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NONFERROUS ALLOYS

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W 0.35 Hf 0.025C
W-HfC

W 4.0 Re 0.35 Hf 0.025C
W·4Re·HfC

1. GENERAL
Tungsten alloys containing 0.35 wt percent hafnium and 0.0250 wt percent carbon and those containing 4 percent Rhenium in addition to the hafnium plus carbon additions have been shown to exhibit unusually high elevated temperature strength (1)(5). Because of their excellent strength the alloys are prime candidates for such applications as wire used for fiber reinforcement in nickel and/or cobalt superalloy matrix (7) and for air vane leading edges on high speed missiles (5). There is some indication that the Re addition lowers the ductile brittle transition temperature by 200F without affecting the elevated temperature properties. This improvement has to be balanced against the high cost of Re.

1.01 Commercial Designation
Tungsten -HfC, Tungsten RHC, W-0.35 w/o HfC, W-4Re-0.35 percent HfC.

1.02 Alternate Designation
None.

1.03 Specifications
None.

1.04 Composition
Table 1.04.

1.05 Heat Treatment
1.051 Microstructurally, W-HfC and W-Re-HfC recrystallize sluggishly with increasing temperature into elongated grains, suggesting that stringers of fine HfC particles pin the grain boundaries in the transverse direction. The approximate temperature for complete recrystallization for worked W-HfC and W-4Re-HfC is 3800F and 4600F respectively (2)(4), Figure 1.051.
1.052 The minimum solution temperature is approximately 4600F (2).
1.053 The optimum aging temperature is approximately 2500F for one hour (2).
1.054 The growth of HfC particles in the W-Re-HfC alloy is fairly rapid above 3500F limiting this alloy to short time usage at this temperature (2).

1.06 Hardness
1.061 The hardness (10 kg VHN) of fully recrystallized, 1 hour at 4400F, W-4Re-HfC alloy is 279. As swaged 0.25 inch rod is 464 on the same scale (3).
1.062 Effects of annealing for 1 hour at various temperatures on hardness of swaged W-Re-HfC, Figure 1.062.

1.07 Forms and Conditions Available
Alloys of this class are currently available as powder metallurgy or arc melted product (5)(8). Billet size made by the powder metallurgy process is approximately 2-3/4 inch diameter x 6 inches long. Arc melted ingots are melted into 2-3/4 inch molds. Extruded rods and shapes are made from these starting materials (5). Wire down to 0.015 inch diameter has been drawn (7). Sheet down to 0.040 inch has been made also (3).

1.08 Melting and Casting Practice
1.081 Vacuum arc melting of W-Re-HfC has been accomplished by the consumable process using pressed and sintered electrodes made from blended high purity elemental powders of W, Re-Hf, and C hydrostatically pressed at 30 to 70 ksi into 10-pound 1.25 inch electrodes. Excess graphite was added to provide for carbon losses that occurred during sintering and melting. The electrodes were sintered in vacuum at 4000F prior to melting into a 2.5 inch diameter water-cooled copper mold. The arc melting was conducted using DC with electrode negative at a chamber pressure of less than 10^{-4} torr (3).
1.082 Vacuum arc melting of W-HfC alloy has been accomplished using the consumable AC process. The consumable electrodes were fabricated from 0.5 inch diameter fully dense tungsten rods, 0.002 inch thick hafnium foil, and graphite yarn. The tungsten rods are bundled into clusters of 10 (for the 3 inch ingot size). Carbon, in the form of graphite yarn, was wrapped in the hafnium foil and was inserted into the interstices of the electrode. The assembled electrodes were held together by GTA tack welding in a high purity helium atmosphere glove box. The melting was accomplished in a $\leq 1 \times 10^{-5}$ Torr vacuum using 4000 to 4500 amps at 30 - 35 volts ac. Carbon control is superior when using elemental alloy additions melted by ac power than by powder techniques using ac or dc (5)(8), Figure 1.082.
1.0821 Power requirements are much less using AC melting, Figure 1.0821.

1.09 Special Considerations
All sintering, melting, welding, or other elevated temperature processes should be done in dry inert gas, vacuum, or dry hydrogen (5).

