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INVESTIGATION OF THE FEASIBILITY OF PRODUCING TUNGSTEN-HAFNIUM --ETC(U)  
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6 INVESTIGATION OF THE FEASIBILITY OF PRODUCING TUNGSTEN-HAFNIUM CARBIDE ALLOY BY POWDER METALLURGICAL TECHNIQUES

11 MAR 1978

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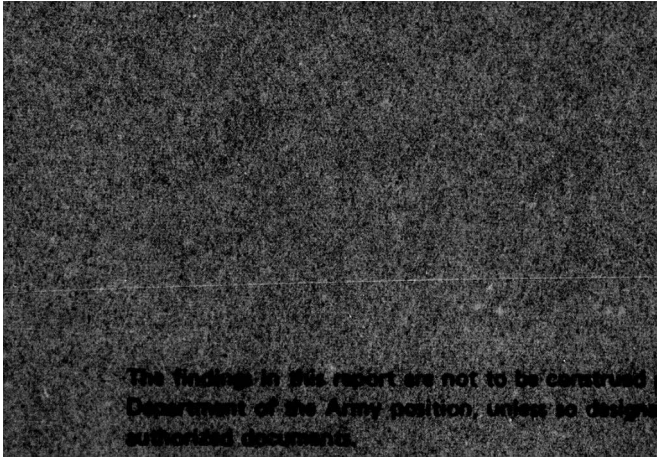
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hydride and graphite powder, encapsulated in mild steel cannisters, and dehydrided under vacuum at elevated temperature. In Process B, deoxidized tungsten powder was blended with degassed hafnium carbide, encapsulated in mild steel cannisters, and evacuated. In Process C, prealloyed W-0.35HfC powder was encapsulated in mild steel cannisters and hydrogen deoxidized at elevated temperatures followed by evacuation. Process A and B powders were consolidated by extrusion at 2300°F. The resulting materials had oxygen levels and controlled carbon levels comparable to arc cast material. Mechanical properties of these materials did not approach those of arc cast material due to incomplete densification and incomplete homogenization of the HfC. Additional thermal-mechanical processing appears to be necessary to improve mechanical properties. The prealloyed WHfC powder, Process C, could not be extruded at 2300°F. However, the material was successfully extruded at 3600°F and had tensile strength equivalent to arc cast material. Tensile strength levels were comparable to arc cast material at all temperatures. Ductility values and strength after annealing were significantly lower than arc cast material due to incomplete densification.

FOREWORD

This report was prepared by the Westinghouse Electric Corporation, Advanced Energy Systems Division, Pittsburgh, Pennsylvania for the Army Materials and Mechanics Research Center, Watertown, Massachusetts under Contract DAAG46-75-C-0098 entitled, "Investigation of Feasibility of Producing Tungsten-Hafnium Carbide Alloy by Powder Metallurgical Techniques". This work is part of the AMMRC program on Development of Hardened ABM Materials, Mr. John F. Dignam, Program Manager. The AMMRC Technical Supervisor was Mr. Lewis R. Aronin.

The work reported herein was conducted from 30 June 1975 through 30 June 1976. Mr. Robert L. Ammon was the Principal Investigator.

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## 1.0 SUMMARY

The objective of this program was the investigation of the feasibility of producing W-0.35HfC\* alloy by powder metallurgical techniques and attaining mechanical properties equivalent to arc-cast and extruded material. The powder metallurgical approach is being evaluated because available arc melting and high temperature extrusion facilities limit the size of billets which can be processed to approximately 3-1/2 inches in diameter. Also, arc-cast ingots contain solidification defects which significantly lower the yield of sound extruded material.

To accomplish this objective, three metal powder consolidation techniques were investigated in parallel. The three powder consolidation approaches consisted of the following:

- Process A - Blending tungsten, hafnium hydride and graphite powder, vacuum dehydrating, and extrusion in a mild steel can at 2300°F to densify the powder compacts. (modified Friedman-Dickinson process)
- Process B - Blending tungsten and hafnium carbide powder, encapsulating in mild steel cannisters, evacuation of the cannisters and extrusion at 2300°F.
- Process C - Encapsulating WHfC prealloyed powder in mild steel cannisters fitted with valved inlet and outlet vent tubes, hydrogen deoxidation at elevated temperature, evacuation of the cannisters, and extrusion at 2300°F.

The consolidation techniques were selected to permit utilization of commercially available equipment to avoid costly capital equipment investment for this feasibility study. The consolidation techniques were also selected to permit ultimate process scale-up in both size and quantity of finished component parts with a minimum development effort required.

\* W-0.35 HfC mol percent = W-0.36HfC weight percent. Throughout this report the alloy composition will be designated in mol percent.



The program consisted of four sequential tasks as follows:

- powder procurement and preparation
- powder blending and consolidation
- heat treatment
- mechanical property evaluation.

In the first task tungsten, hafnium carbide, hafnium hydride and graphite powders were procured. The deoxidation characteristics of the tungsten, hafnium carbide, and graphite powders were investigated in flowing hydrogen, inert gas, and vacuum using a thermal-gravimetric technique. Arc-cast W-0.35HfC prealloyed material was converted to powder by Metallurgical International using the Coldstream process. Degassing characteristics of the prealloyed WHfC powder were also investigated, and a procedure for removing adsorbed gases without decarburizing the alloy powder was developed.

In the powder consolidation task, a procedure was developed for deoxidizing 45 pound batches of tungsten powder and small quantities of graphite and hafnium carbide powder. A vacuum purged glove box was modified to facilitate blending and sealing the blended powders under high purity helium cover gas in mild steel cannisters. Four cannisters of blended deoxidized tungsten, hafnium hydride and deoxidized graphite powder were prepared. The powder mixture was dehydrated under vacuum at 1600°F and sealed. The cannisters containing the W-HfH<sub>2</sub>-C material (Process A) were extruded at 2300°F through a round die to produce material >96 percent of theoretical density. Four cannisters of deoxidized tungsten powder containing deoxidized hafnium carbide (Process B) were prepared in a similar manner. The cannisters were evacuated and sealed. The W-HfC was extruded at 2300°F to produce consolidated material >96 percent of theoretical density. Extruded W-HfH<sub>2</sub>-C and W-HfC material had carbon and oxygen levels comparable to arc-cast material. For the third consolidation approach (Process C), prealloyed WHfC powder was placed in four mild steel

cannisters equipped with valved inlet and outlet tubes containing 500 mesh filters to prevent material loss during the hydrogen deoxidation processing. After deoxidation, the cannisters were evacuated and sealed. Attempts to extrude the prealloyed powder at 2300°F were unsuccessful. Hot pressing was also unsuccessful. To provide material for evaluation, two small molybdenum cans were filled with as-received WHfC prealloyed powder and Dynapak extruded at 3600°F producing a limited amount of consolidated bar stock for evaluation.

In the heat treatment task, recrystallization response of the three consolidated materials to one hour heat treatments in the temperature range 3600 to 4800°F was investigated. The W-HfH<sub>2</sub>-C and W-HfC material recrystallized at temperatures below 3600°F and responded to thermal treatment in a manner similar to unalloyed tungsten. The WHfC prealloyed powder material recrystallized with a duplex grain structure at 4000°F. Solution annealing and aging studies were also carried out and involved only the W-HfH<sub>2</sub>-C and W-HfC material. Insufficient WHfC prealloyed powder material was available for inclusion in this study. Samples annealed at 4600, 4800, and 5000°F for 1/4 hour were aged for one hour at 2500, 3000, and 3500°F. Metallographic examination revealed that the alloys were inhomogeneous and contained microvoids. The W-HfH<sub>2</sub>-C material contained islands of elemental hafnium which were not completely put into solution by the high temperature anneal. The W-HfC material also contained islands of hafnium carbide particles in the tungsten matrix. Both materials contained microvoids associated with the islands of second phase material within the tungsten matrix. Additional thermal-mechanical processing appears to be necessary to eliminate the microvoids and to homogenize the microstructure.

In the final task mechanical properties were determined for as-extruded, and solution annealed and aged material of all three consolidation approaches. In the as-extruded condition the W-HfH<sub>2</sub>-C and W-HfC materials had tensile strength properties which were significantly lower than arc-cast material. Strength levels were, however, well above those for unalloyed tungsten at all test temperatures. For example, W-HfH<sub>2</sub>-C and W-HfC material had strength



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values at 3000°F of 23.5 and 31.7 ksi, respectively, compared to 15.0 ksi for unalloyed tungsten at the same temperature. At 3000°F, arc-cast W-0.35HfC has a tensile strength of 66.7 ksi. WHfC prealloyed powder material had a tensile strength of 84.0 ksi at the same temperature. The lower strength of the W-HfH<sub>2</sub>-C and W-HfC material was attributed to the inhomogeneity of the consolidated powder and the presence of microvoids due to incomplete densification. Solution annealing and aging treatments were deleterious in that the microvoids in all three powder metallurgy materials were coalesced and resulted in reduced strength values and loss of most of the elevated temperature ductility.

## 2.0 INTRODUCTION AND BACKGROUND

W-0.35HfC alloy has been shown to exhibit exceptionally high strength up to 5000°F<sup>(1,2)</sup> as illustrated in Figure 1. This characteristic has made the alloy attractive for a number of applications where a high melting point material with high elevated temperature strength is required. One such application is the leading edge of an air vane on a hypersonic missile<sup>(2)</sup>. Fabrication of the leading edge will require the production of a straight section 24 inches or longer in length. Currently, the W-0.35HfC alloy is being produced by vacuum arc melting followed by direct extrusion at 4000°F. This procedure is expensive due to the required high quality of the starting electrode melting stock, the special handling required to prepare billets for extrusion, and the low yield of sound material from the extrusion process. The arc casting process is currently limited to ingots 3-1/2 inches in diameter. Facilities for melting and extruding larger diameter ingots do not exist at the present time and are not anticipated being available in the near future. Such facilities are highly specialized and expensive to construct. Also, arc cast ingots contain solidification defects which significantly lower the yield of sound extruded material.

A powder metallurgy approach to consolidating the W-0.35HfC alloy is proposed as a means of circumventing the difficulties encountered in vacuum arc casting and direct extrusion processes. The powder processing approach is capable of producing consolidated billets approaching six inches in diameter. Once consolidated to a density of >94 percent of theoretical where interconnected porosity is virtually eliminated, the alloy can be handled in air without fear of contamination by adsorption of oxygen and moisture from the atmosphere. The inherently fine grain microstructure of consolidated powder compacts permits use of a wide variety of working processes such as hot forging and/or rolling to fabricate components.

The powder metallurgy W-0.35HfC tensile property data shown in Figure 1 were generated on a previous program<sup>(1,2)</sup>. The material evaluated was produced by blending tungsten



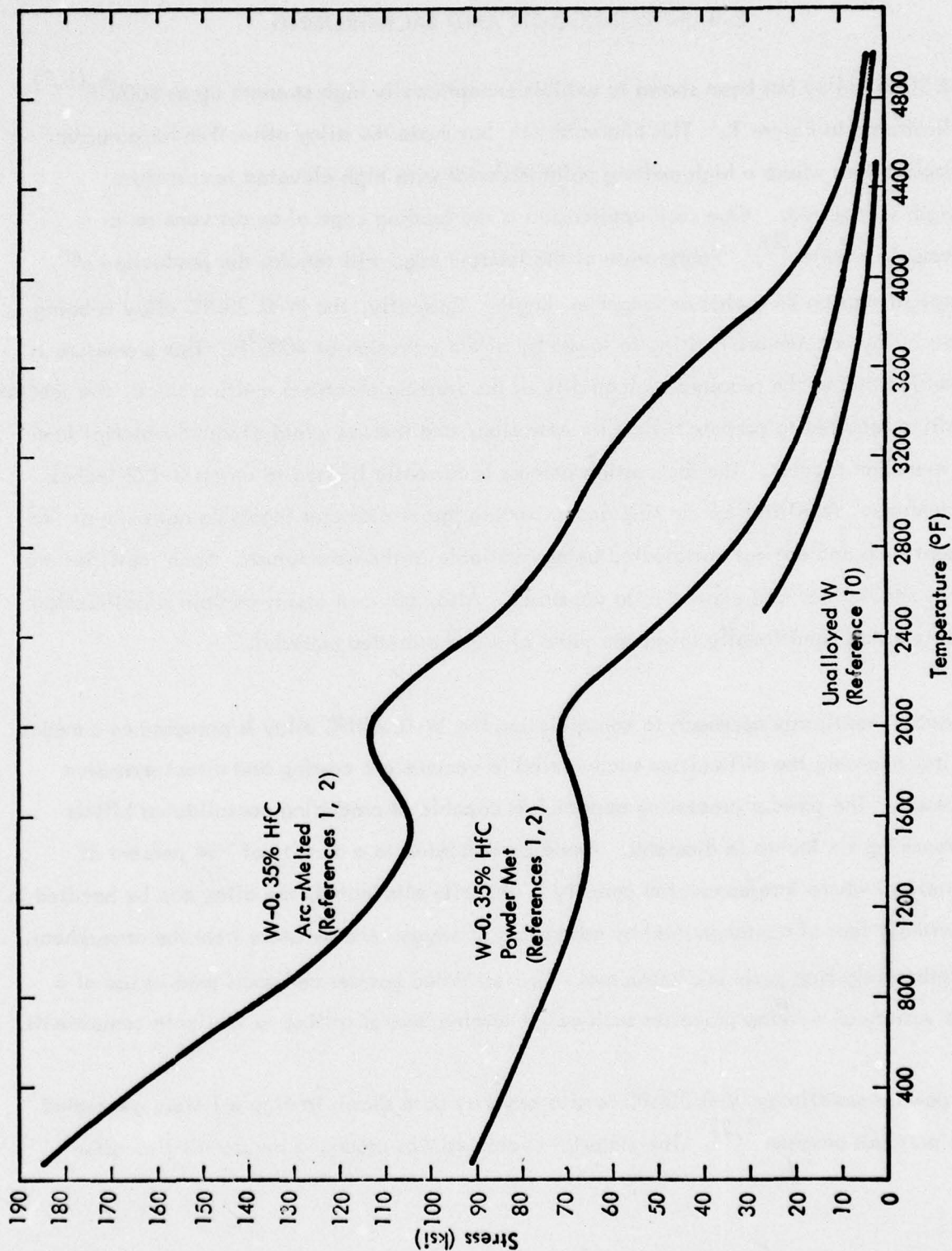


Figure 1. Tensile Properties of W-0.35HfC Alloy

powder (0.6 to 6 micron particle size) with HfC powder (-325 mesh) and consolidated by extrusion at 3200°F in a molybdenum cannister. The material prepared in this manner displayed tensile properties which were significantly lower than those of arc-cast material over the entire temperature range. The purpose of this program is to investigate the feasibility of producing W-0.35HfC alloy with mechanical properties equivalent to arc-cast material.

The first W-HfC powder metallurgy alloys were prepared by Friedman and Dickinson of GTE<sup>(3)</sup>. Four hundred gram billets were prepared by blending and pressing tungsten powder, hafnium hydride, and carbon. The billets were vacuum sintered at 4300°F to remove the hydrogen, alloy the tungsten and hafnium, and to densify the billet. The billets were forged and rolled at elevated temperatures. The processing resulted in heavily worked sheet of 0.040 inch thickness with excellent elevated temperature strength. Work at NASA-Lewis Research Center investigated the W-HfC system using a vacuum arc-cast approach to ingot consolidation. One result of the work at NASA-Lewis Research Center was the narrowing of the optimal composition range to 0.3 to 0.4 percent HfC<sup>(4)</sup>. Attempts to produce ingots within a given compositional range revealed the significance of the problem of oxygen variability in tungsten powder<sup>(5)</sup>, and its affect on final alloy composition. The melting technique developed by Westinghouse Advanced Energy Systems Division circumvented the oxygen problem and resulted in good compositional control in over 50 melts<sup>(6)</sup>.

The key to producing W-0.35HfC alloy by powder metallurgy also involves the control of oxygen. Tungsten powder oxidizes at room temperature by forming a surface layer of  $WO_3 \cdot 2H_2O$ <sup>(7)</sup>. The rate at which the oxide layer forms is dependent on the relative humidity of the air. The total oxygen content in a given quantity of powder is directly proportional to the surface area and hence particle size. Oxygen level can be controlled by proper selection of particle size, deoxidation by heating in a hydrogen environment, storage under vacuum or inert gas, and by blending of deoxidized powders under inert gas. The oxygen level of the tungsten powder must be reduced to a low level, preferably below 100 ppm, prior to blending



with the HfC. Each ppm of oxygen can react with 4 ppm of HfC and thus reduces significantly the quantity of available HfC. The HfC powder must also be vacuum degassed to reduce absorbed oxygen prior to blending. Removing the oxygen from billets pressed from blended non-deoxidized powders by passing hydrogen through the low density billets at elevated temperature does not appear to be thermodynamically feasible. The large disparity in free energy of formation between HfC and HfO<sub>2</sub> (-50 K cal/g mol for HfC vs. -213 K cal/g mol for HfO<sub>2</sub> at 2000°F) favors the formation of HfO<sub>2</sub>. Thermodynamic calculations indicate that the introduction of methane or carbon dioxide into the hydrogen gas to control the carbon activity is not effective in preventing oxidation of the HfC until the temperature approaches 3000°F.<sup>(8)</sup> As a result, it appears that the most prudent approach to producing the W-0.35HfC alloy from powder is to deoxidize the powders before blending and processing under inert gas until > 95% of theoretical density is achieved. Then by means of thermal-mechanical processing attempt to produce a homogeneous product which has mechanical properties equivalent to those of arc melted material.

### 3.0 EXPERIMENTAL PROGRAM

#### 3.1 PROGRAM PLAN

The objective of this study was to demonstrate the feasibility of producing W-0.35 HfC alloy via powder metallurgy with mechanical properties equivalent to arc cast and extruded material. To accomplish this objective, three powder consolidation techniques were investigated in parallel following the program outline shown in Figure 2. Prior to the initiation of the billet consolidation, a preliminary investigation was conducted to develop suitable deoxidizing procedures for treating and handling the starting powders.

Deoxidation treatment investigation was conducted using a Cahn-electrobalance which is sensitive to weight changes on the order of  $2 \times 10^{-6}$  grams. Studies were conducted in both a flowing hydrogen and helium and dynamic vacuum environment. Samples of tungsten powder were exposed at various temperatures (400, 800, 1200, and 1600°F) in flowing hydrogen. Weight loss was measured and recorded as a function of time. From the data, an optimum deoxidizing schedule was developed, and a quantity of starting tungsten powder was treated. The same procedure was repeated for HfC, only the deoxidation process was carried out under a dynamic vacuum.

Three methods of introducing the HfC into the tungsten matrix were evaluated. In the modified Friedman-Dickinson process\*(see Figure 2), tungsten powder, hafnium hydride, and carbon powder were blended and encapsulated in a mild steel can fitted with an exhaust vent and valve. This operation including the welding of the mild steel can was conducted in a high purity helium atmosphere dry box. The inert gas atmosphere contained less than 5 ppm total active impurities. The sealed cans were removed to a furnace and heated to 1600°F to decompose the  $\text{HfH}_2$ . A vacuum pump was used to expedite hydrogen removal. After the hydrogen was removed, the cans were sealed by pinching and welding of the vent tube.

\* The process used in this work differs from the Friedman-Dickinson approach in that the tungsten powders used were deoxidized and the sintering step was omitted.

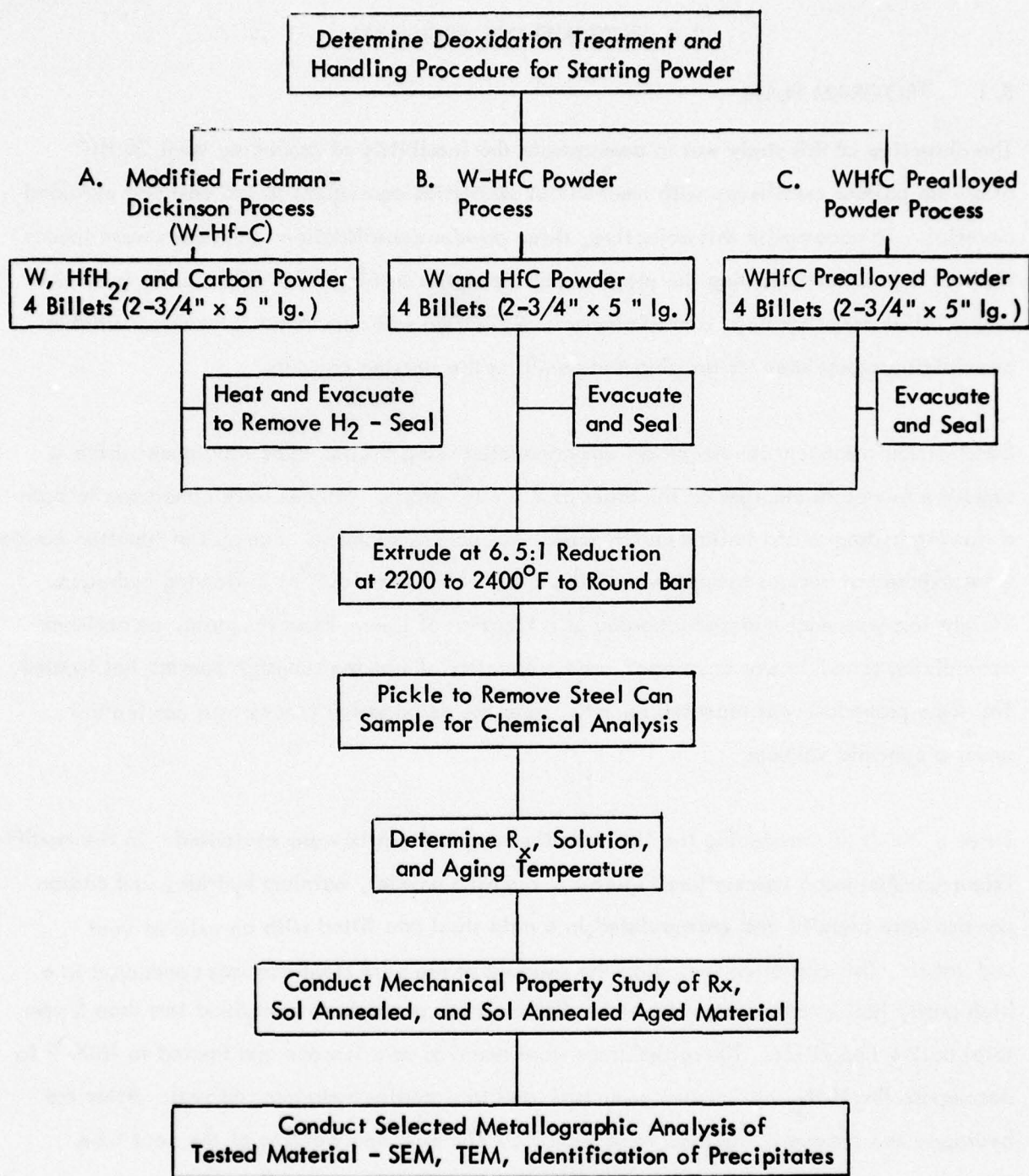


Figure 2. Program Outline for Producing W-0.35HfC Utilizing Powder Metallurgy Processing

In the W-HfC powder process, deoxidized tungsten and HfC powder were blended under inert gas, canned in mild steel, evacuated, and sealed.

For the WHfC prealloyed powder process, approximately 125 pounds of W-0.35HfC alloy produced by arc casting was converted to powder using Metallurgical International's Coldstream process. The powder was screened to various particle fractions. A screening particle size fraction was selected, loaded into a mild steel can, and deoxidized by passing hydrogen through the powder while at 1200°F.

The canned powder of each type of material was processed following the schedule outlined in Figure 2. Extrusion of the billets was accomplished using the facilities of the Air Force Materials Laboratory located at the Wright-Patterson Air Force Base. The extrusion temperature was 2300°F, and the reduction ratio was 6.5:1. The steel cladding was chemically removed from each extrusion. Representative samples were taken from the extrusions for chemical analysis, metallographic, and heat treatment evaluation.

A heat treatment study was conducted to establish the recrystallization temperatures and the solution annealing temperatures for the extruded product. Heat treated samples were examined using both optical and electron microscopy to characterize the microstructure and the form and distribution of the second phase hafnium carbide precipitate.

Mechanical property behavior was determined for material in the as-extruded, recrystallized, and solution annealed and aged condition. Selected specimens were examined using optical and SEM metallographic techniques to correlate microstructure and properties.

