then machined to 3.620 inches diameter to obtain a smooth surface and inspected by ultrasonic, die penetrant, and microstructural techniques for piping, microcracks and other defects. From Table IAIV, it is evident that 1-3/4 inches were discarded from the top due to piping. Two to three inches were cropped because of hairline cracking, indicated by ultrasonic testing, and corroborated by subsequent microstructure examination. The total ingot conditioning losses in melting TZC-1 and TZC-2 were about 45 and 40%, respectively. The two billets then were turned down to 3.490 inches diameter for extrusion, with a 45° nose camfer and a 1.5 inch nose diameter. Figure IA1 shows the two machined billet.

Metallographic Examination

Prior to further processing, a slice 1/2 inch thick was sawed from the top of each casting. This was done after cropping defective material as shown previously in Table IAIV. Each slice was then bisected: The first section was used for hardness, macrostructure and chemical analysis; the second half was cut as shown in Figure IA2, in order to examine the transverse and longitudinal microstructure and to obtain grain size measurements. As shown in Figure IA2, Sections 1, 2, and 3 represent longitudinal sections progressing from the outside to the center of the casting, while Sections 4,5, and 6 represent transverse sections progressing from the center to the outside. Using the ASTM Heyn Intercept method, the grain size of all sections is shown in Table IAV.

Average hardness of five readings on the cast ingots, measured in the radial direction using a 1 kg load,was 233 DPH. Variations of hardness readings were about -6 + 4 DPH. This small variation is significant since it is an indication of the extent of alloying and homogenization obtained in melting.

Metallographic preparation was tedious and accomplished by mechanical polishing then swab etching the specimen in a solution of 2 gr. $K_3Fe(CN)_6$ + 6 gr. NaOH + 600 cc H_2O. The macrostructure as revealed in Figure IA3 shows the extent of grain refinement due to the alloying additions. Typical unalloyed molybdenum has a grain size at least twice as large as that observed for TZC. Examination of the microstructure as shown in Figures IA4 and IA5 reveals a heavy carbide network around each grain and abundant distribution of fine carbide particles within the grains. Identification of the dispersion phases in TZC-type alloys has been made by Chang (1). It is most probable that in both TZC-1 and TZC-2 the coarse particles are Mo_2C and the fine particles are TiC and ZrC.

Chemical Analysis

Complete analysis for metallics as well as Ti and Zr additions and interstitials are shown in Table IAVI. Sections taken from the same slice used in macrostructural studies were consumed in these analyses. It is worth mentioning that the precision in carbon determination is $\pm$10%. Also, the carbon in the castings seems to be 50 to 100 ppm higher than that of the sintered electrodes.

Primary Break-Down

Extrusion of castings TZC-1 and TZC-2 was done at the Research Laboratory of the General Electric Company under the supervision of Mr. John Hughes. The extrusion press used was a 1250-ton Loewy. The billets were heated in a hydrogen atmosphere furnace at 1750 $\pm$5°C for

one hour. Dies with a 130° die angle were plasma sprayed with ZrO_2 and lubricated with No. 7052 glass powder plus graphite. The billet lubricant was No. 7052 glass.

Under these conditions, an extrusion constant of 84,500 psi was obtained for TZC-2 using the theoretical relationship - $P = K \ln Ao/A$ - where P is the breakthrough pressure, Ao/A is the extrusion ratio and K is the extrusion constant. This value agrees well with that obtained by D. R. Carnahan and V. DePierre (2) of approximately 83,000 to 95,000 psi. No K factor could be obtained from extrusion of TZC-1 because of a failure in instrumentation.

Extrusion at a ratio of 6.2:1 was fairly successful in spite of several tears in the extruded bar. The complexities of high extrusion ratios at high temperature with attendant problems of lubricant breakdown and contamination are all at least partly responsible for the surface tears. Figure IA6 shows TZC-1 and TZC-2 extrusions after machining to 1.315 inches and 1.370 inches respectively.

After eliminating about 2 inches from each extruded end, sections from TZC-1 were examined for microstructure and hardness. Figure IA7 reveals a structure which is mostly wrought with the exception of a few small areas which appear to be partially recrystallized, again probably due to the high extrusion temperature and high reduction ratio. The average hardness over the cross-section was 274 $\pm$10 DPH using a 1 kg. load.

TABLE IAI

Description of Sintered TZC Electrodes

Prior to Melting

Electrode Number	Overall Density	Individual Carbon (ppm)				Avg. Carbon (ppm)	Gas Analysis (ppm) O	N	H_3
1	96.2%	829	1136	933	1022	980	9±5	3±3	1±1
2	96.2%	1310	1089	1155	1088	1160	8±5	5±5	1±1
3	96.4%	1272	1247	952	1252	1181	6±5	6±5	1±1
4	96.3%	1203	945	1259	900	1077	8±5	6±5	1±1

Size: 2.27 inches O.D. x 0.74 inches I.D. x 25 inches long

Chemical Analysis of Nickel Powder

Element	ppm	Element	ppm
Al	<8	Cu	4
Ca	<5	W	82
Si	<19	Mn	10
Fe	<35	Mg	<10
Cr	10	Sn	8
Ni	<5		

TABLE IAII

Analysis of Metal Additions to TZC Melting Electrodes

A. Zirconium Rod (0.100 and 0.085 inch diameters)

Vendor (Wah Chang Corporation) Analysis

	Top ppm	Bottom ppm
C	<30	40
H	3.2	3.2
N	17	29
O	60	80
Al	<25	<25
B	<0.2	<0.2
Cb	<100	<100
Cd	<0.3	<0.3
Co	<5	<5
Cr	40	32
Cu	<25	<25
Fe	120	150
Hf	125	1100
Mg	<10	<10
Mn	<10	<10
Mo	<10	<10
Ni	<10	<10
Pb	5	10
Si	<40	<40
Sn	<10	<10
Ta	<200	<200
Ti	<20	<20
V	<5	5
W	<25	<25
Zn	<50	<50
Ca	<10	10
Na	<10	<10
U	<0.5	

B. Titanium Rod (.375 in. dia.)

Vendor (Reactive Metals Inc.) Analysis

Carbon	0.03 wt. %
Nitrogen	.01 wt. %
Oxygen	.16 wt. %
Hydrogen	54/60 ppm

TABLE IAIII

Melting Data - TZC Alloy

Ingot No.	Current Amp.	Voltage Volts	Stirring Amp.	Predominant Vacuum Torr.	Casting inches	Casting lbs.	Melting Rate lb./min.
TZC-1	5000	37-38	.5	1.2×10^{-5}	11.14	49	3.3
TZC-2	5000	37-38	.5	1×10^{-5}	14	62	3.0

TABLE IAIV

Summary of Material Losses Incurred on Casting TZC

TZC-1 Length, inches	TZC-2 Length, inches	
11-1/8	14	As-cast length
1-3/4	1-3/4	Cut from top due to piping
2	3	Cut from top due to hairline cracks
1/2	1/2	Used for microstructure and NASA approval
3/4	7/16	Cut from bottom to remove starting pad
5	5-9/16	Total length lost from original as-cast ingot

TABLE IAV

Grain Size of Arc Cast Molybdenum Alloys (TZC)

grains per square millimeter

Section	TZC-1	TZC-2
1	5	12
2	11	14
3	16	8
4	23	25
5	19	22
6	14	18

TABLE IAVI

Analysis of Molybdenum Alloys (TZC)

Spectro Analysis ppm

Ingot No.	Al	Ca	Si	Fe	Cr	Ni	Cu	Mn	Mg	Sn	Ag	Pb
TZC-1	<8	<5	42	43	<8	6	6	12	<10	<7	<1	<10
TZC-2	<8	<5	29	29	<8	<5	5	<10	<10	<7	<1	<10

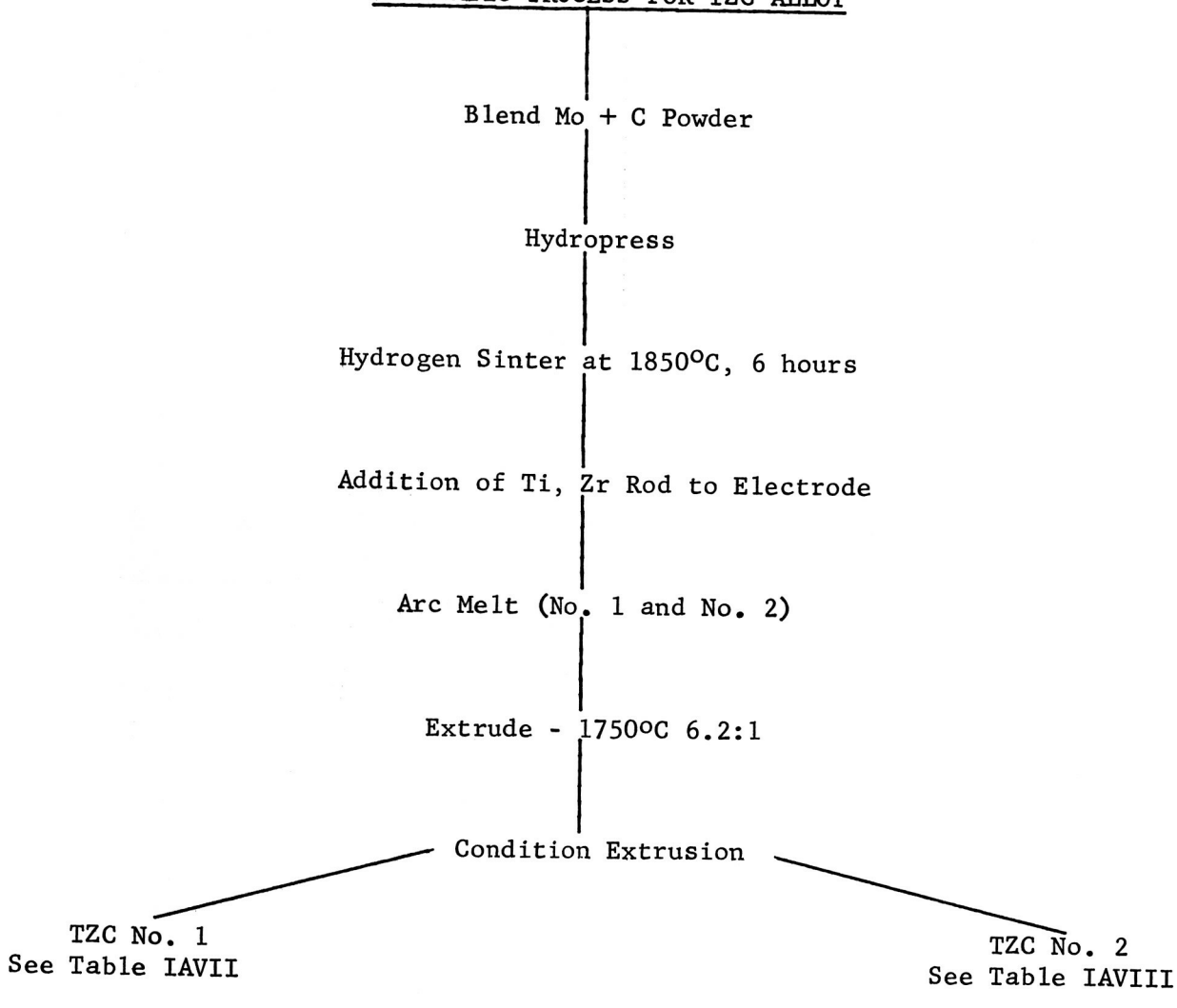
Gas Analysis ppm

Ingot No.	Carbon	Oxygen	Nitrogen	Hydrogen
TZC-1	1257	3±3	1±1	1±1
TZC-2	1326	3±3	1±1	1±1

Chemical Analysis (% by Wt.)

Ingot No.	Titanium	Zirconium
TZC-1	1.2±.1	.26±.04
TZC-2	1.2±.1	.25±.04

SCHEMATIC PROCESS FOR TZC ALLOY



Rod Breakdown and Wire Drawing

The problem of developing a fabrication technique for producing .005 inch diameter TZC wire with optimum creep properties at 2000°F-2200°F was analyzed in parts. The approach was to first develop a workable process to fabricate TZC from 1-1/2 inch rod to .005 inch diameter wire with minimum loss of chemistry (decarburization) and free of contamination and physical defects such as splits, slivers, etc. Once a routine is established, modifications in annealing points and temperatures, coupled with processing variables, could be investigated to develop the most optimum wire for creep properties at 2000°F to 2200°F.

Two extruded bars, one from TZC-1 and one from TZC-2, were conditioned by local grinding to remove tears and seams prior to rolling. In addition, two remaining bars, one from each ingot, were set aside to be processed at a later date, pending the results of the initial trials.

Both bars were rolled on a 3-high rod mill using 10 diamond shaped passes, one oval and a final round pass at .650 inch diameter. The bars were first soaked in a hydrogen furnace at 1475°C for 30±5 minutes, a temperature thought high enough for fabrication and low enough to prevent uncontrolled recrystallization prior to or during rolling. Two rolling passes were made between reheats which were of sufficient duration to return the bar temperature to 1475°C. Exit rolling temperatures ranged from 1375°C to 1275°C. Rolling and swaging details are shown in Table IAVII and TZC-1 and Table IAVIII for TZC-2.

"Alligatoring" (end splitting) occurred on the sixth and ninth pass on TZC-1 and on the ninth pass on TZC-2. After the ninth pass, TZC-2 was cut in half to permit full entry into the furnace for reheating. This is shown as A and B in Table IAVIII. Whenever alligatoring occurred, the rods were cooled to room temperature and the split end cut off at a point where splitting had disappeared. The rods would then be reheated to the 1475°C rolling temperature and processing continued.

At .650" diameter, all three rods were annealed at 1600°C for two hours in hydrogen in an attempt to recrystallize the structure prior to swaging. The degree of strain in the rolled rod was not as high as anticipated because microstructural studies showed the material to be approximately 60% recrystallized with general fiber widening in the non-recrystallized areas. Figure IA8 shows representative areas of the center, mid-radius, and edge at .650" diameter after heat treatment at 1600°C for two hours.

TZC-1 was too short to swage on the regular production lines so it was set aside to be hand swaged. TZC-2 was swaged through 0.560", 0.460", 0.390", and 0.345" diameters without incident. The temperature during swaging ranged from 1350°C to 1250°C in an effort to retain TiC in solution and redistribute what Mo_2C might be present at the grain boundaries. At 0.345" diameter, TZC-2 was recrystallized at 1750-1800°C for 60 minutes in argon. Metallographic samples were taken at this size and Figure IA9 shows representative microstructures before and after recrystallization. The recrystallized grain count was 1200 to 1600 grains per square millimeter for both TZC-2 rods. The structure is relatively clean and free of large carbide particles, so it is evident that most of the TiC was put into solution while the massive Mo_2C presumed to be at the grain boundaries of the ingot and extruded bar have been redistributed or solutioned at this stage of processing. Recrystallized hardness was 178 DPH using a 1 kg. load.

The recrystallized rods were further swaged at 1200°C to .250" diameter and were then centerless ground to 0.236" diameter to assure removal of the decarburized surface that measured approximately 0.004" in depth. The rod was prepared (oxidized) and hot drawn (850°C) through carbide dies to 0.186" diameter in two passes. The material was found to be badly split at this size. Figure IA10 shows a typical worked structure at 0.186" diameter.

Sections of unsplit material from TZC-2 at .186" were swaged at 1050°C to .122" diameter in an effort to attain more "work" in the material in order to overcome the brittle behavior. After three passes on the draw bench, the material was still brittle at .100" diameter. Examination of the surface at 30X revealed fine hairline transverse cracks estimated to be about .002" in depth. The material was etched in molten caustic-Nitrite salts to remove approximately .005" from the diameter and was then found to be ductile. The microstructure did not reveal contamination (Figure IA11) therefore, it is assumed that the brittle behavior was a result of the "stress raiser" effect of the fine transverse cracks.

By using the surface removal techniques described above and following the process shown in Table IAVIII, 1350 feet of 0.005" diameter wire was produced from part of TZC-2.

The work hardening characteristics of the alloy were measured by tensile tests from the .048" anneal point to .010" diameter where the material required another anneal to enable further processing to .005" diameter. The data is shown graphically in Figure IA12.

Samples of .185" diameter wire from TZC-2 were analyzed to determine the effect, if any, of processing contamination or loss of chemistry due to processing. The results are shown in Table IAIX. A slight loss of carbon is observed at this stage in the processing.

TZC-1 was hand-swaged with 20% reductions per pass from 0.650" diameter to 0.460" diameter where it attained enough length to fit the production equipment. From this point, through centerless grinding, (0.236") it was processed similarly to the TZC-2 rods. Swaging proceeded without incident from 0.236" diameter to 0.186" diameter. The rod was drawn from 0.186" to .111" in six passes using carbide dies, graphite lubricant and standard heating practice (800°C). At 0.111" diameter, the wire was still very brittle and failed by transverse cracking. The wire was cleaned, examined and found to be badly split. No further work was done on this section of TZC-1.

Discussion of Results

Fabrication through rolling and swaging was not difficult, temperatures were kept high, and from microstructure examination (after 0.345" recrystallization) the massive carbides evident in the "as extruded" wire bars were successfully broken up and distributed throughout. The decarburized layer that occurred during processing was removed by centerless grinding; however, it is recommended that grinding be eliminated from the conditioning process, based on the results in heavy wire drawing. Figure IA13 shows an area that was spot conditioned by grinding and then swaged two passes of 20% R.A. The photograph shows the surface rupturing that occurred at the ground areas during processing. Surface removal should be accomplished through chemical or electrochemical etching to eliminate the possibility of localized surface stresses.

A quantity of 1,350 feet of .005" diameter TZC-2 was produced from short pieces of rod and wire that did not have splits or transverse cracks by the routine described in Table IAVIII.

Future Recommendations

The remaining extruded bars of TZC-1 and TZC-2 will be processed, one at a time, following the best routine developed during the first six month period.

Rod rolling temperatures will be maintained at 1475°C, but we will resort to double passing and more frequent reheating, in an effort to eliminate the loss due to alligatoring. Swaging temperatures will be dropped to 1200°C and the drafts will be lowered to a uniform 20% R.A. per pass. The anneal after rolling will be eliminated in order to attain a finer grain size at the recrystallization point in swaging.

Swaging will be maintained through at least 85% R.A. after retreat and before going into wire drawing. Surface removal will be accomplished via chemical and electrochemical means at critical points after annealing and before wire drawing. A trial will be made using stress relief anneals rather than full anneals, to see what effect it has on finished properties.

TABLE IAVII

Processing of Extrusion TZC-1

1.478" diameter extruded rod

Rod rolled 12 passes at 1475°C
Reheat every two passes
Finish size: 0.650" diameter
Total R.A. - 80.7%

↓

Annealed at 1600°C - 2 hrs. in H_2

↓

Swaged at 1250°C - 1300°C

↓

.580" - 20% R.A.
.520" - 20% R.A.
.460" - 20% R.A.
.390" - 30% R.A.
.345" - 21% R.A.

↓

Recrystallized 1750°C-1800°C - 60 Min. - Argon

↓

Swaged to

↓

.295" - 27% R.A. - 1175°C
.250" - 28% R.A. - 1050°C

↓

Centerless ground to .235"

↓

Swaged to

↓

.210" - 20% R.A. - 1120°C
.185" - 22% R.A. - 1120°C

↓

Draw Bench

↓

.170" - 15% R.A. - 800°C
.152" - 20% R.A. - 945°C
.132" - 23% R.A. - 900°C
.125" - 10% R.A. - 850°C
.119" - 10% R.A. - 850°C
.111" - 10% R.A. - 850°C

↓

Production on TZC-1 Curtailed
Material 100% Split

TABLE IAVIII

Processing of Extrusion TZC-2

1.466" diameter extruded rod
Rod rolled 12 passes at 1475°C
Reheat every two passes
Finish size: 0.650" diameter
Total R.A. - 80.4%
Material cut in half during rolling due to excessive length and designated TZC-2a and 2b

Annealed at 1600°C - 2 hours in H_2

Swaged at 1250°C-1300°C

.560" - 25% R.A.
.460" - 32% R.A.
.390" - 28% R.A.
.345" - 20% R.A.

Recrystallize 1750°C-1800°C - 60 Min. in Argon

.295" - 27% R.A. - 1200°C
.250" - 28% R.A. - 1200°C

Centerless ground to .235" diameter

Draw Bench

.205" - 23% R.A. - 800°C
.186" - 18% R.A. - 800°C

Both rods 2a and 2b were found to be 50% split. Split sections were cut out, and processing was continued with sound material.

← TZC-2b	TZC-2a →
Swaged at 1050°C-1100°C	Wire Draw
.170" - 15% R.A.	.178" - 8% R.A. - 800°C
.152" - 20% R.A.	.170" - 8% R.A. - 800°C
.136" - 20% R.A.	.165" - 6% R.A. - 800°C
.122" - 20% R.A.	Material broke up - 75% split with many transverse cracks
Wire Drawing at 800°C	
.110" - 14% R.A.	
.105" - 10% R.A.	
.100" - 10% R.A.	
Electroclean and etch to .094" diameter	

TABLE IAVIII (Cont'd.)