2. PHYSICAL AND CHEMICAL PROPERTIES

2.01 Thermal Properties
2.011 Melting range approximately 6120-50F.
2.0111 Recession rate in plasma arc, Table 2.0111.
2.012 Phase changes. The excellent elevated temperature mechanical strength of this alloy is attributed to a submicron dispersion of hafnium monocarbide (HfC) (1)(2) which precipitates from solid solution during cooling from temperatures above 4300F.
2.0121 The lattice parameters, Ao, of extracted carbide particles from W-4Re-0.35 HfC measured 4.608 Å (6). The particles were extracted by electoetching in an aqueous 2 percent NaOH solution.
2.013 Thermal conductivity. 0.038 BTU/ft^2-sec/°F at room temperature for arc cast W-HfC (10).
2.014 Thermal expansion of W-HfC, Figure 2.014.
2.015 Specific heat. 0.036 BTU/lb-°F at room temperature for arc cast W-HfC (10)
2.016 Thermal diffusivity.

2.02 Other Physical Properties
2.021 Density. Arc cast W-HfC is 19.1 gms/cc (5).
2.022 Electrical properties.
2.023 Magnetic properties.
2.024 Emittance.
2.025 Damping capacity.

2.03 Chemical Properties
2.031 Oxidation becomes very rapid above 750F.
2.032 Metallographic specimens can be etched in an acid solution of 30 cc lactic, 10 cc HF, and 10 cc HNO_3 (7).

2.04 Nuclear Properties

3. MECHANICAL PROPERTIES

3.01 Specified Mechanical Properties

3.02 Mechanical Properties at Room Temperature
3.021 Tension-stress/strain diagrams - tension properties.
3.022 Compression-stress/strain diagrams - compression properties.
3.023 Impact.
3.024 Bending.
3.025 Torsion and shear.
3.026 Bearing.
3.027 Stress concentration.
3.0271 Notch properties.
3.0272 Fracture toughness.
3.028 Combined properties.

3.03 Mechanical Properties at Various Temperatures
3.031 Tension-stress/strain diagrams - tension properties.
3.0311 Comparison of swaged and recrystallized W-HfC at elevated temperature, Table 3.0311.
3.0312 Effect of HfC content on 3500F ultimate tensile strength

W
0.35 Hf
0.025C

W-HfC

W
4.0 Re
0.35 Hf
0.025C

W·4Re·HfC

of swaged or recrystallized W-HfC alloys, Figure 3.0312.

3.0313 Typical stress-elongation curve for recrystallized W-HfC at 2500F, Figure 3.0313.

3.0314 Tensile strength of optimum alloy composition W-4Re-0.35 HfC at 2500 to 4000F, Figure 3.0314.

3.0315 Ultimate tensile strength of W-HfC and W-4Re-HfC alloys at 3500F as a function of HfC composition and processing, Figure 3.0315.

3.0316 Ultimate tensile strength of W-HfC, Figure 3.0316.

3.0317 Mechanical behavior of thermomechanically processed W-4Re-HfC alloys, Table 3.0317.

3.0318 Tensile properties of refractory metal wires, Table 3.0318.

3.032 Compression-stress/strain diagrams - compression properties.

3.033 Impact. Tests were conducted using a 3/8 inch diameter glass ball with an impact velocity of 10,000 ft/sec at RT, 1000, and 4000F. W-HfC exhibited impact resistance superior to other arc cast and powder metallurgy W alloys (W-ThO_2, W-Re-HfC) and to tungsten-copper (10).