## 3.2 STARTING MATERIALS

### 3.2.1 Tungsten Powder

One hundred and fifty pounds of tungsten powder was purchased from Li Tungsten Corporation of Glen Cove, Long Island, NY. The powder was produced from scheelite ore from Canada



or GSA surplus. The ore was acid digested to yield tungstic acid, which was then dissolved in aqua ammonia. The ammonium tungstate solution was evaporated to crystallize ammonium paratungstate. These crystals were decomposed thermally under a reducing atmosphere to produce tungsten trioxide which was then hydrogen reduced to metal powder. The particle size distribution is as follows: 8% + 200 mesh, 85% -200 +325 mesh, and 7% -325 mesh. Vendor analysis reports 99.94% tungsten with .02% Mo and 0.03% oxygen or loss on reduction. Typical tungsten powder is shown in the SEM micrograph 3a of Figure 3.

### 3.2.2 Hafnium Carbide and Hafnium Hydride Powders

Hafnium carbide and hafnium hydride were purchased in 1/2 pound quantities. HfC is shown in Figure 3b. Hafnium hydride was not illustrated due to its pyrophoric nature. Both compounds were obtained as -325 mesh powder packed under inert gas. Typical chemical analysis is as follows:

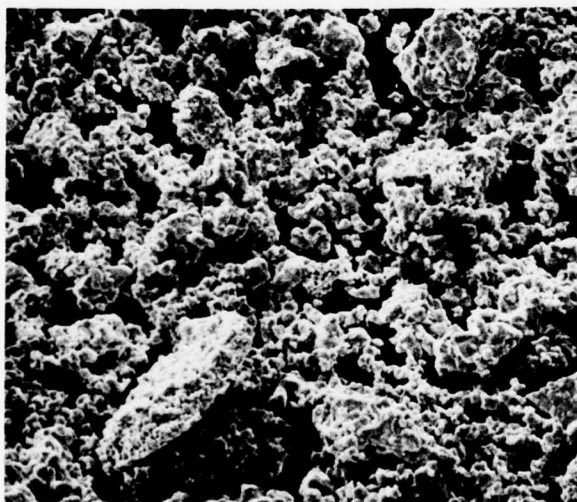
Element	Analysis (ppm)	
	HfC	HfH <sub>2</sub>
Al	25	43
B	.25	< .2
Cd	1	< 1
Co	5	< 5
Cr	10	< 10
Cu	40	< 40
Fe	50	< 50
Mg	10	< 10
Mn	10	< 10
Mo	10	70
N	324	42
Nb	100	< 100
Ni	10	< 10
O	1190	1910
Pb	5	< 5



(a) Tungsten Powder - 100X



(b) Hafnium Carbide (HfC) Powder - 500X



(c) Graphite Powder - 500X



(d) WHfC Prealloyed Powder - 50X

Figure 3. SEM Micrographs of Starting Materials



<u>Element</u>	<u>Analysis (ppm)</u>	
	<u>HfC</u>	<u>HfH<sub>2</sub></u>
Si	-	< 40
Sn	10	< 10
Ta	-	< 200
Ti	850	28
V	-	< 5
W	-	50
Zr	3.50%	3.7%
H	-	1.2%
C	6.21%	-

### 3.2.3 Carbon

Carbon was obtained as -325 mesh graphite powder, 99.5% pure from Ventron-Alfa Products, Beverly, MA, and is shown in Figure 3c.

### 3.2.4 W-0.35HfC

W-0.35HfC prealloyed powder was produced from arc-cast material. Approximately 135 pounds of ingot and defective extrusions were crushed to 1/2 inch chunks. The chunk material was sent to Metallurgical International for conversion to powder utilizing the Coldstream Process. The W-0.35HfC powder was sorted according to particle size. The distribution of material according to particle size was as follows:

+20 mesh	18.5 pounds
-20 +60 mesh	19.1
-60 +200 mesh	37.2
-200 +325 mesh	24.3
-325 mesh	<u>33.4</u>
Total	132.5 pounds

The -60 +325 mesh segment was used in the powder consolidation portion of the program. Alloy powder from the -200 +325 mesh segment is shown in Figure 3d.

### 3.3 DEOXIDATION AND DEGASIFICATION TREATMENTS OF POWDERS

An investigation was conducted to determine the minimum temperature necessary to degas tungsten, hafnium carbide, and graphite powders. Results of this investigation were used to establish the processing procedure for the powder consolidation step. Small samples of each powder material were individually heated in flowing hydrogen, helium or under vacuum conditions in a thermal gravimetric system, shown schematically in Figure 4. A photograph of the system is shown in Figure 5. Sample weight was continuously monitored by means of a Cahn electro-balance, sensitive to weight changes on the order of  $2 \times 10^{-6}$  grams. Powder samples were placed on a molybdenum tray, lowered into the center of a vertical ceramic combustion tube. The system was sealed and a purging flow of helium was initiated. After sufficient time, usually over night, to displace air from the system and to stabilize the weighing mechanism. Helium flow was replaced when required by a calibrated flow of hydrogen at a rate of 100 ml/min. The helium gas used was Matheson grade high purity, 99.995% with a combined oxygen and water level of less than 10 ppm. The water level in the "extra-dry" grade of hydrogen used was less than 10 ppm. The samples were heated rapidly to the test temperature. A thermocouple located adjacent to the weight tray monitored specimen temperature. Sample weight and temperature were continuously monitored as a function of time. Results of the powder degassing investigation are given in Table 1 and are reviewed in the following discussions.

#### 3.3.1 Tungsten Powder

Five deoxidation runs were conducted on the tungsten powder. Individual samples were run at 400, 800, 1200, and 1600°F. The fifth sample was exposed at each temperature starting at 400°F. After weight loss stabilized, the temperature was increased to the next higher level. The percentage of weight loss at each temperature is given in Table 1 and shown in Figure 6. In all five cases the weight loss at 400°F was consistent. Weight losses at 800°F, when time for equilibration was permitted, were also consistent. At higher temperatures,

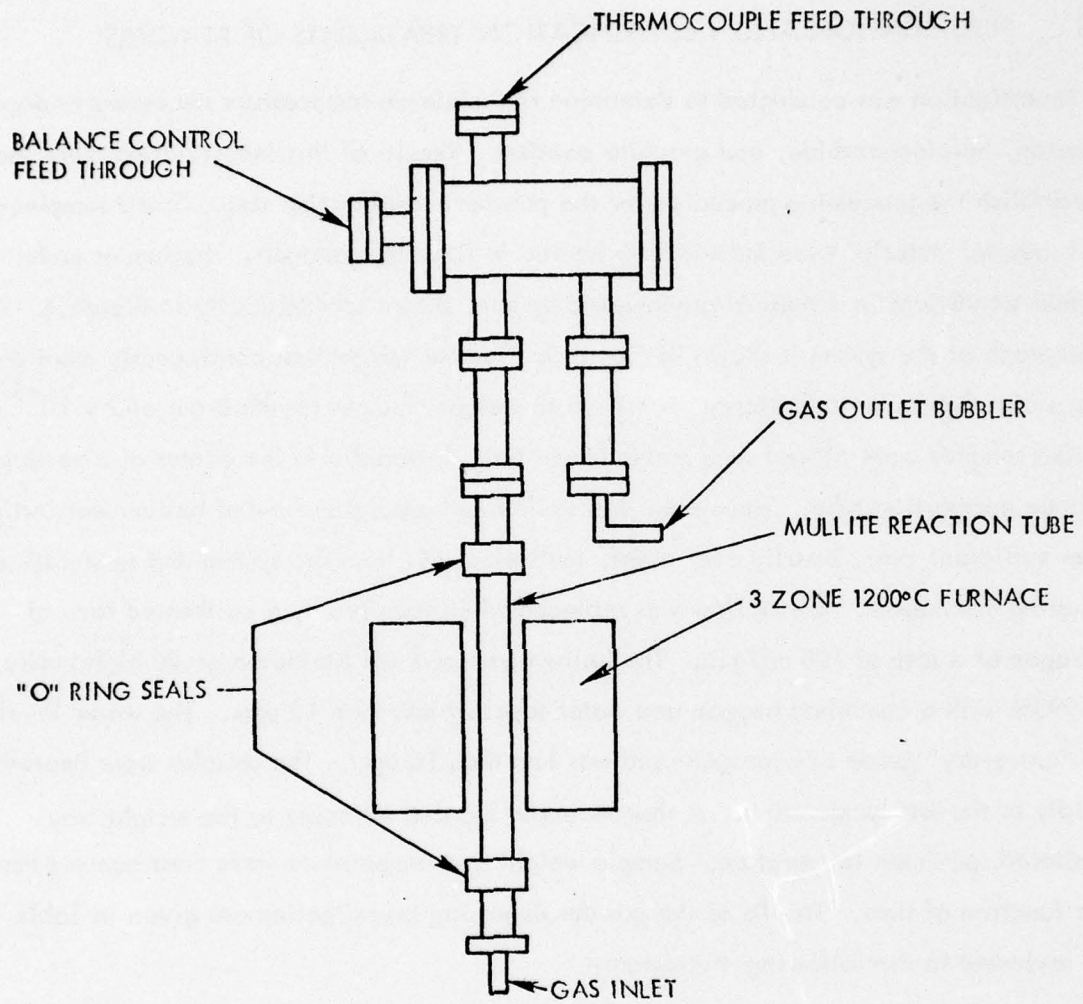


Figure 4. Schematic of Thermal-Gravimetric System Used for Powder Degasification

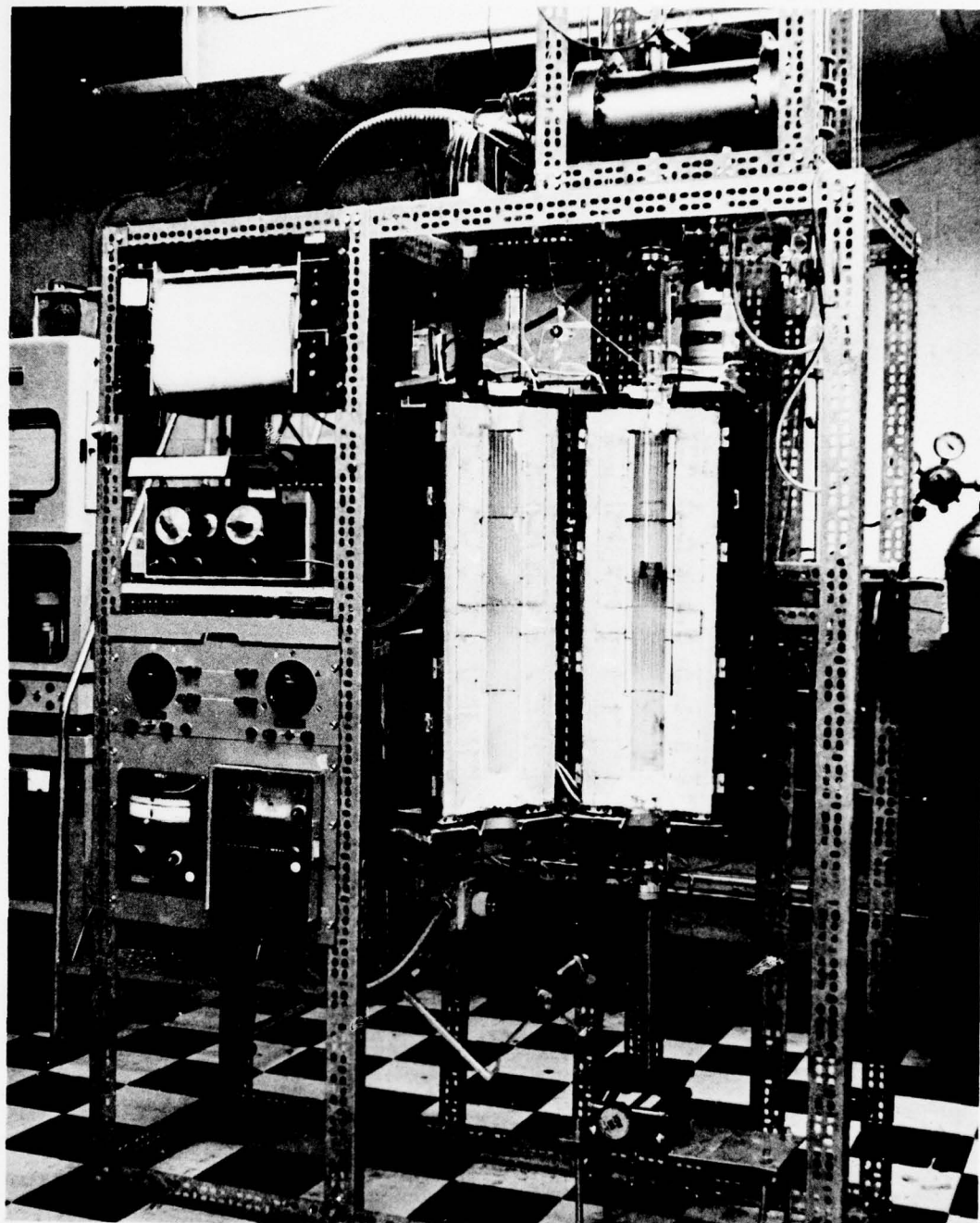


Figure 5. Microbalance and Degassing Apparatus

Table 1. Weight Loss of Powders in Flowing Hydrogen and Helium as a Function of Temperature

Material	Gas	Accumulated % Wt. Loss					Remarks
		400°F	800°F	1200°F	1600°F		
1	W	H <sub>2</sub>	.012	-	-	-	Individual samples heated to each max. temperature. Intermediate wt. losses recorded during sample heat up.
2	W	H <sub>2</sub>	.0130	.045	-	-	
3	W	H <sub>2</sub>	.013	.022	.048	-	
4	W	H <sub>2</sub>	.014	.033	.050	.053	
5	W	H <sub>2</sub>	.013	.046	.048	.052	
6	HfC	H <sub>2</sub>	.058	.089	-	-	One sample exposed at each temperature.
7	HfC	He	.060	.107	-	-	
8	HfC	H <sub>2</sub>	.011	.032	-	-	At 900°F and above sample gained weight rapidly.
9	HfC	H <sub>2</sub> *	.011	.021	.018	.026	
10	HfC	Vac**	.010	.025	.028	.032	At 800°F and above sample gained weight rapidly.
11	C	H <sub>2</sub>	.174	.353	.418	2.7	
12	C	He	.149	.324	.444	.549	Gained weight as temperature increased above 800°F
13	WHfC	H <sub>2</sub>	.016	.032	.034	.053	

Gas Flow Rate - 100 ml/min.

Sample Weight - W - 25 grams

HfC - 20 grams

C - 1.5 grams

\* - High purity H<sub>2</sub> < 1 ppm H<sub>2</sub>O

\*\* - 5 x 10<sup>-5</sup> torr

C reacted with H<sub>2</sub> to form methane above 1200°F.

Experiment stopped after 18 hrs. at 1600°F when sample wt. failed to stabilize.

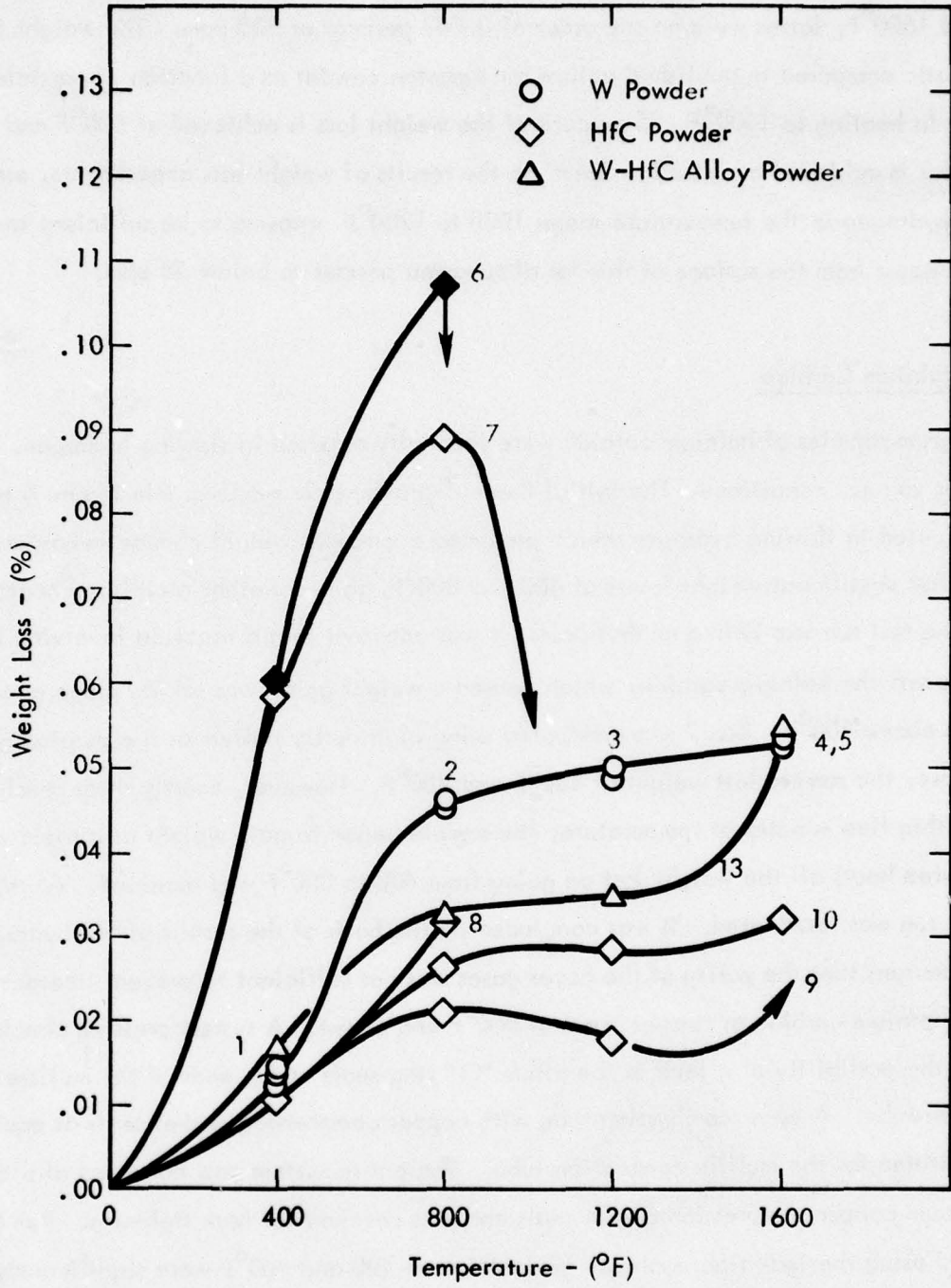


Figure 6. Weight Loss of Tungsten, HfC, and W-HfC Alloy Powder as a Function of Temperature



1200 and 1600°F, losses were on the order of 0.053 percent or 530 ppm. The weight losses are realistic compared to published values for tungsten powder as a function of particle size<sup>(9)</sup>. In heating to 1600°F, 85 percent of the weight loss is achieved at 800°F and 92 percent is achieved at 1200°F. Based on the results of weight loss experiments, exposure to flowing hydrogen in the temperature range 1000 to 1200°F appears to be sufficient to remove adsorbed gases from the surface of this lot of tungsten powder to below 50 ppm.

### 3.3.2 Hafnium Carbide

Five 20 gram samples of hafnium carbide were thermally exposed in flowing hydrogen, helium, and under vacuum conditions. The initial thermal-gravimetric run (No. 6 in Figure 6 and Table 1) was conducted in flowing hydrogen which produced anomalous weight change behavior. The sample after significant weight losses at 400 and 800°F, gained weight rapidly on heating above 900°F. The test run was halted at that point. It was apparent that a reaction involving the hydrogen cover gas and the hafnium carbide, which caused a weight gain, was taking place at temperatures above 800°F. Run 7 was conducted using high purity helium as the purging gas. In this case, the sample lost weight at 400°F and 800°F. However, shortly after reaching 800°F within five minutes at temperature, the sample began to gain weight at a rapid rate. Within three hours all the weight lost on going from 400 to 800°F was regained. At this point the run was terminated. It was concluded on the basis of the results of the hydrogen and helium runs that the purity of the cover gases was not sufficient to prevent interaction with the hafnium carbide at temperatures of 800°F and above. A system pressure check revealed the possibility of a leak at the viton "O" ring seals at the ends of the mullite combustion tube. A vycor combustion tube with copper compression gasket seals at each end was substituted for the mullite combustion tube. The entire system now consisted of ultra-high vacuum copper compression gasket seals and was checked for leak tightness. Run 8 was conducted using the leak tight system. Weight loss at 400 and 800°F were significantly lower than the previous runs. The weight change behavior noted on previous runs, however,

repeated and sample weight began increasing as the sample was held at 800°F. At this point it was concluded that the purity of the hydrogen was not adequate to prevent reaction with the hafnium carbide at temperatures of 800°F and above. A final attempt to degas the hafnium carbide (No. 9) with hydrogen was conducted using ultra-high purity hydrogen produced by an Englehart hydrogen purifier. This system has a heated palladium-silver diffusion membrane which exhibits selective permeability to hydrogen gas and is impervious to all others. Hydrogen is produced with impurities below detection limits as claimed by the manufacturer. Run 9 was conducted using hydrogen with a measured moisture level in the inlet gas below 1 ppm. Weight at 400°F was comparable to the previous run results (No. 8). At 800°F the weight loss was initially lower. However, the sample began to gain weight as in prior runs. The test was continued, and the sample temperature was increased to 1200°F. At 1200°F the sample ceased gaining weight; and as temperature was increased to 1600°F, the sample began to lose weight. This behavior, initial weight gain with temperature in the range 800 to 1200°F followed by weight loss at temperatures above 1400°F was interpreted as a possible hydriding reaction. Elemental hafnium present in the hafnium carbide is most likely responsible for the interaction with hydrogen. It was concluded that the presence of the hydride in the sample made degassing with hydrogen impractical, since accurate weight losses could not be readily determined. The presence of hydride in the hafnium carbide was undesirable as a high temperature vacuum degassing run would be required to remove the hydrogen. A final degassing run was conducted (No. 10) under vacuum conditions. A turbo-molecular pump capable of reducing the pressure in the system to  $4 \times 10^{-5}$  torr or less was used. Weight loss at 400°F was comparable to the two previous runs (8 and 9) in hydrogen. The sample continued to lose weight with increasing temperature. No reversal of weight loss behavior was noted in the temperature range 800 to 1200°F. This behavior tends to confirm the hydriding theory. As a result of this series of degassing runs, it was concluded that vacuum degassing of hafnium carbide was the most effective method for removing adsorbed gases from the surface of the fine powder.





### 3.3.3 Carbon

Graphite powder was also exposed to hydrogen and helium purge gas to determine deoxidation characteristics (Runs 11 and 12 in Figure 6 and Table 1). An impervious ceramic crucible was substituted for the molybdenum tray. In flowing hydrogen, the carbon powder exhibited weight losses at 400, 800, and 1200°F of 1740, 3530, and 4180 ppm, respectively. Above 1200°F, it became apparent that the carbon and hydrogen were reacting with a significant loss in weight of the sample. A switch to helium resulted in similar losses in weight at 400, 800, and 1200°F; however, no catastrophic behavior was noted at 1600°F. Since the weight loss continued at a fairly constant rate with increasing temperature, some of the weight loss can be attributed to reaction of carbon with residual oxygen and water vapor in the helium purge gas. Vacuum degassing of carbon would most likely be more effective at lower temperatures.

### 3.3.4 WHfC Prealloyed Powder

A sample of WHfC prealloyed powder was thermally exposed in flowing hydrogen at the four temperatures of interest. The weight loss at 400°F was comparable to that for unalloyed tungsten powder, however, at 800 and 1200°F the weight losses were somewhat less. At 1600°F, the weight loss behavior of the WHfC prealloyed powder was erratic. When the sample temperature was increased from 1200 to 1600°F, the sample weight began to drop at a constant rate over the next 18 hours. This behavior was in contrast to prior experience where equilibration time decreased as exposure temperature increased, as would be expected. The continued weight loss at 1600°F may indicate a second reaction such as the loss of carbon from the specimen. The experimental results indicate that a safe deoxidation temperature for the WHfC prealloyed powder is most likely at 1200°F.

## 3.4 POWDER CONSOLIDATION

The purpose of the consolidation process was to produce sufficient densified material of each powder alloy approach for evaluation. In each case, four cannisters of powder alloy were

prepared for consolidation by extrusion. The procedures used are briefly outlined in Figure 7 and described in more detail in the following discussions.

### 3.4.1 Modified Friedman-Dickinson Process (W-HfH<sub>2</sub>-C) (Process A)

In this process, degassed tungsten powder was blended with hafnium hydride and graphite powder and charged into mild steel cannisters equipped with a valved vent tube to facilitate dehydriding.