Finish Drawing TZC-2b

.085" dia.	18% R.A.	850°C
.077" dia.	18% R.A.	850°C
.0685" dia.	20% R.A.	850°C
.061" dia.	20% R.A.	850°C
.054" dia.	20% R.A.	850°C
.048" dia.	20% R.A.	850°C

Anneal 1475°C - 30 min. ± 5 min. in H_2

20% drafts to .010" diameter at 700°C

Strand anneal at 1250°C, 2 meters per min. through 10" heat zone in H_2

20% drafts to .005" diameter at 700°C

Electroclean

Yield:	3 spools -	65 meters	(8.3 gms)
		95 meters	(12.2 gms)
		251 meters	(32.2 gms)
	Total -	411 meters or 1,350 feet of .005" TZC	

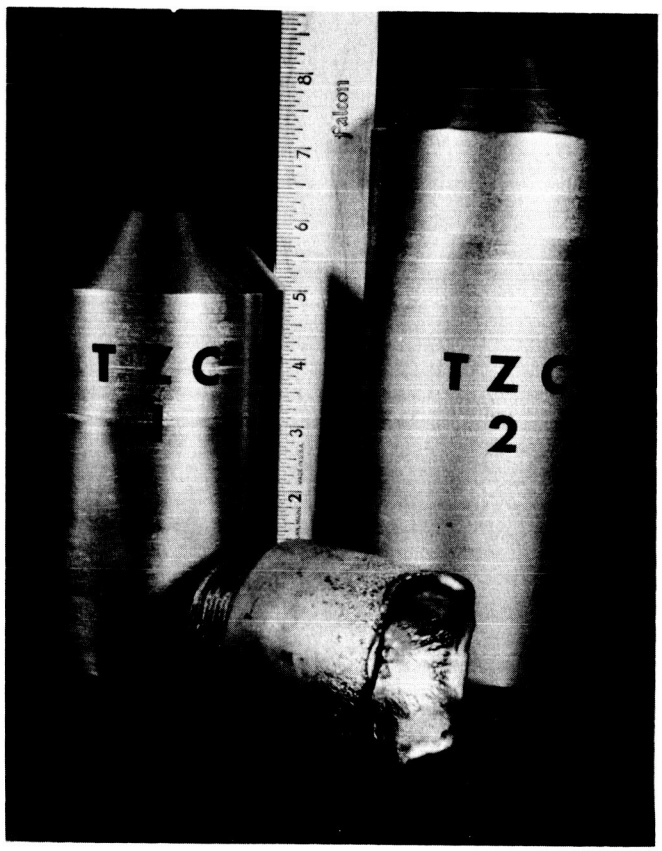


FIGURE IA1 - Machined arc-cast ingots prior to extrusion and stub of melting electrode

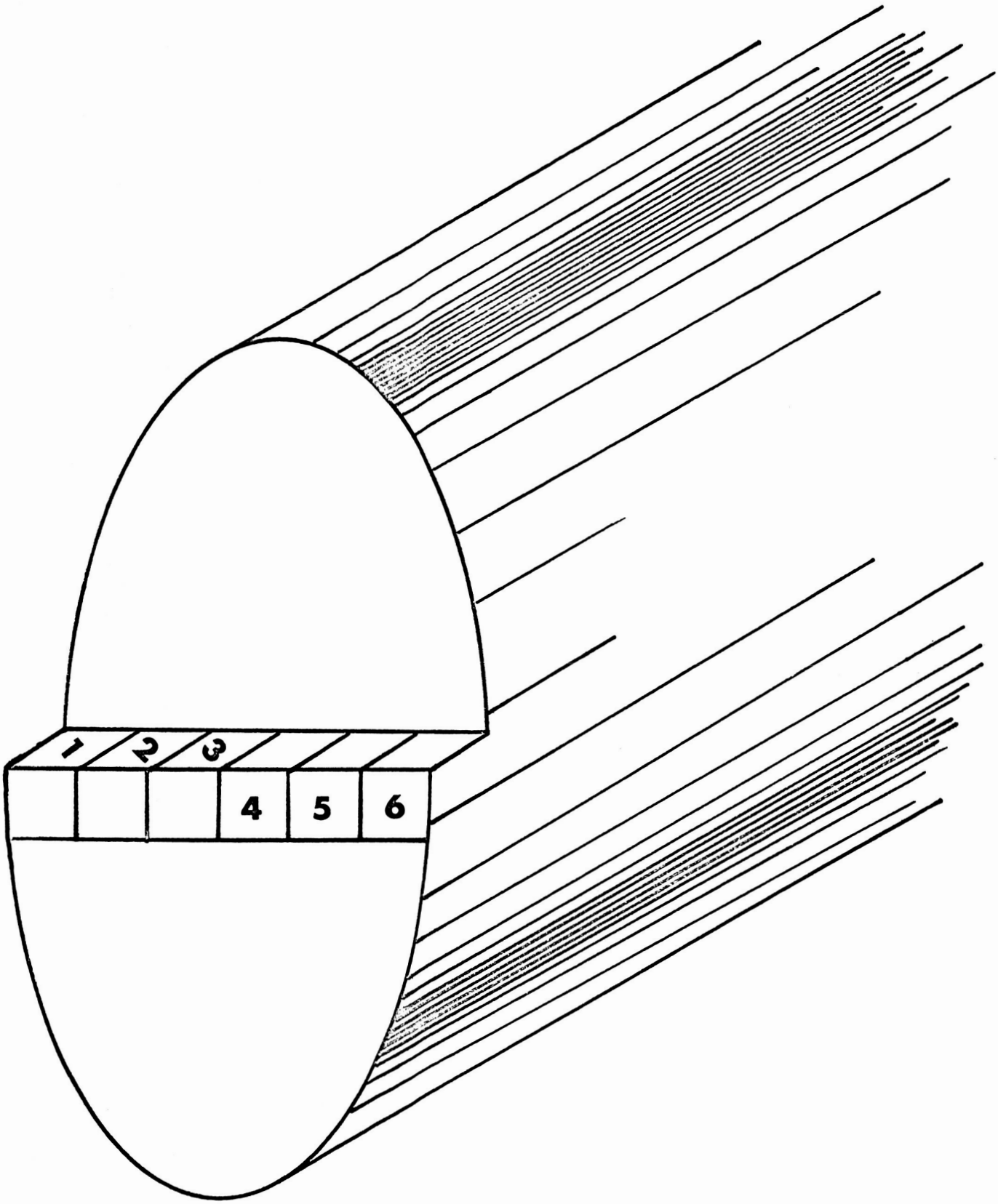


FIGURE IA2 - Metallographic Sections in TZC Cast Billets

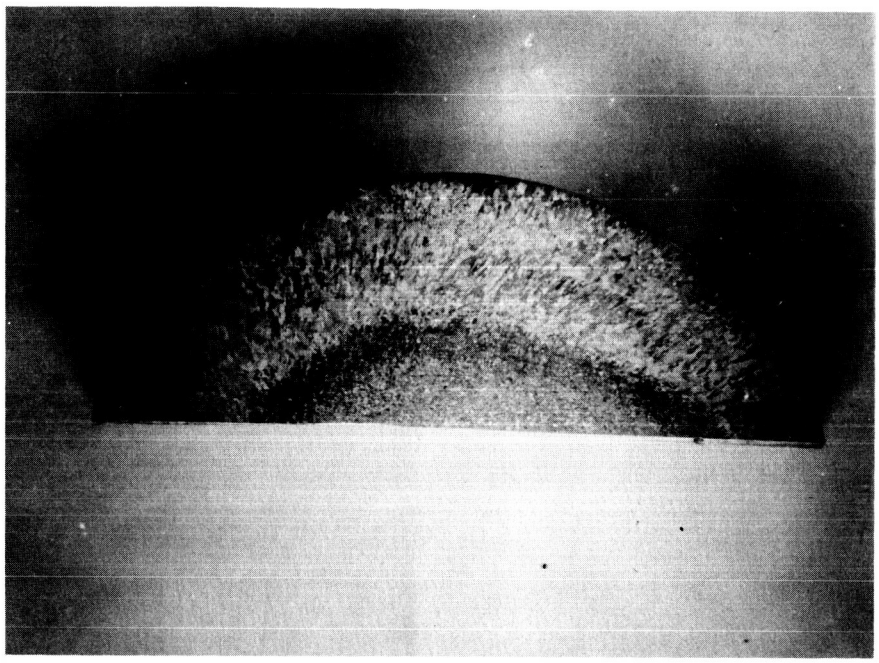
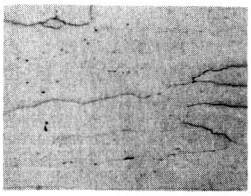
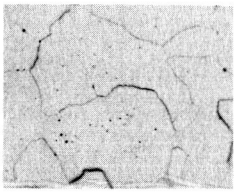


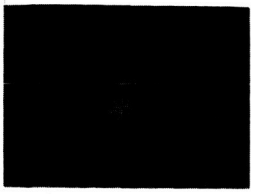
FIGURE IA3 - Macrostructure of cast TZC ingot



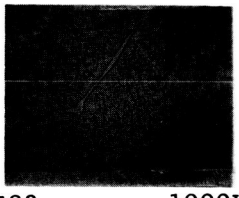
7768 100X



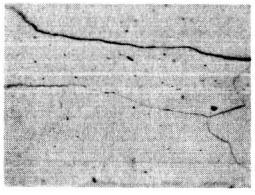
7771 100X



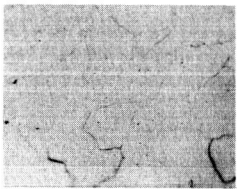
7780 1000X
Longitudinal - Section 1



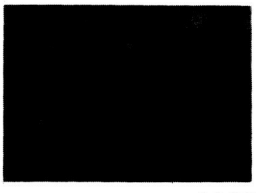
7783 1000X
Transverse - Section 4



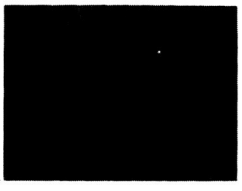
7769 100X



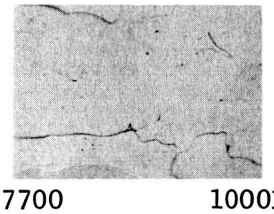
7772 100X



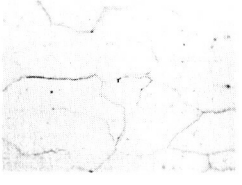
7781 1000X
Longitudinal - Section 2



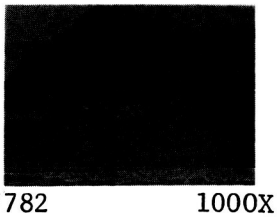
7784 1000X
Transverse - Section 5



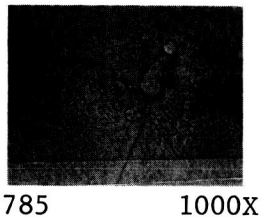
7700 1000X
Longitudinal - Section 1



7773 100X



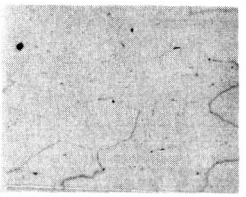
7782 1000X
Longitudinal - Section 3



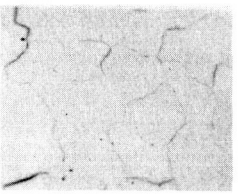
7785 1000X
Transverse - Section 6

FIGURE IA4 - Microstructure of Ingot TZC #1 as indicated in Figure IA2

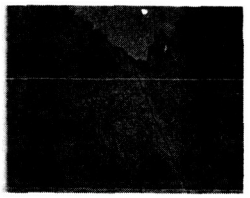
TZC-2



7774 1000X



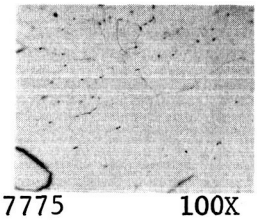
7777 100X



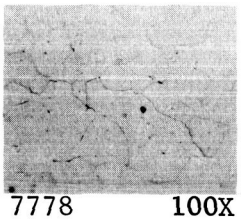
7756 1000X
Longitudinal - Section 1



7789 1000X
Transverse - Section 4



7775 100X



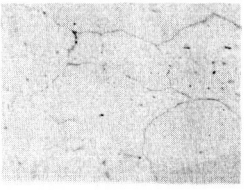
7778 100X



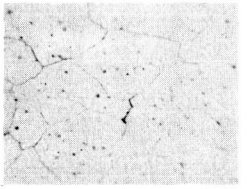
7787 1000X
Longitudinal - Section 2



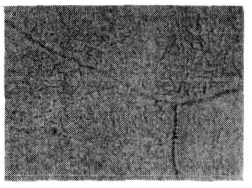
7790 1000X
Transverse - Section 5



7776 100X



7779 100X



7788 1000X
Longitudinal - Section 3



7791 1000X
Transverse - Section 6

FIGURE IA5 - Microstructure of Ingot TZC #2 as indicated in Figure IA2

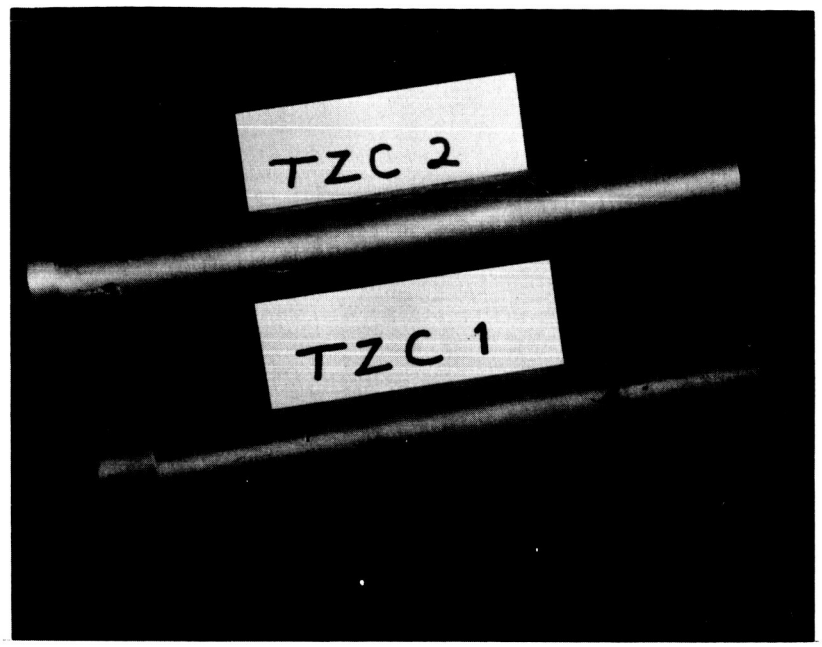
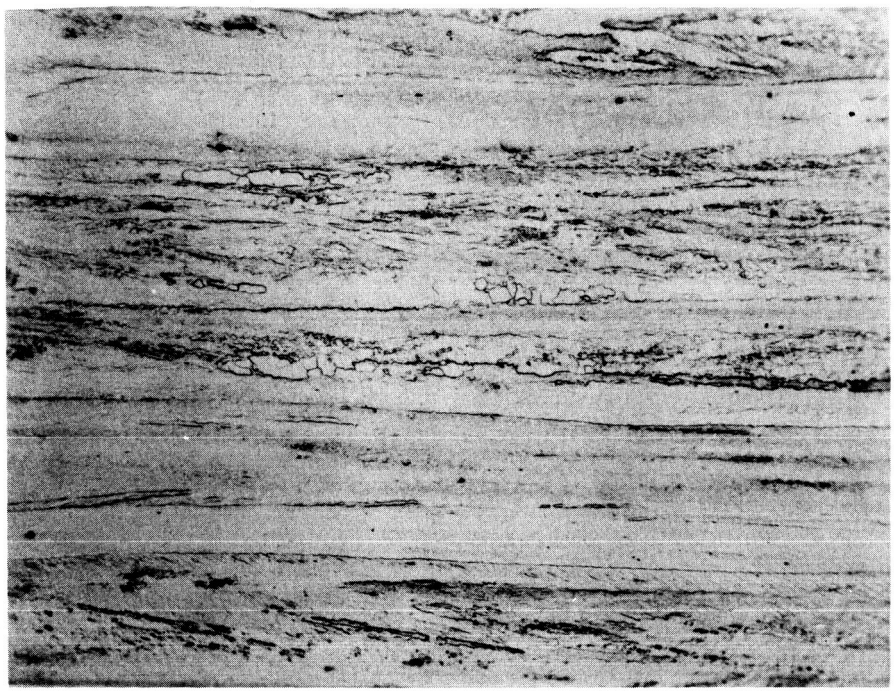
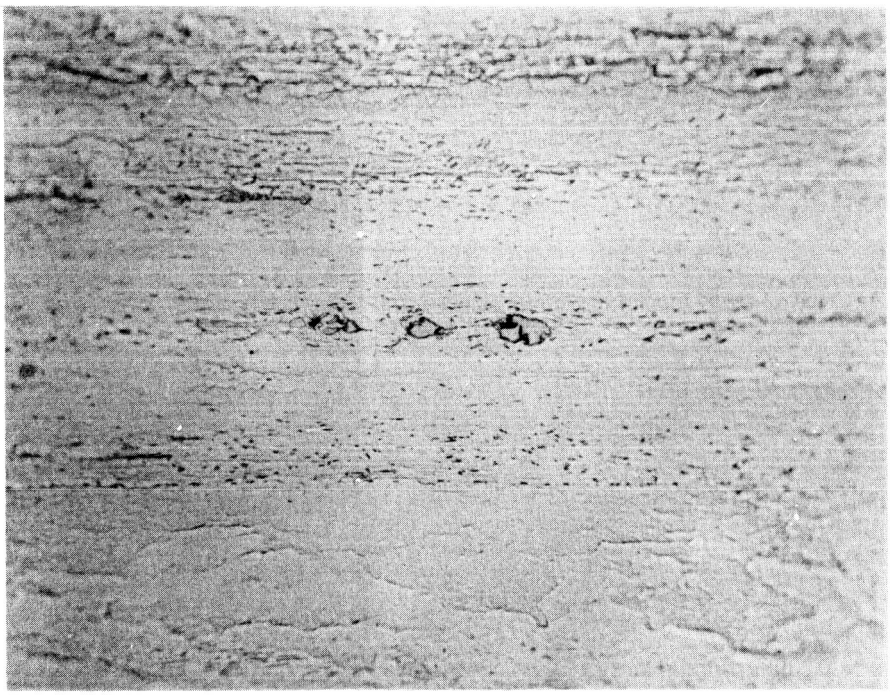


FIGURE IA6 - Machined extrusion of TZC showing localized defects

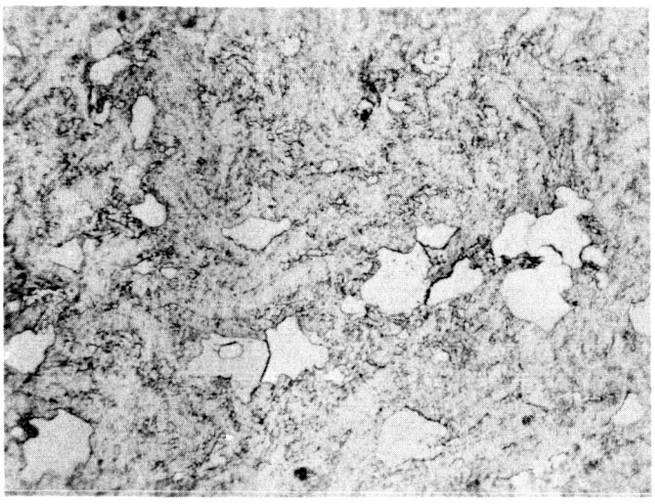


100X

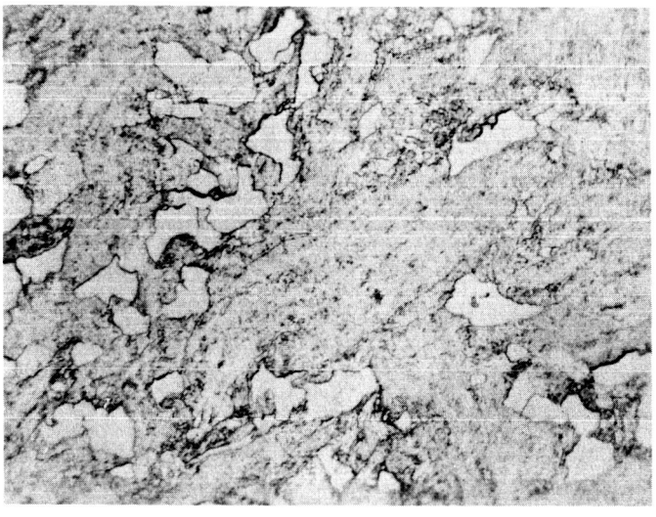


1000X

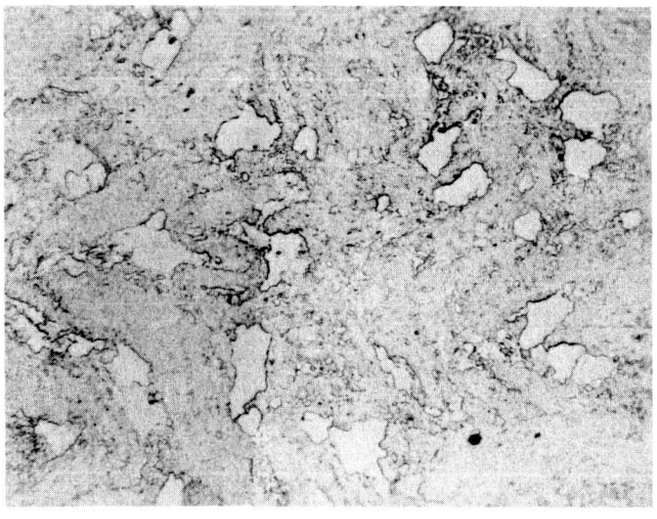
FIGURE IA7 - Microstructure of TZC extrusions showing predominantly cold worked material with small areas of recrystallized, equiaxed grains



314C Transverse Center 250X



314M Transverse Mid-Radius 250X

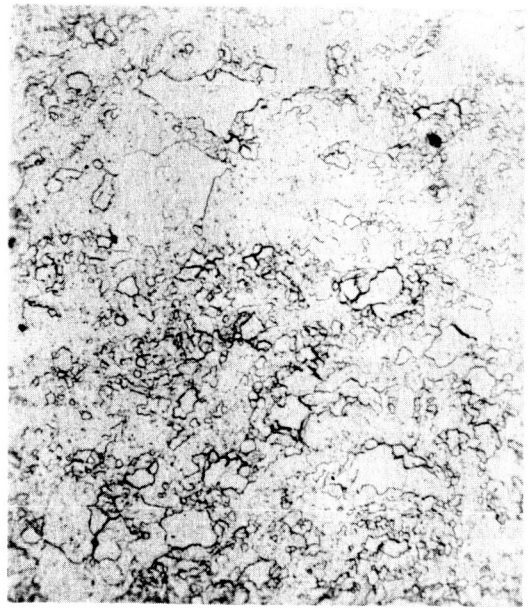


314E Transverse Edge 250X

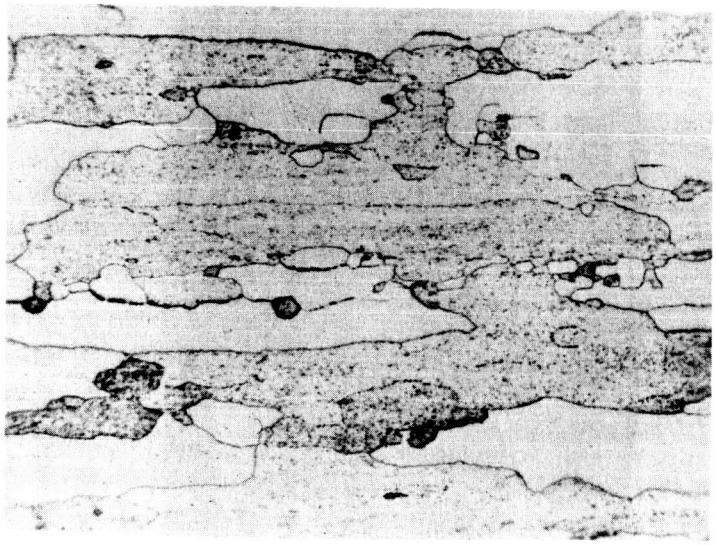
FIGURE IA8 - Typical microstructures of TZC at 0.650" diameter after annealing at 1600°C for two hours in hydrogen



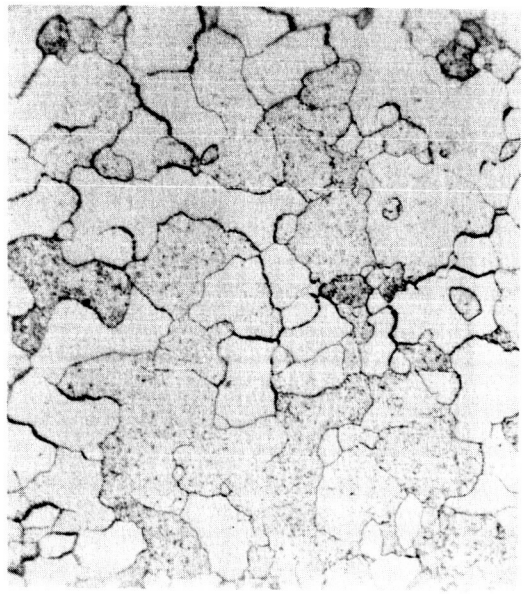
320L Longitudinal 250X



320T Transverse 250X

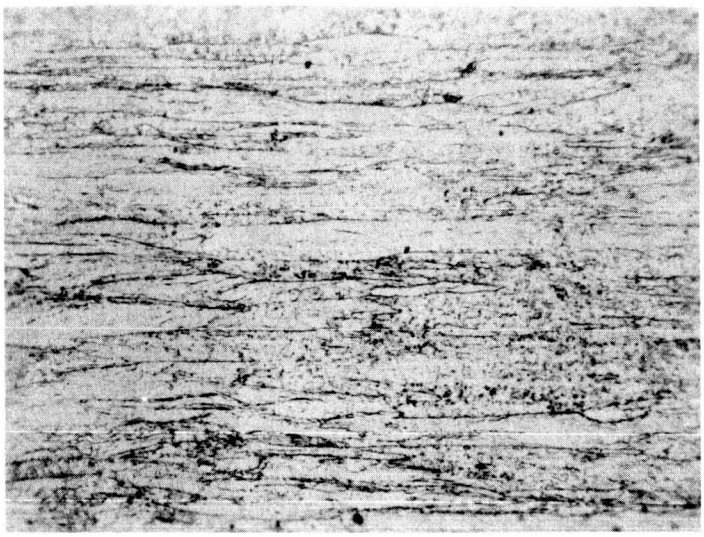


321L Longitudinal 250X

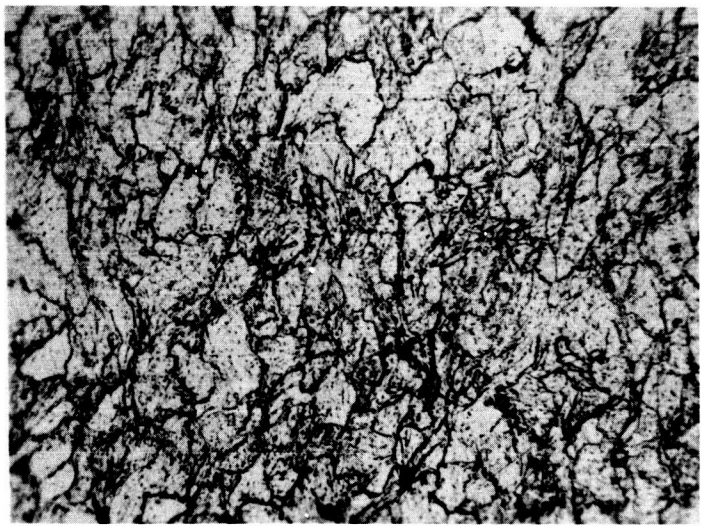


321T Transverse 250X

FIGURE IA9 - Typical microstructures of TZC before and after recrystallization (1800°C - one hour) at 0.345" diameter