3.034 Bending.

3.0341 Ductile-brittle transition temperatures for arc melted W, W-Re, W-HfC, W-4Re-HfC, Figure 3.0341.

3.035 Torsion and shear.

3.036 Bearing.

3.037 Stress concentration.

3.0371 Notch properties.

3.0372 Fracture toughness.

3.038 Combined properties.

3.04 <u>Creep and Creep Rupture Properties</u>

3.041 Effect of HfC content on stress for a minimum creep rate of 10^{-6} sec^{-1} for W-HfC alloys, Figure 3.041.

3.042 Minimum creep rates at 3500F for W-4Re-HfC alloy in various conditions, Figure 3.042.

3.0421 Effect of HfC content on stress for a minimum creep rate of 10^{-6} sec^{-1} for W-Re-HfC alloys, Figure 3.0421.

3.043 Effect of HfC content on rupture life for swaged W-4Re-HfC alloys at 3500F and 15 ksi, Figure 3.043.

3.044 Time to rupture for W-HfC and W-4Re-HfC wire, Figure 3.044.

3.046 Compression creep of W-0.3 HfC at 4050 and 4420F, Table 3.046.

3.05 <u>Fatigue Properties</u>

3.06 <u>Elastic Properties</u>

3.061 Poisson's ratio.

3.062 Modulus of elasticity.

3.063 Modulus of rigidity.

4. FABRICATION

4.01 <u>Forming</u>

4.011 Only a limited amount of information is available on the forming of these alloys from the as cast condition. Cast ingots are machined into billets and canned in molybdenum (produced from sintered powder) or where higher strength of the can is required in Mo-TZM. The canned billet is heated in hydrogen and extruded to rod at about 4000F. Conventional hydraulic presses are used to produce reduction ratios of 8:1. Extrusion dies are generally coated with ZrO_2. Swaging of the extrusion is conducted with the molybdenum cladding intact using preheat temperatures of 3200 to 3300F. Reductions from 10 to 15 percent per pass have been used with total reductions of over 80 percent. Molybdenum clad extruded rods have been rolled with starting temperatures of 3100 to 3300F. In one case, the molybdenum cladding was chemically removed at rolled thickness of 0.25 inch and after conditioning, the material was reduced to final thickness at a temperature of 2900 to 3100F. Wires have been drawn to 0.015 inch both using in process anneals and with no in process anneals (3).

4.02 <u>Machining and Grinding</u>

4.03 <u>Joining</u>

4.04 <u>Surface Treatment</u>

Alloy	W-0.35 HfC		
Source	(2)(3)(5)(6)		
	Powder	W-HfC Arc Cast	W-RHfC Arc Cast
Hafnium, w/o	0.35	0.35	0.35
Rhenium, w/o	-	-	4.0
Carbon, ppm	250	250-300	250-300
Oxygen, ppm	500	25	25
Nitrogen, ppm	10	<5	<5
Iron, ppm	-	-	<5

TABLE 1.04 COMPOSITION

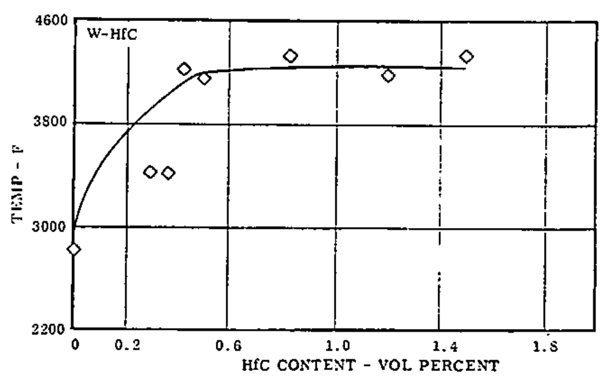

FIG. 1.051 EFFECT OF HfC CONTENT ON 1 HOUR ISOCHRONAL RECRYSTALLIZATION TEMPERATURE OF W-HfC ALLOYS. (2)

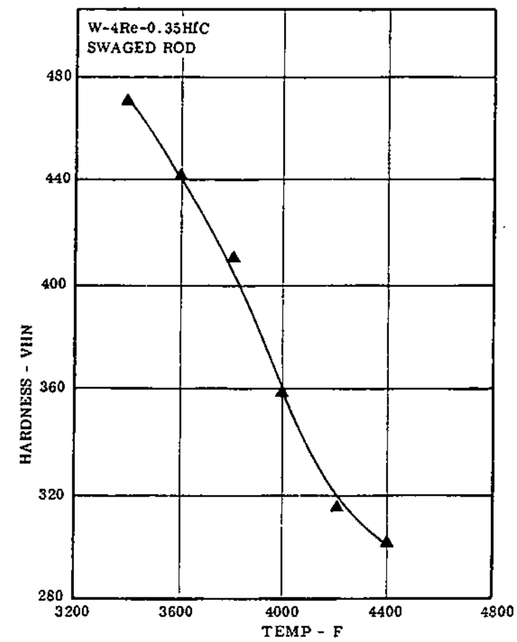

FIG. 1.062 EFFECTS OF ANNEALING FOR 1 HOUR AT VARIOUS TEMPERATURES ON HARDNESS. (3)