The tungsten powder was degassed by first screening to obtain the +325 -200 mesh particle size segment. Hydrogen reduction of this segment was accomplished in a retort illustrated in Figure 8. Forty-five pounds of powder was loaded into the retort which consisted basically of a 4 inch diameter stainless steel tube approximately 14 inches long. The bottom end contained an internal hydrogen diffuser made from pressed and sintered iron flake. The diffuser provided support to the tungsten powder charge while distributing the hydrogen uniformly through the charge similar to a fluidized bed reactor. The top or exit end of the retort contained a 1 inch diameter exit tube equipped with a Swagelok fitting. The exit end of the fitting was reduced to a 3/8 inch diameter tube with a 500 mesh screen welded over the exit to prevent powder carryover during the degassing process. Both the inlet and outlet tubing contained a stainless steel bellows valve with metal-to-metal sealing seats. After charging, the Swagelok fitting was put in place and tightened. The retort was leak checked on a helium leak detector. The charged retort was placed in a vertical tube furnace of the degassing apparatus as shown in Figure 9. The actual apparatus is pictured in Figure 10. Thermocouples were attached to the top, center, and bottom of the retort to monitor temperatures. An Engelhard hydrogen purifier was used to reduce the moisture content of the supply hydrogen to less than 1 ppm (dew point < -105°F). This was accomplished through the use of a heated palladium-silver alloy membrane which exhibits selective permeability to hydrogen gas. Hydrogen gas will diffuse through the palladium-silver alloy while other gases are excluded. The device has a rated output of 20 SCFH ultra-high purity hydrogen at pressures up to 20 psi. The retort was plumbed into

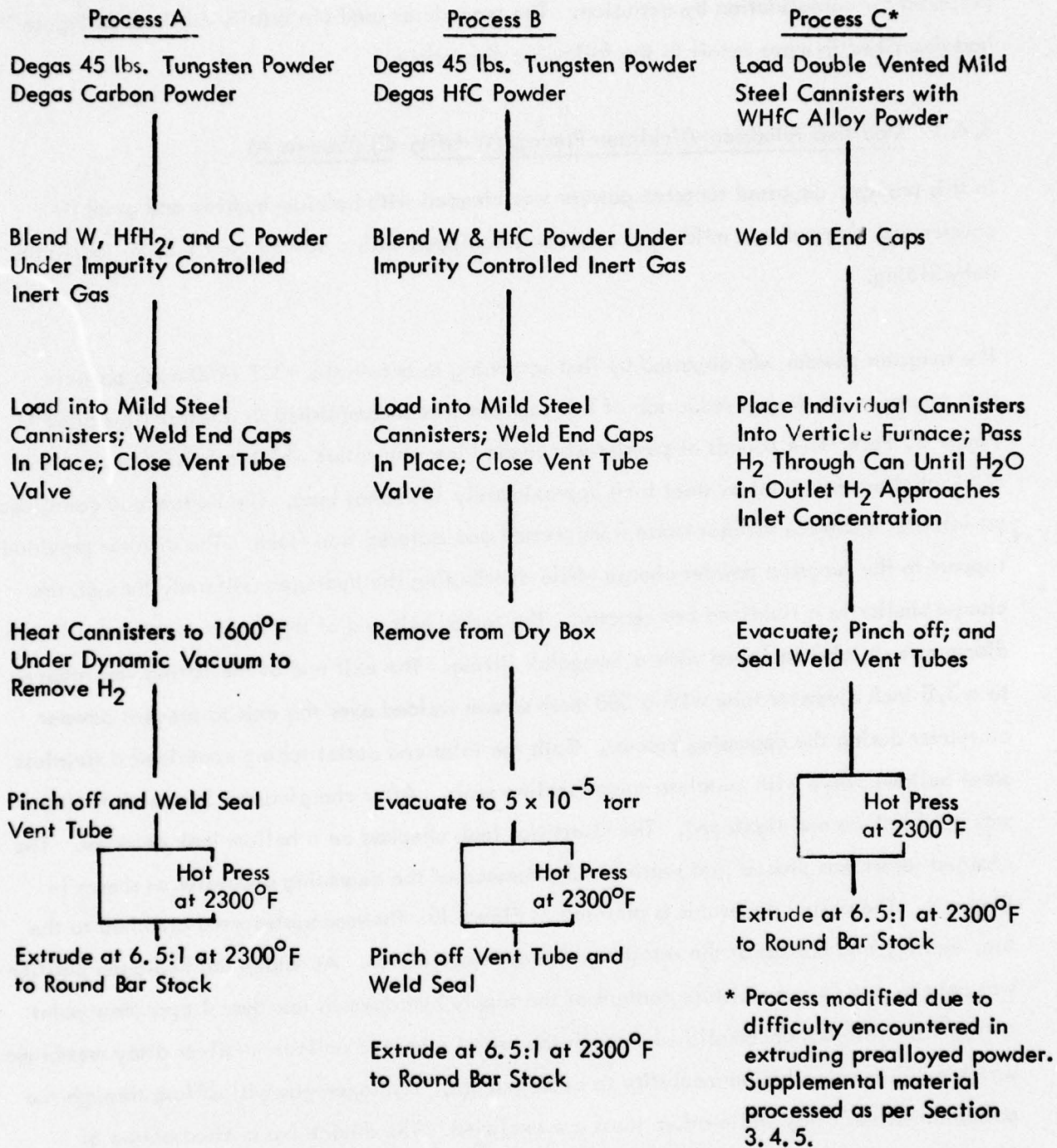


Figure 7. Processing Schedules for Consolidating W-0.35% HfC By Powder Metallurgy Techniques

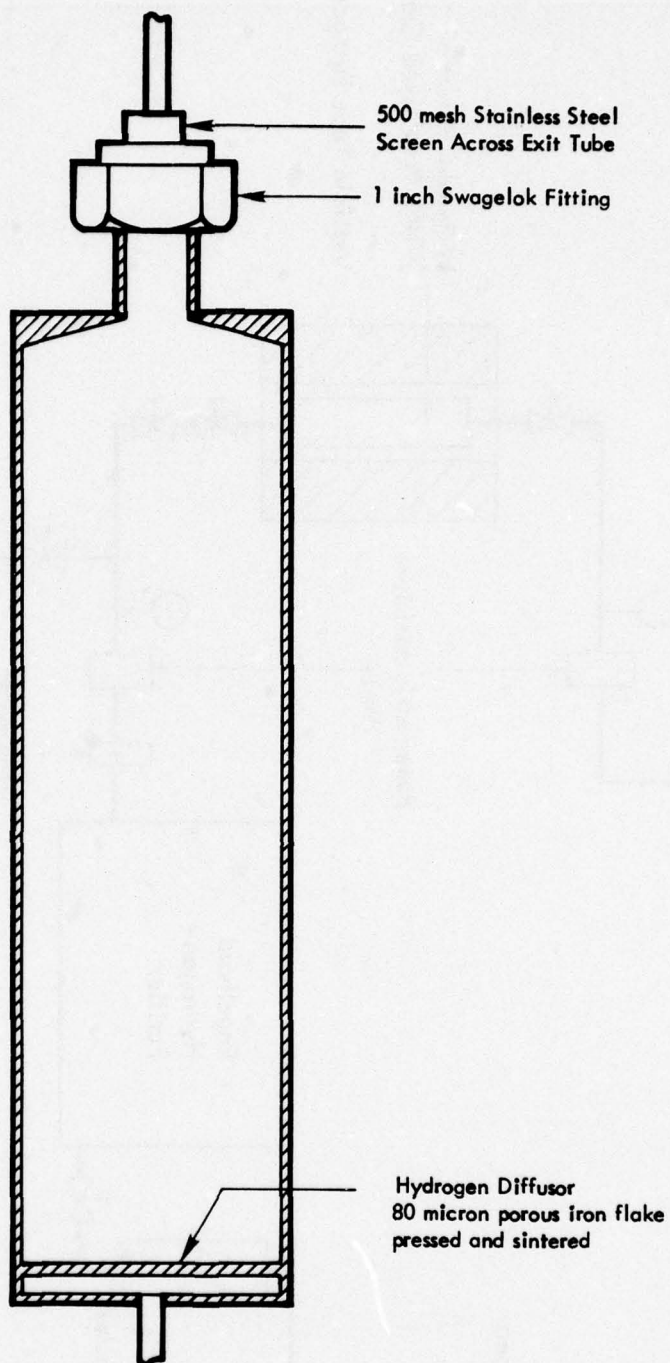


Figure 8. Tungsten Powder Retort

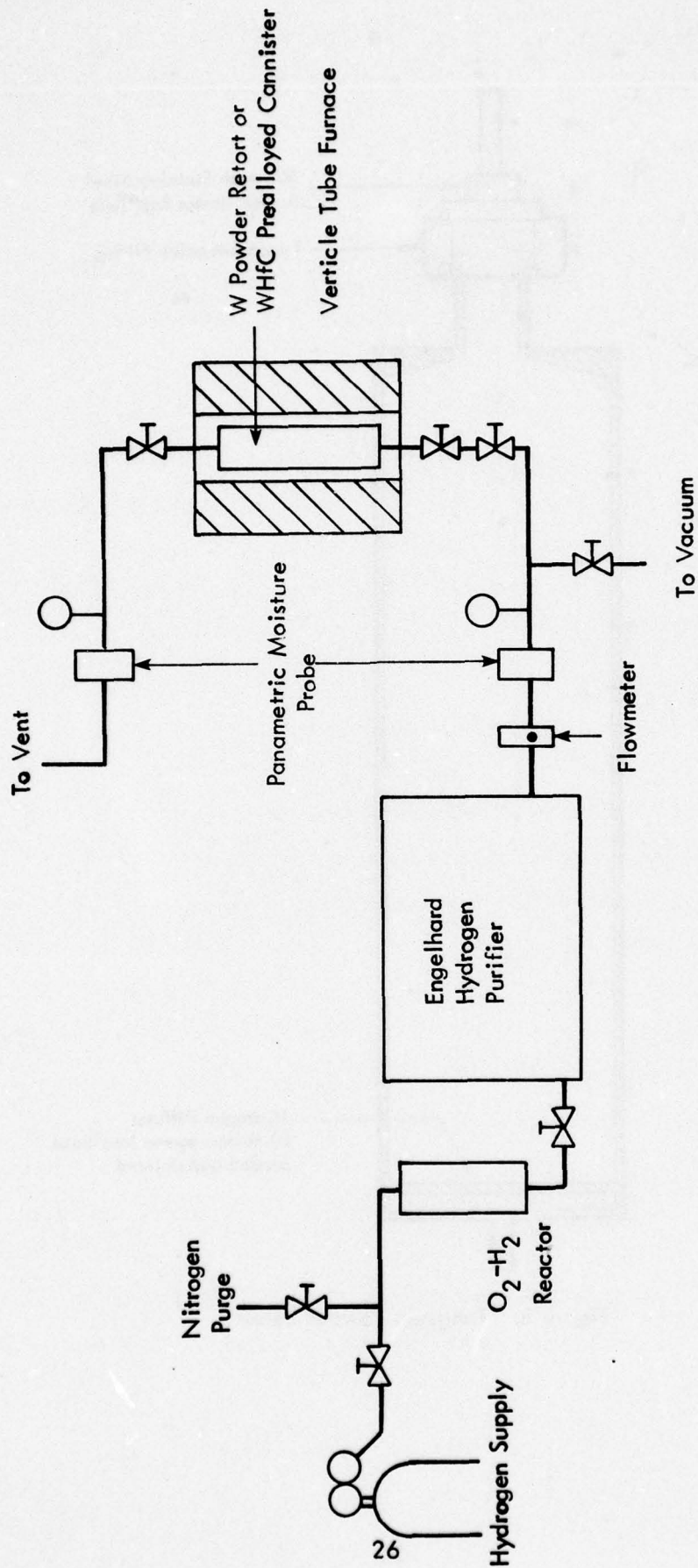


Figure 9 . Powder Degassing Apparatus



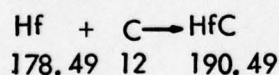
Figure 10. Powder Degassing Apparatus



the outlet of the hydrogen purifier with copper tubing. A Hastings flowmeter monitored hydrogen flow to the retort. A Panametric Hygrometer was used to monitor the moisture level of the retort inlet and outlet hydrogen. Pressure gauges in the inlet and outlet gas lines were used to monitor pressure drop through the retort. Once the retort was in place, the system was pressurized and leak checked. The system was then evacuated, and hydrogen flow was initiated at a rate of 5 liters STP per minute. The retort was heated at a slow rate to 1200°F. Approximately eight hours were required to reach final temperature. The moisture level of both the inlet and outlet hydrogen were recorded along with the retort temperature. Moisture in the hydrogen inlet was less than 1 ppm while the moisture level in the outlet hydrogen reached values in excess of 1000 ppm at times. After 24 hours at temperature, the moisture level in the outlet hydrogen dropped to an essentially constant value of 8 ppm. At this point the furnace power was shut off, hydrogen flow was stopped, the retort was put under vacuum, and insulation around the retort was removed to facilitate rapid cooldown. On reaching ambient temperature, valves in the inlet and outlet lines were closed, and the retort was removed and stored under vacuum.

The recommended composition range for the WHfC alloy is W-0.3 to 0.4 mol % HfC<sup>(4)</sup>. For this program, the upper limit W-0.4 mol % HfC or W-0.42 wt. % HfC was used as the target composition. The 45 pounds of tungsten required the following alloy additions:

$$\text{HfC} = 45 \text{ lbs.} \times 454 \text{ g/lb} \times \frac{.0042}{.9958} = 86.17 \text{ grams}$$



$$\text{Hf required} = \frac{178.49}{190.49} \times 86.17 = 80.74 \text{ grams}$$

$$\text{Carbon} = \frac{12}{190.49} \times 86.17 = 5.43 \text{ grams}$$

Graphite powder was vacuum degassed in a stainless steel container fabricated from 1 inch nominal OD tubing 10 inches long. One end was seal welded with an end closure. The other end was sealed with a Swagelok fitting which adapted down to accommodate 3/8 inch diameter tubing. The required quantity of graphite powder was placed into the tube which was sealed and leak checked. The 3/8 inch diameter vent tube was plumbed into a turbo-molecular vacuum pump with an ultimate pressure capability of  $1 \times 10^{-7}$  torr. The stainless steel capsule was equipped with a thermocouple then inserted into a vertical tube furnace for the thermal degassing operation. Temperature was gradually increased in order to maintain the system pressure at  $5 \times 10^{-5}$  torr or lower. On reaching 900°F, the capsule was held at temperature until the ultimate pressure bottomed out in the low  $10^{-6}$  torr range.

A check run was conducted to verify the carbon degassing process just described. A charge of 5.43 grams of graphite, required to give the target alloy composition, was loaded into the stainless steel capsule and thermally vacuum degassed. After completion of the thermal exposure, the copper tubing was pinched off with a special tool which also seals the tube. The capsule was opened, the graphite powder was removed, and weighed. The 0.02 gram weight loss approximated the predicted value based on the thermal-gravimetric study. The stainless steel capsule was recharged and the degassing process was repeated. The evacuated and sealed carbon degassing capsule was stored in the vacuum purge glove box to await the powder blending step.

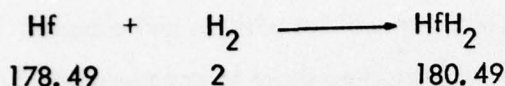
In the Friedman-Dickinson approach, hafnium is added to the powder blend as a hydride and is dissociated in a sintering process prior to thermal-mechanical working. In this program, hafnium hydride was procured as < 325 mesh powder packed under argon. The fine hafnium hydride powder is pyrophoric and therefore was not exposed to the atmosphere. The sealed hafnium hydride container was placed directly into the vacuum purged glove box where the required amount for the powder blending step was weighed out under a protective helium environment. The amount of hafnium required for the 45 pound tungsten powder charge was





Westinghouse

determined as follows:



$$\text{Hf as HfH}_2 \frac{180.49}{178.49} \times 80.74 = 81.64 \text{ grams.}$$

The powder blending step was carried out in a vacuum purged glove box. The glove box was modified to accommodate powder blending under controlled inert gas conditions (high purity helium). The box was equipped with a diffusion pump evacuation system which was capable of reducing the ultimate pressure in the clean empty box into the high  $10^{-7}$  torr range. A Vee blender with a volume capacity to handle 45 pounds of tungsten powder was modified for vacuum operation. The gear boxes were cleaned and refilled with vacuum grease. Outlets for two 250 watt heat lamps were installed. A water cooled electric welding "torch" was also installed. The interior of the glove box is shown in Figure 11.

An external helium purification loop was also provided to maintain the purity of the cover gas at a high level during the blending and cannister loading operations. The purification loop consisted of a gas pump, flow meter, titanium sponge furnace, and a Panametrics moisture probe. A schematic diagram showing component layout is shown in Figure 12. All the components were joined with stainless steel tubing. A supply of Matheson grade helium, 99.9999% He, was plumbed to the glove box through a stainless steel tube. A Westinghouse oxygen meter was used to monitor the oxygen level of the helium in the glove box. A Panametrics moisture probe was located at the top of the glove box to monitor the glove box environment under vacuum and helium backfilled conditions.

The glove box was loaded with the retorts containing tungsten and graphite powders, the container of hafnium hydride, a balance scale, tungsten welding electrodes, four mild steel cannisters with one end welded in place, four end caps with valved vent tubes, and miscellaneous tools.

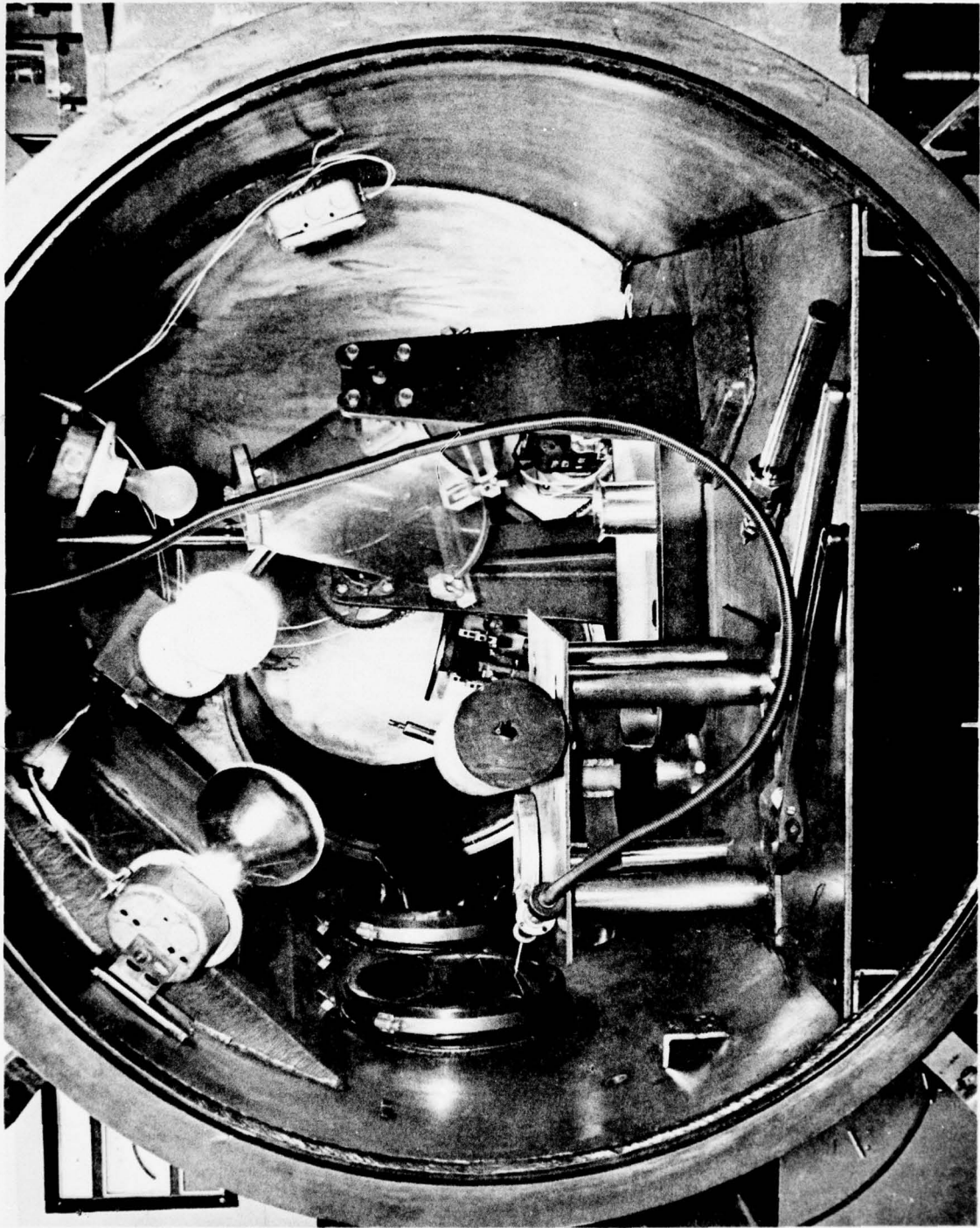


Figure 11. Interior of Vacuum Purged Glove Box

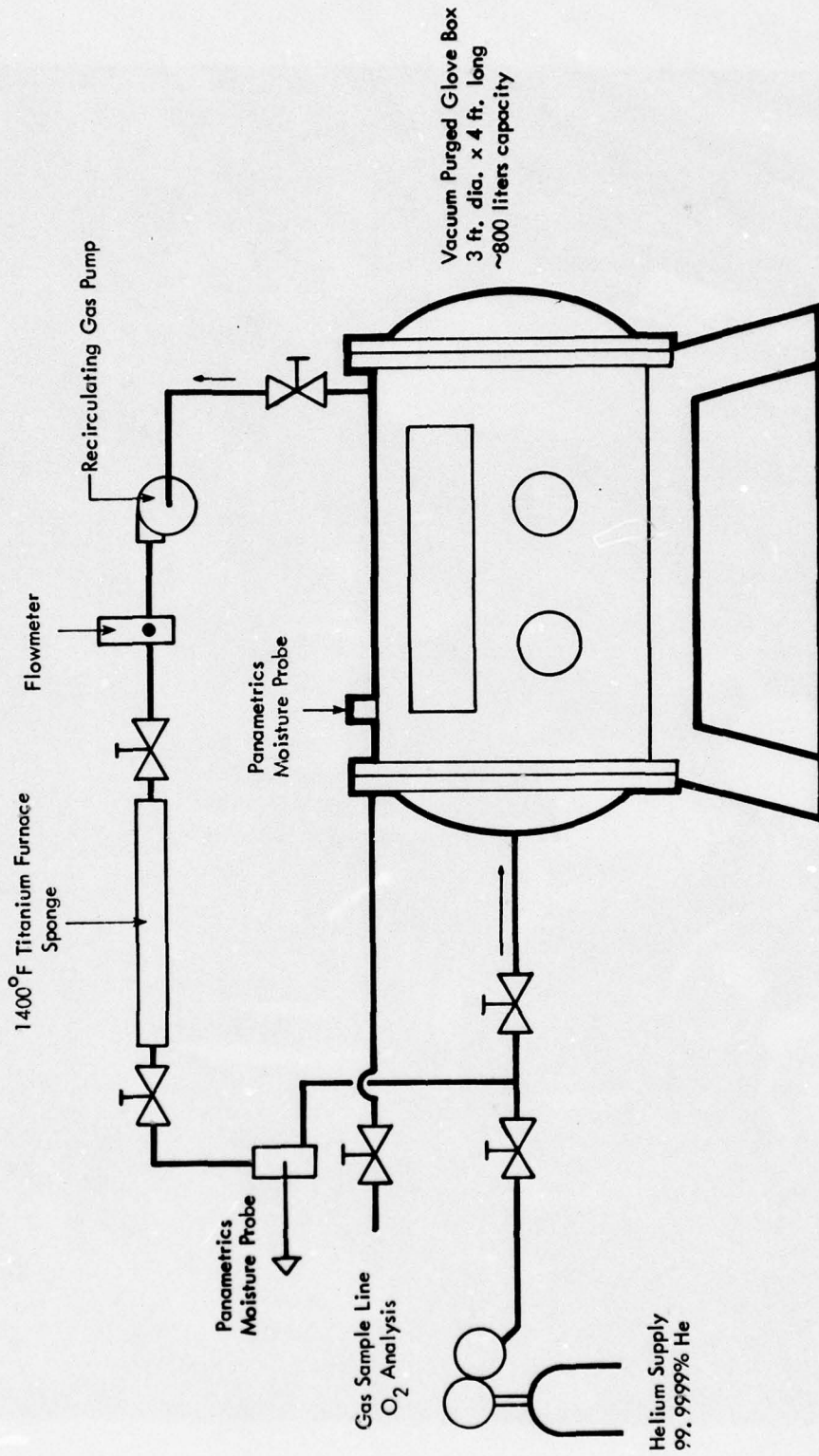


Figure 12. Vacuum Purged Glove Box Schematic

The box was evacuated to an ultimate pressure of  $4 \times 10^{-5}$  torr and the internal heat lamps were turned on to bake the moisture off the surfaces inside the glove box. This condition was maintained overnight for approximately 14 hours. The pressure in the box increased to  $2 \times 10^{-4}$  torr. After the heat lamps were turned off, pressure reduced to  $8 \times 10^{-6}$  torr as the system temperature returned to ambient. The lines to the external helium purification system were opened and power to the titanium sponge furnace was turned on. The recirculating tubes to the purification system were heated while under dynamic vacuum. The glove box was then backfilled with ultra-high purity helium to approximately 1 atmosphere. When the titanium sponge furnace reached  $1400^{\circ}\text{F}$ , the recirculating pump was started, and a flow rate of 10 liters per minute was initiated. The moisture content of the return helium to the glove box and the glove box moisture level were continuously recorded. Oxygen level of the glove box helium was measured intermittently. The initial moisture and oxygen level at the start of the operation in the glove box was less than 1 ppm for each impurity.