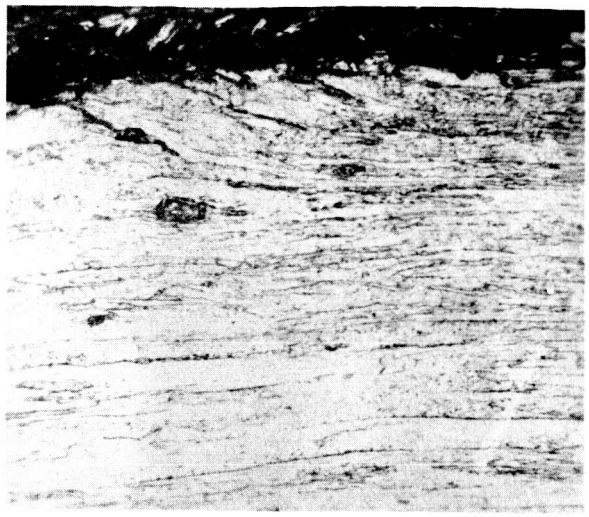


331L Longitudinal 250X



331T Transverse 250X

FIGURE IA10 - Typical as worked microstructure of TZC at 0.186" diameter

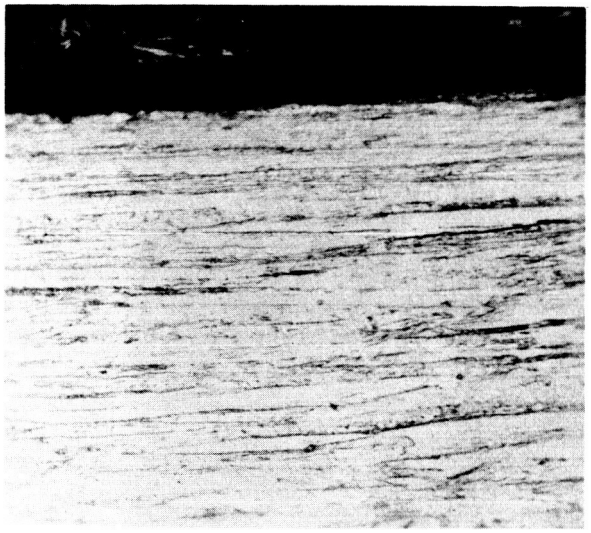


361L 250X

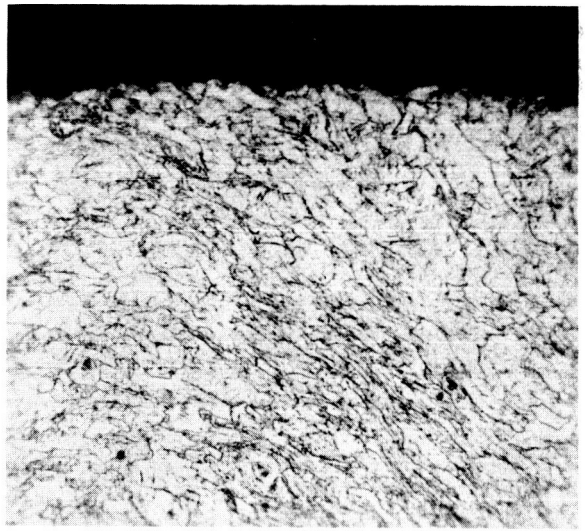


361T 250X

Unetched Surfaces



361L 250X



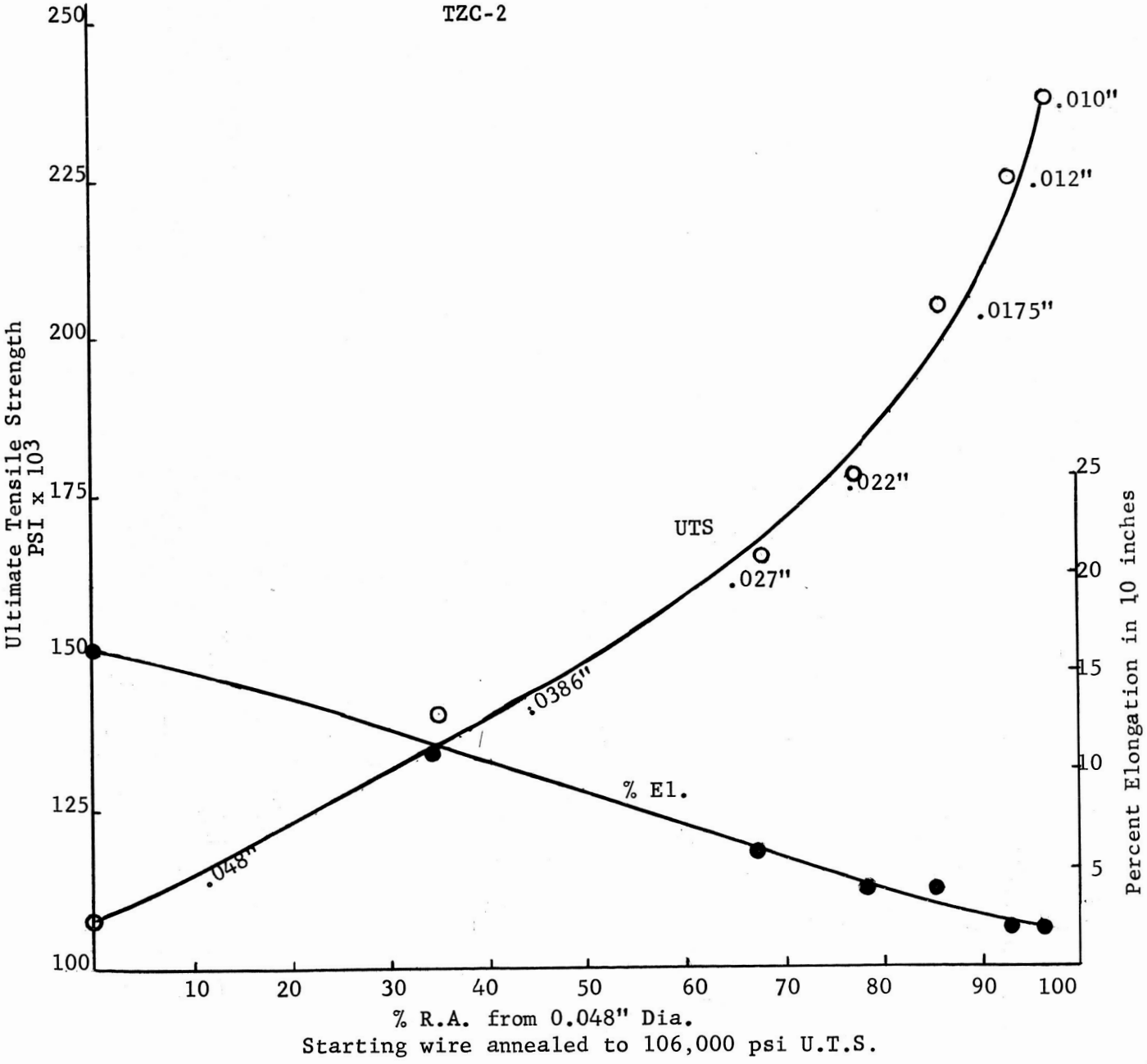
361T 250X

Etched Surfaces

FIGURE IA11 - **Surfaces** of TZC rod (0.100" diameter) indicating "cracks" possibly responsible for brittle behavior (top) and surface after etching. Lack of microstructural evidence of surface contamination is also apparent.

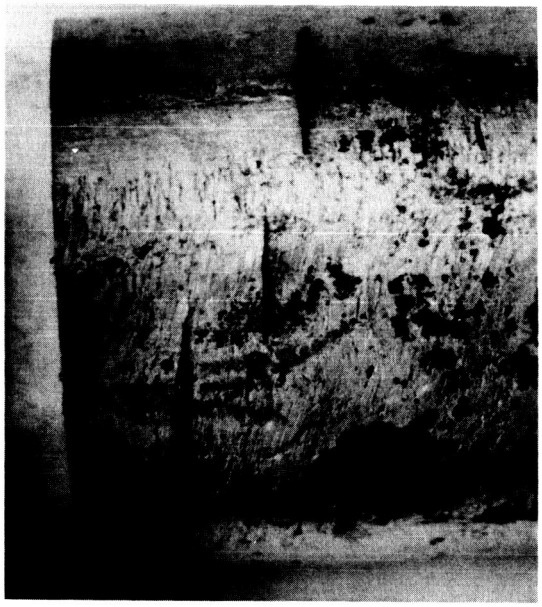
FIGURE-IA12

Change in Room Temperature Tensile Strength
and Percent Elongation Versus Percent
Reduction in Area
TZC-2



Notes:

1. Yield strength data was not recorded because chart speed was too slow to accurately determine intersection at 0.1% offset.
2. Starting material was .048" diameter TZC-2b annealed 1475°C for 30 min., process temperature during wire drawing was 700°C-800°C
3. Strain rate was 0.2 in./in./min.



485 30X

FIGURE IA13 - Section of TZC rod spot conditioned by grinding and swaged showing evidence of surface rupturing.

B. Cb-Base Alloy, AS-30
Cb+(19-21)W+(0.8-1.0)Zr+(0.08-0.1)C

Electrode Preparation

Columbium granules were purchased from duPont deNemours and Company because of their low interstitial content, as presented in the vendor's analysis in Table IBI. The zirconium chips, obtained from Wah Chang Corporation, were attrition-milled to round shapes (-20 +40 mesh) which were more suitable for blending than the chips. Table IBII is a complete analysis of the zirconium. Tungsten "granules" in the -20 +40 mesh size were used as the tungsten addition. Carbon was added as "G" powder obtained from Fisher Scientific.

The blending of the components was performed in a V-cone blender, using a mixing time of 15 minutes. Prior experience had indicated that longer blending times lead to segregation of the widely variant density metals. After blending, the powder was packed into a columbium foil lined rubber mold to prevent the powder from sticking to the rubber. The mold was then hydrostatically pressed at 35,400 psi. Six logs, measuring approximately two inches in diameter were pressed. Figure IBI shows an as-pressed AS-30 log contained in Cb-foil. The as-pressed electrodes were strong enough to be handled as long as the Cb-foil was intact.

Sintering

The electrodes were individually sintered in a vacuum self-resistance furnace. This furnace provides for heating compressed powder ingots by means of their own electrical resistance. 720 KW of powder is available between a stationary top electrode and a movable lower electrode, both of which are made of copper and are water cooled. A vacuum of about 5×10^{-6} Torr. pressure is maintained by means of a 10 inch diffusion pump (using liquid nitrogen) backed by a six inch oil booster and a 140 $feet^3$/minute mechanical pump. Figure IB2 shows the described vacuum furnace.

Sintering increased the mechanical strength and electrical conductivity of the green compacts. A summary of the sintering parameters follows:

Log No.	Length Pounds	Length Inches	Sintering Temp. C	Sintering Hours	Vacuum X10^{-5} Torr.	Leak Rate Micron/hour
A	20.7	27	1750	1	8	1
B	22.2	26.25	1550	1	5	1
C	18.7	22	1500	2	2	.4
D	14.1	16	1500	2	2.8	.9
E	12.8	15	1600	2	1.4	.6
F	11.0	12.75	1500	2	4	1
Total	99.5	119				

Examination of the above data shows that the leak rate was about <1 micron/hour, and therefore, sintering was done predominantly at 10^{-5} Torr. pressure.

Sintering Log A at 1750°C for one hour caused considerable buckling of the electrode. Therefore, the rest of the electrodes were sintered at a lower temperature. Sintering the remaining electrodes at about 1550 ±50°C for two hours resulted in fairly straight, continuous lengths. A detailed description of the sintering schedule is shown in Table IBIII.

About one inch was cropped from each electrode end after sintering. The ends were cooler during sintering because they are held in the water cooled copper clamp. End losses amounted to about 10% of the electrode weight. After sintering, the Cb-foil was easily stripped off. Figure IB3 represents a typical cross section of sintered electrode.

Arc Melting

Two melting electrodes were prepared by joining the sintered bars using tungsten-inert-gas welding methods. Electrodes B, C, and D were joined together to form a 57 inch length weighing 48.5 pounds. Electrodes A, E, and F were welded together to form another melting electrode, 52 inches long weighing 42.5 pounds. A "starting pad" for the bottom of the melting crucible, weighing 16 pounds (of AS-30 composition), was hydropressed and then sintered by radiation heating at 1500°C for two hours. The final pad size was 3.908 inches in diameter x 6.5 inches long.

Two ingots, AS-30 No. 1 and AS-30 No. 2 were conventionally consumably melted from the above electrodes into a four inch copper crucible. Melting was done at the Refractory Metals Plant of the General Electric Company, Euclid, Ohio. The as-cast diameter of the ingot was 3.9 inches. Melting parameters are shown in Table IBIV.

Melting and Chemistry Approval

After machining the two ingots to 3.820 inches diameter to obtain a smooth surface and cropping about 1/2 inch from the top of the ingot, a slice 1/4 inch thick was taken for structure and chemistry analyses. Figure IB4a reveals the microstructure of AS-30 No. 1. It clearly shows that incomplete fusion of tungsten granules occurred during arc melting. The microstructure, at higher magnification, revealed the presence of a fine second phase(s) as shown in Figure IB4b.

Interstitial analysis of ingot AS-30 No. 2 was as follows:

C	789±80 ppm
O	23± 5 ppm
N	10± 5 ppm
H	1± 1 ppm

Future Plans

The incomplete tungsten fusion and the low carbon content will necessitate double melting. The two ingots as they now stand will be quartered and made into two new melting electrodes by welding the quartered sections together. Adjustment of carbon will also be made to raise the carbon level to 900 ppm ±100 ppm after remelting.

The double melted material will then be jacketed and extruded to provide starting material for rod and wire processing.

TABLE IBI

Analysis of Columbium Granules (ppm)

E. I. duPont deNemours and Company

O	77	Fe	<50
H	-	Cr	<30
N	5	Ni	38
C	12	Ti	<50
Ta	700	W	<50

TABLE IBII

Analysis of Zirconium Additions to AS-30 (ppm)

Wah Chang Corporation

Al	32	Mg	<10	Ti	36
B	0.4	Mn.	10	V	<5
C	80	Mo	<10	W	<25
Cb	<100	N	31	Zn	<50
Cd	<0.3	Ni	15	P	<10
Co	<5	O	1142	U	<0.5
Cr	155	Pb	6		
Cu	<25	Si	<46		
Fe	928	Sn	10		
Hf	69	Ta	<200		

TABLE IBIII

Typical Sintering Schedule of AS-30 Electrodes

(Electrode C)

Leak Rate, .4 micron/hour

Time Min.	Pressure Torr.	Amperes Approx. amp	Voltage Approx. volt	Temp. °C ±25	Note
Start	6×10^{-6}				
9	8×10^{-5}		2.5		
15	2×10^{-5}	800	5		
17	2×10^{-4}	960	5	~600	
18	9×10^{-5}	400	2.5	~600	Lowering power
27	9×10^{-5}	800	3	~600	
62	5.6×10^{-5}	800	3	~700	First hold for 35 min.
82	5.2×10^{-5}	1200	3.25	900	
89	6×10^{-5}	1600	3.75	1000	
102	7×10^{-5}	2400	4.25	1200	
107	9×10^{-5}	3200	5	1300	
117	3.4×10^{-5}	3200	5	1300	
132	3×10^{-5}	3800	5.4	1350	
147	3.6×10^{-5}	4500	5.6	1450	
162	4.5×10^{-5}	4800	5.8	1500	Final hold one hour
172	3.6×10^{-5}	4800	5.8	1500	
179	4.2×10^{-5}	4800	6.0	1500	
182	3.0×10^{-5}	4800	6.0	1500	
192	2.4×10^{-5}	4800	6.0	1500	
200	2.2×10^{-5}	4800	6.0	1500	
212	2.0×10^{-5}	4800	6.0	1500	
217	1.8×10^{-5}	4800	6.0	1500	
222	1.8×10^{-5}	Power off			

TABLE IBIV

Melting Data for AS-30

Ingot No.	Current Amp	Electrodes Used	Predominant Vacuum Torr.	Casting Inches	Casting Pounds	Melting Rate Lb/Min.
AS-30 No. 1	4300	B,C,D	4×15^{-4}	11.86	48.5	2.5
AS-30 No. 2	3800	A,E,F	5×15^{-5}	10.5	42.5	2.7

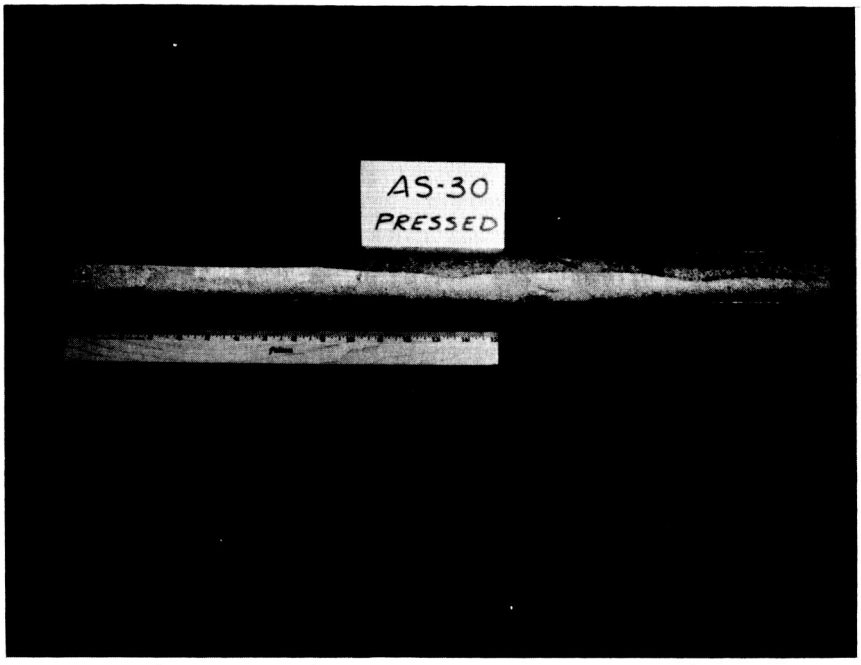


FIGURE IB1 - Cb-Base alloy, AS-30 electrode in the pressed condition

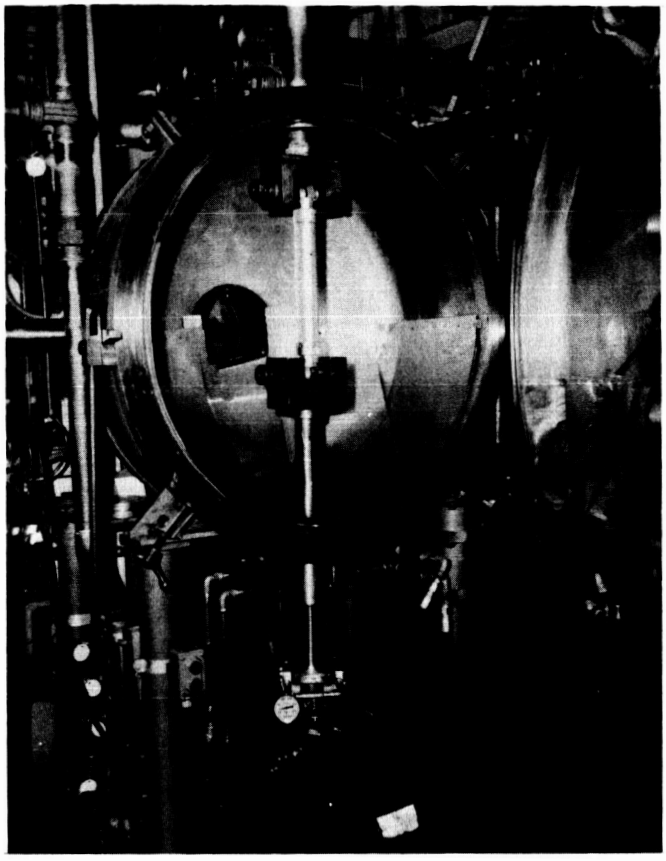
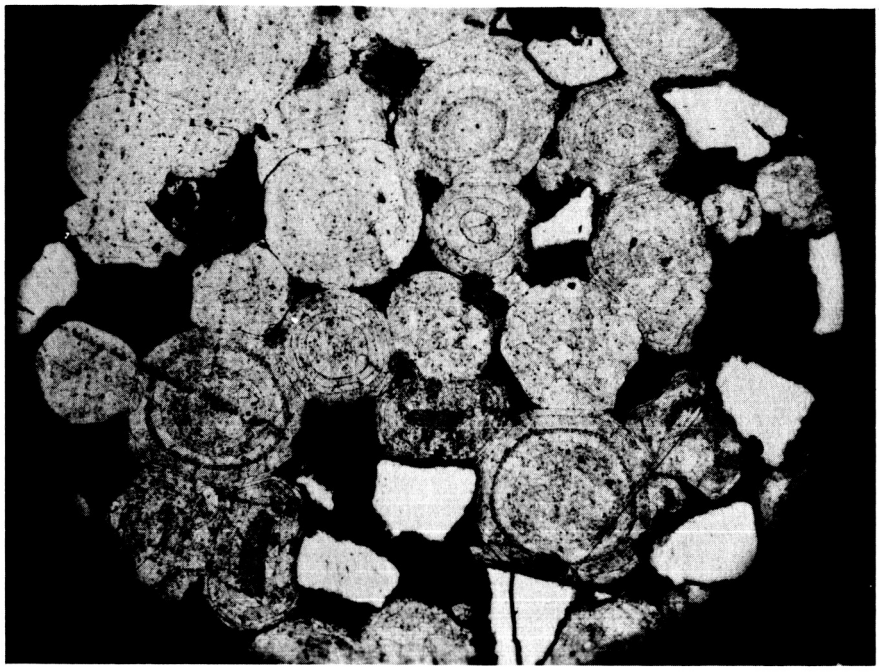
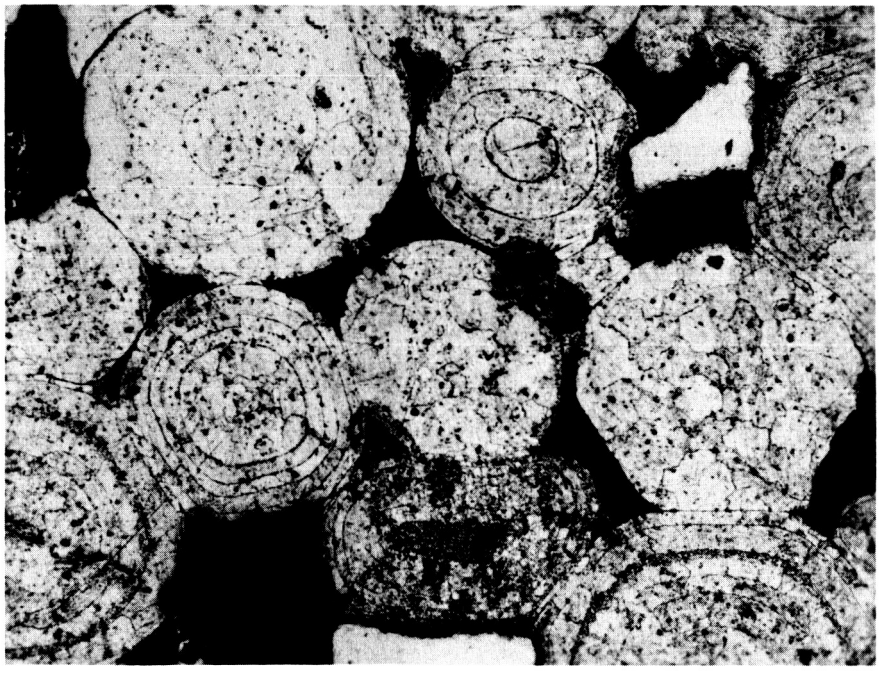