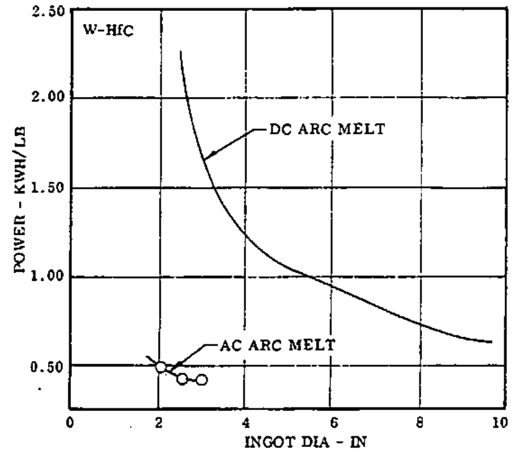

FIG. 1.0821 EFFECT OF INGOT DIAMETER ON THE POWER REQUIRED FOR MELTING TUNGSTEN AND TUNGSTEN ALLOY. (S)

W
0.35 Hf
0.025C

W- HfC

W
4.0 Re
0.35 Hf
0.025C

W·4Re·HfC

Alloy	W-0.35 HfC		
Source	(10)		
Form	Arc Cast and Extruded Rod, 0.20 inch		
Test Apparatus	5 MW Plasma Arc		
Cold Wall Heat Flux, BTU/ft^2-sec	11,400	9,800	8,300
Bulk Stagnation Enthalpy, BTU/lb	5,000	4,000	2,800
Centerline Stagnation Enthalpy, BTU/lb	6,600	5,400	4,850
Stagnation Pressure, ATM	11.6	12.8	11.4
Recession Rate, in/sec	0.455	0.325	0.173

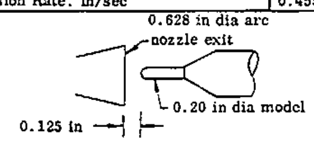

TABLE 2.0111 RECESSION RATE IN PLASMA ARC.

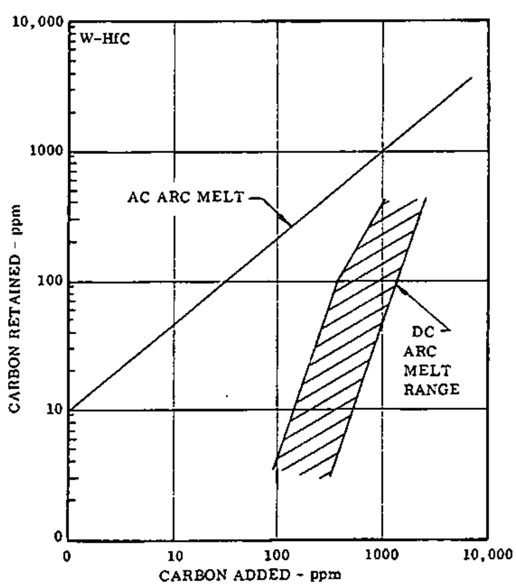

FIG. 1.082 CARBON RETENTIONS FOR VARIOUS ARC MELTED W ALLOYS. (8)

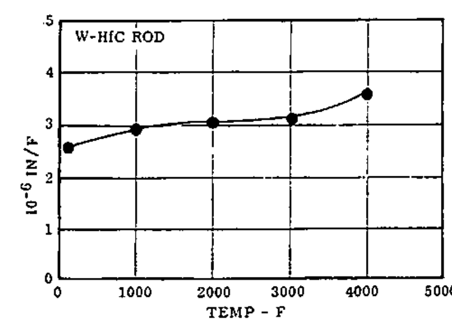

FIG. 2.014 COEFFICIENT OF THERMAL EXPANSION. (5)