The tungsten powder retort was opened and the tungsten powder was transferred to the Vee blender. The preweighed graphite powder was removed from the sealed capsule and transferred to the Vee blender. The hafnium hydride container was opened and the hafnium hydride charge was weighed out on the balance scale within the glove box. The hafnium hydride was added to the Vee blender. The blender was closed and run for two hours. The blended powder was loaded into the four mild steel cannisters, and the end caps with the valved vent tube were welded into place. Each cannister contained approximately 11 pounds of blended powder at a tap density of 58 to 60 percent of theoretical. The vent valve on each cannister was closed. Oxygen and moisture level in the glove box remained constant during the blending and loading operation. The impurity level in the helium cover gas rose slightly during the welding operation. Moisture and oxygen levels in the helium cover gas at the completion of the welding operation were less than 3 ppm total.



The W-HfH<sub>2</sub>-C powder cannisters were removed from the glove box and helium leak checked to insure a sound end cap weld. Each cannister was then individually attached to a turbo-molecular pumping system. The cannisters were heated to 1500°F in a vertical tube furnace to dissociate the hafnium hydride. The dehydrating process required six hours per cannister to remove all the hydrogen and reduce the pressure to  $5 \times 10^{-6}$  torr or less. The cannisters were then removed from the furnace and cooled to ambient while attached to the vacuum pumping system. The vent valves were closed, and the vent tubes were heated, pinched, and weld-cut to seal the cannisters.

#### 3.4.2 Tungsten Powder Plus Hafnium Carbide Approach (W-HfC) (Process B)

In this approach degassed tungsten powder was blended with degassed hafnium carbide powder which was loaded into mild steel cannisters equipped with a valved vent tube to facilitate evacuation prior to extrusion. Tungsten powder, -200 +325 mesh, was degassed in the retort as per the process described in detail in the previous section. A charge of 45 pounds of tungsten powder and 86.17 grams of hafnium carbide were processed. The hafnium carbide was weighed with sufficient excess to achieve the target level after the degassing step. The hafnium carbide was heated under dynamic vacuum to 700°F in the stainless steel capsule. The copper vent tube was pinched off to seal the capsule. The tungsten retort with degassed tungsten powder and the sealed stainless capsule containing the degassed hafnium carbide were placed into the vacuum purged glove box. The powder blending, cannister loading and cannister sealing process was carried out as described for the W-HfH<sub>2</sub>-C process. The filled cannisters were removed from the glove box, attached to a helium leak detector, evacuated, and leak checked. The evacuated cannisters were sealed by heating the vent tubes, flattened by pinching the tube with a special tool, and weld cut to form a permanent seal.

#### 3.4.3 WHfC Prealloyed Powder Process (Process C)

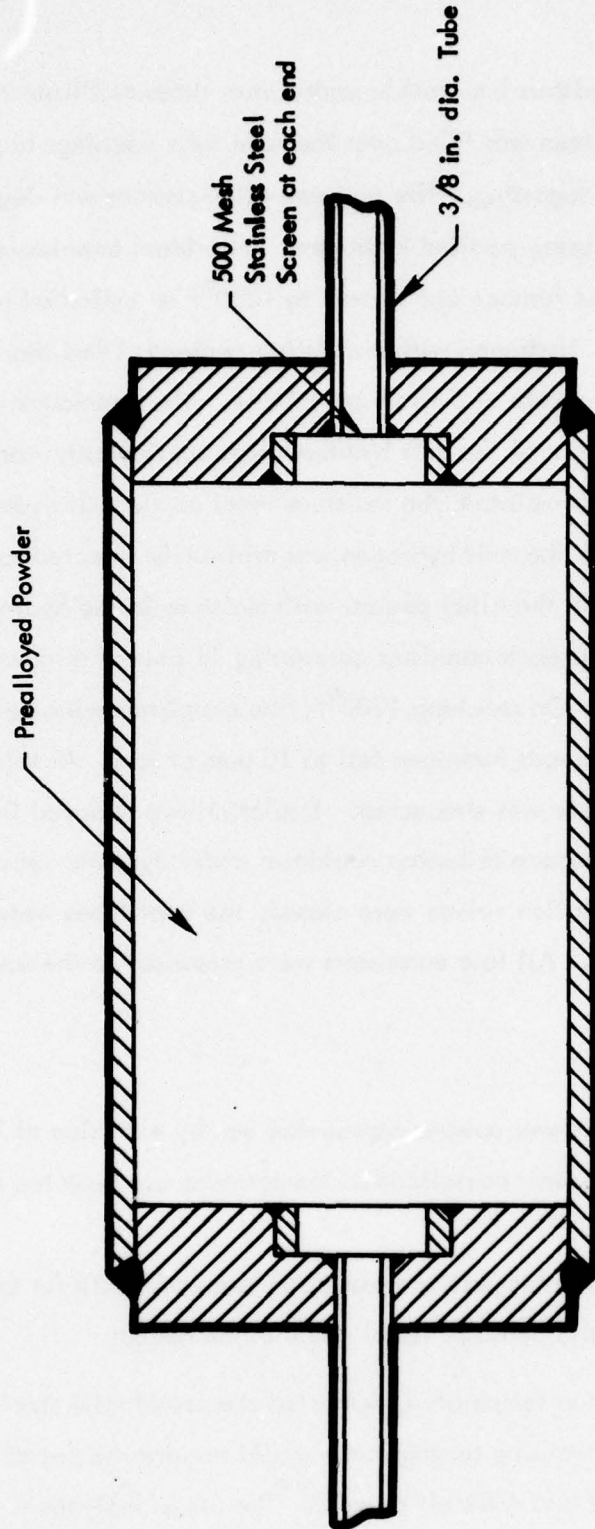
Tungsten alloy powder produced from arc-cast material by the Coldstream Process was loaded into mild steel cannisters. The charge consisted of the -60 +325 mesh segment of the alloy

powder. The mild steel cannisters had double ended vent tubes as illustrated in Figure 13. A 500 mesh stainless steel screen was fixed over the vent tube openings to prevent loss of powder during handling and degassing. The tungsten alloy powder was degassed in the apparatus shown in Figure 9 using purified hydrogen. Individual cannisters, Figure 14, were placed into the vertical tube furnace and heated to 1200°F as indicated by the degassing study conducted previously. Hydrogen with a moisture content of less than 0.8 ppm was fed through the cannisters at a rate of 5 liters per minute. The cannisters were heated gradually while the moisture content of the exit hydrogen was continuously monitored. The heating rate was controlled in order to maintain the moisture level of the exit hydrogen below 100 ppm. The 100 ppm moisture level in the exit hydrogen was arbitrarily selected to minimize the possible reaction of the HfC in the alloy powder with moisture in the hydrogen. Approximately 12 hours was required to degas each cannister containing 11 pounds of powder at a tap density of 58 percent of theoretical. On reaching 1200°F, the cannisters were held at temperature until the moisture level in the exit hydrogen fell to 10 ppm or less. At this point, hydrogen flow was halted, and the system was evacuated. Insulation was removed from the top and bottom of the vertical tube furnace to hasten cooldown under dynamic vacuum. At near ambient temperature, the isolation valves were closed, the vent tubes were heated, pinched closed, and weld-cut to seal. All four cannisters were processed in the same described manner.

#### 3.4.4 Extrusion

The consolidation step for all three powder approaches was by extrusion at 2300°F at a reduction ratio of 6.5:1. The relatively low consolidation temperature was selected for a number of reasons.

- The 2300°F extrusion temperature was considered adequate for consolidation purposes in that fully dense material could be produced.
- The 2300°F extrusion temperature permitted the use of mild steel as the cannister material. Higher working temperatures would require the use of molybdenum which is expensive and difficult to weld. The use of molybdenum cannisters



Outside Dimensions - 2.95 inches OD x 6.0 inches long  
Inside Dimensions - 2.70 inches ID x 5.0 inches long  
Wall Thickness - 0.120 inch

Figure 13. Mild Steel Extrusion Cannister

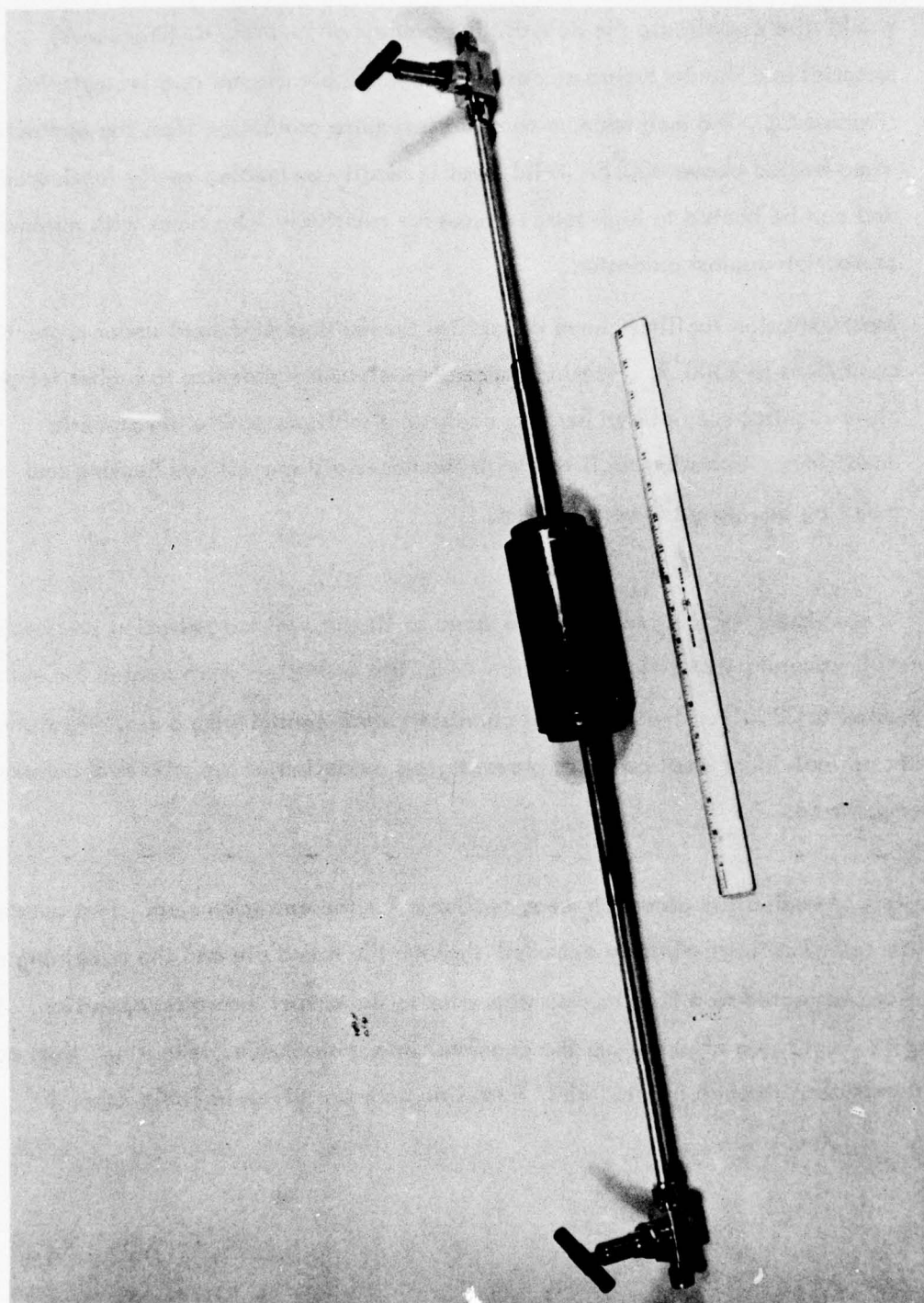


Figure 14. Double Ended Cannister for Prealloyed W-HfC Powder (Process C)





would also complicate the dehydriding process of W-HfH<sub>2</sub>-C (Process A) material and the degassing process of the WHfC prealloyed powder material (Process C). The molybdenum containers require protection from the atmosphere when heated above 800°F. Mild steel is readily weldable, easily fabricated, and can be heated to high temperatures for relatively long times with minimal protection against oxidation.

- Most extrusion facilities have capability for heating mild steel under protective conditions to 2300°F. Heating materials such as molybdenum to higher temperature requires specialized heating equipment with protective atmospheric conditions. Extrusion facilities with the necessary specialized heating and handling equipment is very limited.

The extrusion cannisters for this program were sized to fit the 700 ton extrusion press at the Air Force Materials Laboratory at Wright-Patterson AFB. The cannisters were heated for extrusion in a furnace heated to 2300°F. The mild steel cannisters were coated with a graphite slurry and placed under an individual steel cover to prevent gross oxidation of the mild steel cannisters while at temperature.

Four cannisters of each alloy approach were available for the extrusion step. Two cannisters of each alloy approach were directly extruded through the round die and the remaining two cannisters were subjected to a hot pressing step prior to the actual extrusion operation. The hot pressing step consisted of extruding the cannister into a blank die, reheating, then conventionally extruding through a round die. Extrusion data are given in Table 2.

Table 2. Extrusion Data

Cannister Ident.	Extrusion No.	Material	Total Run Force		Ram Speed in./min.	Comment	Process
			Break-through (tons)	Run through (tons)			
A	6517	W-HfH <sub>2</sub> -C Pwdr.	620 - 580		3.5	Directly extruded	A
B	6518	W-HfH <sub>2</sub> -C Pwdr.	700 - 600		4.5	Directly extruded	
C	6522	W-HfH <sub>2</sub> -C Pwdr.	620 - 600		4.8	Hot pressed	
D	6524	W-HfH <sub>2</sub> -C Pwdr.	620 - 600		5.0	Hot pressed	
1	6513	W-HfC Powder	610 - 560		5.0	Directly extruded	B
2	6514	W-HfC Powder	620 - 520		5.0	Directly extruded	
3	6520	W-HfC Powder	690 - 600		3.0	Hot pressed	
4	6521	W-HfC Powder	690 - 600		3.5	Hot pressed	
1-A	6469	Alloy Powder	700 -		Did not extrude		C
1-B	6470	Alloy Powder	710 -		Did not extrude	Hot pressed	
1-C	6471	Alloy Powder	715 -		--	Hot pressed only	
1-D	6472	Alloy Powder	720 -		--	Hot pressed only	

Extrusion ratio 6.5:1

Extrusion temperature 2300°F



The W-HfH<sub>2</sub>-C (Process A) and W-HfC (Process B) powder cannisters were successfully extruded. Both the hot pressed and the unpressed material were consolidated by extrusion.

Typical extrusions are shown in Figure 15. Figure 15a shows the extrusions with the mild steel clad in place. The rippled skin effect was due to the hydraulic behavior of the mild steel at the extrusion temperature since it tended to extrude more rapidly than the core material as it passed through the die. Figure 15b shows the extrusion with the steel clad chemically removed. All the extrusions exhibited some degree of nose burst. The surfaces were smooth with only a slight ripple due to the mild steel hydraulic effect. The de-clad diameter was approximately 1-1/4 inches.

Attempts to extrude the W-HfC prealloyed powder (Process C) cannisters were unsuccessful. Initially an effort was made to extrude one hot pressed and one unpressed billet. Both billets stalled the extrusion press. The remaining two cannisters were hot pressed to densify the alloy powder for possible further consolidation attempts by other means. Both cannisters, which failed to extrude, were inspected. The mild steel clad was chemically removed from the hot pressed billet using hydrochloric acid to dissolve the iron. The cannister, which failed to extrude directly and for which no prior hot pressing step was conducted, was partially machined to remove the steel clad. The resulting billets are shown in Figure 15b and 16b. Both compacts, which were essentially hot pressed by the attempted extrusion at 2300°F, are severely laminated. This working temperature for compacting the WHfC prealloyed powder is apparently too low.

#### 3.4.5 Supplemental WHfC Prealloyed Powder Extrusion

In order to provide some material of the WHfC prealloyed powder approach for evaluation, two molybdenum TZM cans were prepared for Dynapak extrusion. One can was filled with powder taken from the -60 +325 mesh size segment. The other was filled with larger particle material from the -20 +60 mesh segment. The cans were 4 inches long with an OD of 1-7/8 inch



(a) Extrusions A6517 and B6518 - W-HfH<sub>2</sub>-C Material with Steel Clad in Place (Process A)



(b) Extrusions 1-6513 and 2-6514 (W-HfC) Material with Steel Clad Chemically Removed (Process B)

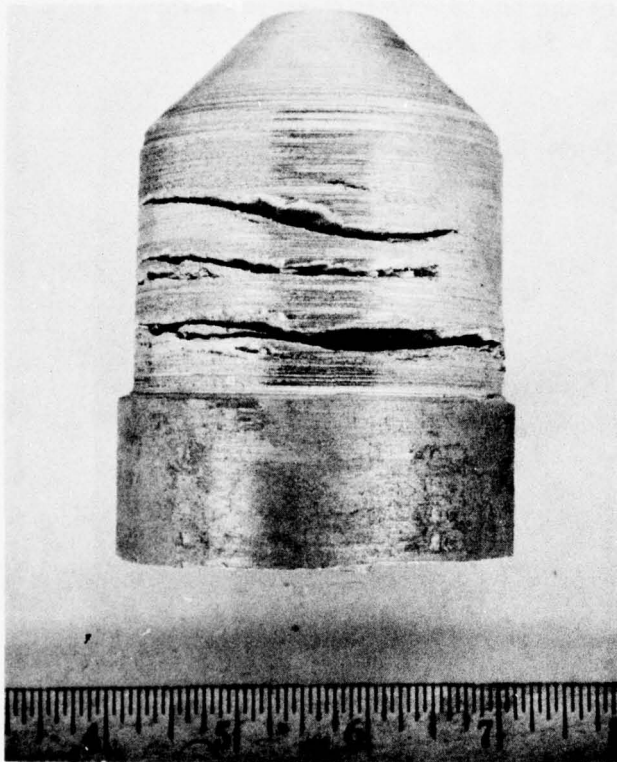
Figure 15. Typical Extrusions of W-HfH<sub>2</sub>-C (Process A) and W-HfC (Process B)



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(a) Declad Hot Pressed  
WHfC Prealloyed  
Powder Compact



(b) Partially Machined  
WHfC Prealloyed  
Powder Compact Which  
Failed Direct Extrusion

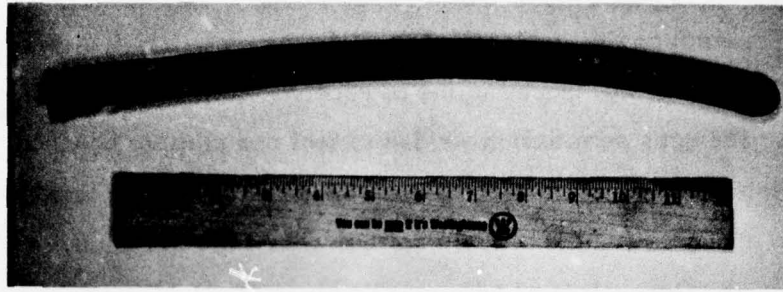
Figure 16. Declad WHfC Prealloyed Powder Compact Hot Pressed at 2300°F and Partially Machined Cannister Which Failed Direct Extrusion at 2300°F

diameter. The internal cavity, which contained the powder, was 1.6 inches ID by 3-1/2 inches long. The powder was loaded in the as-received condition, no degassing processing was conducted. The cans were fusion welded to seal and pressure checked for leak tightness. The powder billets were heated to 3600°F in an induction heater enclosed in a chamber with a flowing argon atmosphere. The billets were transferred to the Dynapak and extruded at 7:1 reduction ratio. The Dynapak is a high energy rate metal-working machine. The billet containing the fine WHfC alloy powder was only partially extruded. Less than 1/2 of the powder passed through the die. An insufficient fire pressure was responsible for the incomplete extrusion. The coarse powder billet, however, was successfully extruded completely through the die and is shown in Figure 17. The figure includes the extrusion with and without the co-extruded molybdenum TZM clad and a closeup of the extrusion surface to illustrate the high quality of the extruded alloy powder. Sufficient material was available to permit limited metallographic evaluation and tensile tests. The evaluation of this material was included where appropriate with the evaluation of the W-HfH<sub>2</sub>-C and W-HfC materials.

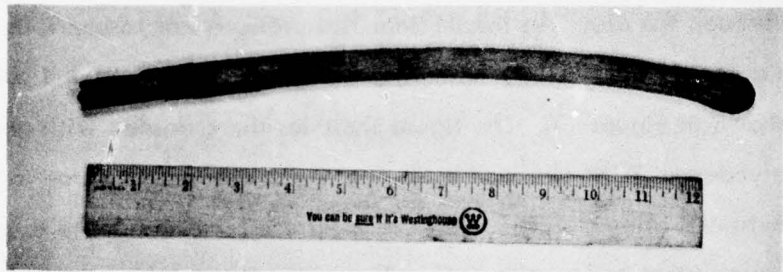
### 3.5 CHEMICAL ANALYSIS OF EXTRUDED MATERIAL

#### 3.5.1 Chemical Analyses

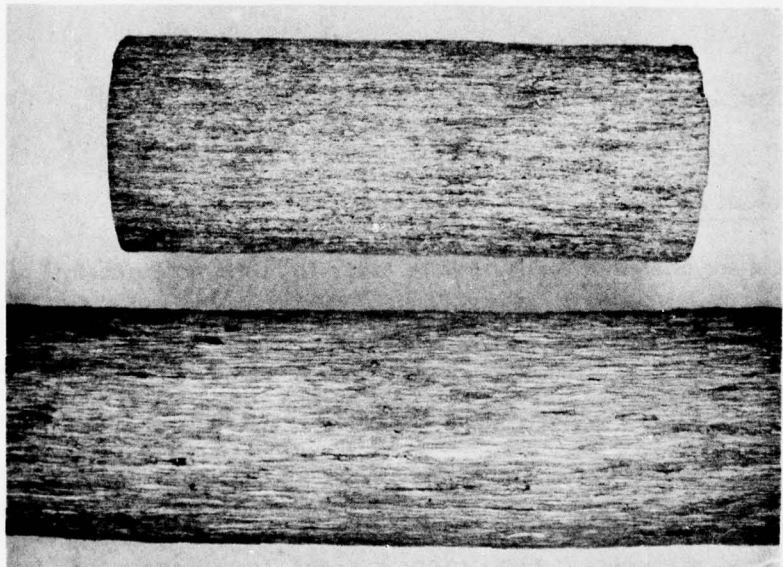
Samples suitable for chemical analysis were taken from the nose and tail of each extrusion. In addition, samples for density measurements were also taken from the tail section of each extrusion. Results are given in Table 3. Material produced from blended tungsten, hafnium hydride and graphite powder, designated as W-HfH<sub>2</sub>-C (Process A) had carbon levels which ranged from 360 to 390 ppm by weight. Hafnium levels averaged 0.33 percent by weight for the eight analyses. Assuming stoichiometric combination of the carbon with the hafnium, an excess of carbon on the order of 160 to 180 ppm was present. The material produced by blending tungsten powder and hafnium carbide, W-HfC, (Process B) also exhibited excess carbon on the order of 160 ppm above stoichiometry. Since no intentional addition of carbon was made to



(a) As-extruded with Mo Clad



(b) As-extruded with Mo Clad Removed



(c) Closeup of As-extruded Surface - 2X  
Top - Fine Powder  
Bottom - Coarse Powder

Figure 17. Dynapak Extrusion of WHfC Prealloyed Powder in Molybdenum Can at 3600°F

Table 3. Chemical Analyses and Densities of Extruded W-HfH<sub>2</sub>-C (Process A) and W-HfC (Process B) Material

Process	Sample Identification	Material	Density*		Chemical Analyses (wt. %)						
			g/cm <sup>3</sup>	%	C	O <sub>2</sub>	N <sub>2</sub>	Hf			
A	A-6517 - tail	W-HfH <sub>2</sub> -C	18.5	96.4	0.039	0.0031	<0.0010	0.32	Direct Extrusion		
	A-6517 - nose	W-HfH <sub>2</sub> -C	-	-	0.036	0.0058	0.0018	0.36			
	B-6518 - tail	W-HfH <sub>2</sub> -C	18.5	96.4	0.039	0.0024	0.0015	0.30	Hot Pressed		
	B-6518 - nose	W-HfH <sub>2</sub> -C	-	-	0.035	0.0030	<0.0010	0.34			
	C-6522 - tail	W-HfH <sub>2</sub> -C	19.1	99.5	0.036	0.0025	<0.0010	0.34	Hot Pressed		
	C-6522 - nose	W-HfH <sub>2</sub> -C	-	-	0.037	0.0064	0.0039	0.30			
D-6524 - tail	W-HfH <sub>2</sub> -C	18.9	98.4	0.036	0.0040	0.0011	0.33	Direct Extrusion			
D-6524 - nose	W-HfH <sub>2</sub> -C	-	-	0.036	0.0027	<0.0010	0.32				
B	1 - 6513 - tail	W-HfC	18.5	96.4	0.042	0.0034	<0.0010	0.38	Direct Extrusion		
	1 - 6513 - nose	W-HfC	-	-	0.030	0.0058	<0.0010	0.24			
	2 - 6514 - tail	W-HfC	19.0	99.0	0.038	0.0030	0.0010	0.30	Hot Pressed		
	2 - 6514 - nose	W-HfC	-	-	0.040	0.0027	0.0010	0.30			
	3 - 6520 - tail	W-HfC	18.6	96.9	0.037	0.0030	0.0018	0.31	Hot Pressed		
	3 - 6520 - nose	W-HfC	-	-	0.031	0.0040	0.0016	0.24			
4 - 6521 - tail	W-HfC	19.2	100	0.034	0.0027	<0.0010	0.31	Hot Pressed			
4 - 6521 - nose	W-HfC	-	-	0.032	0.0024	0.0014	0.24				
C	1-A 6469**	WHfC Prealloyed Pwdrip.	Not Measured		0.032	0.0042	0.0010	0.35			

\* Density as percent of arc cast.