FIGURE IB2 - High vacuum resistance sintering furnace

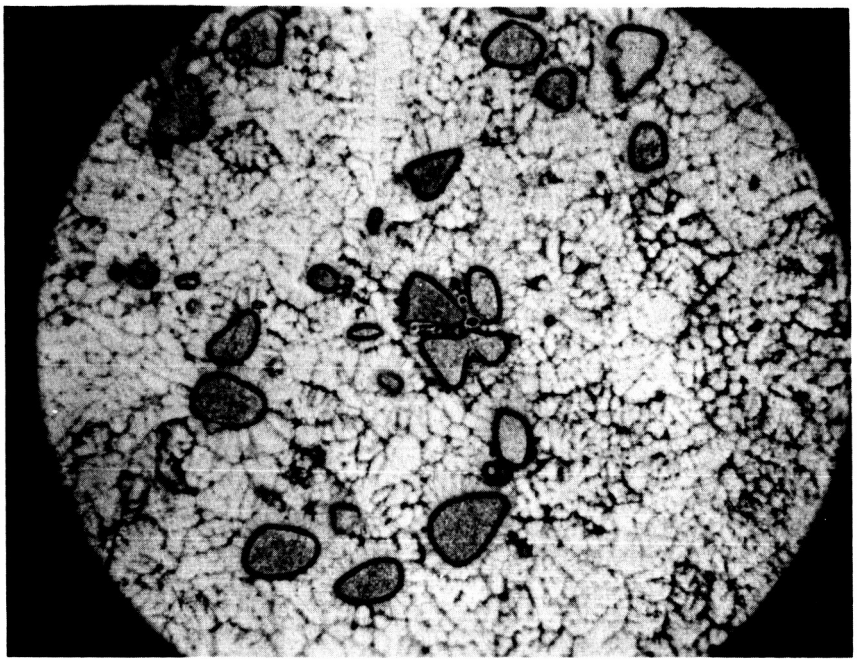


25X 7817



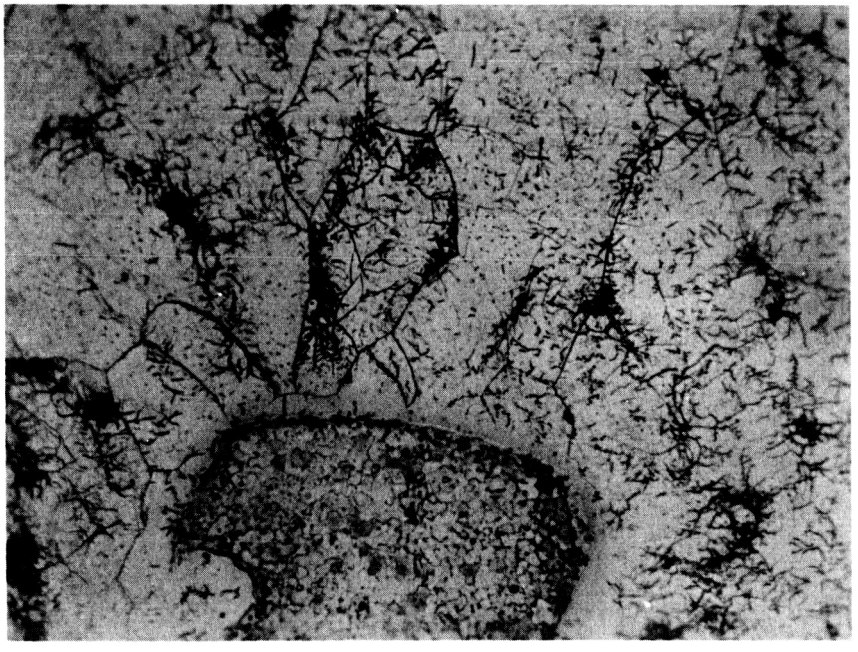
50X 7818

FIGURE IB3 - AS30 pressed and sintered "logs" made from columbium granules



25X 7835

FIGURE IB4a - Macrostructure of AS-30 No. 1



200X 7836

FIGURE IB4b - Microstructure of Cb-Base Alloy, AS-30 No. 1

C. Tungsten-Rhenium-Thoria Alloy
$W+(4-6)Re+(2-4)ThO_2$

Powder and Ingot Preparation

The development of a fabricable tungsten-rhenium-thoria ingot or bar, by powder metallurgy techniques, has progressed from the learning to the pre-production stage. Initially, problems were encountered with segregation of rhenium and with low, as-sintered, density. These problems now appear to be solved and attention has been shifted to ingot breakdown techniques and subsequent drawing.

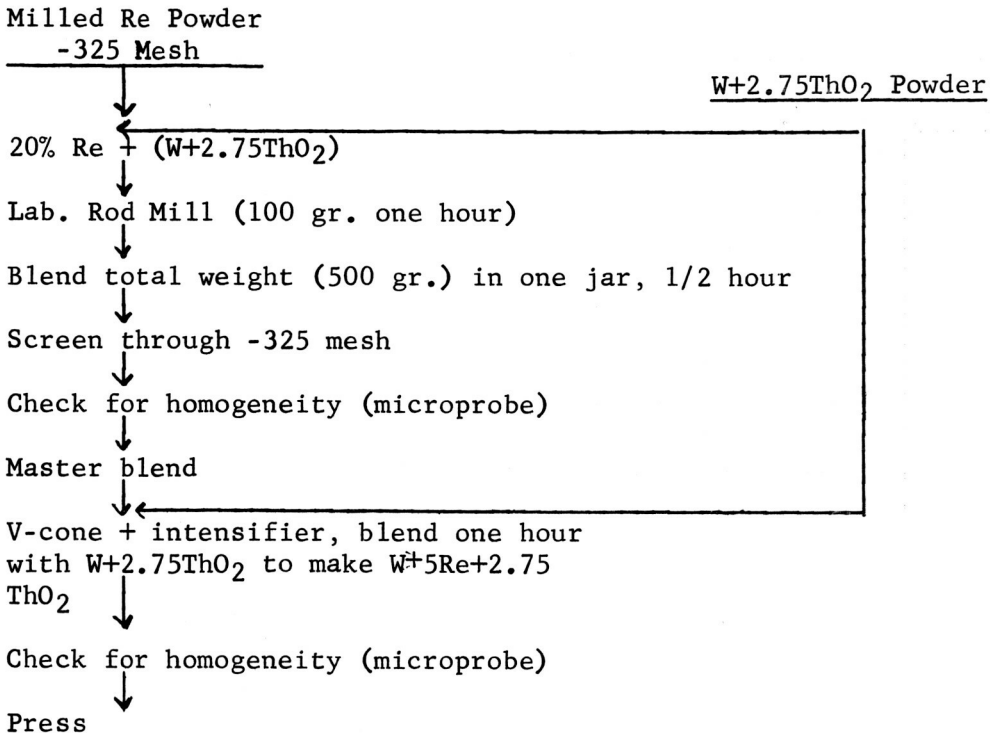
A special blend of tungsten plus 2.75 percent, by weight, of ThO_2 was prepared using commercial procedures. An aqueous solution of thorium nitrate $[Th(NO_3)_4 \cdot H_2O]$ was added to ammonium paratungstate crystal, dried, and then the mixture was fired at 1100°C to green oxide. The oxide was attrition milled, and then reduced to metal powder by firing in a hydrogen atmosphere at about 1000°C. Table ICI lists a complete analysis of the tungsten-thoria powder used in these experiments.

Table ICII shows the vendor analysis of rhenium powder purchased from the Chase Brass Company. The as-received rhenium powder was milled for one hour and then screened through -325 mesh. Five weight percent rhenium was added to the W-2.75 ThO_2 powder followed by blending for one half hour in a V-cone blender. Because rhenium is a costly metal, small powder batches and small ingots or bars were pressed during this learning stage. The ingot mold produced bars measuring 5/8" x 13/16" x 16" when a pressure of 22.5 tons per square inch was used to compress the powder. Each tungsten alloy bar was numbered consecutively, as it was pressed, to identify it through subsequent processes.

The first bar successfully removed from the ingot mold (WRT-1) was presintered for one hour at 1200°C, in hydrogen, to improve the green strength. It was then resistance sintered in a hydrogen "bottle" at 2830°C for one half hour. The sintered ingot showed segregation of rhenium and had a density of around 92%. Experience indicated that this density was not sufficient for fabrication.

Improved Blending and Sintering Technique

To alleviate the problem of rhenium segregation, a new and more thorough blending technique was followed as summarized below:



The new powder mixture was pressed and presintered for one hour at 1200°C in a muffle furnace using a hydrogen atmosphere, followed by an additional presintering treatment at 1850°C for six hours. The bars were then resistance-sintered in a hydrogen atmosphere according to a prescribed schedule as shown in Table ICIII. Initially, there were three high temperature holding periods with a 2700°C final hold. This original plan was later modified to include a fourth holding period at 2900°C for 1/2 hour to obtain the high density (over 95% theoretical) required. Table ICIV summarizes the various techniques and results that were obtained on all ingots produced to date.

The final method that was developed to produce uniform, homogeneous ingots of this alloy differs from that previously described in the literature, Ratliffe et al. (1). The differences are primarily in the methods of powder preparation and consolidation: mechanical pressing and self-resistance sintering in this investigation versus gas pressure bonding. Workable ingots apparently can be produced by both techniques. Further fabrication processing and final mechanical property testing, on the material produced in this investigation, will be compared with that obtained in the referenced study.

Metallographic Examinations

Slices cut from the ends of each sintered ingot were examined. The microstructure of Ingot WRT1 as shown in Figure IC1, indicated localized rhenium melting which upon freezing resulted in shrinkage cavities. The reasons for this failure were a combination of inadequate and poor blending as well as insufficient sintering time for complete dissolution of the rhenium particles in the tungsten matrix.

Improvements in blending techniques allowed a more uniform rhenium distribution to be obtained in the W+ThO_2 matrix. Using a microprobe examination technique, it was shown (Figure IC2) that the rhenium can be fairly evenly distributed in a green compact, made from the same starting constituents, by varying only the blending procedure. Also, the microprobe method demonstrated that the as-sintered ingots were fairly homogeneous alloys. In Figure IC3 the microstructure of representative ingots (WRT4, WRT5, WRT8, WRT9) and the dispersion alloy WRT12 are shown for comparison. The photomicrographs reveal that no gross rhenium segregation occurred. The thoria dispersion was uniform and no evidence of ThO_2 gross agglomeration was observed. Grain size measurements indicated that a great deal of grain refinement had occurred. Table ICIV shows that the grain size ranged from 32,000 to 53,000 grains/mm^2 for the W-Re-ThO_2 alloy. Unalloyed tungsten processed under similar conditions would be in the range of 20,000 grains/mm^2. This grain refinement is attributed mostly to the addition of the thorium oxide rather than the rhenium metal. It is obvious that grain refinement, as evidenced in the W-ThO_2 alloy, (Ingot W23) has been due to the ThO_2 dispersion.

The results of blending and sintering can be summarized as follows:

1. There was complete solid solution of rhenium in tungsten. No sigma phase was evident.

2. Elimination of internal defects, i.e., large holes, shrink cavities, etc., was accomplished.

3. High density; well over 95% of theoretical was obtained.

4. Thoria seemed to be well dispersed and no gross agglomeration was observed.

5. A high degree of grain refinement was obtained, as well as grain size uniformity across the cross section of the sintered ingot.

Ingot Breakdown

In the first attempt to fabricate this alloy, Ingot WRT2 (W+5Re+2.6ThO_2) was rolled three passes before it split by alligatoring.

Ingot WRT2

Pass	Time	Temperature	Remarks
1	10 min.	1730°C	1-1/2" long split at nose
Recrystallize by resistance heating at 5000 amps			
2	10 min.	1710°C	No cracks visible
3	10 min.	1710°C	Split full length

In view of the rolling difficulty, swaging was attempted with Ingot WRT3 (W+5Re+2.75ThO_2). Ingots WRT4 and WRT5 (W+5Re+2.75ThO_2) were shipped to the General Electric Plant at Dover, Ohio, for cladding with molybdenum prior to rolling. The swaging and rolling results, respectively, are shown below:

Ingot WRT3 (Swaged)

Pass	Time	Temperature	Remarks
1	10 min.	1800°C	Light pass to break corners
2	10 min.	1800°C	Transverse cracks. Swaging terminated.

Ingot WRT4 (Rolled)

1	30 min.	1700°C	Light pass to shape - Mo cladding
2	15 min.	1700°C	Good appearance
3	15 min.	1700°C	Good appearance
4	10 min.	1700°C	Good appearance
5	15 min.	1450°C	Good appearance

The rod was pickled after the fifth pass to remove the molybdenum cladding for inspection. The finished diameter was approximately .550". Further processing will be terminated because of transverse cracks and tears.

Ingot WRT5 (Rolled)

The above schedule was used for Ingot WRT5, except for a fourth pass reheat temperature of 1450°C. The molybdenum cladding has not been removed, but several tears are evident in the clad surface. The cladding will be removed by pickling for inspection.

To determine the feasibility of rod rolling high percentage thoria alloys beyond the third pass, Ingots WRT12 and WRT13 (W+2.75ThO_2) were rolled. No rhenium additions were made to these ingots. Inspection of the as-sintered ingots showed a marked improvement in quality. These ingots were virtually free of the small surface chips, and defects noted for Ingot WRT2.

Ingot WRT12

Pass	Time	Temperature	Remarks
1	20 min.	1680°C	Fractured at tail. Transverse cracks, checks and shipping appear to be related to ingot consolidation.

Ingot WRT13

1	20 min.	1680°C	No cracks visible
2	20 min.	1630°C	1-1/2" split on nose
Recrystallize by resistance at 3650 amps in H_2			
3	20 min.	1630°C	Slight nose and tail cracks
4	20 min.	1595°C	No cracks visible
5	10 min.	1530°C	No cracks visible, ready for swaging

The above rolling practices incorporated three changes suggested by the initial attempt to roll WRT2:

1. Preheat time was increased from 10 minutes to 20 minutes.

2. Elongation/pass was increased from 10 to 15%/pass to <20%.

3. Recrystallization was moved from after the first pass to after the second pass.

Figures IC4 and IC5 show that change No. 3 produced a significant improvement in grain size uniformity.

Based on the encouraging results with Ingot WRT13, W+5Re ingots with two different thoria levels were rolled. Surface quality of these ingots was comparable to Ingots 12 and 13.

Ingot WRT9 (W+5Re+2.2ThO_2)

Pass	Time	Temperature	Remarks
1	20 min.	1710°C	Split 1-1/2" at nose
2	20 min.	1650°C	No cracks visible

Further rolling planned after recrystallization

Ingot WRT10 (W+5Re+2.2ThO_2)

1	20 min.	1710°C	Split 1-1/2" at nose
2	20 min.	1650°C	Split 1-1/2" at nose

Further rolling planned after recrystallization

Ingot WRT11 (W+5Re+2.2ThO_2)

1	20 min.	1710°C	Transverse crack at tail.
2	20 min.	1650°C	Would not enter guide, will be rolled after modification of guide.

Ingot WRT6 (W+5Re+2.75ThO_2)

1	20 min.	1720°C	No cracks visible
2	20 min.	1650°C	No cracks visible

Further rolling planned after recrystallization

Ingot WRT8 (W+5Re+2.75ThO_2)

1	20 min.	1720°C	Transverse tears along bottom surfaces. No further processing.

Because Ingot WRT8 was shorter than the guide, some difficulty was encountered with starting the ingot into the rolls. Cracking may have been due to excessive heat loss. Ingot WRT7 (W+5Re+2.75ThO_2) was extremely short. To facilitate handling this ingot a tungsten rod has been welded to one end.

Future Plans

Further fabrication process work will be performed on those ingots that have not failed during the initial breakdown operations. Determination of proper recrystallization sizes and temperatures will be determined. Examination of the microstructure throughout processing will provide a means for controlling the process and assure reproducibility of future material.

References

Ratliffe, J. L., Abbott, W. H., Maykuth, D. J., Ogden H. R. Blocher, J. M., Jr., Jaffe, R. I., "Further Development of a Ductile Tungsten Base Sheet Alloy", 2nd Quarterly Progress Report, December 19, 1964, Bur. Nav. Weaps. Contract N600 (14) 61982.

TABLE ICI

Analysis of W+2.75ThO_2 (Nominal)

Below are listed the analyses of the tungsten powder lot No. ID 65-8-56. This material was transferred on 8/23/65. Qty. 50.000 kgs.

Spectrographic Analysis

Element	ppm	Element	ppm
Al	<6	Ni	20
Ca	17	Cu	<3
Si	11	Mn	<6
Mo	52	Mg	7
Fe	18	Sn	10
Cr	5		

Flame Photometry Analysis

Sodium - 1 ppm
Potassium - 25 ppm

LECO Analysis

Carbon - 11 ppm

Average Particle Diameter by Fisher Sub-Sieve Sizer

	as supplied	Lab. milled
Number (microns)	2.57	2.49
Porosity	.659	.488

ThO_2 - 2.6±.1% (by x-ray fluorescence)

Apparent Density by Scott-Schaeffer-White Volumeter (ASTM B-329 58)

67.7 gms. per cu. in.

Wt. % Particle Size Distribution by Photelometer

Micron Range	Lab Milled
0- 1	2.4
1- 2	17.6
2- 3	38.3
3- 4	27.8
4- 5	10.4
5- 6	.7
6- 7	.8
7- 8	.9
8- 9	1.0
9-10	-
10-11	
11-12	
12-13	
13-14	
14-15	
15-20	
20-25	

TABLE ICII

Physical, Chemical Analysis of Rhenium Powder
Chase Brass Company

Batch 446

Description - Rhenium Grade 1 -200 mesh

Microns - 2.35

Scott Density gm/in^3 - 27.6

Spectrographic Analysis (ppm)

Element	ppm	Element	ppm
Al	<1	Mg	<1
Ca	<1	Mo	<1
Cr	<1	Ni	1
Cu	1	Si	<1
Fe	15		

Gas Analysis - performed by the General Electric Company, Oxygen = 2860 ppm

TABLE ICIII

Sintering Schedule of W-Re-ThO_2 Alloys (Typical)

Presintered one hour at 1200°C and six hours at 1850°C, followed by resistance sintering according to the following schedule:

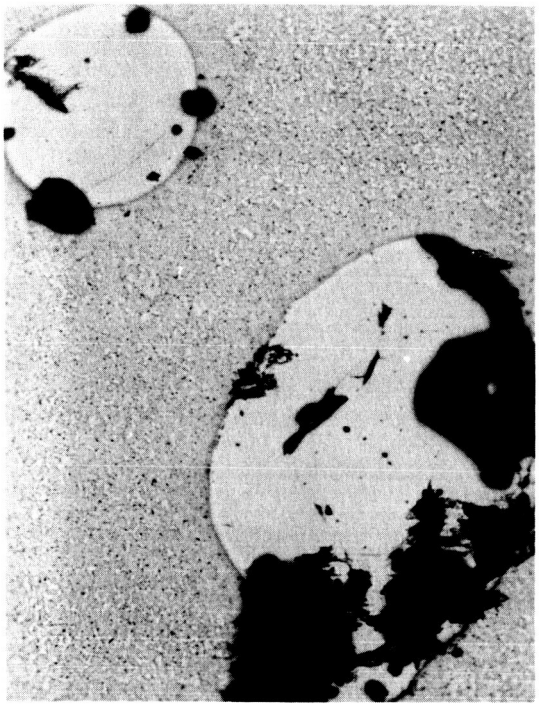
Time Min.	Current Amps	Temperature °C±25
1	1200	
2	1600	1750
3	2000	
4	2400	
5	2800	
5-1/2	3000	2270
6	3200	
7	3600	
8	4000	2500
18	1st hold for 10 min.	
18-1/2	4500	2570
48-1/2	2nd hold for 30 min.	
49	5000	2700
79	3rd hold for 30 min.	
80	5300	2900
110	4th hold for 30 min.	