W
0.35 Hf
0.025C

W- HfC

W
4.0 Re
0.35 Hf
0.025C

W·4Re·HfC

Alloy	W-0.35 HfC					
Source	(2)					
Condition	Arc Cast, Extruded, and Swaged					
Specimen	0.125 inch to 0.160 inch dia x 1.03 inch long					
	As Swaged			Recrystallized (a)		
Test Temp, F	3000	3500	4000	2500	3000	3500
F_{ty}, ksi	48.1	39.3	19.1	34.9	28.6	27.8
F_{tu}, ksi	66.4	42.7	22.4	58.3	72.0	30.4
e (in), percent	16.2	16.3	-	21.2	7.2	13.6
RA, percent	76.3	80.8	93.4	61.5	14.1	44.7
(a) One hour at 4400F.						

TABLE 3.0311 COMPARISON OF SWAGED AND RECRYSTALLIZED W-HfC AT ELEVATED TEMPERATURE.

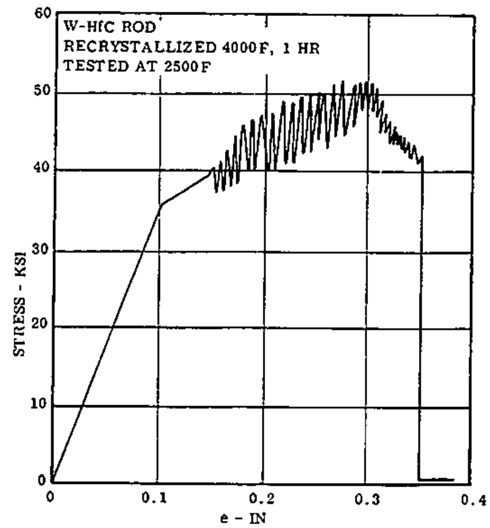

FIG. 3.0313 STRESS ELONGATION CURVE FOR RECRYSTALLIZED W-HfC ALLOY. (2)

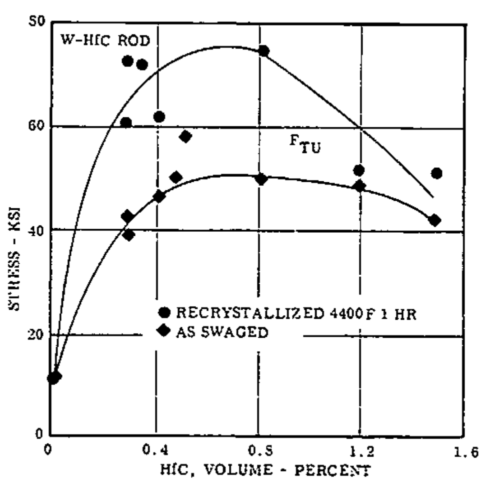

FIG. 3.0312 EFFECT OF HfC CONTENT ON 3500F TENSILE STRENGTH OF SWAGED OR RECRYSTALLIZED W-HfC ALLOYS. (2)

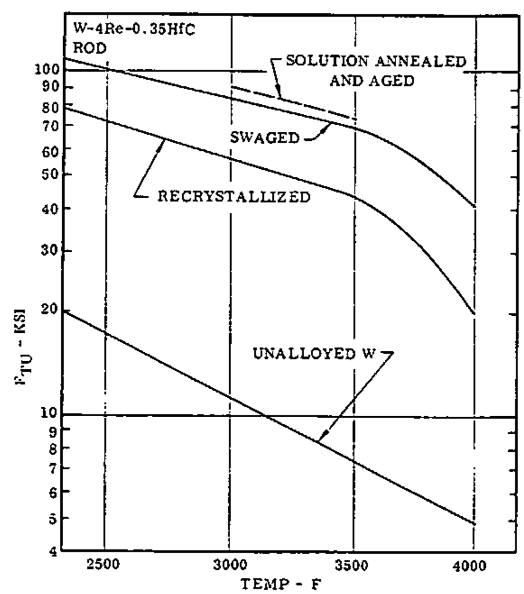

FIG. 3.0314 TENSILE STRENGTH OF OPTIMUM ALLOY COMPOSITION W-4Re-0.35 HfC COMPARED WITH UNALLOYED TUNGSTEN. (3)