\*\* Sample taken from top of billet which failed to extrude. Density as percent of density of arc-cast material.





this material, W-HfC, it was concluded that the excess carbon was present in the starting tungsten powder. The carbon present in the starting tungsten powder was not included in the carbon charge calculation. Typical vendor analysis indicated the possible presence of up to 500 ppm carbon maximum. As a result, carbon levels for both materials were in excess of stoichiometry.

The most significant analytical results are for oxygen and nitrogen levels. The reported values reflect the efficiency of the powder degasification process. Oxygen values ranged from 24 to 64 ppm with an average value of 37 ppm. Nitrogen values were below the limits of detectability in most cases with a maximum value of 39 ppm. The results for oxygen and nitrogen are comparable to levels produced in arc-melted material. The control of oxygen level in the consolidation of W-Hf-C alloy is the key to producing consistent alloy compositions from heat-to-heat. The reported analytical results indicate that the process used in this investigation to consolidate W-Hf-C alloy by powder metallurgical techniques was successful in controlling the interstitial level in the final consolidated product. The WHfC prealloyed powder produced from arc-cast material, which failed to extrude, was also analyzed. The hydrogen degassing heat treatment conducted in the mild steel cannisters did not reduce the carbon level in the alloy powder. These results indicate that the oxygen level in the WHfC prealloyed powder can be controlled without loss of carbon. The alloy powder handling procedure and degasification treatment were sufficient to control the interstitial level of the pressed alloy powder.

### 3.5.2 Density Measurements

Density measurements of the extruded material were also conducted. Two methods were used, a water displacement pycnometer and an air comparison pycnometer. A reference density of  $19.2 \text{ g/cm}^3$  for WHfC alloy was taken from arc-cast and extruded material measured by each technique. Extrusion at  $2300^\circ\text{F}$  in the mild steel cannisters produced material which was less than 100 percent dense in all but one case. Extrusions designated as C-6522, D-6524, 3-6520, and 4-6521 were hot pressed prior to extrusion; the others were extruded directly.

The prior hot pressing appears to have an effect on the consolidation of the W-HfH<sub>2</sub>-C material. Directly extruded material had a density of 18.5 g/cm<sup>3</sup> while the density of prior hot pressed material was 18.9 and 19.1 g/cm<sup>3</sup> or a difference of approximately 3 percent. Density of the extruded W-HfC material (Process B) was not as consistent since both the directly extruded and the prior hot pressed material had high and low density values. The measured extruded values appear to be inconsistent with metallographic examination of the microstructure of extruded material. As will be shown in the following section, the microstructure at a magnification of 500X appears to be 100 percent dense.

### 3.6 HEAT TREATMENT STUDIES

Heat treatment studies were carried out on material from each powder metallurgical non-consolidation technique. The objectives of the heat treatment studies were:

- Determination of the recrystallization behavior of the extruded material.
- Determination of the optimum solution annealing and aging temperatures.

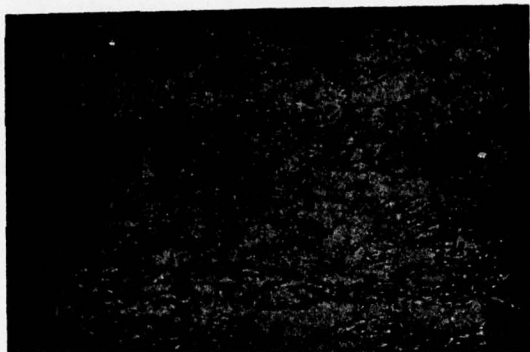
#### 3.6.1 Determination of Recrystallization Behavior of Extruded Material

To determine the recrystallization behavior, samples of the W-HfH<sub>2</sub>-C and W-HfC extruded material were heat treated for one hour at 3600, 3800, 4000, 4200, 4400, and 4600°F. A limited amount of WHfC prealloyed powder material consolidated by Dynapak extrusion of non-degassed powder at 3600°F in a molybdenum can was also included in the recrystallization study. The microstructures of the "as-extruded" and heat treated W-HfH<sub>2</sub>-C and W-HfC materials are shown in Figures 18 and 19.

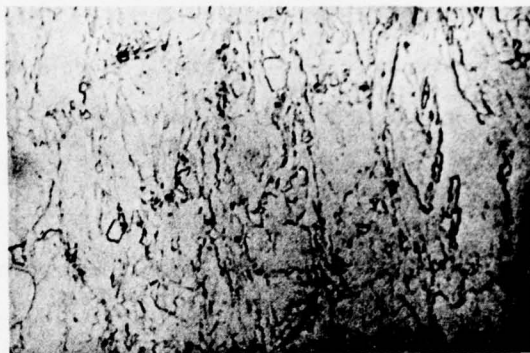
In the as-extruded condition, the W-HfH<sub>2</sub>-C material (Process A) displayed a wrought microstructure (Figure 18). At 500X some evidence of metallic hafnium produced during the dehydrating process was visible. The material appeared to be very nearly 100 percent dense with no gross indications of voids. The microstructure was very clean with little or no indications of the presence of oxides. Samples of as-extruded



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200X

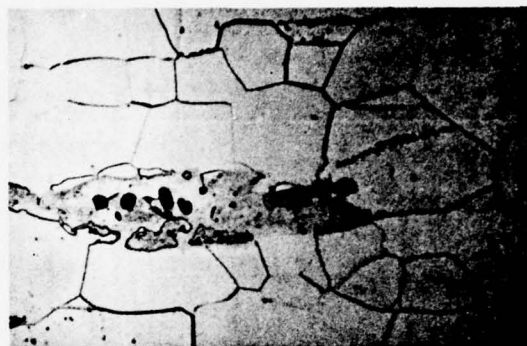


500X

As-Extruded - Longitudinal



100X

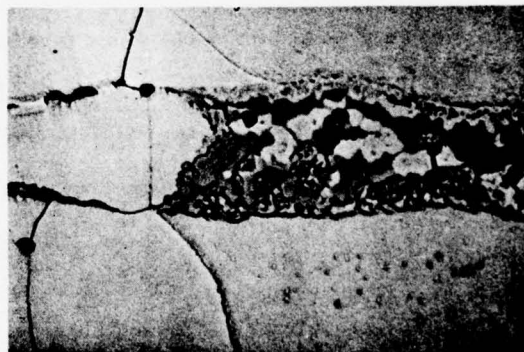


500X

Extruded + 1 Hour/3600°F - Longitudinal



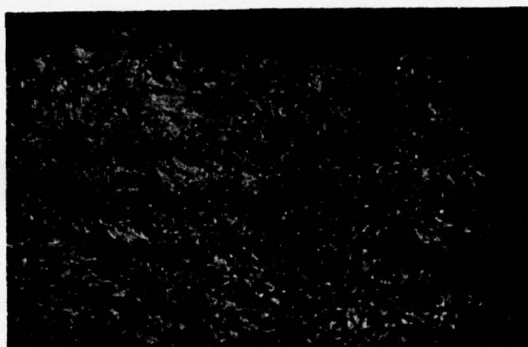
100X



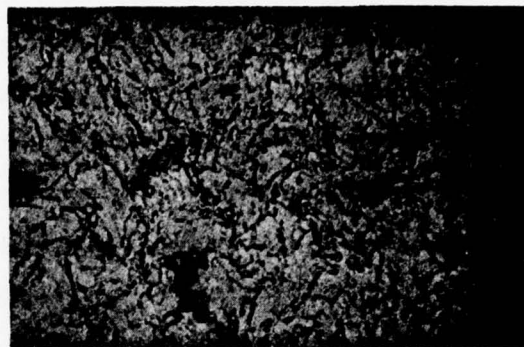
1000X

Extruded + 1 Hour/4600°F - Longitudinal

FIGURE 18. MICROSTRUCTURES OF EXTRUDED AND HEAT TREATED W-HfH<sub>2</sub>-C MATERIAL (PROCESS A) (ETCH - MURIKAMI'S REAGENT)



200X

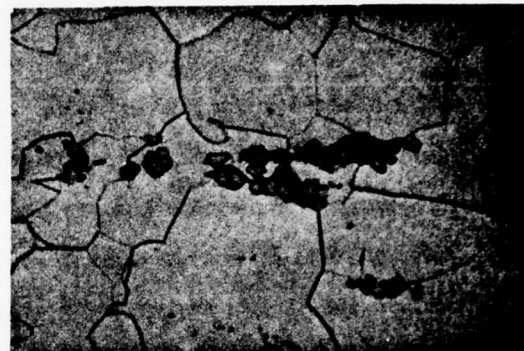


500X

As-Extruded - Longitudinal

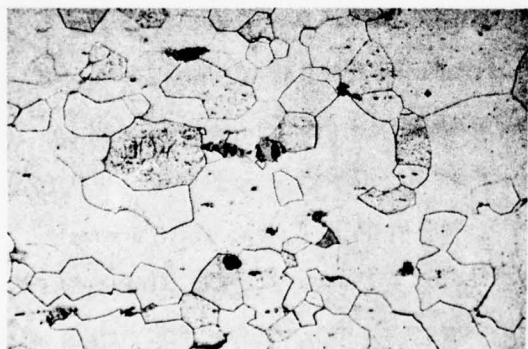


100X



500X

Extruded + 1 Hour/3600°F - Longitudinal



100X



1000X

Extruded + 1 Hour/4600°F - Longitudinal

FIGURE 19. MICROSTRUCTURES OF EXTRUDED AND HEAT TREATED W-HfC MATERIAL (PROCESS B) (ETCH - MURIKAMI'S REAGENT)



material were given anneals of 1 hour at 3600, 3800, 4000, 4200, 4400, and 4600°F. The microstructure of the material annealed at 3600°F and 4600°F are shown in Figure 18. The microstructure of the material annealed at 3600°F exhibits a completely recrystallized microstructure with no significant evidence of interaction between the elemental hafnium and the tungsten matrix. As the annealing temperature was increased, the grain size of the tungsten matrix also increased. The microstructures of the material annealed at 3800, 4000, 4200, and 4400°F, which are not shown, were essentially the same as the material annealed at 3600°F, only the tungsten matrix grain size was larger for each successive increase in annealing temperature. The grain size exhibited for each annealed condition was typical of unalloyed powder metallurgy tungsten sheet. The material annealed at 4600°F had a grain size of 0.062 mm (ASTM 5). At 500X, etch pits outline the development of a substructure which is typical of unalloyed tungsten. Some evidence of interaction between the elemental hafnium and tungsten matrix was noted for material annealed at 4600°F. The interaction is illustrated in the photomicrograph taken at 1000X, Figure 18. A stringer-like formation of hafnium which was heated well above its melting point, 3866°F, shows evidence of solutioning reaction with the tungsten matrix.

The W-HfC material (Process B) exhibited similar microstructures in the extruded and heat treated conditions (Figure 19). The as-extruded W-HfC material exhibited a clean, wrought microstructure with hafnium carbide particles uniformly distributed throughout the matrix. After 1 hour at 3600°F, the material was completely recrystallized with a grain size of 0.0246 mm (ASTM 8). As the annealing temperature was increased to 4600°F, the grain size also increased to 0.047 mm (ASTM 6). Material annealed at 4600°F exhibited little or no evidence of interaction between the hafnium carbide and the tungsten matrix. High magnification micrographs (1000X) illustrate the disposition of hafnium carbide particles in the tungsten matrix after a 1 hour heat treatment at 4600°F, Figure 19. The particles are located at grain boundaries and contain voids which appear to be due to the geometry of the hafnium carbide particle. In some cases there is evidence of coherency of the carbide particles with the tungsten matrix.

Heat treatment of the WHfC prealloyed powder material (Process C) was carried out for 1 hour at 4000, 4200, 4400, and 4800°F. The microstructures shown in Figure 20 include transverse and longitudinal sections of the as-extruded condition for material produced from coarse powder, -50 +200 mesh. In both micrographs large grains are surrounded with fine particles. Evidence of deformation was present in the larger grains; there were no indications of classical recrystallization as a result of the 3600°F extrusion operation. On annealing for 1 hour at 4000°F, a duplex grain structure was produced with very large, apparently strain-free grains and regions of significantly smaller grains also apparently strain free. The duplex grain structure persisted after heat treatments at 4200 and 4400°F. In each case the resulting grain sizes increased with increasing temperature. At 4800°F the duplex structure was not as pronounced. The grain structure was more or less uniform. Material from a second extrusion made from WHfC prealloyed powder of a finer size, +325 -200 mesh, was also heat treated in a similar manner. The response of the fine and coarse grained material was the same, only the resultant grain size was smaller for the initially fine material as would be expected.

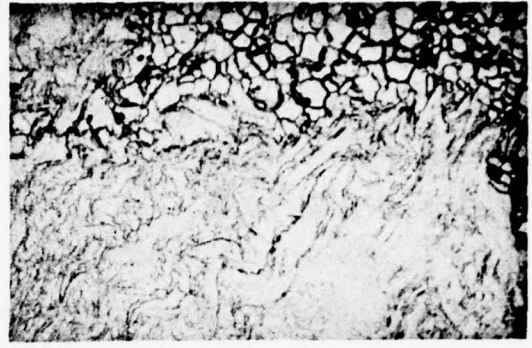
Hardness data for material produced by each of the powder consolidation approaches are given in Table 4 and Figure 21. The WHfC alloy powder material exhibited hardness values of 466DPH for as-extruded fine grained material and 542 DPH for as-extruded coarse grained material. The hardness of as-extruded W-HfH<sub>2</sub>-C and W-HfC material was very similar, 502 and 496, respectively. A hardness value of 528 DPH for arc-cast material was included as a reference. The room temperature hardness of material involving elemental tungsten powder in the consolidation process (W-HfH<sub>2</sub>-C and W-HfC) ranged in hardness from 348 to 372 DPH for all of the annealing temperatures. The WHfC prealloyed powder material exhibited significantly higher hardness values at all annealing temperatures. The difference in hardness behavior is due to the difference in the distribution and morphology of the alloy constituents. In the W-HfH<sub>2</sub>-C and W-HfC materials, the optimum distribution of the hafnium carbide phase throughout the tungsten matrix has not as yet been accomplished at this stage of processing, while the optimum distribution of hafnium carbide produced during arc-melting has been retained in the alloy powder product.



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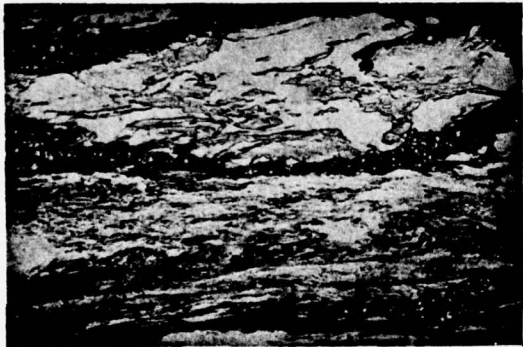


100X

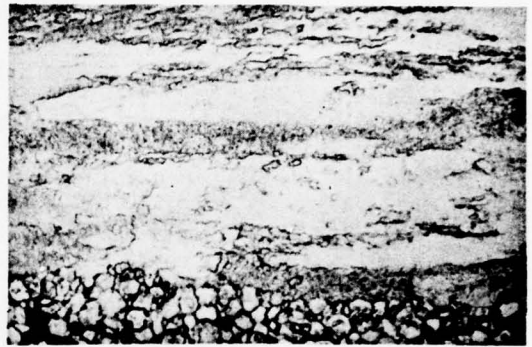


500X

As-Extruded - Transverse



100X

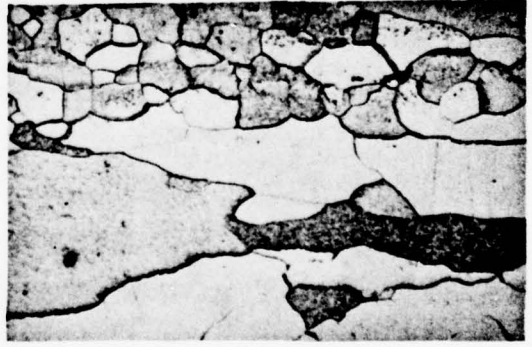


500X

As-Extruded - Longitudinal



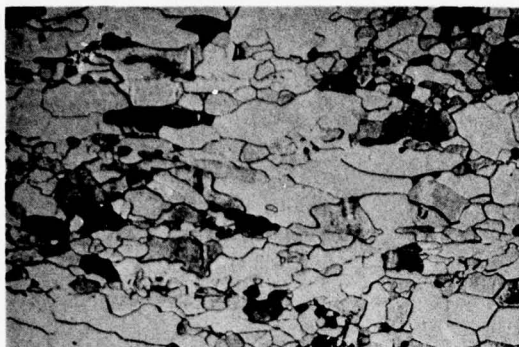
100X



500X

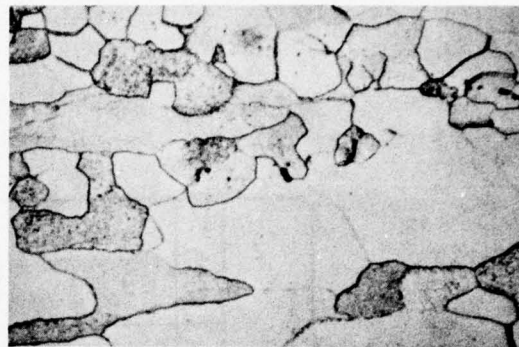
Extruded + 1 Hour/4000°F - Longitudinal

FIGURE 20. MICROSTRUCTURES OF EXTRUDED AND HEAT TREATED WHFC PRE-ALLOYED POWDER MATERIAL (ETCH - MURKIAMI'S REAGENT)

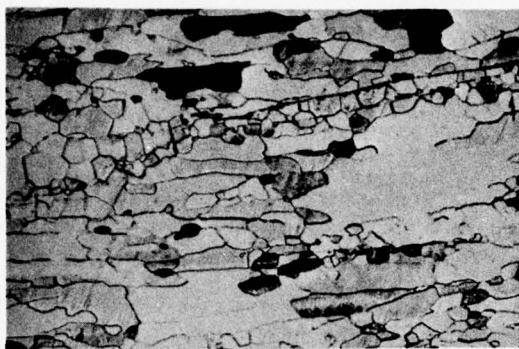


100X

Extruded + 1 Hour/4200°F - Longitudinal

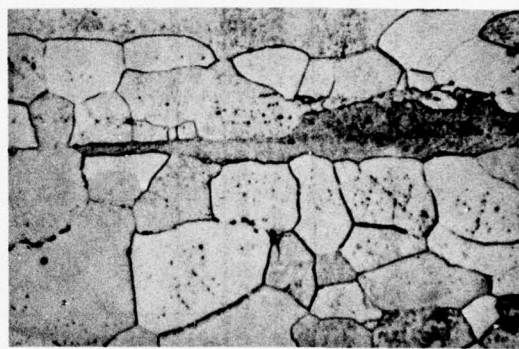


500X



100X

Extruded + 1 Hour/4400°F - Longitudinal

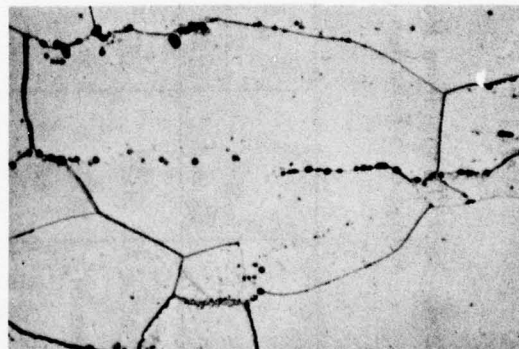


500X



100X

Extruded + 1 Hour/4800°F - Longitudinal



500X

Figure 20 (Cont'd.). Microstructures of Extruded and Heat Treated WHfC Prealloyed Powder Material (Etch - Murikami's Reagent)



Table 4. Room Temperature Hardness (DPH) of Various Powder Metallurgy WHfC Alloys as a Function of Condition and Heat Treatment

Material	As-Extruded	As-Extruded Plus One Hour Anneal at the Indicated Temperature (°F) DPH						
		3600	3800	4000	4200	4400	4600	4800
W-HfH <sub>2</sub> -C (Process A)	502	370	359	360	366	359	352	-
W-HfC (Process B)	496	364	362	362	372	356	348	-
WHfC (Prealloyed Pwdr.) Fine Particle	465	-	-	391	392	378	-	357
Coarse Particle	553	-	-	405	388	373	-	363
WHfC (arc-cast)	526	-	-	-	-	-	388	-

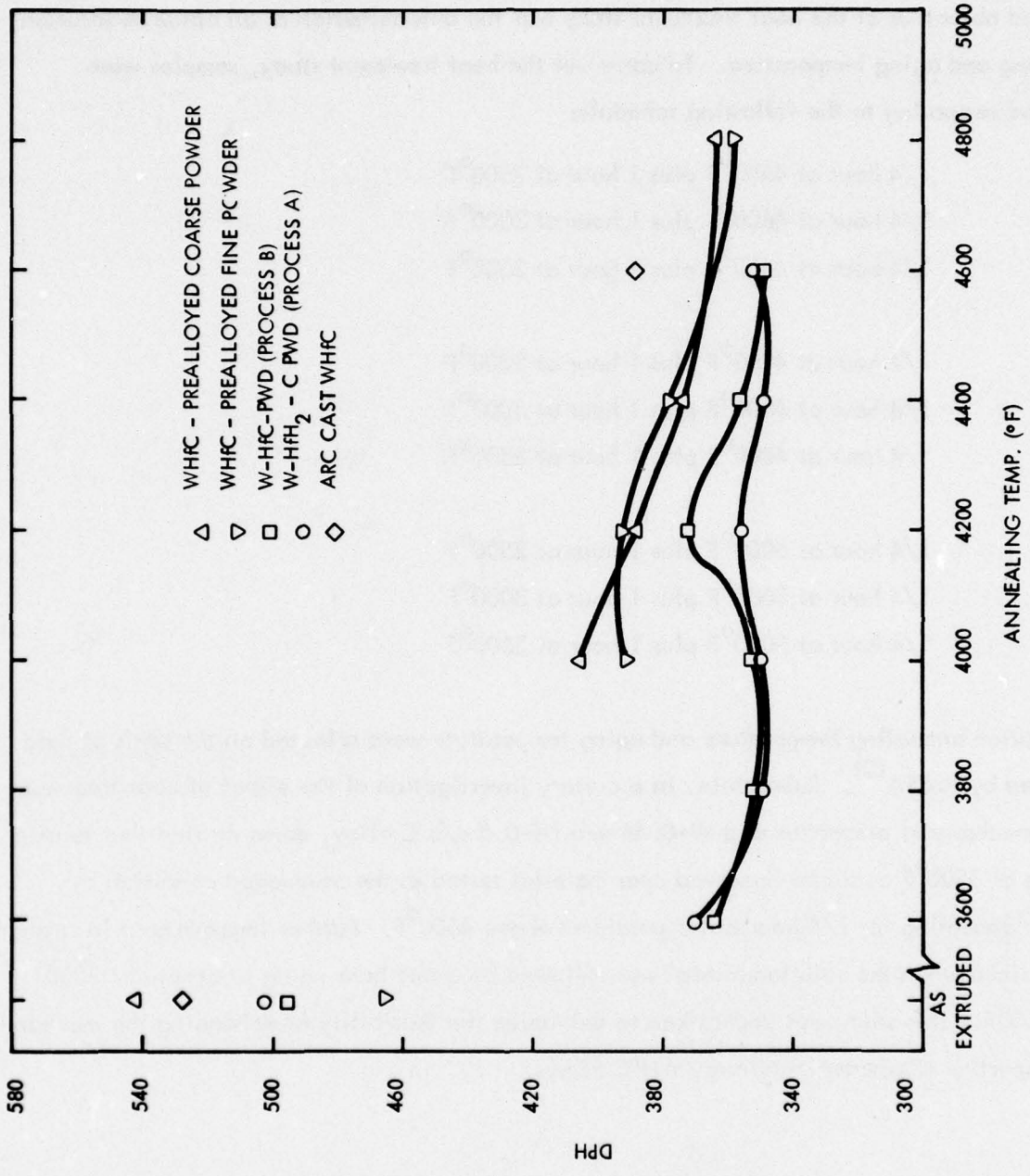


Figure 21. The Effect of Heat Treatment on the Room Temperature Hardness of W-Hf-C Alloys



### 3.6.2 Determination of the Effect of Solution Treatment and Aging on the Microstructure of Extruded Material

A second objective of the heat treatment study was the determination of an optimum solution annealing and aging temperature. To carry out the heat treatment study, samples were annealed according to the following schedule:

1/4 hour at 4600°F plus 1 hour at 2500°F

1/4 hour at 4600°F plus 1 hour at 3000°F

1/4 hour at 4600°F plus 1 hour at 3500°F

1/4 hour at 4800°F plus 1 hour at 2500°F

1/4 hour at 4800°F plus 1 hour at 3000°F

1/4 hour at 4800°F plus 1 hour at 3500°F

1/4 hour at 5000°F plus 1 hour at 2500°F

1/4 hour at 5000°F plus 1 hour at 3000°F

1/4 hour at 5000°F plus 1 hour at 3500°F

The solution annealing temperature and aging temperature were selected on the basis of data published by NASA<sup>(5)</sup>. Rubenstein, in a cursory investigation of the effect of heat treatment on the mechanical properties of a W-0.48 a/o Hf-0.5 a/o C alloy, demonstrated that tensile strength at 3500°F could be improved over material tested in the as-swaged condition by solution annealing for 1/4 hour at temperatures above 4600°F. Further improvement in strength was attained when the solution anneal was followed by a one hour aging treatment at 2500 and 3000°F. This study was undertaken to determine the feasibility of enhancing the mechanical properties of powder metallurgy WHfC alloys.