TABLE ICIV

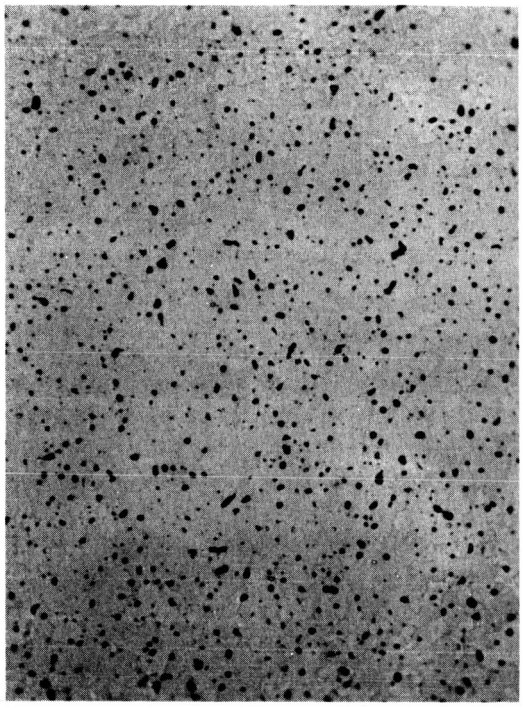
Summary of Sintering Conditions and Properties of
Tungsten + Rhenium + Thoria Alloys

Ingot No.	Additions Wt.%	H_2 Sintering, 1/2 Hr. 1st Temp. °C ±25	2nd Temp.	Grain Size Grains/mm² X1000	*Theoretical g/cm³	Density, ± .15 g/cm³ 1st density g/cm³	2nd density g/cm³	Remarks
WRT1	5Re+2.75ThO_2	2830	-	-	18.9	17.30	-	Poor blending, low density
WRT2	5Re+2.75ThO_2	2830	-	-	-	17.60	-	Good blending, low density
WRT3	5Re+2.75ThO_2	2830	-	-	-	17.75	-	" "
WRT4	5Re+2.75ThO_2	2830	-	-	-	17.65	-	" "
WRT5	5Re+2.75ThO_2	2830	-	-	-	17.75	-	" "
WRT6	5Re+2.75ThO_2	2800	2900	53	-	17.27	17.92	Good blending, increased density
WRT7	5Re+2.75ThO_2	2800	2900	53	-	17.35	18.01	" "
WRT8	5Re+2.75ThO_2	2800	2900	46	-	17.38	18.01	" "
WRT9	5Re+2.20ThO_2	2830	2900	34	19.0	17.40	18.01	" "
WRT10	5Re+2.20ThO_2	2830	2900	49	-	17.40	18.11	" "
WRT11	5Re+2.20ThO_2	2830	2900	32	-	17.40	18.10	" "
WRT12	2.75ThO_2	2800	2900	40	18.8	17.00	17.96	" "
WRT13	2.75ThO_2	2800	2900	-	-	17.00	17.96	" "

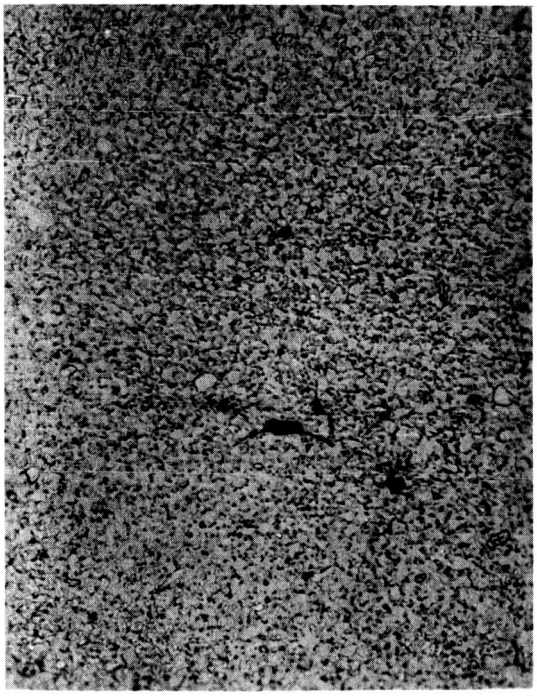
*Calculated using formula $\frac{1}{d_T} = \frac{\text{Wt. \% A}}{d_A} + \frac{\text{Wt. \% B}}{d_B} + \ldots$, where densities of Re, W and ThO_2 are 21.04, 19.30 and 10.03 g/cm³ respectively.



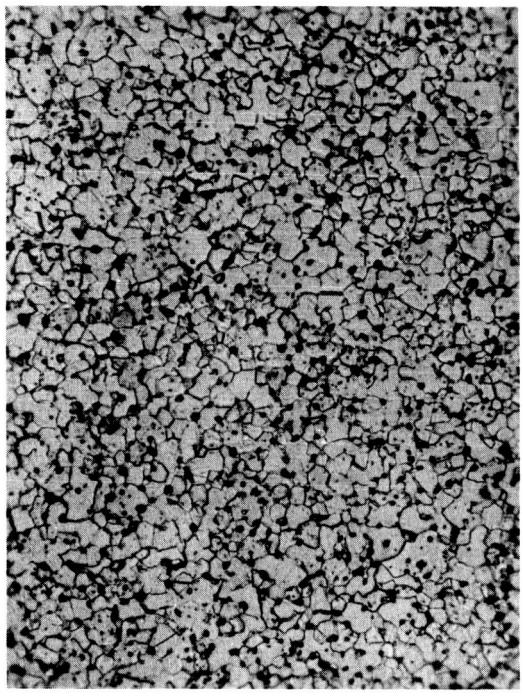
Polished showing localized Re melting



Polished showing ThO_2 phase

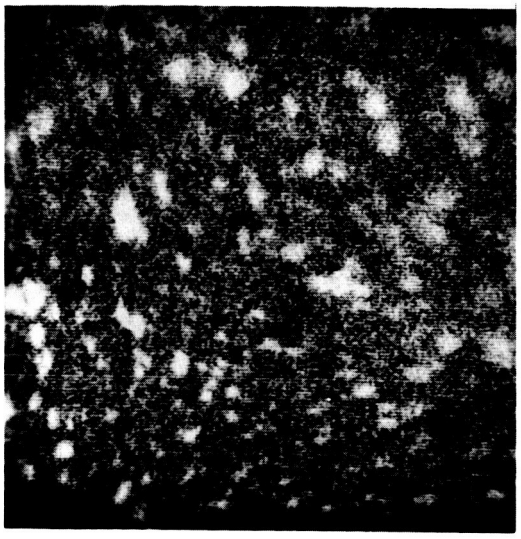


Large porosity-polished.

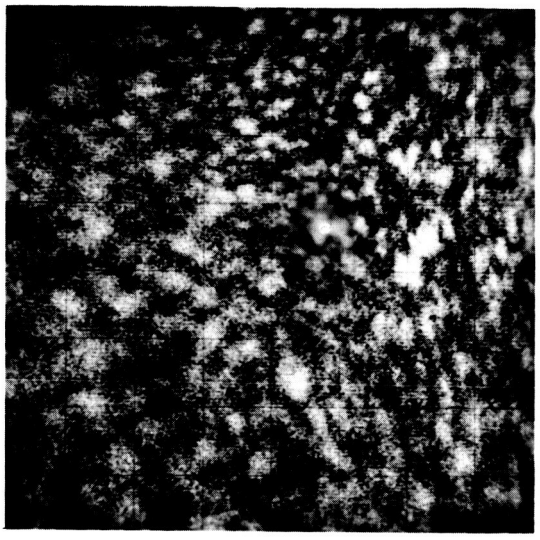


Grain refinement-Murakami etch

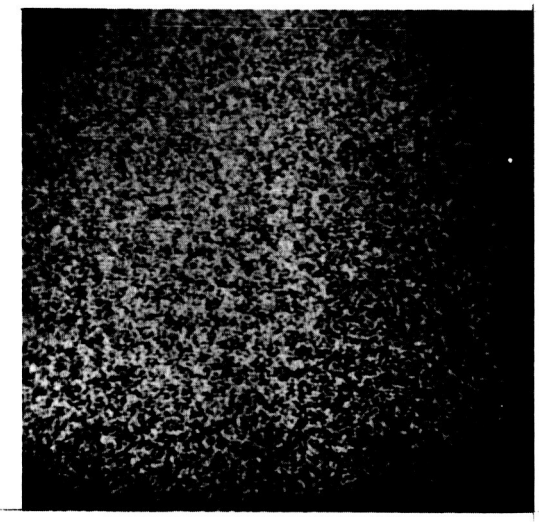
FIGURE IC1 - Typical microstructures which may occur in W - Re - ThO_2 alloy (WRT-1). 400X



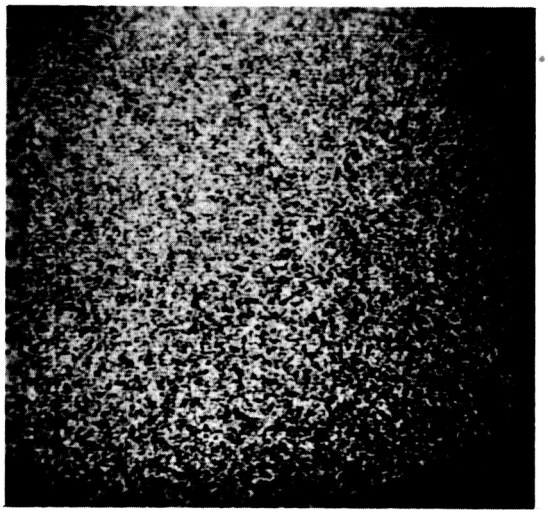
A
WRT-1 Poor Blend



B
WRT-3 Good Blend



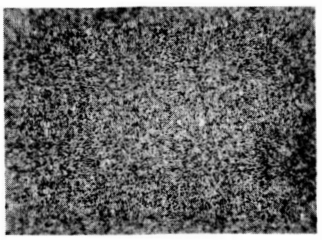
C
Sintered - Good Ingot



D
Sintered - Good Ingot

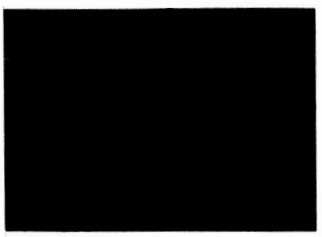
FIGURE IC2 - W + 5 Re + 2.75 ThO_2 Alloys. Electron microprobe examination. White areas show presence of rhenium. 222X

100X



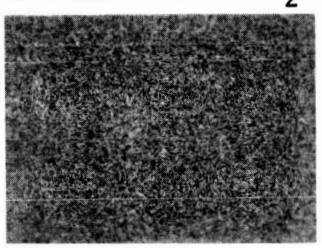
WRT-2 A7760

W + 5 Re + 2.75 ThO_2



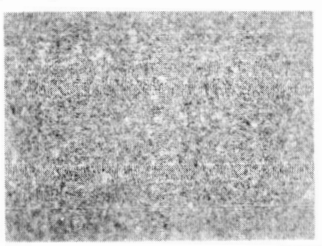
WRT-5 A7811

W + Re + 2.75 ThO_2



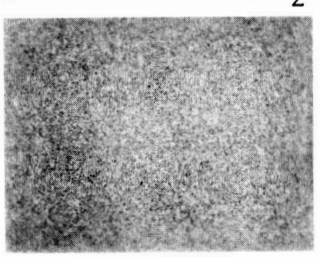
WRT-8 A7839

W + 5 Re + 2.75 ThO_2



WRT-9 A7855

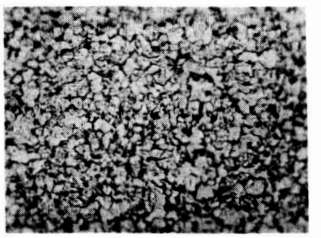
W + 5 Re + 2.2 ThO_2



WRT-12 A7833

W + 2.75 ThO_2

1000X



WRT-2 A7761

W + 5 Re + 2.75 ThO_2



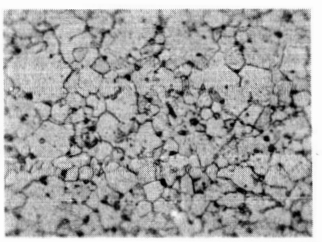
WRT-3 A7814

W + Re + 2.75 ThO_2



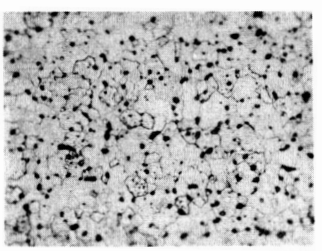
WRT-8 A7842

W + 5 Re + 2.75 ThO_2



WRT-9 A7860

W + 5 Re + 2.2 ThO_2



WRT-12 A7834

W + 2.75 ThO_2

FIGURE IC3 - Typical microstructure of as-sintered W-Re-ThO_2 ingots - all etched in Murakami except WRT-5 which was buff etched

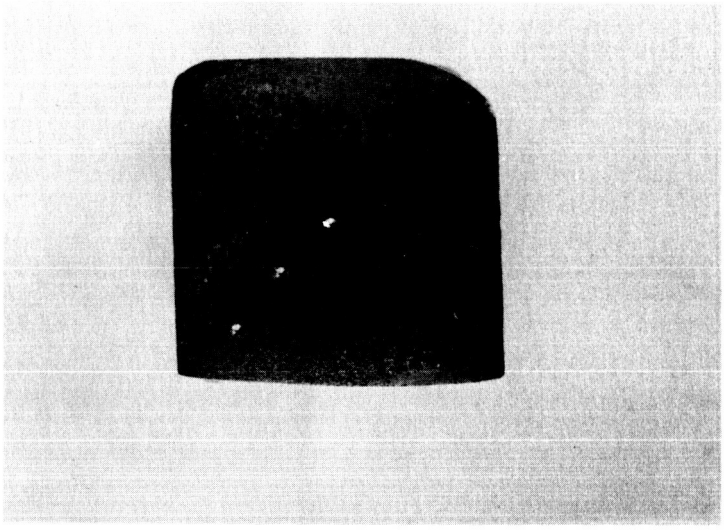


FIGURE IC4 - Macrostructure of Ingot WRT-2,
Rolled 1st Pass and Recrystallized.
3X Magnification.

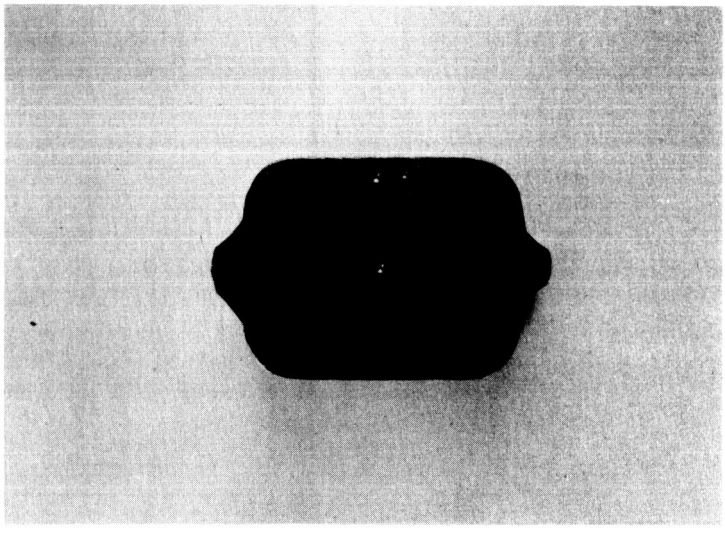


FIGURE IC5 - Macrostructure of Ingot WRT-13,
Rolled 2 Passes and Recrystallized.
3X Magnification.

D. Tungsten-Hafnium-Carbon Alloy W+(1-3)Hf+(0.005-0.02)C

Powder and Ingot Preparation

The first selection of tungsten metal powder had a Fisher sub-sieve size of 4.0. This type of powder normally results in adequate as-pressed green strength to allow handling without breakage. When mixed with hafnium hydride and carbon, however, it was found that the green strength of the pressed ingot was very low. A 2.1 Fisher sub-sieve size powder was selected next and resulted in adequate green strength. The complete analysis of this powder is shown in Table IDI. Hafnium was added to the tungsten base metal as hafnium hydride obtained from Metals Hydrides Incorporated, Beverly, Massachusetts. Table IDII is the vendor's analysis of the hafnium hydride. Lamp black was used in all the experiments as the carbon additive.

Compacts of the blended powders were prepared by mechanical pressing into 5/8" x 13/16" x 16" long bars. A pressure of 44.6 tons/sq. in. was used to assure sufficient green strength for handling. The pressed ingots were then transferred to the vacuum furnace described in Section IB for sintering.

Upon initial heating, the hafnium hydride dissociated at approximately 500°C. After the hydride dissociation, the pressure was maintained in the 10^{-5} Torr. range throughout the sintering cycle. Table IDIII shows a typical sintering schedule. The table indicates that during sintering there were five holding periods. The first hold at 1200°C was done primarily to strengthen the compact since little sintering was accomplished at the 500°C hydride dissociation temperature. The other holding periods were for the purpose of homogeneously alloying the material.

Ingots WHC1, WHC2 and WHC3 were sintered at a final holding temperature in the range of 2800-2830°C $\pm$ 25°C. Metallographic examination indicated that possible localized melting was occurring during sintering. It should be noted that hafnium oxide has a melting point of about 2810°C. All subsequent final sintering temperatures were therefore limited to a maximum of 2800°C. These first three ingots in the W-Hf-C system, prepared as described above, were not homogeneously alloyed and exhibited coarse second phase particles identified as hafnium oxide by microprobe examination. A different method of preparing the compacts was therefore developed for all subsequent ingots.

As in the case of the W-Re-ThO_2 alloys, improved blending techniques were employed. Small batches of a master blend were prepared from the tungsten powder, hafnium hydride and carbon. The master mix was then blended back to the desired composition with unalloyed tungsten. In order to minimize oxygen pickup during blending, re-reduced tungsten powder was obtained (from the original powder lot) and kept in argon-filled polyethylene bags and stored in metal cans. Weighing of the powders was done in an inert (argon) atmosphere by using a dry-box, shown in Figure ID1. Mixing was also done in an argon atmosphere using a twin-shell blender with an intensifier. Pressing and sintering conditions were not substantially changed from the original experiments. Table IDIV summarizes all the sintering experiments that have been performed to date.

Chemistry

Analysis of WHC1 and WHC2 for hafnium retention indicated that very small losses occurred. Hafnium was determined by both wet chemical and x-ray spectrographic methods. The wet chemical method indicated that hafnium was present as hafnium oxide to the extent of 0.36% and 0.24% in WHC1 and WHC2 respectively. The remaining hafnium (2.04% and 2.18%) should therefore be in solid solution in the tungsten matrix or present as hafnium carbide. All percentages are on a weight basis.

Interstitial content of the sintered ingots was not acceptable, especially with regard to oxygen content. Despite precautions that were taken in storing, weighing, blending, and sintering there appears to be no easy way, at the present, to reduce the oxygen content of the sintered ingot. Similar difficulties were encountered in other investigations related to this alloy system (1). Ingot WHC4 was sintered in a dry hydrogen atmosphere to try and reduce the oxygen level; however, this was not successful. Ingot WHC7 was sintered by radiation heating rather than self resistance, but this also was unsuccessful. Table IDV shows the chemistry results, to date, of the various ingots prepared. A complete spectrographic analysis for metallic impurities in ingots WHC1 and WHC2 is also given in Table IDV. Initially, it was difficult to adjust the carbon content to the level desired, 50 to 200 ppm. There were two reasons for this problem; carbon pickup was occurring due to back diffusion of oil and secondly, carbon that was added in hopes of "deoxidizing" the ingot was not effective, probably because of the affinity of the hafnium for both oxygen and carbon. In order to obtain the desired carbon level addition in the range of 100 to 125 ppm were added as in Ingots WHC11, 12 and 13.

Metallographic Examination

In order to evaluate the structure and characterize the sintered ingots, sections from each sintered ingot were conventionally polished and then etched in:

50 parts 1N NaOH

50 parts 30% $K_3Fe(CN_6)$

All the W-Hf-C alloy ingots prepared to date have exhibited large second phase particles within the matrix. Figure ID2 shows the structure of representative ingots at 100 and 1000 magnifications. Microprobe examination to date has revealed only hafnium oxide. There is a good possibility that the smaller particles may be hafnium carbide; however, this has not been determined analytically. Microstructure examination has also shown that a modest degree of grain refinement occurs in the W-Hf-C system; however, it is not as pronounced as is the W-Re-ThO_2 alloys. A variation of grain size from edge to center was also observed in many of the sections examined, the edge grains being about twice as large as grains near the center of the ingot. This grain size variation may affect workability and may also indicate a chemistry variation from edge to center.

The average hardness of the various ingots was about R_c33 regardless of composition or sintering schedule.

Microprobe Examination

Microprobe techniques were employed to study the extent of uniformity in blending the powders and also to check the degree of alloying after sintering. Figure ID3-c indicates that a relatively uniform mixture of hafnium hydride in tungsten was obtained using the improved blending technique. After sintering microprobe examination indicated that agglomeration occurred. Figure ID3-a and b show local concentration of hafnium (as hafnium oxide). The intense white area in Figure ID3-b is suspected to be an area where localized melting occurred during sintering.

Summary of Sintering W-Hf-C Alloys

The ingots prepared, to date, have been unsatisfactory for one or more of the following reasons:

1. Dispersion of a large second phase.
2. Localized melting due to too high of a sintering temperature.
3. Agglomeration of the second phase, hafnium oxide.

Ingot Breakdown

Rolling has been attempted only on Ingot WHC3. Using a preheat of 1740°C, for 10 minutes, the material failed in a brittle manner in the first pass. Seven other ingots are ready for breakdown rolling but the extremely brittle nature of the alloy noted thus far is not encouraging. Ingot WHC12 was broken in an attempt to hot straighten it at 1600°C.

Future Plans

In order to obtain a fabricable ingot, the approach of melting and extruding, recently demonstrated by Raffo and Klopp (2), is being considered as a method of consolidation for the W-Hf-C alloy. Before this approach is taken, however, further fabrication processing work will be attempted. High energy rate extrusion (Dynapak) of the presently available ingots and molybdenum jacketed ingots for rod rolling attempts will also be investigated. It is anticipated that once the initial breakdown of the ingot is achieved, further processing will be less difficult until very small wire diameters are approached

References

1. Stephen Foldes, "The Effect of Alloying Additions on the Low and High Temperature Properties of a Tungsten-Molybdenum Base Alloy", Presented at the Fourth Symposium on Refractory Metals, Sponsored by the AIME, October, 1965.

2. Peter L. Raffo and William D. Klopp, "Solid Solution and Carbide Strengthened Arc Melted Tungsten Alloys", Presented at the Fourth Symposium on Refractory Metals, Sponsored by the AIME, October, 1965.

TABLE IDI

Tungsten Powder
U2.1-5071

Spectro Analysis of Powder (ppm)

Al	-6	Mg	5
Ca	14	Sn	8
Si	-7	Co	-3
Fe	6	Ti	-6
Cr	-3	Ag	-3
Ni	10	Pb	-6
Cu	-3	Nb	-20
W/Mo	68	Zr	-3
Mn	-6		

Chemical Analysis of Powder (ppm)

O_2	380
C	18

Physical Measurements

Cubic Inch	38.7
Tap Test	
Fisher No.	2.10
Porosity	.717
Milled Fisher	1.98
Milled Porosity	.540

Photelometer Distribution

Micron Size	% by Weight (as is)	(milled)
1.		8.7
2.		42.4
3.		29.0
4.		12.6
5.		6.2
6.		.9
7.		
8.		
9.		
10.		
11.		
12.		
13.		
14.		
15.		
20.		
25.		
30.		
40.		

TABLE IDII

Hafnium Hydride
(Prepared from Hafnium Crystal Bar)
Metal Hydrides Inc.