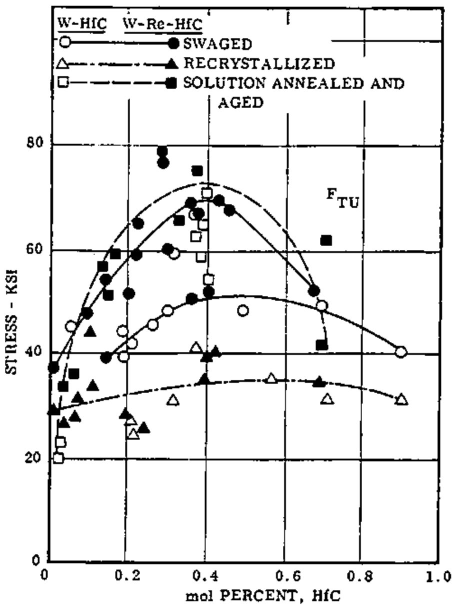

FIG. 3.0315 ULTIMATE TENSILE STRENGTH OF W-HfC AND W-4Re-HfC AT 3500F AS A FUNCTION OF HfC COMPOSITION AND PROCESSING. (4)

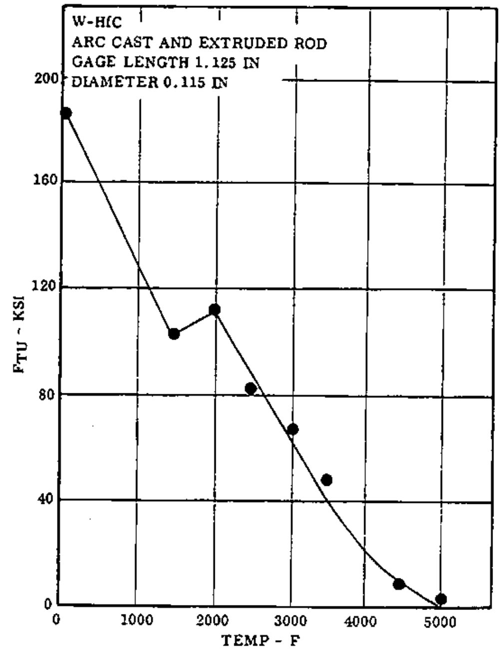

FIG. 3.0316 ULTIMATE TENSILE STRENGTH. (5)

W
0.35 Hf
0.025C

W- HfC

W
4.0 Re
0.35 Hf
0.025C

W-4Re-HfC

Alloy	W-4Re-HfC	
Source	(6)	
Form	Rod, ~0.250 dia	
Condition	Extruded at 4000F and Swaged	Double Extruded at 4800 and 4000F
Composition	W-4.1 Re-0.42 Hf-0.26C	W-3.2 Re-0.30 Hf-0.24C
Test Temp., F	3500	3500
F_{ty}, ksi, 0.2 percent	40.3	45.2
F_{tu}, ksi	49.7	63.2
e (1 in) percent	35	20
RA, percent	88	60
Post test Carbon content, percent	0.22	0.24
Creep at 15 ksi		
Min. creep rate, sec^{-1}	$(2.6-7.6) \times 10^{-7}$	1.2×10^{-8}
Rupture life, hr.	17.3 - 28.8	42.7
e, total percent	15 - 19	6
Post test Carbon content, percent	0.25 - 0.26	0.22
Ductility		
Bend, DBTTT, F	80	175
RA, percent at 500F	5	1

TABLE 3.0317 MECHANICAL BEHAVIOR OF THERMOMECHANICALLY PROCESSED W-4Re-HfC ALLOYS.

W
0.35 Hf
0.025C

W- HfC

W
4.0 Re
0.35 Hf
0.025C

W·4Re·HfC

Alloy	W-HfC and W-4Re-HfC								
Source	(7)								
Form	0.015 inch Diameter Wire								
Composition, w/o	W-0.33 Hf - 0.042 C						W-4.1Re-0.38Hf-0.021C		
Test Temp. F	RT		2000		2200		RT	2000	2200
Condition (a)	A	B	A	B	A	B	B	B	B
F_{tu}, ksi	392	326	207	253	201	224	458	314	281
e, (1 in) percent	5.4	2.8	-	-	-	-	4.8	-	-
RA, percent	21.1	1.9	67.8	44.2	70.9	46.9	27.5	24.7	37.6
(a) A - In process annealed, B - hard drawn.									