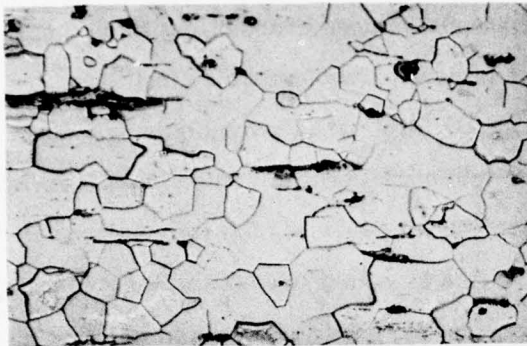
The heat treatments were carried out in a diffusion pumped vacuum chamber containing a tungsten mesh, resistance heating element. System pressures were generally less than  $1 \times 10^{-6}$  torr at ambient temperature and less than  $5 \times 10^{-5}$  torr at solution annealing temperatures. Samples were wrapped in tantalum foil to minimize possible contamination during heat treatment. After exposure at the solution annealing temperature, the furnace temperature was rapidly reduced to the aging temperature without cycling to ambient temperature. Due to insufficient material, the WHfC prealloyed powder material, which was consolidated by Dynapak extrusion, was not included in this study. Photomicrographs of the heat treated samples are shown in Figures 22 and 23. Micrographs are shown for material solution annealed at all three temperatures investigated and for only one aging temperature. The aging heat treatment had little visible effect on the microstructure.

In Figure 22 (Process A material) the effect of the solution anneal is evident in the behavior of the elemental hafnium produced by the dehydrating process prior to consolidation. It is evident from the microstructure that while the hafnium was fairly uniformly distributed throughout the tungsten matrix, it existed as discrete islands surrounded by a relatively large volume of unalloyed tungsten. The degree of interaction between the elemental hafnium and the tungsten matrix increased with increasing temperature as would be expected. In many cases microvoids were associated with the elemental metallic hafnium islands. Two plausible explanations exist for the presence of the microvoids. The incomplete densification during the powder consolidation process as reflected by the density measurements is one. The other explanation involves the mobility or diffusivity of the hafnium at the solution temperature. The large difference in diffusivity of hafnium and tungsten may have produced Kirkendall void formation. In any case numerous voids associated with the hafnium rich areas were noted.

The behavior of the W-HfC material (Process B) in response to the solution annealing and aging treatments is shown in Figure 23. The disposition of the hafnium carbide particles in the tungsten matrix was very similar to the behavior of the elemental metallic hafnium in the W-HfH<sub>2</sub>-C

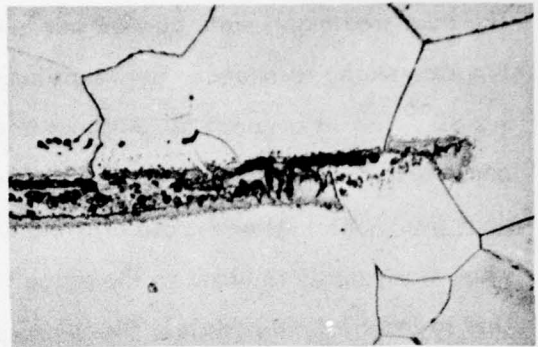


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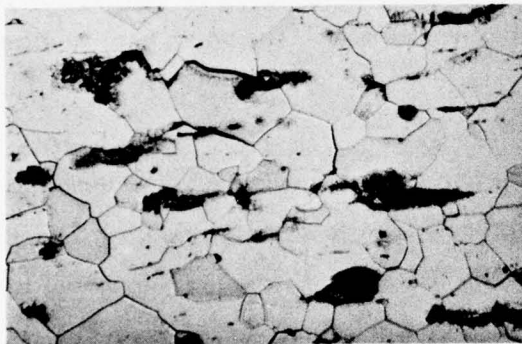


100X

Solution Annealed 1/4 Hour/4600°F + 1 Hour/3500°F - Longitudinal

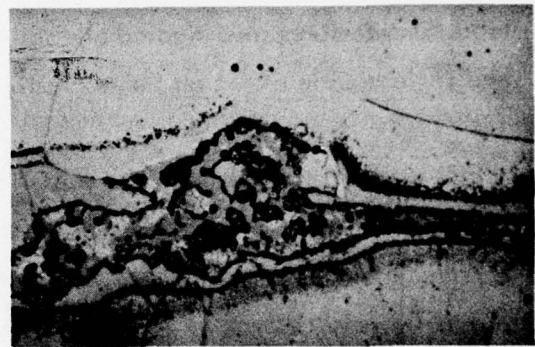


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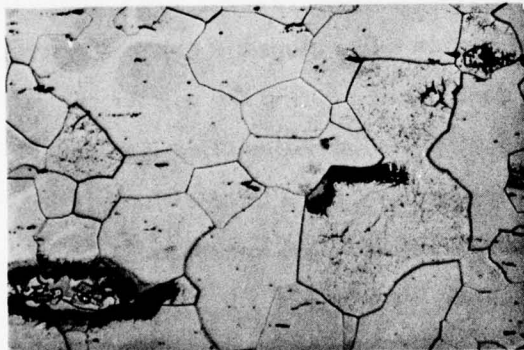


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Solution Annealed 1/4 Hour/4800°F + 1 Hour/3500°F - Longitudinal

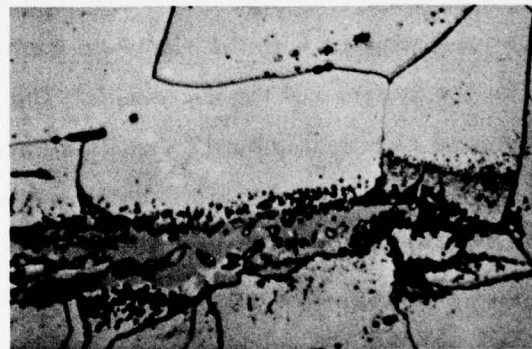


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Solution Annealed 1/4 Hour/5000°F + 1 Hour/3500°F - Longitudinal



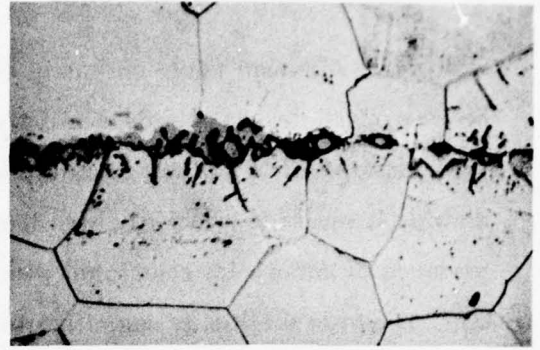
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Figure 22. Microstructures of Solution Treated and Aged W-HfH<sub>2</sub>-C Material (Process A) (Etch - Murikami's Reagent)

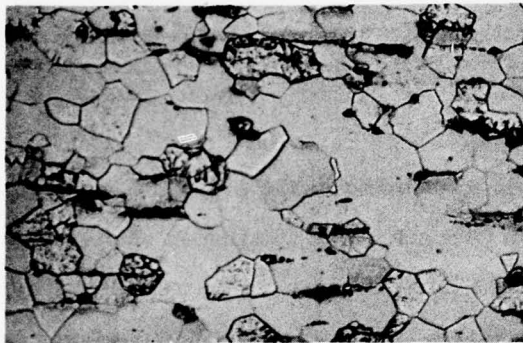


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Solution Annealed 1/4 Hour/4600°F + 1 Hour/2500°F - Longitudinal

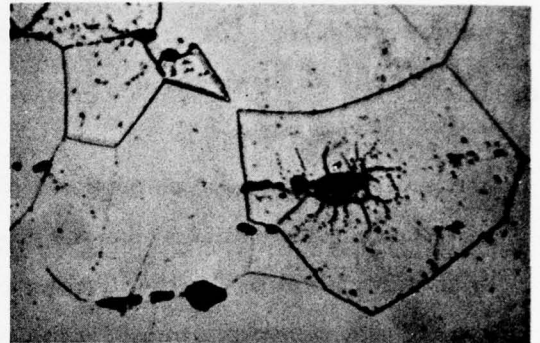


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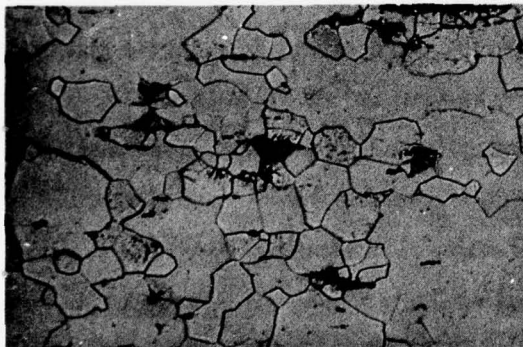


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Solution Annealed 1/4 Hour/4800°F + 1 Hour/3000°F - Longitudinal

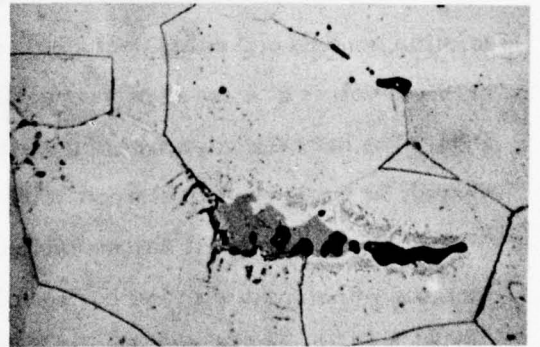


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100X

Solution Annealed 1/4 Hour/5000°F + 1 Hour/2500°F - Longitudinal



500X

Figure 23. Microstructures of Solution Annealed and Aged W-HfC Material (Process B) (Etch - Murikami's Reagent)



material. Although fairly uniformly distributed throughout the matrix, the mean free distance between particle islands was relatively large. Reactivity between the hafnium carbide and the tungsten matrix was not as extensive as was the case with elemental hafnium. Hafnium carbide is stable to relatively high temperatures. Metallographic examination revealed the presence of microvoids associated with the hafnium carbide particles also. The microvoids can be seen in the higher magnification micrographs as dark areas adjacent to hafnium carbide particles. In some cases the particles appear to contain internal voids which extend to the particle surface. These voids are obviously due to the morphology of the starting hafnium carbide particles. Other voids present were most likely due to incomplete densification during the consolidation process.

The purpose of the solution anneals was to facilitate solutioning of the elemental metallic hafnium into the tungsten matrix in the W-HfH<sub>2</sub>-C material (Process A) and dissolution of the hafnium carbide particles in the W-HfC (Process B) material. The purpose of the aging treatments was to promote the optimum reprecipitation of hafnium carbide particles. Since the solutioning process was not completed for either material, the aging heat treatments were rendered ineffective. Room temperature hardness measurements are listed in Table 5 for each material after the solution anneals and aging heat treatments. The W-HfC material exhibited little change in hardness values as a result of the heat treatments. Hardness values ranged from 352 to 364 DPH. The hardness values were comparable to those obtained for material given one hour anneals in the temperature range 3600 to 4600°F and reported in Table 4 and illustrated in Figure 21. The hardness values for the W-HfH<sub>2</sub>-C material displayed a slight but positive increase in hardness with increasing solution annealing temperature. This hardness increase was most likely due to the alloying effect of hafnium going into solution. Arc cast and extruded WHfC material has a hardness of 391 DPH after one-half hour exposure at 5000°F compared to an average hardness value of 366 DPH for W-HfH<sub>2</sub>-C material annealed at the same temperature and a 354 DPH hardness for W-HfC material. These results indicate that each powder metallurgy material requires additional thermal-mechanical processing in order to produce a homogeneous alloy comparable to arc-melted material.

Table 5. Room Temperature Hardness of Solution Annealed and Aged W-HfH<sub>2</sub>-C and W-HfC Material

Material Condition	Room Temperature Hardness (DPH)	
	W-HfH <sub>2</sub> -C	W-HfC
1/4 hour/4600°F + 1 hour/2500°F	(Process A) 359	(Process B) 364
1/4 hour/4600°F + 1 hour/3000°F	360	355
1/4 hour/4600°F + 1 hour/3500°F	356	364
1/4 hour/4800°F + 1 hour/2500°F	362	358
1/4 hour/4800°F + 1 hour/3000°F	366	358
1/4 hour/4800°F + 1 hour/3500°F	363	356
1/4 hour/5000°F + 1 hour/2500°F	362	353
1/4 hour/5000°F + 1 hour/3000°F	371	352
1/4 hour/5000°F + 1 hour/3500°F	364	358

Average of 5 readings





### 3.7 MECHANICAL PROPERTY EVALUATION

The objective of the mechanical property evaluation was the determination of the tensile properties of each material in the "as-extruded," recrystallized and solution annealed and aged condition in accordance with the following schedule:

Table 6. Mechanical Property Test Schedule

Test Temp. (°F)	<u>Material Condition</u>					
	As Extruded	Recrystallized	Solution Annealed	Solution Treated and Aged One Hour at		
				2500°F	3000°F	3500°F
RT	X	X	X	X	X	X
1500	X					
2000	X					
2500	X	X	X	X	X	X
3000	X					
3500	X	X	X	X	X	X
4000	X					
4500	X			X	X	X

Sections of the "as extruded" bar were cut into two inch lengths. The two inch long bars were sectioned axially in a pie shaped cross section to provide six tensile specimen blanks per bar. A total of 33 blanks were cut for each material (W-HfH<sub>2</sub>-C and W-HfC). Although only 26 tensile specimens were required to carry out the proposed test program, extra specimen blanks were included to cover breakage during machining and to provide duplicate specimens where required. Nine specimen blanks were broken during machining, and five more were broken during handling and loading into test equipment.

A limited amount of the WHfC prealloyed powder material produced by Dynapak extrusion was available. Consequently only six tensile specimens of this material were produced.

### 3.7.1 Tensile Specimen Geometry

Tensile specimens having a 1.125 inch long gauge section 0.115 inch in diameter were machined from the specimen blanks. The ends were button type 0.290 inch in diameter with a 0.125 inch radius to the point of tangency on the gauge section. Required heat treatments were carried out on machined specimens using the procedures and equipment described in the Heat Treatment Studies section.

### 3.7.2 Test Equipment

Tensile testing was carried out in a 10,000 pound load capacity Instron test unit equipped with a Brew model 1064 vacuum test chamber. The test chamber was evacuated by means of a mechanical pump backed 5 inch CVC oil diffusion pump equipped with a freon refrigerated cold trap. The system had an ultimate pressure capability of less than  $1 \times 10^{-6}$  torr at ambient and  $5 \times 10^{-5}$  torr at maximum test temperature of  $5000^{\circ}\text{F}$ . The test specimens were heated by means of a tungsten mesh resistance heater element four inches long by two inches in diameter. A radiation shield pack consisting of two tungsten foil inner shields and three outer shields of tantalum foil was used to attain operating temperatures up to  $5000^{\circ}\text{F}$ .

### 3.7.3 Tensile Test Results

#### 3.7.3.1 Material Tested in the As Extruded Condition

Tensile test results for as-extruded W-HfH<sub>2</sub>-C, W-HfC, and WHfC prealloyed powder materials are given in Tables 7, 8, and 9, respectively. The ultimate strength values are plotted in Figure 24 along with reference data from other sources. The W-HfH<sub>2</sub>-C (Process A) and W-HfC (Process B) exhibited elevated temperature tensile properties which were comparable to powder metallurgy W-HfC consolidated by extrusion in a molybdenum can at  $3600^{\circ}\text{F}^{(2)}$ . While all three consolidation



Table 7. Tensile Properties of W-HfH<sub>2</sub>-C Material  
(Process A)

Condition	Test Temperature (°F)	Ultimate Strength (KSI)	Yield Strength (KSI)	Elong. (%)	Reduction in Area (%)
As Extruded	RT	70.2	---	---	---
	1500	84.7	82.4	8.5	46.4
	2000	74.8	70.3	14.2	55.3
	2500	39.1	28.9	40.1	---
	3000	23.5	14.5	38.0	65.0
	3500	15.4	9.5	26.9	35.2
	4000	9.3	5.4	42.4	32.3
	4500	6.3	4.6	20.6	33.5
Annealed 1/4 Hr/4800°F	RT	33.4	---	---	---
	2500	51.7	24.6	---	---
	3500	25.6	15.8	6.5	14.4
Annealed 1/4 Hr/4800°F + 1 Hr/2500°F	RT	32.8	---	---	---
	2500	49.9	24.2	14.2	---
	3500	6.9	5.2	30.0	30.8
Annealed 1/4 Hr/4800°F + 1 Hr/3000°F	RT	29.8	---	---	---
	2500	41.7	15.8	18.4	56.6
	3500	23.7	15.3	5.8	20.4
	4500	---	---	---	---
Annealed 1/4 Hr/4800°F + 1 Hr/3500°F	RT	32.8	---	---	---
	2500	42.0	23.9	29.2	71.2
	3500	17.6	11.7	7.1	13.5
	4500	6.4	5.4	9.3	10.9

Strain Rate 0.05/min.

Table 8. Tensile Properties of W-HfC Material (Process B)

Condition	Test Temperature (°F)	Ultimate Strength (KSI)	Yield Strength (KSI)	Elong. (%)	Reduction In Area (%)
As Extruded	RT	57.8	---	---	---
	1500	80.0	77.8	6.8	39.1
	2000	76.4	74.7	12.0	59.1
	2500	37.2	22.3	42.3	76.8
	3000	31.7	16.6	49.5	98.0
	3500	13.0	9.4	12.9	15.2
	4000	7.8	6.8	9.0	---
	4500	3.5	3.0	7.2	8.3
Annealed 1/4 Hr/4800°F	RT	17.3	---	---	---
	2500	37.7	16.6	14.7	39.6
	3500	16.7	13.1	3.3	8.8
Annealed 1/4 Hr/4800°F + 1 Hr/2500°F	RT	22.4	---	---	---
	2500	37.7	16.6	14.7	39.6
	3500	16.7	13.1	3.3	8.8
	4500	5.6	4.5	8.6	12.0
Annealed 1/4 Hr/4800°F + 1 Hr/3000°F	RT	44.2	---	---	---
	2500	26.3	14.9	---	---
	3500	16.3-19.2	-- 14.9	-- 3.0	-- 4.3
	4500	6.1	5.4	7.9	7.7
Annealed 1/4 Hr/4800°F + 1 Hr/3500°F	RT	10.6	---	---	---
	2500	34.6	18.5	8.0	27.0
	3500	15.3	10.6	4.0	5.7
	4500	6.0	4.7	15.1	14.2
Recrystallized 1 Hr/ 2500°F	RT	62.6	---	---	---
	2500	35.0	16.0	45.9	73.3
	3500	12.6	8.9	12.6	8.8



Table 9. Tensile Properties of WHFC Prealloyed Powder Material

Condition	Test Temperature (°F)	Ultimate Strength (KSI)	Yield Strength (KSI)	Elong. (%)	Reduction In Area (%)
As Extruded	2000	94.4	---	---	---
	2500	80.0	---	---	---
	3000	84.0	84.0	0.2	0.2
	3500	47.8	---	---	---
Annealed 1/4 Hr/4800°F	3500	24.8	---	---	---
Annealed 1/4 Hr/4800°F + 1 Hr/2500°F	3500	27.6	---	---	---

Strain Rate 0.05/min.