Chemical Analyses (Wt. %)

H	-	1.06
N	-	<.0010
O	-	<.0500
Ca	-	<.0050
Cu	-	<.0050
Al	-	<.0050
Ni	-	<.0050
Fe	-	.0012
Mg	-	.0016
Si	-	.0012
Mn	-	.0001
Ti	-	.0125
Zr	-	1.86

TABLE IDIII

A Summary of a Typical Sintering Schedule of W-Hf-C Alloys

Ingot WHC12

Time Min.	Pressure Torr.	Volts	Amp	Temp. °C ±25	
0	Leak rate 1 micron/hour				
25	1×10^{-4}	2-1/2			H_2 evolution
45	1×10^{-4}	2-1/2		(Red Color)	H_2 evolution
52	8×10^{-5}	4	800	935	
60	5×10^{-5}	4	1200	1200	
Hold for one hour					(1)
130	2×10^{-5}	4-1/2	1680	1450	
135	1.5×10^{-5}	5	1840	1555	
140	3×10^{-5}	6-1/2	2200	1800	
Hold for one hour					(2)
205	7×10^{-5}	7	3040	2150	
215	9×10^{-5}	7-1/2	3200	2250	
Hold for 1/3 hour					(3)
240	9×10^{-5}	8-1/4	3600	2450	
Hold for 1/4 hour					(4)
249	8×10^{-5}	8-1/2	3840	2600	
252	4×10^{-5}	10-1/2	4240	2780	
Hold for one hour					(5)
212	3×10^{-5}	10-1/2	4240	2780	Power off

TABLE IDIV

Summary of Sintering Conditions and Properties of Tungsten + Hafnium + Carbon Alloys

Ingot No.	Additions Wt. %	Sintering			Grain Size Grains/mm^2 1000X	Density gm/cm^3
		Atm.	Temp. ^{o}C ±25	Time, Hour		
WHC1	2.44 HfH_2 + .02C	Vac.	2830	1/6		18.16
WHC2	2.44 HfH_2 + .02C	Vac.	2830	3		18.50
WHC3	2.44 HfH_2 + .05C	Vac.	2800	1/2		18.10
WHC4	2.44 HfH_2 + .045C	H_2	2750	1/2		18.41
WHC5	2.44 HfH_2 + .045C	Vac.	2750	1.0		18.31
WHC6	2.44 HfH_2 + .045C	Vac.	2750	1.0		18.07
*WHC7	1.5 HfH_2 + .045C	Vac.	2750	1.0		18.30
WHC8	1.5 HfH_2 + .045C	Vac.	2750	1.0		18.31
WHC9	1.5 HfH_2 + .03C	Vac.	2460	1/3		17.47
WHC10	1.5 HfH_2 + .03C	Vac.	2780	1/2		18.50
WHC11	1.5 HfH_2 + .03C	Vac.	2000	1/3	Discontinued sintering because of high carbon in WHC10	
WHC12	1.5 HfH_2 + .012C	Vac.	2780	1/2	8600	18.40
WHC13	1.5 HfH_2 + .012C	Vac.	2760	1/2	3700	18.29
WHC14	1.5 HfH_2 + .012C	Vac.	2760	1/2		

*Sintered in a Brew type furnace by radiation heating

TABLE IDV

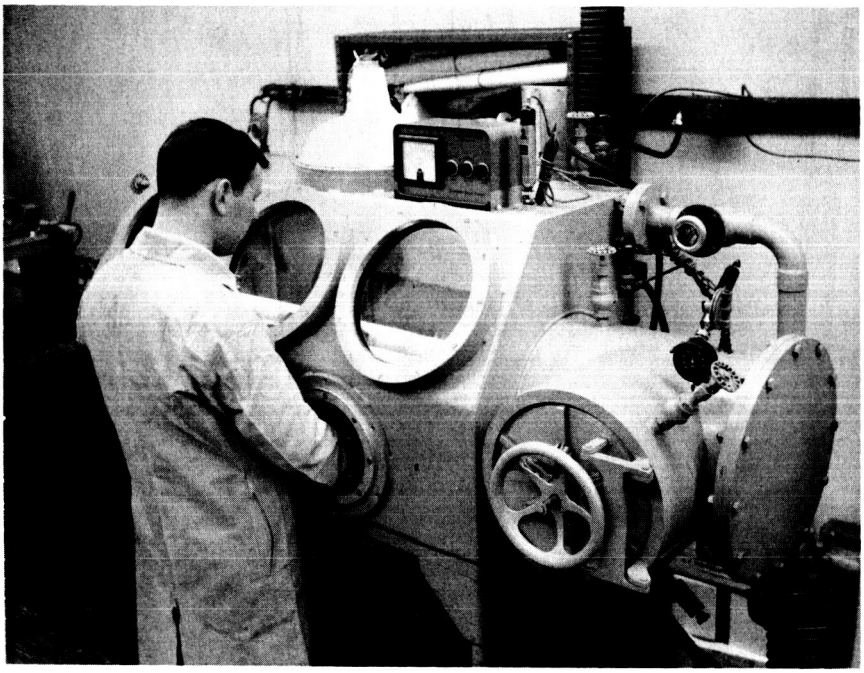
Chemical Analysis of Tungsten + Hafnium + Carbon Alloys

A. Chemical and Gas Analysis

Ingot No.	Nominal Additions Wt. %	Analysis				
		Wt. % Hf	ppm C	ppm O	ppm H	ppm N
WHC1	2.44 HfH_2 + .02C	2.40	260	518	3	5
WHC2	2.44 HfH_2 + .02C	2.42	300	791	1	38
				806	1	30
WHC3	2.44 HfH2 + .05C		174			
WHC4	2.44 HfH_2 + .045C					
WHC5	2.44 HfH_2 + .045C		700	774	1	34
WHC6	2.44 HfH_2 + .045C		439	663	1	20
WHC7	1.5 HfH_2 + .045C		291			
WHC8	1.5 HfH_2 + .045C		378			
WHC9	1.5 HfH_2 + .03C	1.5				
WHC10	1.5 HfH_2 + .03C		311			
WHC11	1.5 HfH_2 + .03C					
WHC12	1.5 HfH_2 + .012C		160			
WHC13	1.5 HfH_2 + .012C		161			
WHC14	1.5 HfH_2 + .012C					

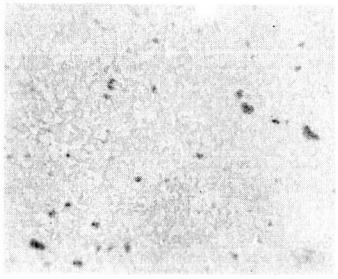
B. Spectro Analysis of Ingots WHC1 and WHC2

Element	W-1 (ppm)	W-2 (ppm)	Element	W-1 (ppm)	W-2 (ppm)
Al	15	14	Mn	6	<6
Ca	19	19	Mg	7	13
Si	36	46	Sn	<6	<6
Mo	125	230	Co	8	9
Fe	17	17	Ti	<6	<6
Cr	6	5	Ag	<3	<3
Ni	6	8	Pb	<6	<6
Cu	<3	<3	Zr	64	63
Cb	<20	<20			

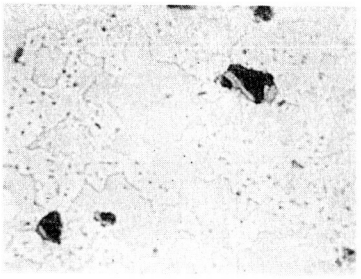


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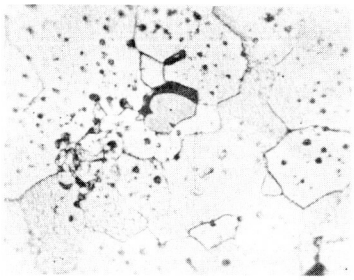
FIGURE ID1 - Dry box used to screen, blend, and prepare W-Hf-C powders prior to pressing



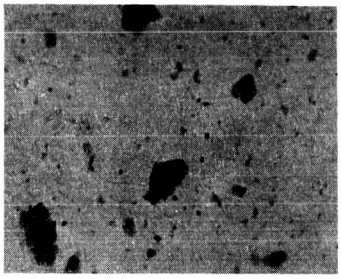
WHC-1 A7735
100X
W + 2.44 Hf + .02 C



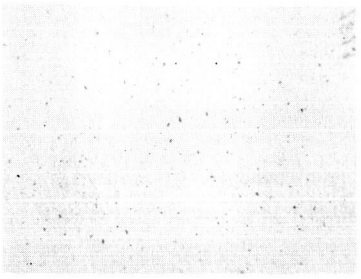
WHC-1 A7736
1000X



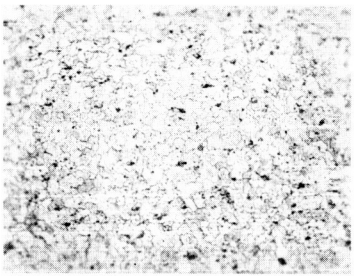
WHC-3 A7762
1000X
W + 2.44 HfH_2 + .05C



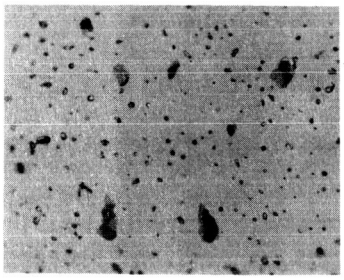
WHC-5 A7812
1000X
W + 2.44 HfH_2 + .045 C



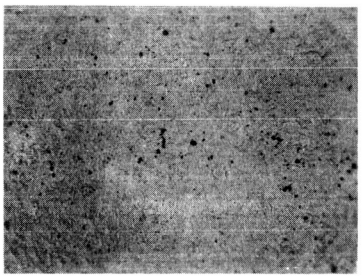
WHC-5 A7813
100X



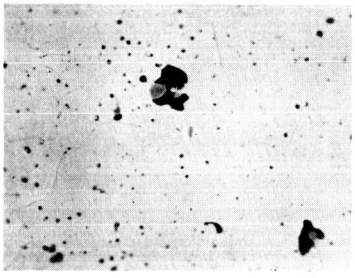
WHC-3 A7759
100X



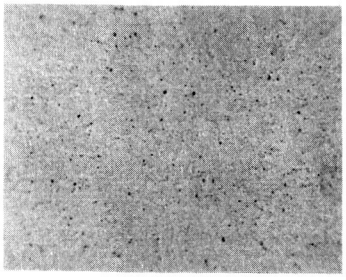
WHC-10 A7843
1000X
W + 1.5 HfH_2 + .03 C



WHC-12 A7849
100X
W + 1.5 HfH_2 + .012 C



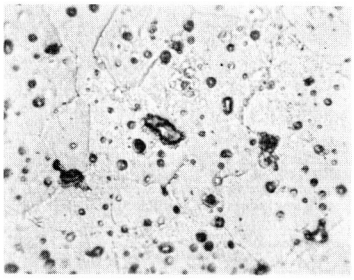
WHC-12 A7850
1000X



WHC-10 A7844
100X

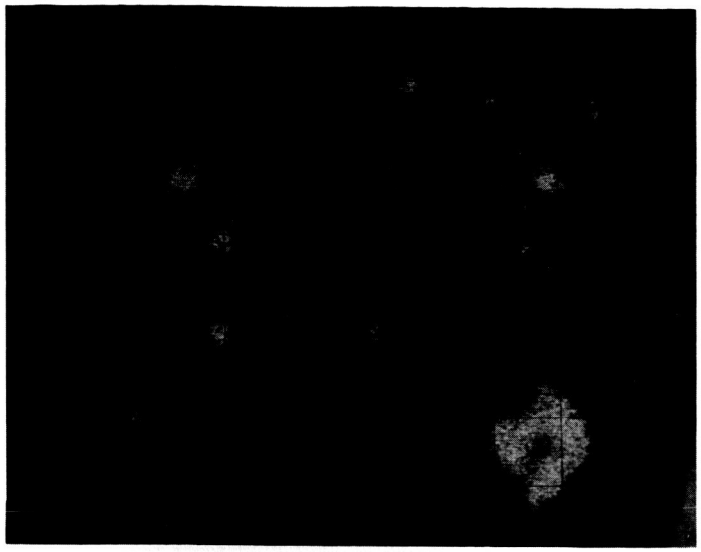


WHC-13 A7852
100X
W + 1.5 HfH_2 + .012 C

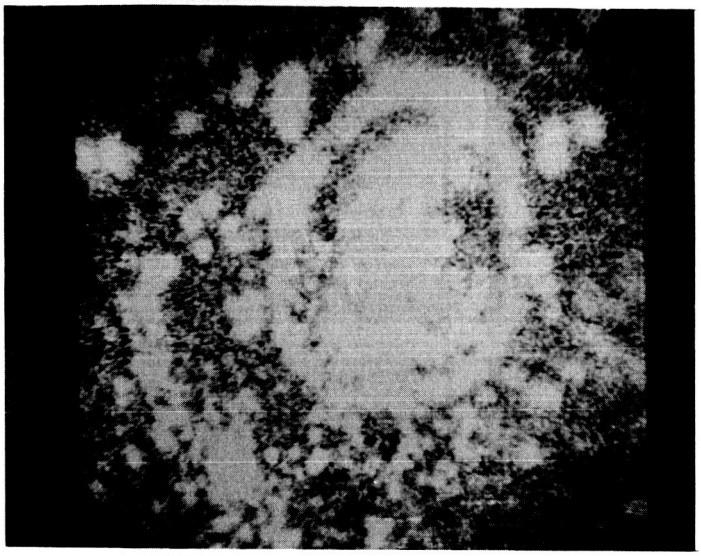


WHC-13 A7853
1000X

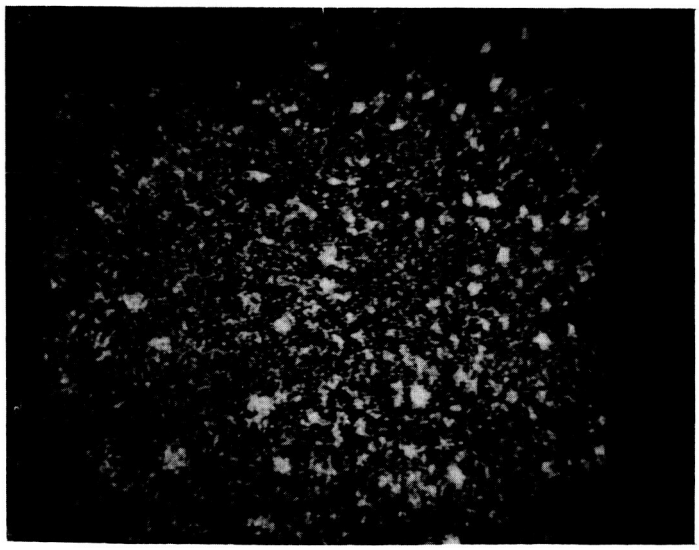
FIGURE ID2 - Microstructure of Sintered W-Hf-C Alloys
Illustrating Second Phase



A. WHC-1, As-Sintered
W + 2.44 HfH_2 + .02C



B. WHC-3, As-Sintered
W + 2.44 HfH_2 + .05C



C. WHC-5, Powder Compact
W + 2.44 HfH_2 + .05C

FIGURE ID3 - Microprobe Examination of W-Hf-C. White Areas Indicate Hafnium
222X

E. Columbium Alloy FS-85
Cb+(27-29)Ta+(9.5-10.5)W+(0.7-1.1)C

Commercial availability of columbium alloy, FS-85, indicated that the production of wire from the alloy could be expedited by purchasing rod stock suitable for redraw. Specifications and process details were negotiated with the vendor and an order for 80 pounds of 1/4" diameter rod was placed in July 1965 with Fansteel Metallurgical Corporation. Table IEI details the chemical composition specification which was negotiated with the vendor. It was also agreed that processing information along with a slice of the cast ingot and microstructure evaluation of the ingot would be supplied by the vendor.

Upon receipt of the 1/4" diameter rod, complete chemical, microstructural and mechanical property evaluations will be performed in order to prepare a "Raw Materials Description". Future procurement of this alloy, if necessary, would then be based on the "Raw Materials Description".

Unfortunately, due to a number of difficulties experienced by the vendor while preparing this alloy, delivery has been delayed to January 1966 from the originally scheduled delivery date of September 1965. As a result of this delay, no progress has been made in fabrication of columbium alloy FS-85 during this reporting period.

TABLE IEI

Chemistry Specification
Columbium Alloy FS-85

Ta	28 ± 1%
W	10 ± 0.5%
Zr	0.9 ± 0.2%
C	50 ppm max.
O	150 ppm max.
N	150 ppm max.
H	10 ppm max.
Fe	100 ppm max.
Si	100 ppm max.
Cb	Balance

F. Tantalum Alloy T-222
Ta+(9.1-10.1)W+(2.1-2.7)Hf+(80-120 ppm)C

Like columbium alloy FS-85, the tantalum base alloy, T-222, is commercially available and the production of wire could be expedited by purchasing rod for redraw purposes. Specifications and process information details were negotiated with the vendor. An order for 95 pounds of 1/4" diameter rod was placed in July 1965 with Fansteel Metallurgical Corporation. Table IFI lists the chemical composition specification negotiated with the vendor. Processing information and a slice of the cast ingot and microstructure evaluation of the ingot will be supplied by the vendor.

Upon receipt of the 1/4" diameter rod complete chemical, microstructural and mechanical property evaluations will be performed in order to prepare a "Raw Materials Description". Again, as in the case of the columbium alloy, FS-85, future procurement of this alloy would then be based on the "Raw Materials Description".

Because of difficulties experienced by the vendor, delivery of the 1/4" diameter rod has been delayed until the end of January 1966. As a result of this delay, no progress has been made in fabrication of tantalum alloy, T-222, during this reporting period.

TABLE IFI

Chemistry Specification
Tantalum Alloy T-222

W	9.6 $\pm$ 0.5%
Hf	2.4 $\pm$ 0.3%
C	100 ppm $\pm$ 20 ppm
$O_2 + N_2$	<60 ppm

Section II - The Evaluation of Materials

A. The Multi-Station Creep and Stress Rupture Apparatus

Introduction

The design of a multi-station stress-rupture and creep apparatus for testing wire of less than 10 mils diameter was undertaken after receipt of the contract. Some of the basic features of this apparatus which needed to be incorporated in the design were:

1. Testing capability to a maximum temperature of 2800°F.
2. Vacuum capability to pressures of 10^{-9} to 5 x 10^{-11} Torr.
3. Continuous operation for periods up to 1500 hours.
4. Measurement of creep deformation to a precision of 50 x 10^{-6} inches.

Within 90 calendar days the basic design was completed and detail design drawings had been submitted to the NASA Project Manager for approval prior to the start of fabrication. Upon receipt of design drawing approvals and after the incorporation of suggested changes, corrections or improvements, the fabrication and/or purchase of individual items of the apparatus was begun.

Summary and Overall Description of the Equipment

The Basic Components of the Apparatus

1. An ultra-high vacuum chamber for housing six individual creep-rupture test stations is shown in Figure IIA1. The chamber is constructed of stainless steel and uses metal gasket seals. Therefore, it is capable of being baked out to a temperature of at least 500°F. The bakeout is accomplished by utilizing strip-type heaters on the chamber. The entire chamber is equipped with an insulated aluminum outer shroud. Water cooling channels are welded to the chamber and are used together with a blower for cooling after the bakeout procedure.

   The stainless steel shell of the chamber is flanged so as to be bolted to the Main Base Plate and a large metal gasket serves as the vacuum seal (Figure IIA2). In addition, the Main Base Plate is so constructed that the six-creep-rupture test stations are individually mounted on the Base Plate by means of flanges and metal gasket seals.

2. Individual Test Stations (See Figure IIA2)

Each test station is fabricated, assembled and aligned onto a separate flange which in turn may be independently bolted to the Main Base Plate. Therefore, each one can be replaced by a blank flange, if the need arises. This has the advantage of allowing for the replacement of one or more stations with a blank flange, the need for vacuum checkout of individual stations, or the use of less than six stations.

3. The Vacuum Pumping System (See Figure IIA1)

For rough pumping the test chamber to approximately 10^{-2} Torr., the system is provided with three sorption-type pumps attached to a roughing manifold through three non-bakeable valves and one bakeable valve. To attain pressures of the order of 10^{-9} to 5×10^{-11} Torr., the system has a bakeable 500 liter/sec. triode pump and a titanium sublimation pump. The titanium sublimation pump has a removable liquid nitrogen or water-cooled cryopanel of 500 square inches surface area for receiving the titanium film from the pump.

4. Equipment Controls

Controls for the vacuum system include the following:

a. Ion pump control
b. Titanium sublimation pump control
c. Chamber and pump bakeout control, timer and temperature indicator
d. Ionization gage control
e. Thermocouple gage control
f. Ion pump pressure relay

Temperature recorders and controllers

The system for controlling and recording the temperature of each test station utilizes a General Electric Instrument Department system which consists of the following: step-down transformer; SCR Power Pack; Type 550 MV/I transmitter for use with two W-5% Re/W-26% Re thermocouples in a range of 1000 to 3000°F; a Type 521-1/2% - 2-pen recorder; and a Type 560 dual alarm for automatically switching the control system from the temperature controlling thermocouple to the temperature recording thermocouple. In addition, a Minneapolis-Honeywell manual switch allows the switching of thermocouples at the operator's discretion.

This extra emphasis on the thermocouple switching arrangement was deemed appropriate in order to decrease the risk of loss of data due to thermocouple failure during a run.

Automatic controls and timer for bakeout are also included in the control system.

5. The Hoist System (See Figure IIA1)

An electrically hydraulic hoist system, provided with safety latches and control valves, furnishes vibration-free lifting of the outer stainless steel shell, thus exposing the individual test stations mounted on the Main Base Plate.

Elements of a Creep Rupture Station

The basic elements of a Creep Rupture Station are shown in Figure IIA2 and are as follows:

1. Invar Posts

These serve as the stationary support for the specimen train. They are constructed of low coefficient of expansion material to minimize errors in the creep measurement.

A zero mark or fiducial reference point is positioned on the invar post. Provision for sighting this reference point with a cathetometer through a window is made for alignment adjustments at set-up time and for measuring or corroborating measurements of extensions during test.

2. Water Cooled Copper Wall, Radiation Shields and Heating Elements

The heating element and radiation shields are made from 5 mil Ta-10% W sheet and are housed inside a water-cooled jacket.

The tungsten-rhenium thermocouples (W-5% Re/W-26% Re) are positioned inside the furnace element, in close proximity to the wire sample, for recording and controlling the test temperature.

3. Wire Samples

Wire of approximately five mils diameter is electrolytically etched to a slightly smaller diameter and to a length of one inch in order to define the gage length. The sample is clamped to the upper invar post and then attached to the desired load (weights). The weights are suspended by a pivoted lever arrangement and are released only when the test conditions are achieved.

4. Creep Sensing System

For measuring the extension of the wire sample under stress an LVDT (Linear Variable Differential Transformer) method, designed and built by Schaevitz Engineering Corporation, is employed. This consists of a nickel-iron core rod attached to the weights and is a part of the total load on the specimen. This core rod hangs within a stainless steel tube welded to the test station flange. The LVDT coils are positioned externally around the tube and core. The movement of the core rod within the field produces an electrical signal which can, by calibration, be related to creep deformation (See below). In addition to the usual LVDT coils, an additional coil has been designed into the system for use as a "Specimen Break" detector signal.

The Creep Measuring System

The extension of the loaded specimen with time requires measurement of deformation perhaps as great as 0.5", to precision as high as 50 microinches and with expected testing times as long as 1,000 hours.

The LVDT system of measurement (see above) is identical for each of the six test stations. Movement of the Ni-Fe core suspended from the specimen is monitored by the signal induced in the surrounding LVDT coils. Convenient calibration of the LVDT system is effected by measuring the change in output of the LVDT when the outside coils are moved a known distance. A sensitive mechanical adjustment of the position of the external coils is available and the displacement can be measured directly.

The primaries of the LVDT's are excited by a 2.5 KC carrier at 3 VAC. The output voltage from each differential winding of the LVDT's leads into a separate carrier-amplifier-demodulator where it is converted to an analog DC voltage for presentation on a multichannel recorder. In addition, this output may be switched to a single channel recorder for continuous recording required for rapid changes during initial stages of creep.

A range selector switch at the output of the amplifier-demodulator will select full scale measurement ranges for this displacement equivalent to 0.005", 0.050", 0.100", 0.250" and 0.500".

Each LVDT output is fed into a six channel Bristol recorder with color dot printout. The input to the recorder is 0 to 50 millivolts. Chart speed is one inch/hour and sampling rate is one print/minute for a total cycle time of six minutes.

The LVDT system contains an additional coil which will produce a signal when specimen rupture occurs. The signal through the control relays to the multi-channel recorder will give a record of rupture within six minutes of actual rupture time.

The second recorder, a single channel recorder, is used to accept any one of the six station outputs for recording continuously when desired. This recorder has a 0 to 50 millivolt range and chart speeds of one inch/hour and one inch/minute.

Design and Construction

Design

The design of the various components of the equipment were completed by September 15, 1965, and approval of the detailed drawings has been received.

The Flow Diagrams (Electrical and Water) have also been completed as of the date of this report and have been submitted for approval.

Final design changes and corrections of detail drawings are to be made after the equipment has been assembled and debugged. An accurate and complete set of prints will then be submitted to NASA.

Fabrication and Construction

All phases of equipment fabrication and/or purchasing of specific and specialized instrumentation for the vacuum, temperature and measurement systems were initiated as soon as approvals were received.

Facilities

General Electric laboratory facilities have been rearranged in order to provide a separate room for the assembly, and operation of the equipment. Services and, in addition, air conditioning have been installed.