TABLE 3.0318 TENSILE PROPERTIES OF REFRACTORY METAL WIRES.

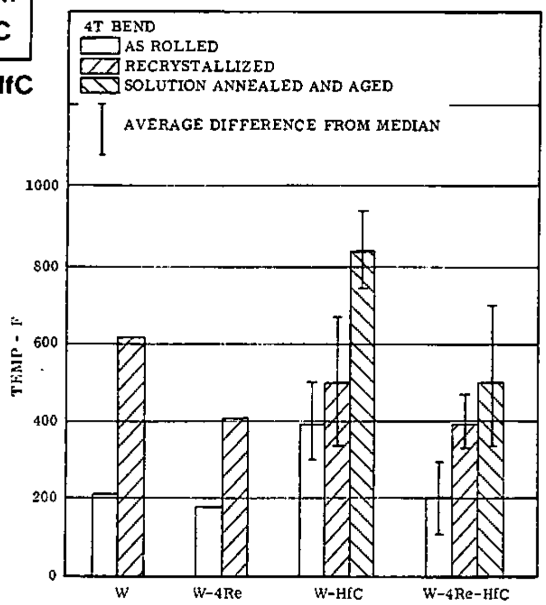

FIG. 3.0341 DUCTILE BRITTLE TRANSITION TEMPERATURES FOR ARC MELTED W, W-Re, W-HfC, W-Re-HfC. (3)

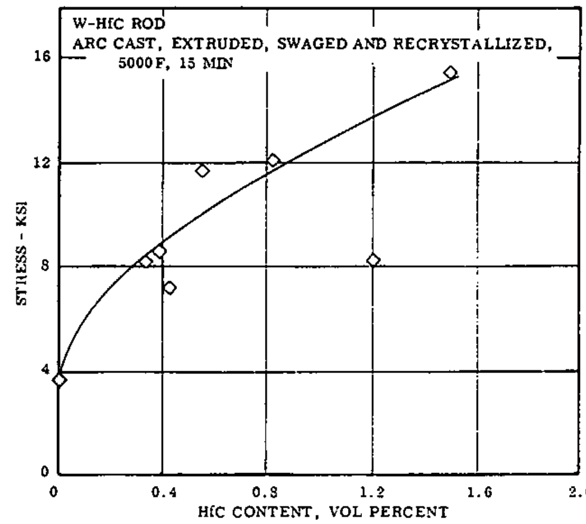

FIG. 3.041 EFFECT OF HfC CONTENT ON STRESS FOR A MINIMUM CREEP RATE OF 10^{-6}SEC^{-1} FOR W-HfC ALLOYS. (2)

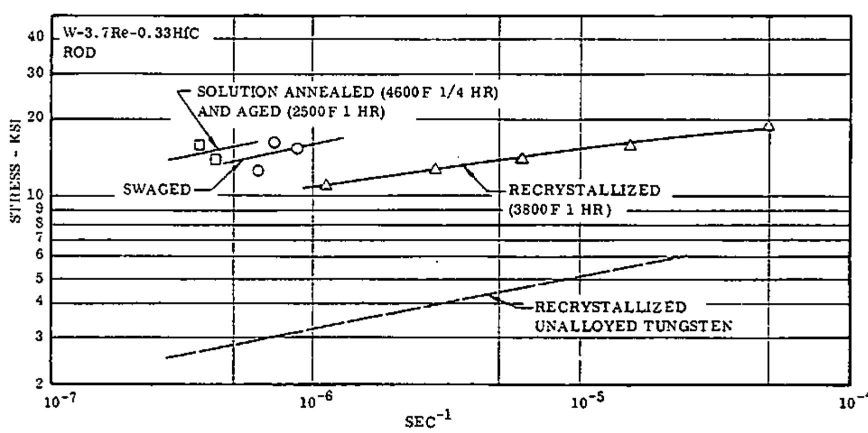

FIG. 3.042 MINIMUM CREEP RATES AT 3500F FOR W-4Re-HfC ALLOY IN VARIOUS CONDITIONS. (3)