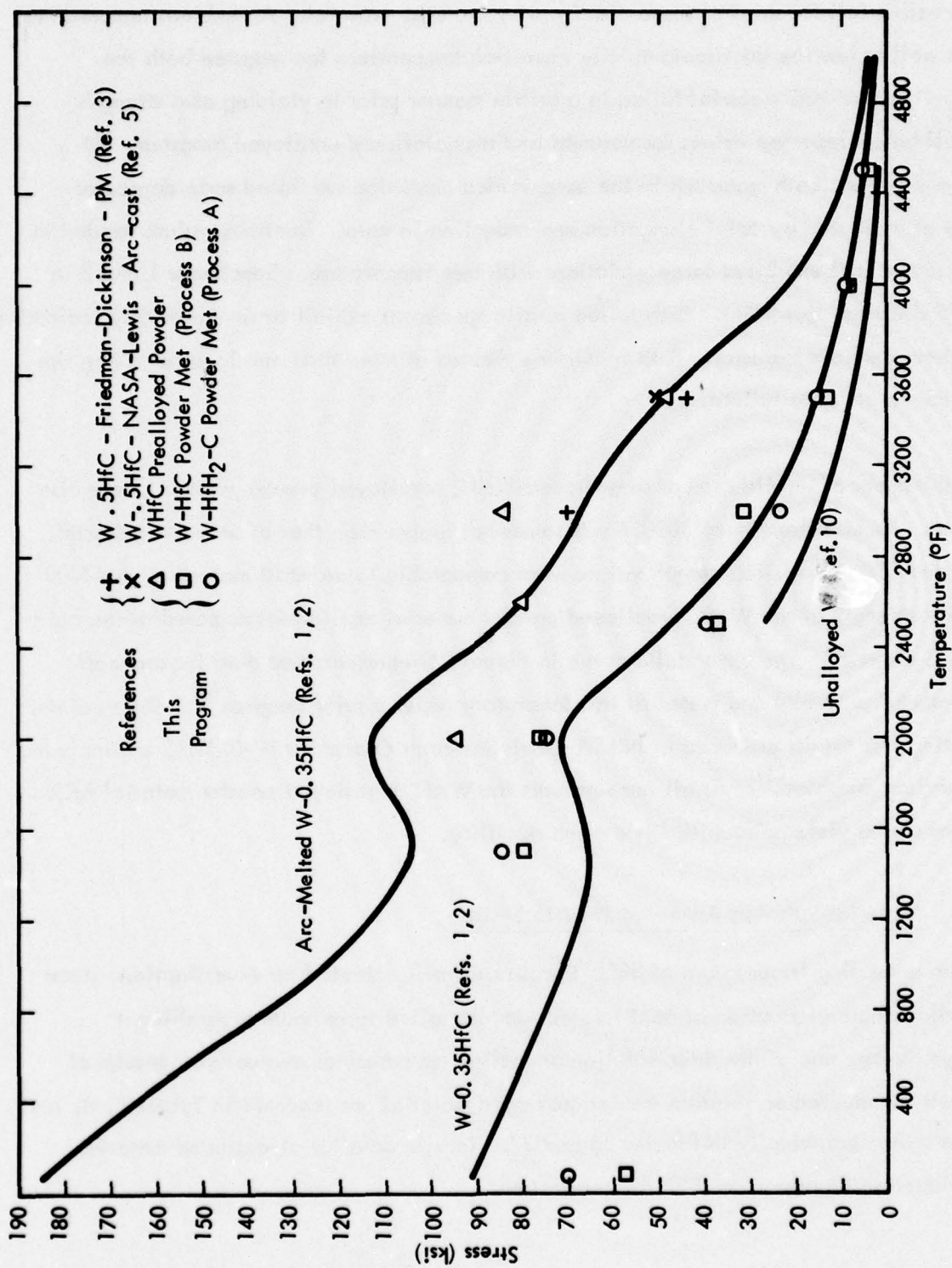


Figure 24. Mechanical Properties of As-extruded WHfC Alloys as a Function of Test Temperature

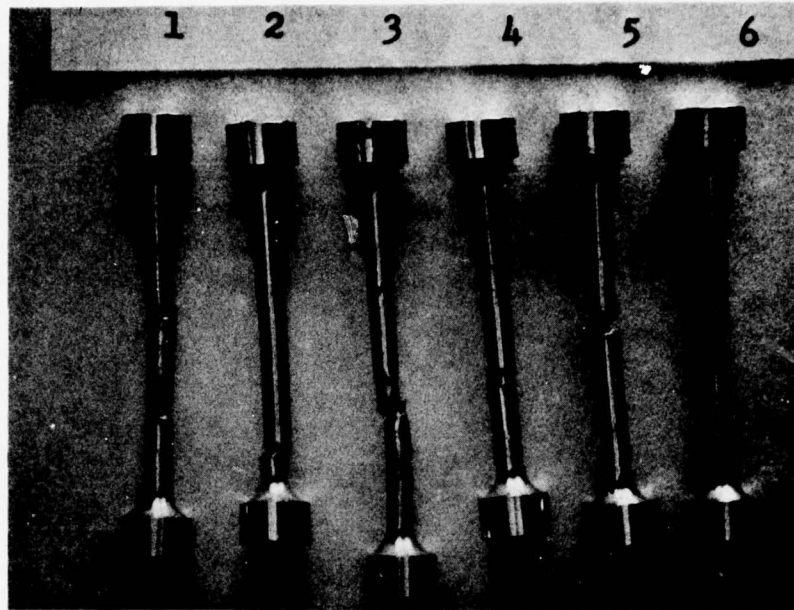


approaches produced material with improved strength over unalloyed tungsten, tensile strength values fell far short of those displayed by arc cast material. At ambient temperature, which is well below the ductile-to-brittle transition temperature for tungsten both the W-HfH<sub>2</sub>-C and W-HfC material failed in a brittle manner prior to yielding at a strength level well below reported values for wrought and recrystallized unalloyed tungsten. At 1500°F and above, both materials in the as-extruded condition exhibited some degree of ductility as indicated by total elongation and reduction in area. Ductility values tended to be inconsistent and exhibited large variations with test temperature. Specimens 1 and 3 in Figure 25 illustrate this point. Both failed tensile specimens exhibit strain instability indicative of a nonhomogeneous material. Both specimens yielded at more than one location along the gauge prior to ultimate failure.

A limited number of tensile tests of as-extruded WHfC prealloyed powder material were also conducted. Tensile strength at 3000°F was somewhat higher than that of arc-cast material. At 2500 and 3500°F tensile strength values were comparable to arc-cast material. At 2000°F the tensile strength of the WHfC prealloyed powder material was lower compared to the arc-cast WHfC material. The upper solid curve in Figure 24 represents test data for arc-cast WHfC material produced and tested at this laboratory under a prior program<sup>(1)</sup>. Data points, representing test results produced at NASA-Lewis Research Center for W-0.5HfC are included for comparison purposes<sup>(5)</sup>. At all temperatures the WHfC prealloyed powder material failed prior to or at the yield point with little or no ductility.

### 3.7.3.2 Material Solution Annealed Prior to Testing

A solution annealing temperature of 4800°F was arbitrarily selected for investigation, since the metallographic evaluation of heat treated samples failed to indicate a significant advantage for any one of the three solution annealing temperatures evaluated. Results of tensile tests conducted on solution treated and aged material are reported in Tables 7, 8, and 9 and are shown graphically in Figures 26 and 27. Tensile data for as-extruded material were included in Figures 26 and 27 for comparison.



<u>Specimen No.</u>	<u>Material</u>	<u>Condition</u>
1	W-HfC	As-Extruded
2	W-HfC	1/4 Hr/4800°F
3	W-HfH <sub>2</sub> C	As-Extruded
4	W-HfC	1/4 Hr/4800°F + 1 Hr/3000°F
5	W-HfH <sub>2</sub> -C	1/4 Hr/4800°F
6	W-HfH <sub>2</sub> -C	1/4 Hr/4800°F + 1 Hr/3000°F

Figure 25. Failed Tensile Specimen of W-HfH<sub>2</sub>-C (Process A) and W-HfC (Process B) Material Tensile Tested at 3500°F





Westinghouse

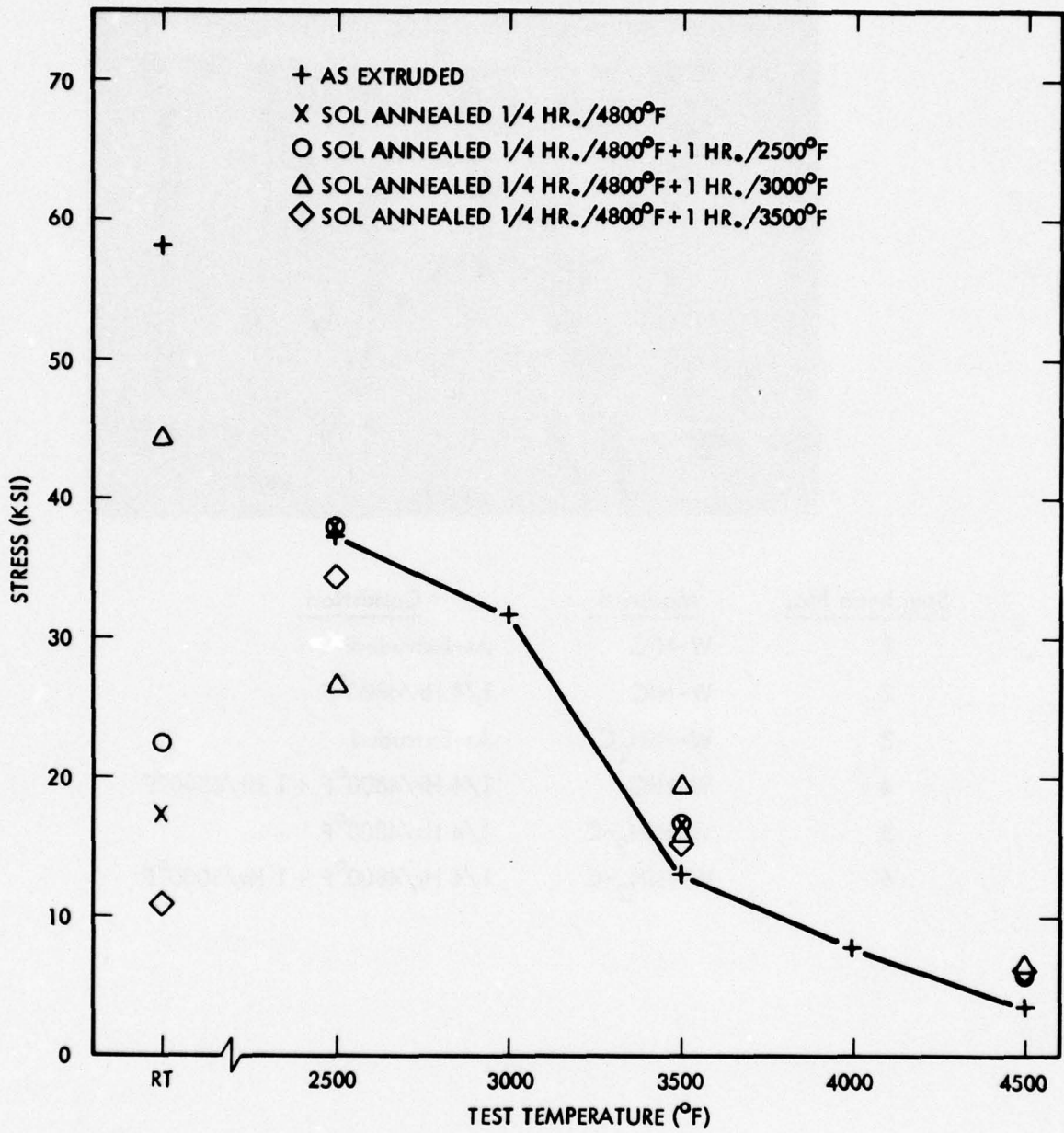


Figure 26. Effect of Heat Treatment on Tensile Strength of W-HfH<sub>2</sub>-C Material (Process A)

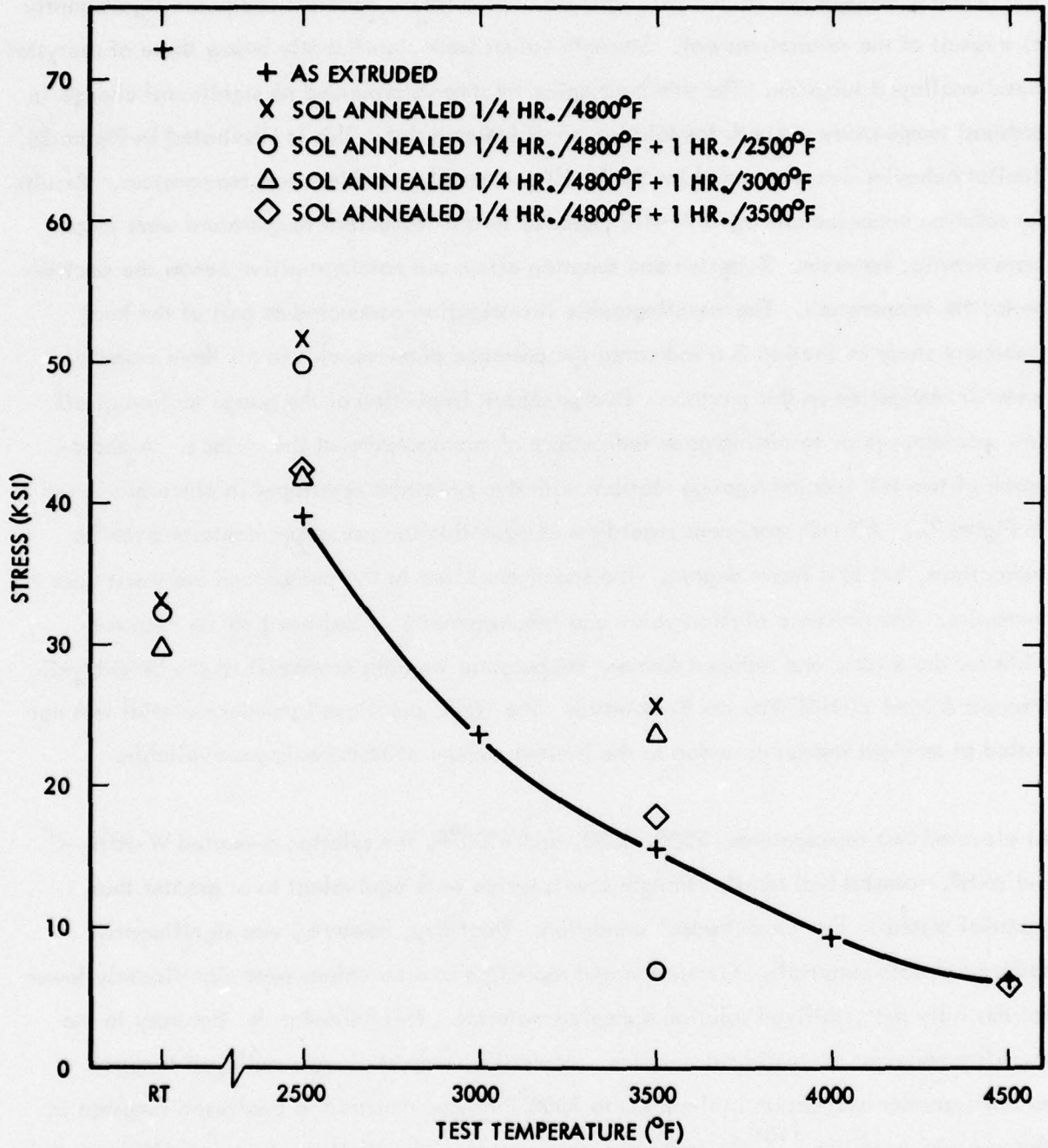


Figure 27. Effect of Heat Treatment on Tensile Strength of W-HfC Material (Process B)



The ambient temperature (RT) tensile strength of W-HfH<sub>2</sub>-C material decreased significantly as a result of the solution anneal. Strength values were significantly below those of recrystallized unalloyed tungsten. The one hour aging treatments produced no significant change in ambient temperature strength for solution annealed material. This is illustrated in Figure 26. Similar behavior was also noted for the W-HfC material at ambient test temperature. Results for solution annealed and aged W-HfC material tested at ambient temperature were much more erratic, however. Tungsten and tungsten alloys are notch-sensitive below the ductile-to-brittle temperature. The metallographic investigation conducted as part of the heat treatment study in Section 3.6 indicated the presence of microvoids in all three materials under investigation in this program. Dye penetrant inspection of the gauge section of all test specimens prior to testing gave indications of microporosity at the surface. A photograph of two test specimen gauge sections with dye penetrant developer in place are shown in Figure 28. All test specimens regardless of consolidation procedure contained similar indications, but to a lesser degree. The specimens cited in the photograph are worst case examples. The presence of microvoids and inhomogeneity is believed to be responsible for the erratic and reduced ambient temperature strength properties of the W-HfH<sub>2</sub>-C (Process A) and W-HfC (Process B) material. The WHfC prealloyed powder material was not tested at ambient temperature due to the limited number of test specimens available.

At elevated test temperatures, 2500, 3500, and 4500°F, the solution annealed W-HfH<sub>2</sub>-C and W-HfC material had tensile strength levels which were equivalent to or greater than material tested in the "as extruded" condition. Ductility, however, was significantly reduced in both materials. Elongation and reduction in area values were significantly lower for the fully recrystallized solution annealed material. This behavior is contrary to the ductility behavior of unalloyed tungsten. Normally, recrystallized unalloyed tungsten exhibits greater elongation in the 2500 to 3500°F range compared to unalloyed tungsten in the wrought condition.<sup>(10)</sup> The inhomogeneous nature of the W-HfH<sub>2</sub>-C and W-HfC materials which produced the microvoids associated with the elemental hafnium in the W-HfH<sub>2</sub>-C material and with the hafnium carbide particles in the W-HfC material was most likely responsible for the reduction in ductility.

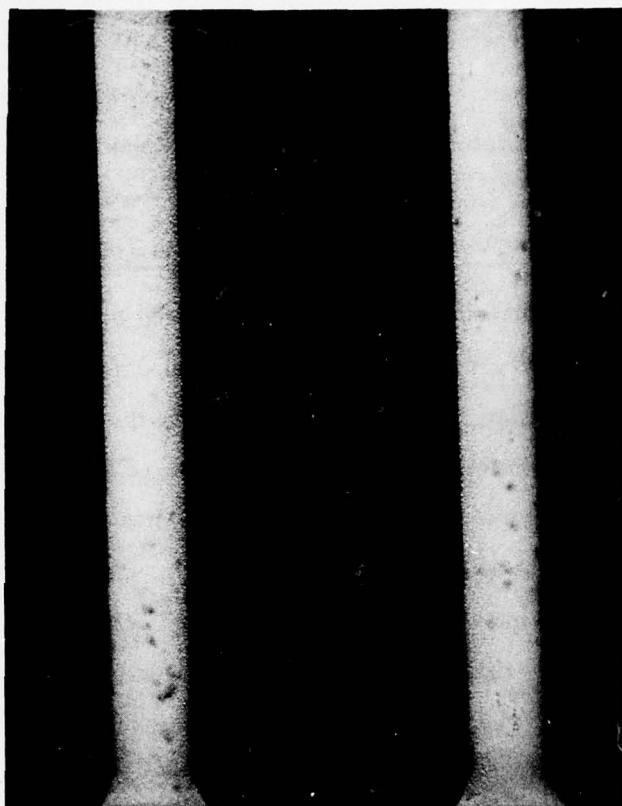


Figure 28. Gauge Sections of Tensile Test Specimens Prior to Testing with Dye Penetrant Developer in Place



The solution annealed WHfC prealloyed powder material was also tested at 3500°F. The tensile strength was drastically reduced compared to as-extruded material. Microvoids resulting from incomplete densification were most likely responsible for the loss in strength. The solution anneal caused the voids to coalesce in the grain boundaries. Inasmuch as the prealloyed powder material which was extruded in the molybdenum cans was not deoxidized prior to extrusion, it is suspected that it may have a high oxygen level which also plays a role in loss of strength as a result of high temperature annealing.

### 3.7.3.3 Material Solution Annealed and Aged Prior to Testing

The aging treatments conducted after the solution anneal at 4800°F produced inconclusive results. In Figure 26 the W-HfH<sub>2</sub>-C material tested at 2500 and 3500°F, exhibited decreasing strength with increasing aging temperature compared to the strength of solution annealed material. In each case, however, tensile strength values for solution annealed and aged material were greater than material tested in the as-extruded condition. Test results at 4500°F showed little effect of solutionizing and aging. The aging phenomenon in the WHfC alloy is predicated on having sufficient hafnium and carbon in solution to promote nucleation and growth of a classically dispersed hafnium carbide phase within the tungsten matrix. Metallographic evidence discussed in Section 3.6.2 indicates that this condition was not achieved in the W-HfH<sub>2</sub>-C material.

Tensile test results for solution annealed and aged W-HfC material are shown graphically in Figure 27. Material tested at 2500°F, after aging at 2500, 3000, and 3500°F, exhibited a decrease in strength at each aging condition compared to material which received only the solution annealing treatment. Material aged at 3000°F displayed the largest decrease. At the 3500°F test condition, the opposite behavior was noted. Aged material had a slightly higher strength level compared to solution annealed material with the greatest effect noted for material aged at 3000°F. Material tested at 4500°F, exhibited slightly higher values compared to material tested in the as extruded condition.

Only one specimen of WHfC prealloyed powder material was available for evaluation in the solution annealed and aged condition. The specimen was heat treated for 1/4 hour at 4800°F and aged one hour at 2500°F prior to tensile testing at 3500°F. The specimen failed prior to yielding with essentially nil ductility. The ultimate strength was approximately the same as for material tested in the solution annealed condition. The solution anneal caused the microvoids in the less than 100 percent dense WHfC prealloyed powder material to coalesce reducing the effective cross sectional area of the specimen and provided sources for the initiation of failure.

#### 3.7.3.4 Material Recrystallized Prior to Testing

The test program scheduled testing of material in the recrystallized condition. Because of a limited amount of WHfC prealloyed powder material and specimen breakage of W-HfH<sub>2</sub>-C test specimens during handling and machine loading, only W-HfC (Process B) material was tested in the recrystallized condition. The recrystallization study of as-extruded material, Section 3.6, revealed that the W-HfH<sub>2</sub>-C and W-HfC material responded to thermal treatments in a manner similar to unalloyed tungsten. The recrystallization temperature of W-HfC material (Process B) was determined to be approximately 2500°F from examination of as-extruded material tensile tested at 2000, 2500, and 3000°F. Test specimens were heat treated one hour at 2500°F prior to testing at ambient temperature, 2500 and 3500°F. Test results are recorded in Table 8. The ambient temperature test results were slightly higher compared to material tested in the as-extruded condition and significantly higher than material solution annealed and aged. The results for recrystallized W-HfC material (Process B) tested at 2500 and 3500°F were comparable to material in the as-extruded condition and in the solution annealed and aged condition. This is further evidence that due to alloy inhomogeneity classical solutionizing and aging did not occur.



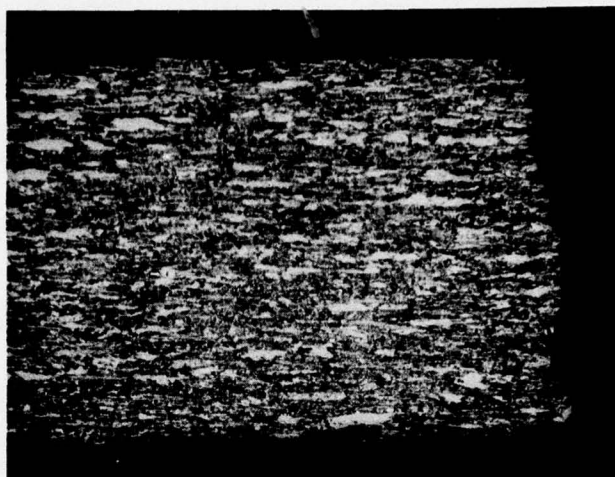
### 3.7.4 Metallography of Tensile Test Specimens

All failed tensile test specimens were examined metallographically. Selected specimens were examined using Scanning Electron Microscopy (SEM).

#### 3.7.4.1 Metallography of Failed W-HfH<sub>2</sub>-C Tensile Specimens (Process A)

Typical photo micrographs of W-HfH<sub>2</sub>-C failed tensile specimens are shown in Figures 29, 30, 31, and 32. The room temperature specimen of W-HfH<sub>2</sub>-C material tested in the as extruded condition is shown in Figure 29 Top. The wrought material failed in a brittle manner typical of wrought tungsten. The material tested at 3000°F shown in Figure 29 Bottom, exhibited an essentially recrystallized microstructure which failed in a ductile manner. Some evidence of grain boundary separation was present near the fractured surface in the upper half of the specimen. The microstructure of the tensile specimen tested at 3500°F is shown in Figure 30 Top. The failed specimen is also shown in Figure 25, as specimen 3. The grain size was slightly larger than in the 3000°F tensile specimen. The as-extruded material was recrystallized during the hold time for temperature equilibration prior to tensile testing. The solution annealed material shown in Figure 30 Bottom, which was also tested at 3500°F displayed reduced ductility. The large grain size was produced during the 1/4 hour solution anneal at 4800°F. SEM micrographs, Figure 31, illustrate microvoids associated with metallic hafnium. The voids resulted from either incomplete densification during the consolidation process, or were a manifestation of Kirkendall void formation which occurred during the solution anneal at 4800°F. A third possible explanation for the presence of microvoids involves the melting and solidification of metallic hafnium. During the solution anneal, hafnium which has a melting point of 4030°F, expands on melting and contracts during solidification resulting in the formation of a void. All three phenomena most likely are responsible for the microvoids in the solution annealed W-HfH<sub>2</sub>-C material. Solution annealed and aged W-HfH<sub>2</sub>-C material tested at 2500 and 3500°F exhibited lower ductility compared to as-extruded material. A typical microstructure is shown in Figure 32. Little evidence of deformation was noted in the grains near the fracture surface. Fracture propagated along grain boundaries.