Future Plans

The various components of the Multi-Station creep tester are scheduled for completion and shipment to G. E. by mid-February 1966. The equipment will then be assembled and the debugging, reworking and calibration of the apparatus will start.

Within the next six months period, general familiarization with the equipment and the development of procedures and techniques of its operation will be accomplished. Creep testing of wire specimens will also be done.

A manual of operation including the operation procedures and techniques for testing will be written up for NASA. Included in this manual will be a general maintenance and troubleshooting section.

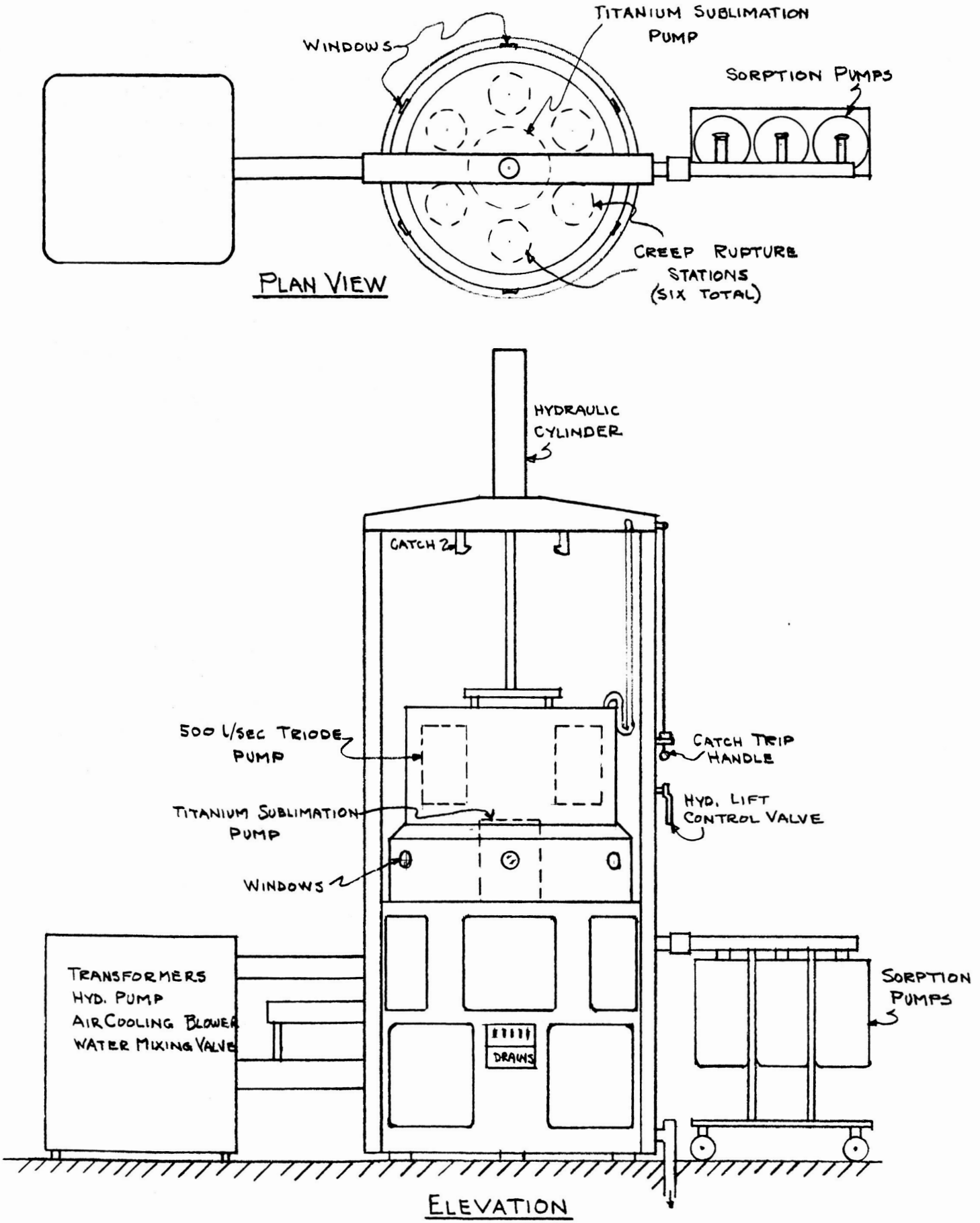


FIG. II A1- CREEP RUPTURE APPARATUS

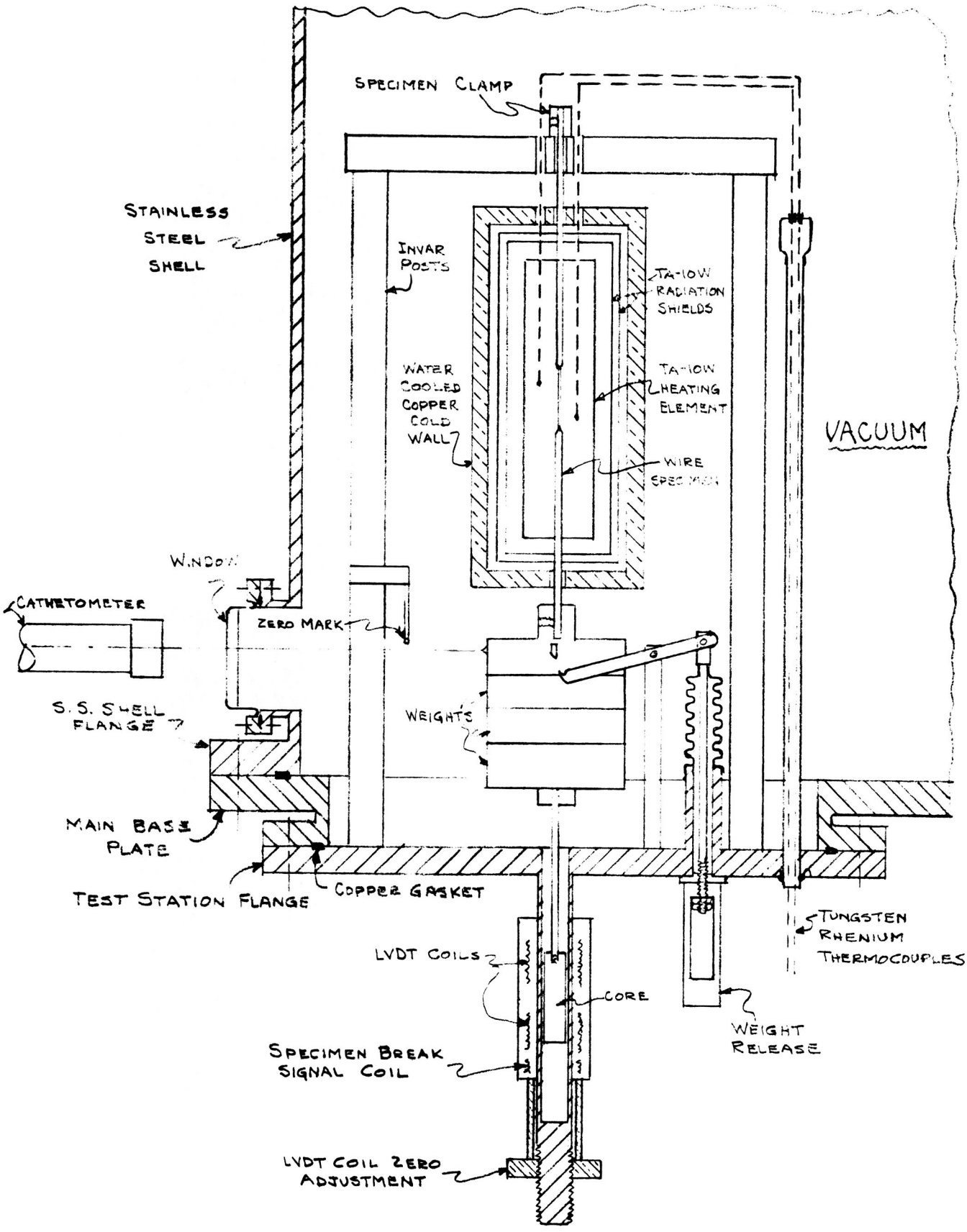


FIG. II A 2 - CREEP RUPTURE STATION

Section II - The Evaluation of Materials

B. The Tensile Testing Apparatus

A description of this ultra-high vacuum tester will be included in the next report. It is now in the final build stage. This equipment is not part of the contract work.

Section II - The Evaluation of Materials

C. Preliminary Investigations

Specimen Gage Length

Introduction

In order to define the length of wire specimen being deformed during a creep-rupture test, it was necessary to find a method to reduce uniformly the diameter of a section of wire exactly one inch long. Preliminary experiments using electrochemical etching revealed that a more uniform diameter gage length could be obtained by use of alternating current rather than direct current. In addition, it was found that rotation of the wire on its axis during electrochemical etching produced a preferred and better specimen. Specifically, this method yields smoother and more gradual diameter changes at the ends of the gage length.

Etching Apparatus (See Figure IIC1)

The apparatus designed for etching the one inch gage section is shown in Figure IIC1. The basic features of this apparatus are:

1. Plexiglass etching container
2. Braided tungsten wire coil
3. Capillary glass tubing
4. Variable speed motor
5. A.C. voltage variable transformers and voltmeter

The plexiglass container is fabricated so that its internal diameter is exactly one inch. Through the walls of the container are two diametrically opposed .015 inch diameter holes. A tungsten coil (nine wires of .065" diameter braided wire one inch in length and an I.D. of 5/16") is inserted into the one normal NaOH solution and serves as the anode. This coil is positioned such that the wire specimen passes through its center when the specimen is threaded through capillary glass tubing and plexiglass container. One end of the wire is gripped by a pin vise chuck which is rotated by a variable speed motor.

Procedure

The wire specimen was inserted through the plexiglass container, tungsten coil anode and capillary glass tubing and attached to the variable speed motor by the pin vise chuck. The variable speed motor for these experiments was a Dremel Model-2 Moto-Tool, the speed being controlled by controlling the input voltage with a variable AC transformer. No attempt was made to measure the actual rotational speed as the voltage was varied. The speed was varied to determine the effect of rotation on uniformity of etching. The AC voltage for etching was controlled and varied by using a Powerstat variable transformer in the circuit. The etching voltage used was measured by a voltmeter. Preliminary experiments for the determination of feasibility of this method were tried on .007" diameter 218 tungsten wire under the following experimental conditions:

	Experimental Conditions		
Experiment No.	Moto-Tool Rotation Speed (AC Volts)	Etching Voltage (AC Volts)	Etching Time (Seconds)
1	25	9	5
2	25	9	10
3	25	9	20
4	40	9	20
5	60	9	20
6	25	4.5	40
7	25	2	90

After each wire specimen was etched as described above, dimensional measurements were made on the etched section using an optical microscope with a 10X objective lens and the Bausch and Lomb filar micrometer eyepiece from a Tukon Microhardness Machine. The filar micrometer was calibrated directly by means of a stage micrometer. The sensitivity of this method is calculated to be 70 micro inches. Diameter measurements were then made by traversing the gage length and making measurements at 1/4 inch intervals. Measurements to show the transition from the etched section to the original diameter were not made. However, photographs of typical junctions were taken.

Results from these experiments indicated that electrochemical etching method could be used to obtain a reasonably uniform one inch gage length with a diameter less than that of original wire. The final gage length diameter is dependent on the etching parameters, such as time, etching voltage and rotational speed.

The next step was to determine whether or not the etching process caused a significant change in mechanical properties. Tensile tests at room temperature and at 1670°C were made on unetched wire and wire etched approximately .0005" and .002". The .2% offset yield stress, ultimate tensile strength and percent elongation were determined from the load-deflection test data record of an Instron tensile testing machine.

From the experience gained with 218 W wire, TZC .005" diameter wire, drawn for property evaluation in this contract, was etched using the same technique and the same electrolyte. The etching parameters for the TZC were as follows:

	Experimental Conditions		
Experiment No.	Moto-Tool Rotation Speed (AC Voltage)	Etching Voltage (AC Voltage)	Etching Time (Seconds)
1	25	4.5	15
2	25	4.5	20
3	25	5	15
4	25	2.5	40

Room temperature tensile tests were made on these materials to again see whether the mechanical properties were affected by the etching process.

Results of Etching Experiments

218 Tungsten .007" Diameter Wire

Figure IIC2 shows a graph of the variations in diameter of the gage length profile. In addition, the influence of variations in rotational speed, etching voltage and time are shown. It can be seen that the variations in diameter from one end of the gage length to the other are quite small (approximately .0001") for the poorest case and are significantly better if the proper etching conditions are selected (such as 25-9-20).

Photographs of the gage section and the area of transition from the original to the etched diameters are shown in Figures IIC3, 4, 5 and 6. Figures IIC3 and IIC5 show the gradual reduction of diameter at 100X magnification for the 25-9-5 (diameter decreased by .0005") and the 25-9-20 (diameter reduced .002") respectively. Figures IIC4 and IIC6 show the entire gage length at 10X magnification for these same etching parameters.

Table IICI is a compilation of the room temperature and 1670°C tensile properties of etched and unetched 218 tungsten wire. Although the data presently available should be considered as quite limited, some tentative observations and conclusions are suggested. At both room temperature and 1670°C the ultimate tensile strength of 218 tungsten wire does not appear to be influenced by the etching process. For example, at room temperature five samples of unetched wire gave an average ultimate tensile value of 425,500 psi (range of values 423,600 psi to 426,200 psi). The etched samples gave room temperature ultimate tensile averaging 413,300 psi (range 408,900 psi to 417,800 psi). Thus, agreement is indicated within approximately three percent. At 1690°C the ultimate tensiles of an unetched sample 93,100 psi compares very favorably with three values listed for etched samples (average = 92,400 psi).

For the .2% yield strength, at room temperature, the average value for etched samples is 361,000 psi compared to the average 363,800 psi for unetched wire. At 1690°C the average value of 90,400 psi is within 4% of the single value now available for an unetched sample. The room temperature elongation data (of which there is admittedly a paucity) indicate that with a change in diameter of .0015" or greater from etching, the elongation is approximately 1/3 that of the unetched material. However, with a diameter change of only .0004", the elongation of the etched material is about 3/4 that of the unetched. At 1670°C, the elongation of etched samples is 1/2 that of the unetched. The amount of material removed by etching does not appear to be as important at this elevated temperature.

TZC .005" Diameter Wire

Figure IIC7 shows the variation of diameter with gage length profile. In this case, a constant speed of rotation was chosen and the etching voltages and times varied. Of significance here is the fact that the etching voltage needed to be decreased to roughly 1/2 that used for the 218 W .007" diameter wire. At this decreased etching voltage measurements of the resulting etched diameter revealed extremely good uniformity in the gage section.

Photographs at 100X magnification in Figures IIC8 and IIC9 show that portion of the etched wire at the junction of the original and gage length diameters. Figure IIC8 is the TZC sample decreased approximately .0005" in diameter by etching conditions of 25-4.5-15 and Figure IIC9 is the TZC sample representative of a .001" decrease in diameter by 25-5.0-15 etching conditions.

Table IICII is a compilation of the room temperature tensile property data for TZC samples etched by the technique discussed above. Comparison of the strength properties reveals no significant influence on the ultimate tensile strength of the material by the etching process. The average ultimate tensile strength for etched wire (215,600 psi) is almost identical to the average value of 215,700 psi for unetched wire. On the other hand, the data for .2% yield strength shows the unetched wire to have an average value (189,800 psi) lower than the average (199,600 psi) for etched samples. This difference is approximately five percent of the unetched value. All percent elongation values for etched wire are lower than for the unetched. It is not now apparent that this can be correlated with the degree of etching.

Conclusions

From the results of the etching experiments presented here, it seems to be apparent that this technique can be used to establish a uniform gage length section in a wire specimen in order to define the deformation zone during mechanical property tests. The data seem to indicate that the properties of the etched material approximate those of the unetched material. For the ultimate strengths and .2% yield strength, correspondence has been demonstrated to within 5% for 218 tungsten wire at room temperature and 1670°C and for TZC at room temperature. Apparent significant differences in percent elongation have been observed both in tungsten and TZC. In all cases, percent elongation is lower for etched specimens.

Control Thermocouple Switching Experiments

To establish the feasibility of an automatic temperature control switching arrangement on each of the test stations, it was necessary to estimate the rate of change of temperature with time at power interruption. Experiments in a Brew vacuum furnace (Vacuum - 5×10^{-6} Torr. and temperature 2400°F) were made where the change in temperature at the center of the furnace, as measured by a thermocouple, was recorded on an X-Y recorder as a function of time when the power to the furnace was instantaneously shut off.

The average results of five such experiments are graphed in Figure IIC10. The data are shown for the actual temperature vs. cooling time and also as the change in temperature vs. the cooling time. From these experiments, it can be seen that in five seconds after complete power shutoff (a condition which approximates the automatic switching from the control thermocouple to the recording thermocouple for control) the furnace cooled 2.5°F. For time intervals of seven, eight, and ten seconds, the furnace cooled 12°F, 22°F, and 62°F respectively.

Provided that this experiment adequately approximates the test furnaces to be constructed for the multi-station tester, then it is desirable for the temperature control switching system to transfer control from one thermocouple to the other within a 0 to 7 second period. This requirement has, therefore, been designed into the equipment.

TABLE IICI

218 Tungsten .007" Diameter Wire

Etching Procedure	Test Temperature	Average G.L. Diameter	Ultimate Tensile Strength in psi	.2% Yield Strength in psi	% Elongation
25-9-5A	1670°C	.00644	95,400	93,400	0.4
25-9-5B	25°C	.00659	417,800	325,400	3.22
25-9-20A	1670°C	.00520	95,500	93,500	0.4
25-9-20B	25°C	.00522	408,900	369,200	1.47
25-4.5-40A	1670°C	.00546	86,200	84,500	0.4
25-4.5-40B	25°C	.00534	415,200	388,400	1.35
Unetched	1670°C	.00700	93,100	87,100	0.8
Unetched	25°C	.00700	425,500*	363,800*	4.33*

*Average results of five tensile test on unetched wire

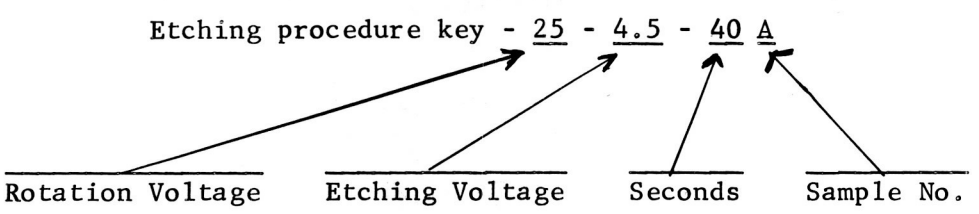
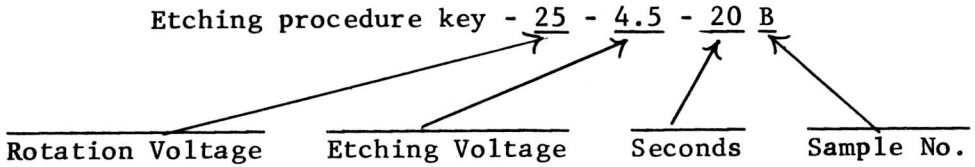


TABLE IICII

TZC .005" Diameter Wire

Etching Procedure	Test Temperature	Average G.L. Diameter	Ultimate Tensile Strength in psi	.2% Yield Strength in psi	% Elongation
25-4.5-20B	Room Temp.	.00366	218,200	200,200	1.88
25-4.5-20C	Room Temp.	.00363	217,600	196,300	1.47
25-9-5A	Room Temp.	.00446	214,900	202,100	1.44
25-4.5-15A	Room Temp.	.00415	217,700	201,500	2.24
25-4.5-15B	Room Temp.	.00421	218,800	201,600	2.06
25-5-15B	Room Temp.	.00402	223,500	206,300	2.54
25-5-15C	Room Temp.	.00398	212,900	194,400	2.26
25-2.5-40C	Room Temp.	.00398	206,100	190,800	2.68
25-2.5-40B	Room Temp.	.00396	210,900	194,700	2.37
Unetched*	Room Temp.	.00500	215,700*	189,800*	3.93*