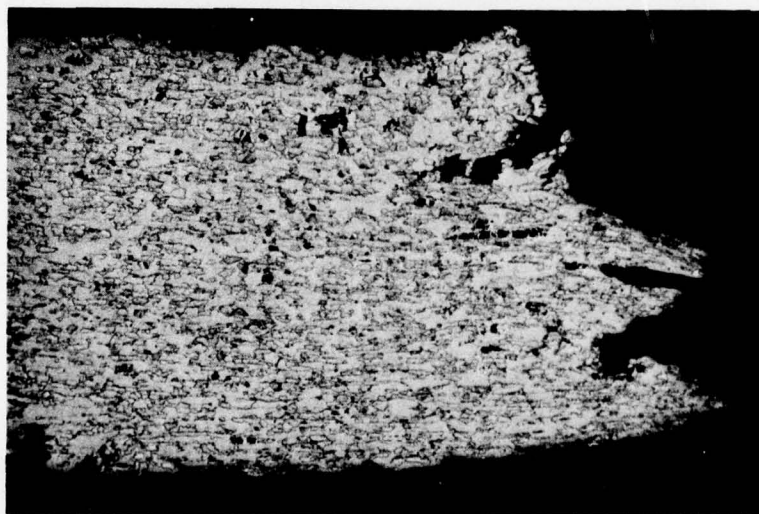
Strain  
Axis



40X

Room Temperature Tensile Test  
W-HfH<sub>2</sub>-C - As Extruded

Strain  
Axis



40X

3000°F Tensile Test  
W-HfH<sub>2</sub>-C - As Extruded

Figure 29. Microstructure of W-HfH<sub>2</sub>-C Tensile Specimens  
(Process A)



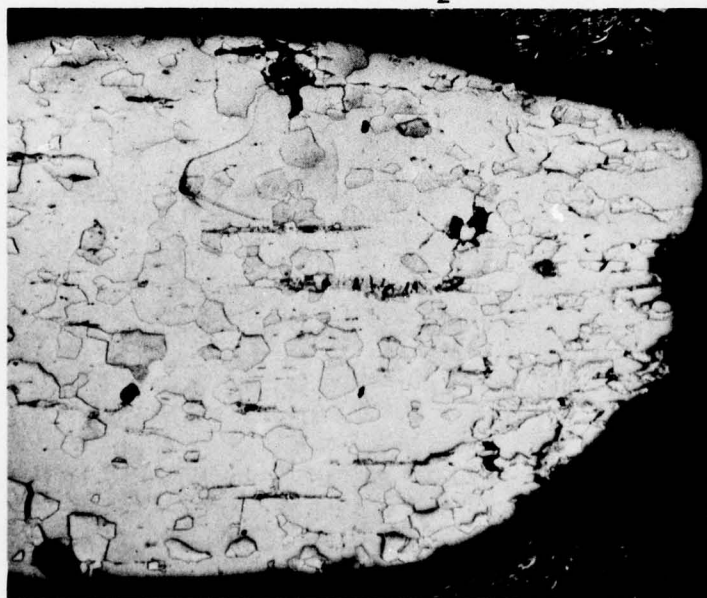
Strain  
Axis  
→



40X

3500°F Tensile Test - W-HfH<sub>2</sub>-C - As Extruded

Strain  
Axis  
→

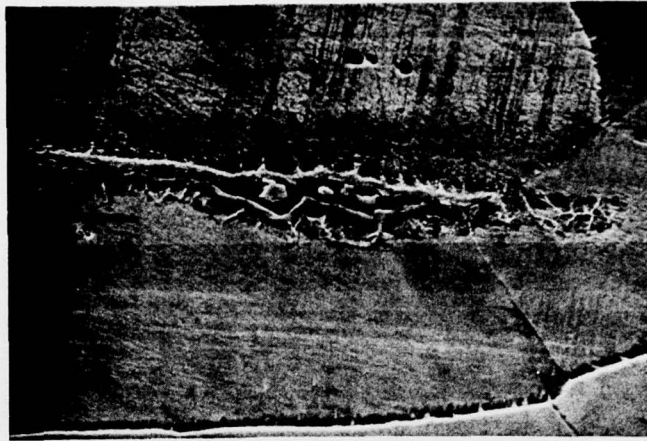


40X

3500°F Tensile Test - W-HfH<sub>2</sub>-C  
Annealed 1/4 Hr/4800°F

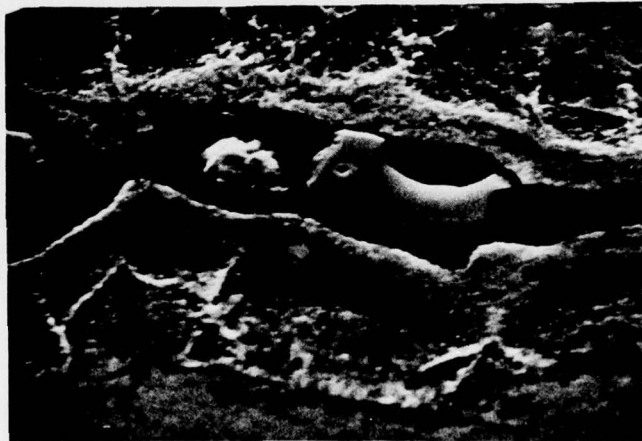
Figure 30. Microstructure of W-HfH<sub>2</sub>-C Tensile Specimens (Process A)

Strain  
Axis  
→



SEM 1100X

Strain  
Axis  
→



SEM 5500X

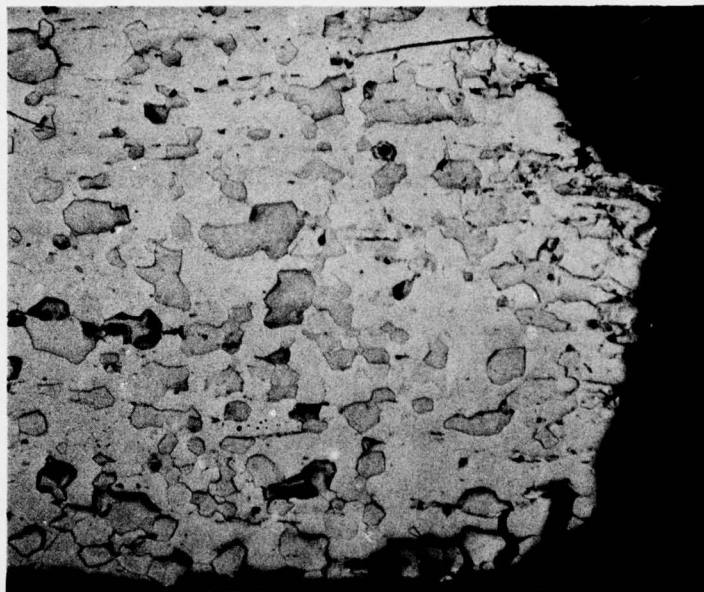
3500°F Tensile Test W-HfH<sub>2</sub>-C Solution Annealed 1/4 Hr/4800°F

Figure 31. Microstructure of W-HfH<sub>2</sub>-C Tensile Specimens (Process A)



Westinghouse

Strain  
Axis



40X

3500°F Tensile Test - W-HfH<sub>2</sub>-C - Annealed 1/4 Hr/4800°F + 1 Hr/3000°F

Figure 32. Microstructure of W-HfH<sub>2</sub>-C Tensile Specimens (Process A)

#### 3.7.4.2 Metallography of Failed W-HfC Tensile Specimens (Process B)

The microstructure of failed W-HfC tensile specimens are shown in Figures 33, 34, 35 and 36. At ambient temperature, the wrought W-HfC material fractured in a brittle manner with nil ductility. At temperatures up to 3000°F, the W-HfC material displayed tensile properties typical of powder metallurgy unalloyed tungsten. Ductility as measured by elongation and reduction in area reached a maximum at 3000°F then declined as test temperatures were increased. The failure mode changed on going from 3000°F (Figure 34, Top) to 3500°F (Figure 34, Bottom). At 3000°F, deformation occurred essentially by deformation of the grains and the fracture was transgranular. At 3500°F, deformation occurred by sliding along grain boundaries. Fracture was intergranular with a marked reduction in ductility. This behavior is typical for bcc metals as test temperatures increase above  $0.5T_m$  (homologous temperature).

Solution annealed material tested at 3500°F, Figure 35 Top, behaved in a similar manner. Fracture was transgranular. SEM micrographs, Figure 35 Bottom and Figure 36 Top, illustrate microvoids associated with hafnium carbide particles in solution annealed W-HfC material. The voids appear to be associated with the hafnium carbide geometry and failure of the tungsten matrix to completely fill the surrounding volume around the carbide particles during the consolidation process. Some reaction indicating solutioning of the carbide is evident in the SEM micrographs. Figure 36 Bottom, illustrates more clearly the typical high temperature grain boundary failure mode.

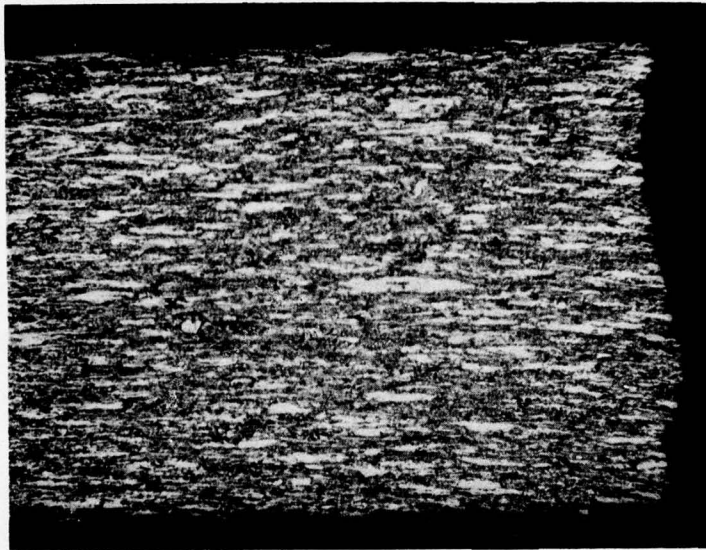
#### 3.7.4.3 Metallography of WHfC Prealloyed Powder Material Tensile Specimens

A limited amount of material was produced by Dynapak extrusion of prealloyed W-HfC powder at 3600°F in a molybdenum can. Tensile tests were conducted in the "as extruded" condition at 2000, 2500, 3000 and 3500°F. One specimen was solution annealed 1/4 hour at 4800°F prior to tensile testing at 3500°F. Another specimen was solution annealed and aged one hour prior to tensile testing, also at 3500°F. In Figure 37 Top, the 3000°F tensile test



Westinghouse

Strain  
Axis

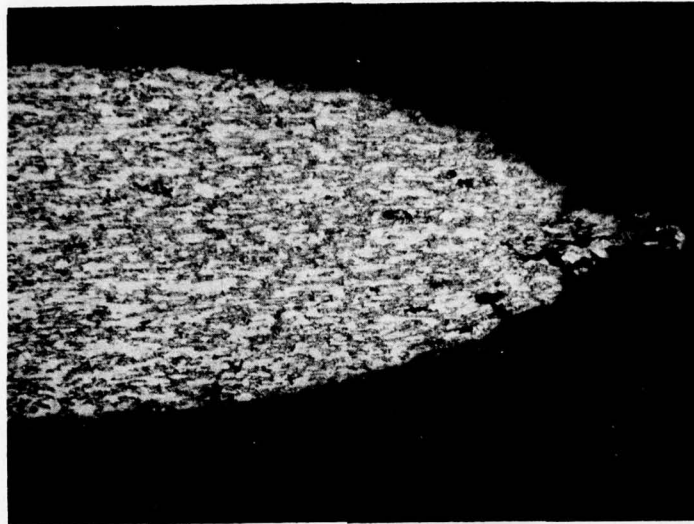


40X

Room Temperature Tensile Test - W-HfC - As Extruded

Figure 33. Microstructure of W-HfC Tensile Specimens (Process B)

Strain  
Axis  
→



40X

3000°F Tensile Test - W-HfC - As Extruded

Strain  
Axis  
→



40X

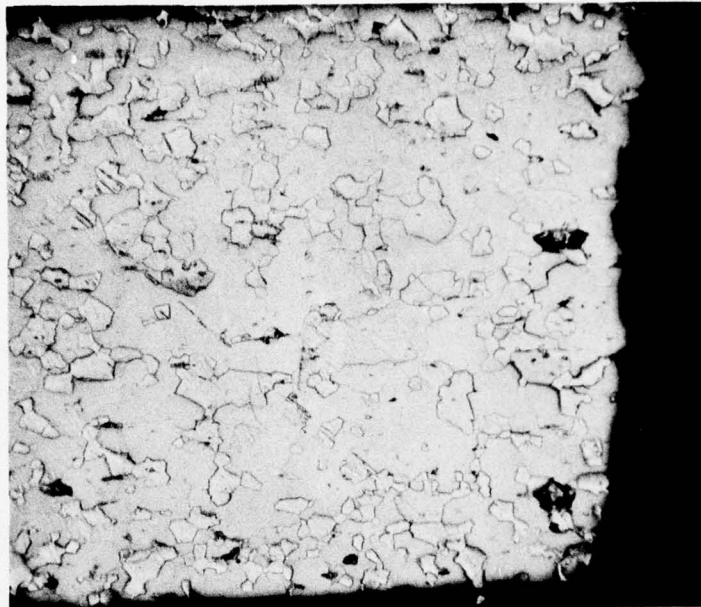
3500°F Tensile Test - W-HfC - As Extruded

Figure 34. Microstructure of W-HfC Tensile Specimens  
(Process B)



Westinghouse

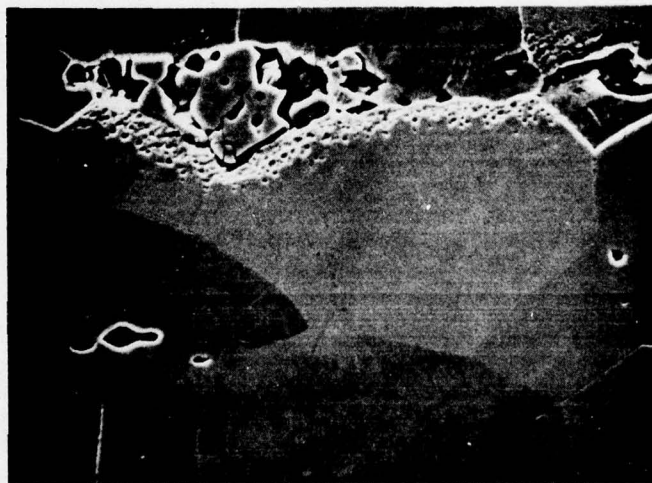
Strain  
Axis



40X

3500°F Tensile Test - W-HfC Annealed 1/4 Hr/4800°F

Strain  
Axis

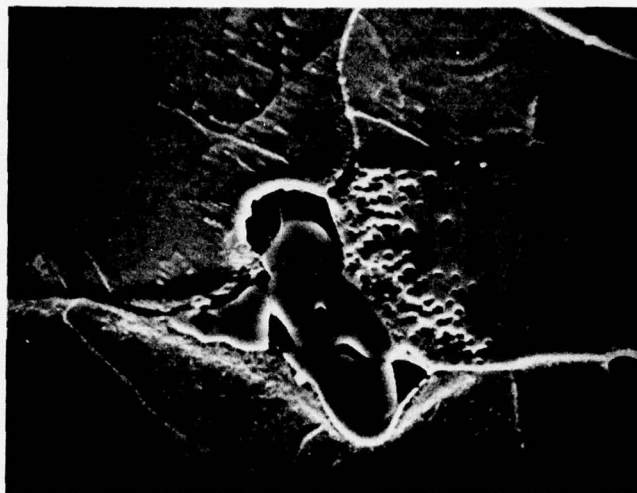


SEM 1090X

3500°F Tensile Test - W-HfC Annealed 1/4 Hr/4800°F

Figure 35. Microstructure of W-HfC Tensile Specimens  
(Process B)

Strain  
Axis  
→



SEM 2150X

3500°F Tensile Test - W-HfC Annealed 1/4 Hr/4800°F

Strain  
Axis  
→



40X

3500°F Tensile Test - W-HfC Annealed 1/4 Hr/4800°F + 1 Hr/3000°F

Figure 36 . Microstructure of W-HfC Tensile Specimens  
(Process B)





specimen microstructure is shown. This specimen had an ultimate strength of 84.0 Ksi which was significantly higher than arc cast material. However, the as-extruded material failed with only a slight measurable amount of elongation and reduction in area. The microstructure was composed of large elongated deformed regions surrounded by a finely divided crystalline like structure. Material tested at 3500°F, Figure 37 Bottom, also exhibited a similar duplex microstructure. At the higher test temperature, yielding appears to have occurred primarily in the fine grained regions by grain boundary separation while the large wrought regions indicate some degree of ductile deformation in the fracture surface. The tensile strength of the material produced from the prealloyed WHfC powder shown in Figure 37, Bottom, was comparable to the tensile strength of arc cast material.

WHfC prealloyed powder material solution annealed 1/4 hour at 4800°F, Figure 38 Top, and solution annealed and aged one hour at 2500°F, Figure 39 Bottom, had tensile strengths at 3500°F which were reduced to approximately one half the strength of as extruded material tested at the same temperature. SEM micrographs of the solution annealed material are shown in Figure 38 Bottom and Figure 39 Top. In each case, the microstructure was relatively clean except for the rounded microvoids located in the grain boundaries. The microvoids were apparently responsible for the reduction in strength of the heat treated WHfC prealloyed powder material and also contributed to the lack of ductility of the material. The microvoids most probably resulted from incomplete densification during the consolidation process. Energy dispersive x-ray analysis of the microvoids failed to indicate the presence of foreign material. Trapped inert gas which was used to protect the material during heat-up for extrusion may be responsible for generating the microvoids during the extrusion process.

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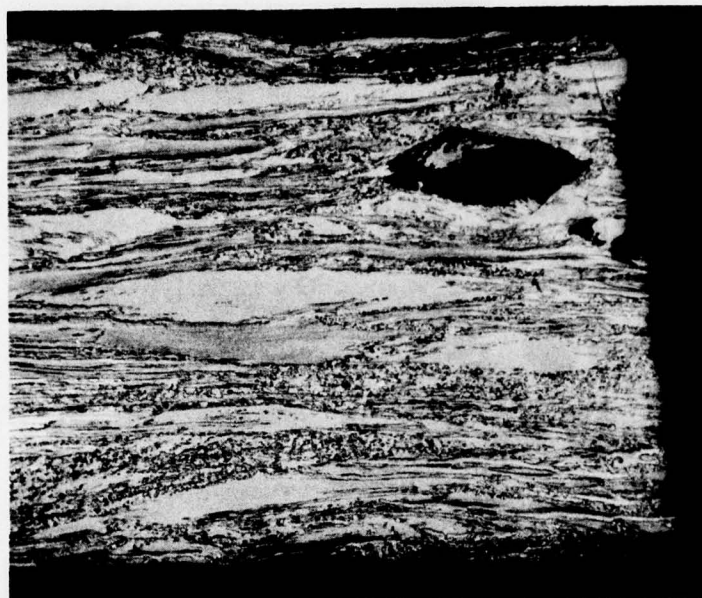
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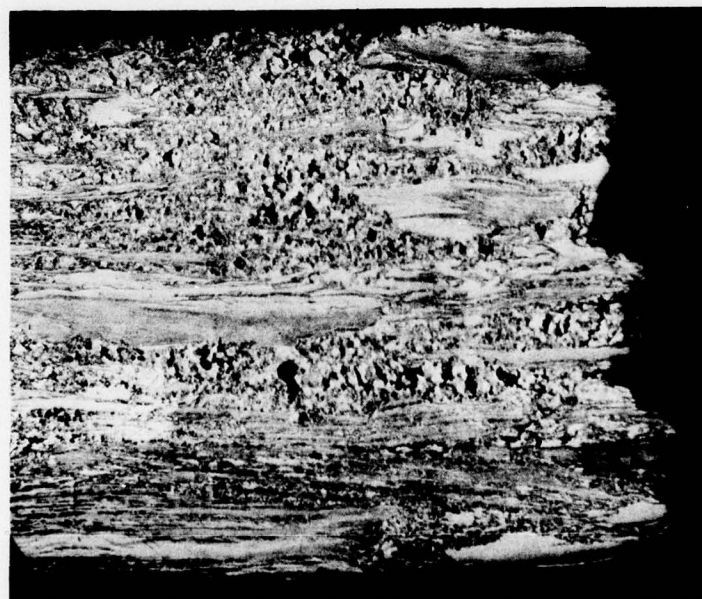
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40X

3000°F Tensile Test - WHfC Prealloyed Powder - As-Extruded

Strain  
Axis



40X

3500°F Tensile Test - WHfC Prealloyed Powder - As-Extruded

Figure 37. Microstructure of WHfC Prealloyed Powder Material Tensile Tests



Westinghouse

Strain  
Axis  
→



40X

3500°F Tensile Test - WHfC Prealloyed Powder Annealed 1/4 Hr/4800°F

Strain  
Axis  
→



SEM 5000X

3500°F Tensile Test - WHfC Prealloyed Powder Annealed 1/4 Hr/4800°F

Figure 38. Microstructure of WHfC Prealloyed Powder Material Tensile Tests

Strain  
Axis  
→



SEM 1000X

3500°F Tensile Test - WHfC Prealloyed Powder Annealed 1/4 Hr/4800°F

Strain  
Axis  
→



40X

3500°F Tensile Test - WHfC Prealloyed Powder Annealed 1/4 Hr/4800°F + 1 Hr/2500°F

Figure 39. Microstructure of WHfC Prealloyed Powder Material Tensile Tests



#### 4.0 DISCUSSION OF RESULTS AND CONCLUSIONS

1. The work performed in this program accomplished a necessary first step toward the objective of developing powder metallurgy W-0.35% HfC alloys with mechanical strength equivalent to arc cast material. Powder deoxidation and handling procedures developed in this program permit material of W-0.35% HfC composition to be consolidated with controlled carbon and oxygen levels comparable to material produced by vacuum arc melting. These procedures are amenable to scale-up and provide a practical basis for fabrication of large size WHfC components.
2. Materials consolidated thus far did not achieve mechanical properties equivalent to arc cast WHfC due to the fact that full densification and homogeneous distribution of hafnium carbide did not result from the limited mechanical working. It was demonstrated that W-HfH<sub>2</sub>-C material (Process A) and W-HfC material (Process B) could be consolidated to a density of greater than 96 percent of theoretical at a working temperature of 2300°F. Material in this condition can be subjected to further extensive thermomechanical working to achieve desired density and microstructure. This point was demonstrated in work by Friedman and Dickinson<sup>(3)</sup> in the processing of small scale pressed and sintered buttons which were hot rolled to sheet and displayed high strength. It is anticipated that similar results can be duplicated on larger pieces consolidated by powder metallurgy procedures investigated in this program.
3. Development of a homogeneous distribution of hafnium carbide within the tungsten alloy matrix can also be facilitated by utilizing a finer starting tungsten powder size. Reducing the tungsten particle size reduces the length of the diffusion path for hafnium and thus enhances homogenization during subsequent thermomechanical processing. However, the

benefits to be derived from a finer particle size must be traded off against the undesirable effects of a larger surface area for adsorption of oxygen and lower tap densities achievable in powder loading.

4. It was shown that a temperature of 3600°F or higher is required to consolidate WHfC prealloyed powder (Process C) to a density of greater than 99 percent of theoretical. High temperature tensile strengths of material produced from prealloyed powder were comparable to values for arc cast material. Although high strengths were achieved for this material in this program, ductility values at elevated temperatures were significantly lower than for arc cast material. The high strength of the prealloyed material is attributed to the fact that the classical distribution of HfC produced in the tungsten matrix during the cooldown after arc melting was retained during the consolidation process. The lack of ductility is most likely due to the presence of microvoids at grain boundaries resulting from incomplete densification during consolidation. The drastic reduction of strength properties after solution annealing was due to the coalescence of these microvoids as a result of the heat treatment.



## 5.0 REFERENCES

1. Ossin, A. and Aronin, L., "Refractory Metal Air Vane Leading Edge for Ballistic Missiles Defense Interceptor", AIAA Journal V 14, No. 6, June 1976, pp 781-788.
2. Hall, R. C., Ossin, A., Aronin, L., Ammon, R. L., and Buckman, R. W., "Processing and Characterization of Several Tungsten Alloys", 20th National SAMPE Symposium, San Diego, CA, April 29-May 1, 1975.
3. Friedman, S. and Dickinson, C. D., "Powder Metallurgy Tungsten Alloys Based on Carbide Dispersion", Refractory Metals and Alloys IV, Vol. 41, Metallurgical Society Conference, French Lick, IN, October 1965.
4. Rubenstein, L. S., "Effects of Composition and Heat Treatment on High Temperature Strength of Arc Melted Tungsten-Hafnium-Carbon Alloys", NASA-TN-D-4379, February 1968.
5. Raffo, P. L. and Klopp, W. D., "Mechanical Properties of Solid Solution and Carbide Strengthened Arc Melted Tungsten Alloys", NASA-TN-D-3248, February 1966.
6. Ammon, R. L. and Buckman, R. W., Jr., "Vacuum Arc Melting of Tungsten-Hafnium-Carbon Alloy", Journal of Vacuum Society, Vol. II, No. 1, January/February 1974.
7. Friedrich, K., "Oxydation Von Molybdän, Wolfram und Rhenium Pulver Bei Raumtemperatur an Luft Unterschiedlichen Feuchtigkeitsgehaltes", Journal of Less Common Metals 16, 1968.
8. Dr. F. Harvey, Westinghouse Research and Development Center, private communication.
9. Tungsten Metal Powder, General Electric Catalog 1100, Lamp Metals and Components Department, Cleveland, OH.
10. "The Engineering Properties of Tungsten and Tungsten Alloys", DMIC Report 191, September, 1963.



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