*Average results of six tensile test on unetched wire



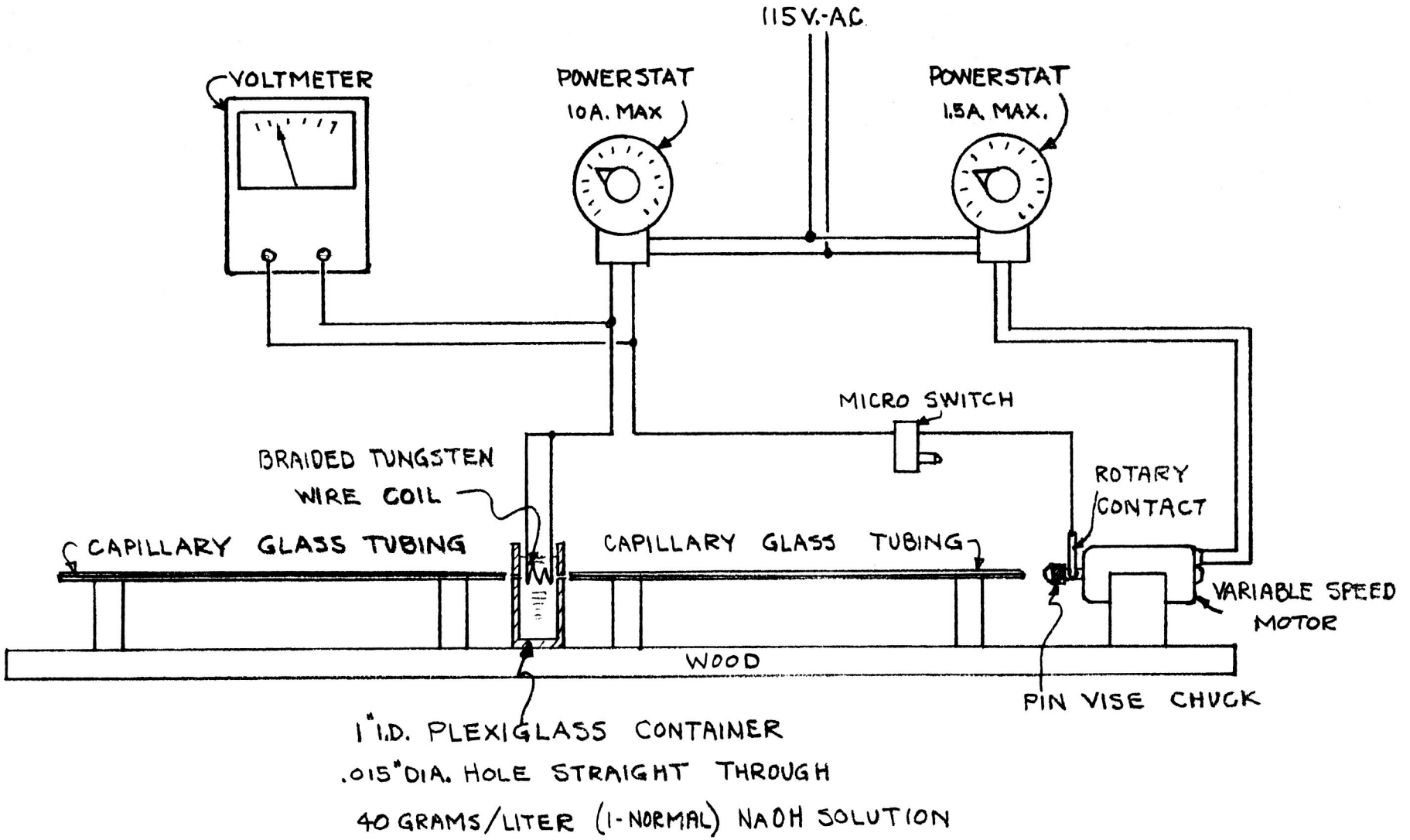


FIG. II C1 - WIRE ETCHING DEVICE

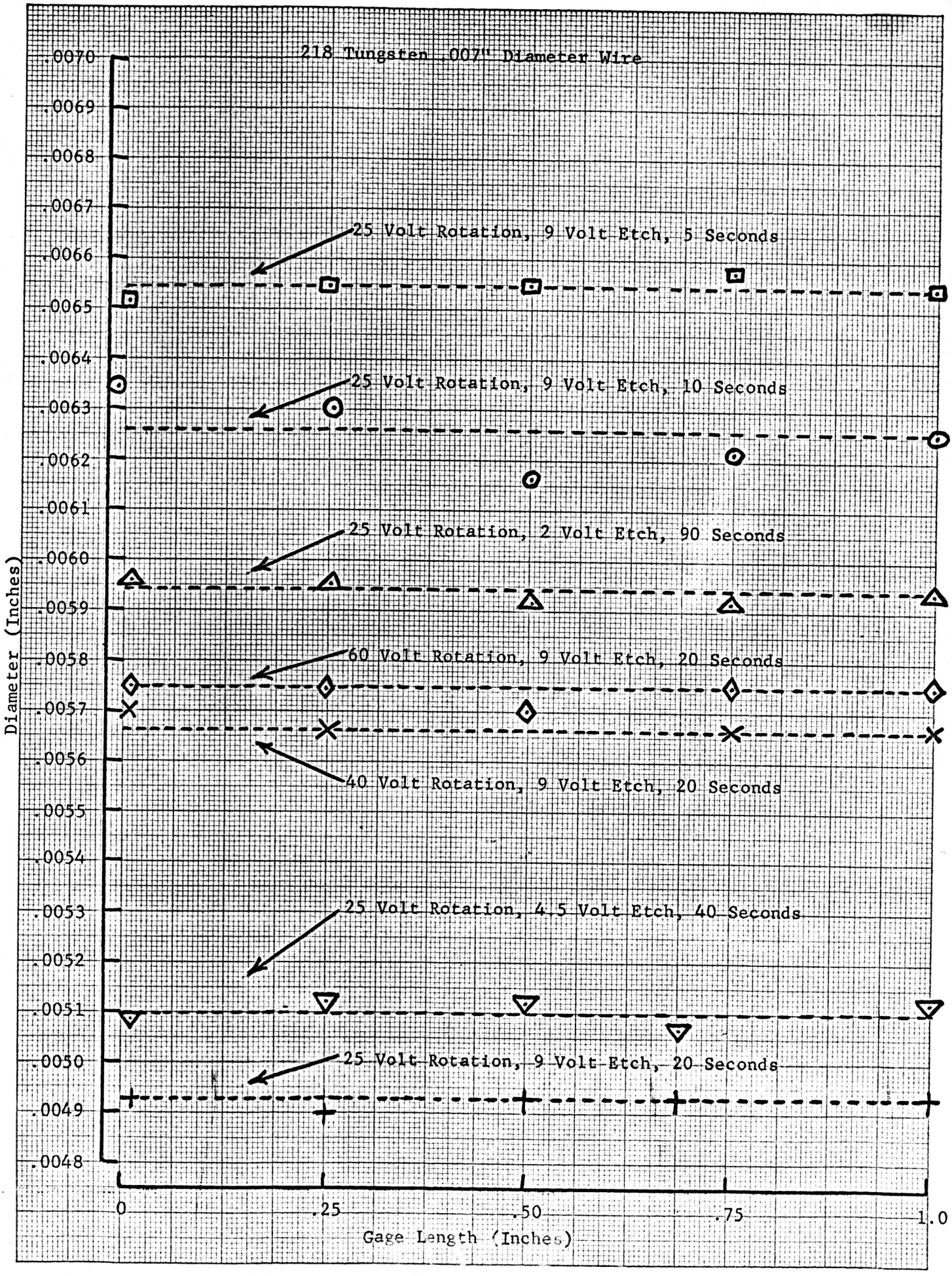

218 Tungsten .007" Diameter Wire
.0070
.0069
.0068
.0067
.0066
.0065
.0064
.0063
.0062
.0061
.0060
.0059
.0058
.0057
.0056
.0055
.0054
.0053
.0052
.0051
.0050
.0049
.0048
Diameter (Inches)
25 Volt Rotation, 9 Volt Etch, 5 Seconds
25 Volt Rotation, 9 Volt Etch, 10 Seconds
25 Volt Rotation, 2 Volt Etch, 90 Seconds
60 Volt Rotation, 9 Volt Etch, 20 Seconds
40 Volt Rotation, 9 Volt Etch, 20 Seconds
25 Volt Rotation, 4.5 Volt Etch, 40 Seconds
25 Volt Rotation, 9 Volt Etch, 20 Seconds
0
.25
.50
.75
1.0
Gage Length (Inches)

FIGURE - IIC2

218 Tungsten Wire

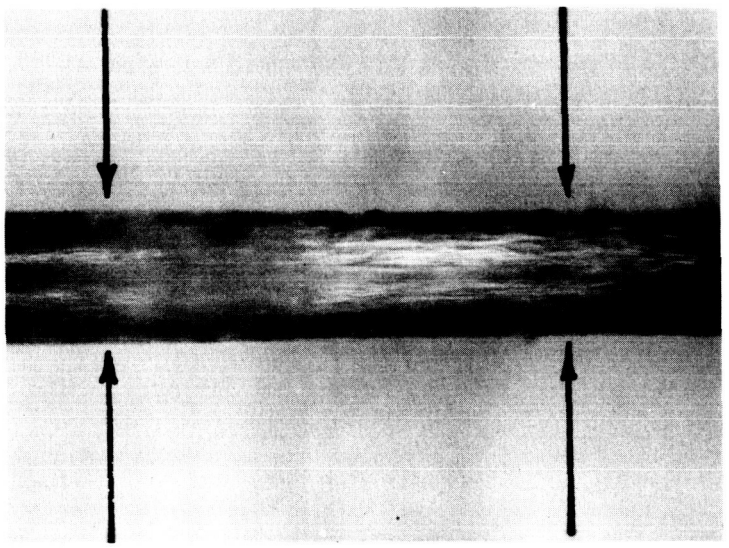


FIGURE IIC3 - 25 Volt Rotation, 9 Volt Etch
5 Seconds, 100X

218 Tungsten Wire

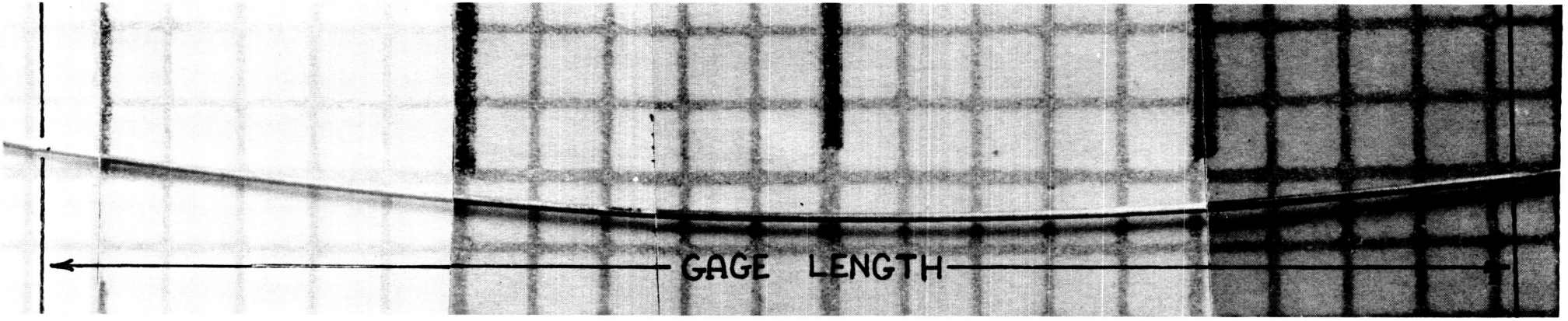
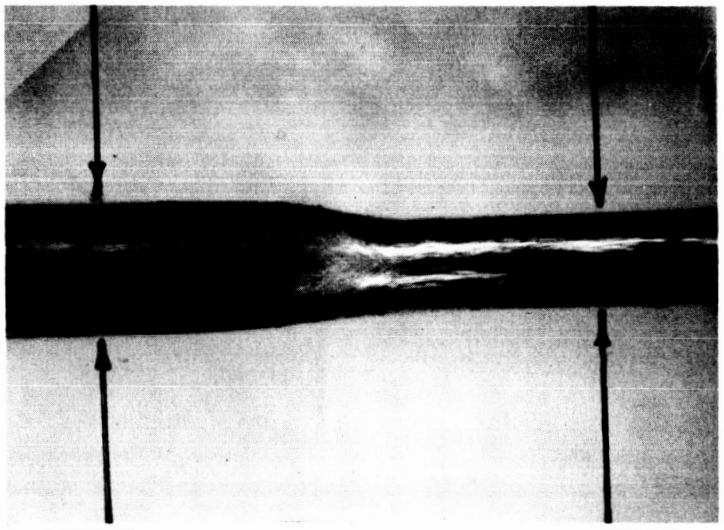


FIGURE IIC4 - 25 Volt Rotation, 9 Volt Etch, 5 Seconds, 10 X

218 Tungsten Wire



.00700" .0049"

FIGURE IIC5 - 25 Volt Rotation, 9 Volt
Etch, 20 Seconds, 100X

218 Tungsten Wire

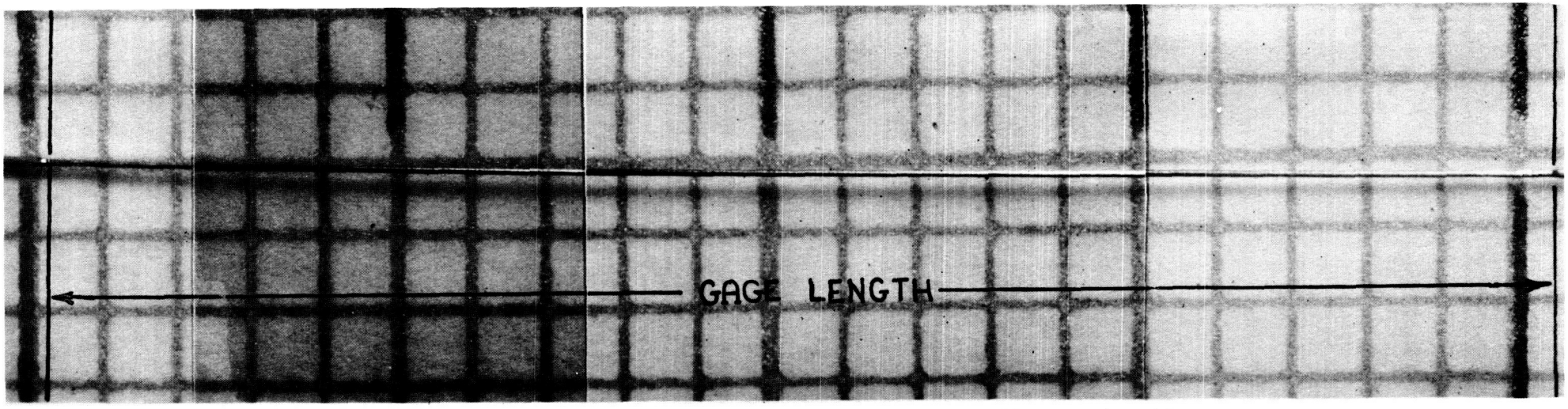


FIGURE IIC6 - 25 Volt Rotation, 9 Volt Etch, 20 Seconds, 10 X

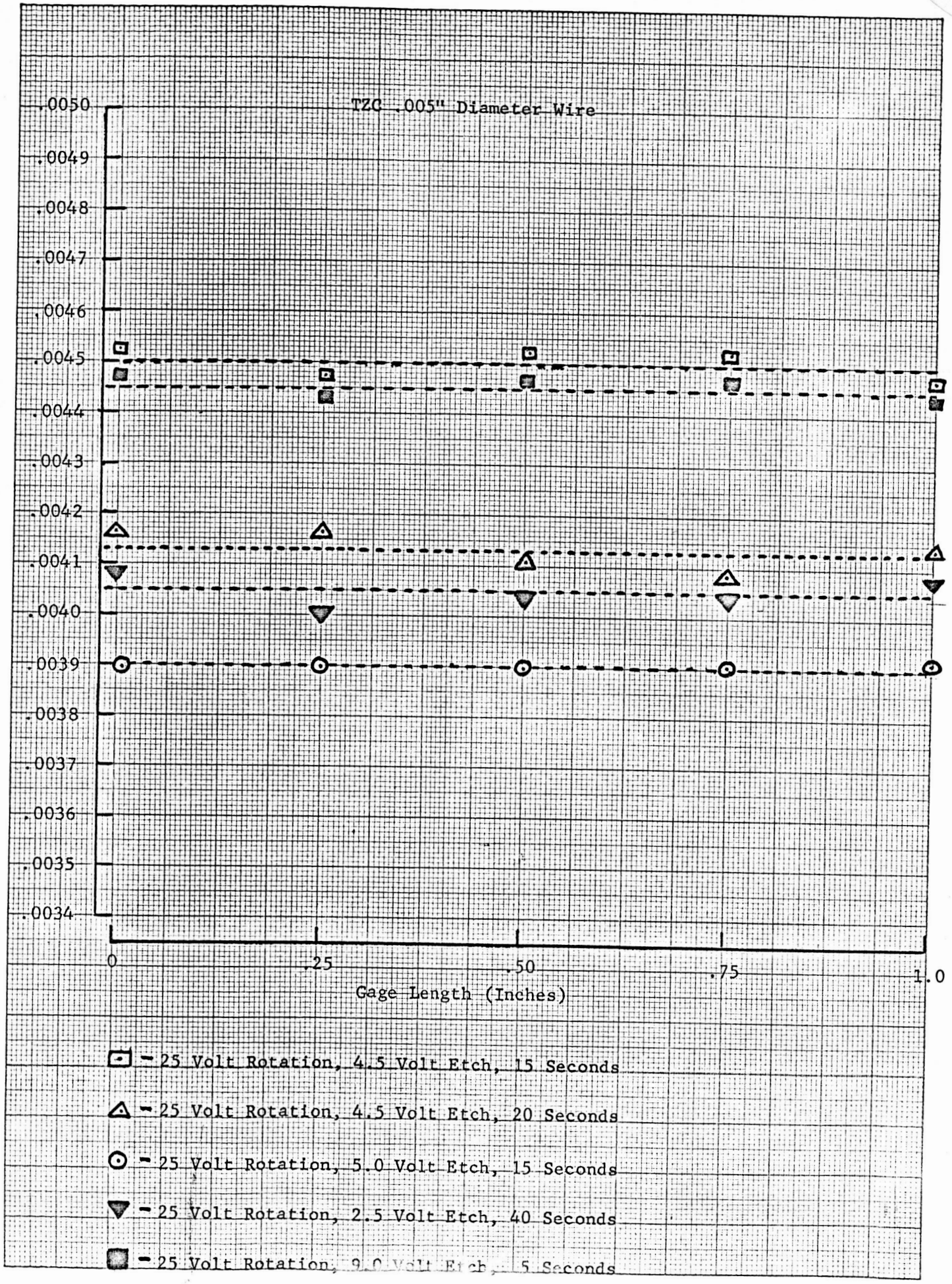
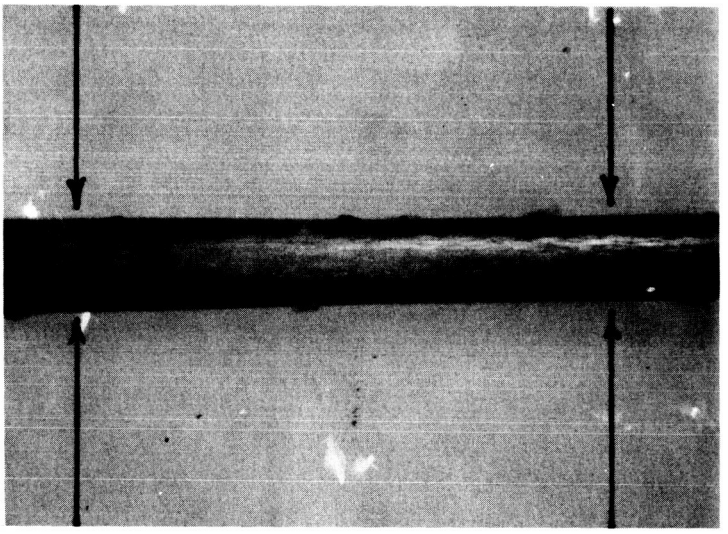

TZC .005" Diameter Wire
.0050
.0049
.0048
.0047
.0046
.0045
.0044
.0043
.0042
.0041
.0040
.0039
.0038
.0037
.0036
.0035
.0034
Diameter (Inches)
0
.25
.50
.75
1.0
Gage Length (Inches)
- 25 Volt Rotation, 4.5 Volt Etch, 15 Seconds
- 25 Volt Rotation, 4.5 Volt Etch, 20 Seconds
- 25 Volt Rotation, 5.0 Volt Etch, 15 Seconds
- 25 Volt Rotation, 2.5 Volt Etch, 40 Seconds
- 25 Volt Rotation, 9.0 Volt Etch, 5 Seconds

FIGURE - IIC7

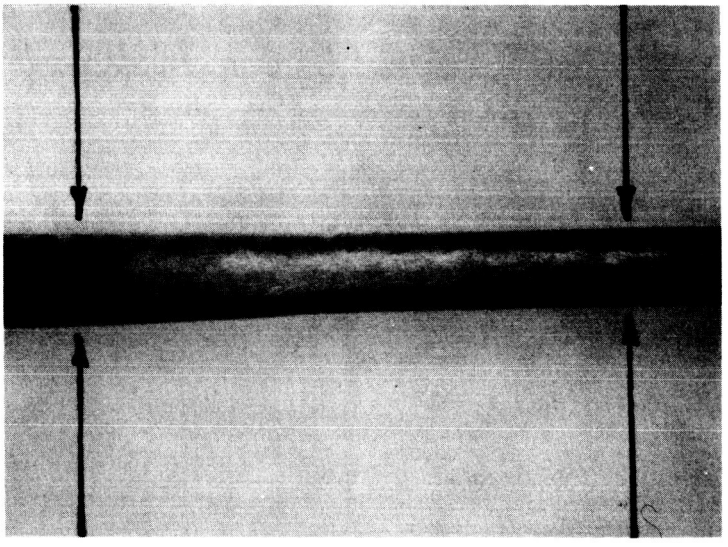
TZC Wire



.0050" .0045"

FIGURE IIC8 - 25 Volt Rotation, 4.5 Volt Etch
15 Seconds, 100X

TZC Wire



.0050" .0040"

FIGURE IIC9 - 25 Volt Rotation, 5 Volt Etch
15 Seconds, 100X

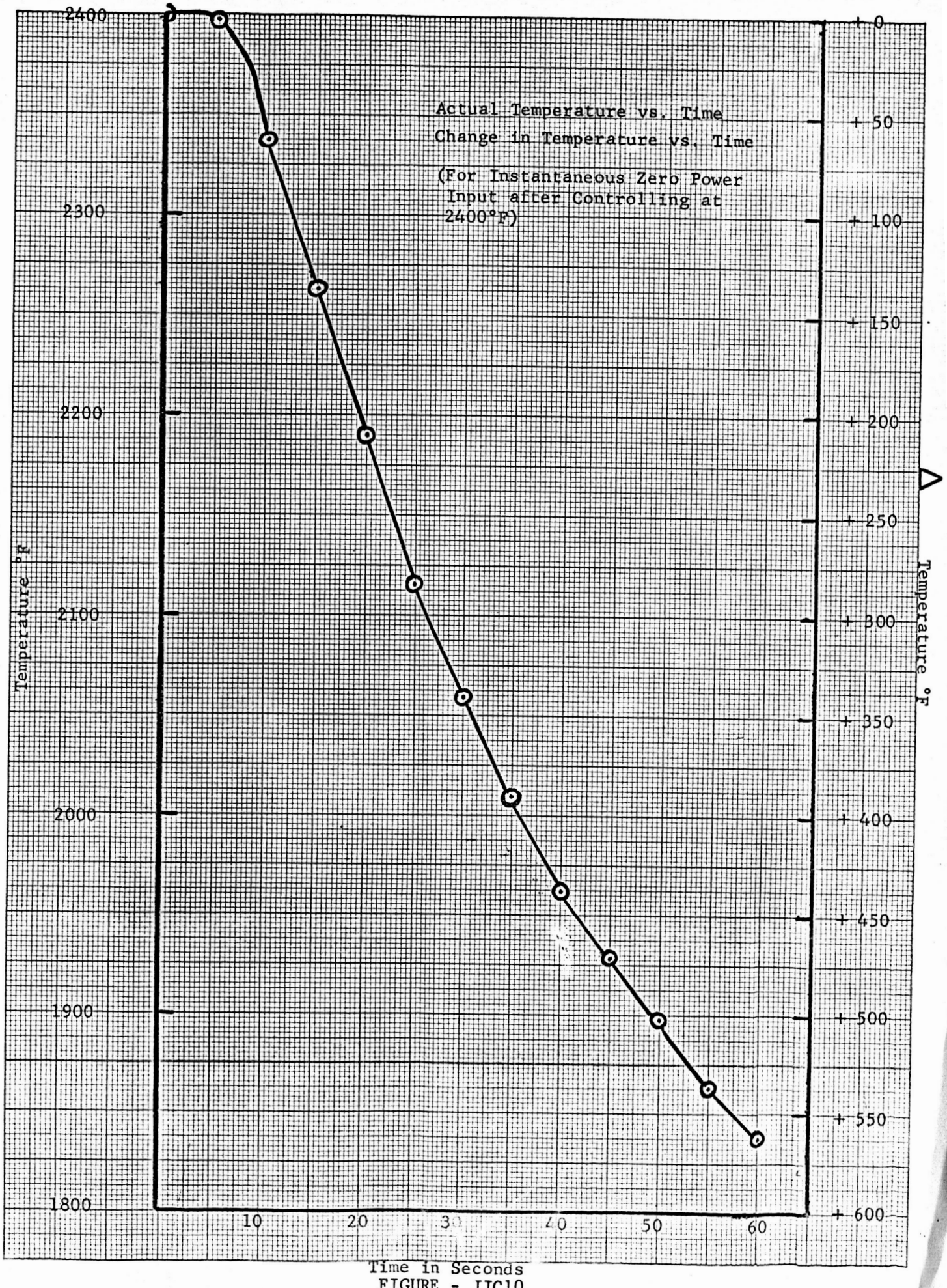


FIGURE - IIC10

Acknowledgements

A relatively large number of people have contributed to various phases of this contract. A brief acknowledgement of the names and the attendant areas of contribution will convey an idea of the effort being expended in this development contract.

Material acquisition, melting, or preparation has been supervised primarily by Mr. R. Barto and especially L. Amra.

Breakdown of powder metal ingots or extruded rods has been followed by Mr. F. R. Adams at the Cleveland laboratory or by Mr. L. F. Chamberlain at the Dover, Ohio, location.

The predominant amount of wire processing development will be done at Dover, under Mr. Chamberlain or Mr. K. A. Hofacker, although it is possible that the tungsten base alloys may have to be run in the Engineering Pilot Plant at Cleveland, under Mr. C. W. Hewitt.

The designing and building of the multi-station creep, stress-rupture test apparatus has been mainly a joint effort of Mr. W. C. Gates and Mr. J. F. Tavernelli. Mr. Tavernelli will also be in charge of all physical testing of the wire produced for this contract.

Valuable assistance in the form of consultation has been received from Dr. C. A. Brown and Dr. D. T. Hurd.