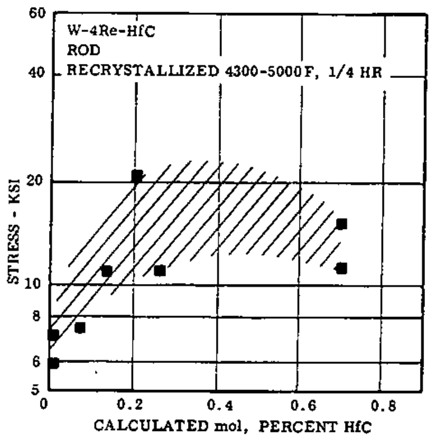

FIG. 3.0421 EFFECT OF HfC CONTENT ON STRESS FOR A MINIMUM CREEP RATE OF $10^{-6}SEC^{-1}$ FOR W-Re-HfC ALLOYS. (3)

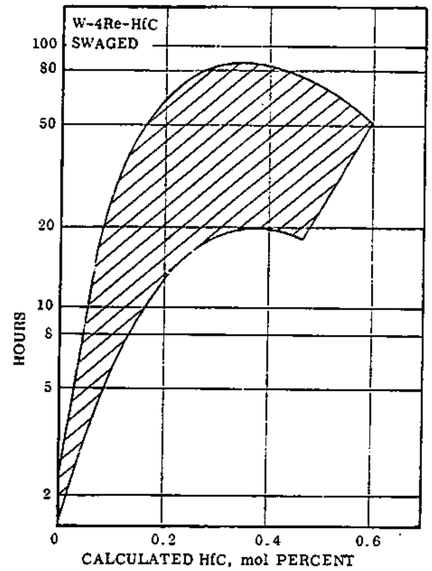

FIG. 3.043 EFFECT OF HfC CONTENT ON RUPTURE LIFE FOR W-4Re-HfC AT 3500F AND 15 KSI. (6)

W
0.35 Hf
0.025C

W- HfC

	W
4.0	Re
0.35	Hf
0.025C	

W·4Re·HfC

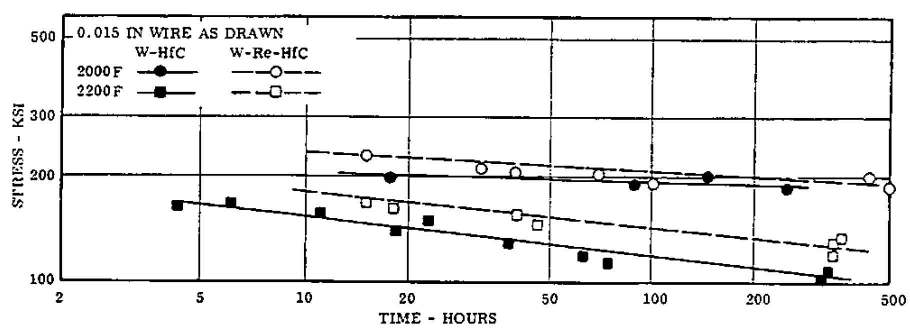

FIG. 3.044 TIME TO RUPTURE FOR W-HfC AND W-4Re-HfC WIRE. (7)

W
0.35 Hf
0.025C

W- HfC

W
4.0 Re
0.35 Hf
0.025C

W·4Re·HfC

Source	(9)							
Alloy	W-0.3 a/o HfC (W-0.35 w/o Hf-0.025 w/o C)							
Form and Condition	2 inch dia. consumable arc melted ingot extruded at 3700F using 7:1 reduction ratio							
Compression specimen	0.375 inch dia. x 0.75 inch long							
Test	Graphite heated furnace, helium atmosphere, tantalum wrapped specimen							
Test temp., F	4050	4420	4420			4050		
Material condition (a)	B	A	B			A		
Stress, ksi	2.5	2.5	5.0	7.5	12.5	5.0	7.5	12.0
Min. creep rate, percent/hr	0	0	0.04	0.14	18.3	0.07	0.27	9.15
Time at stress, hrs.	5.5	6.5	1.0	2.2	4.6	1.0	2.2	5.7
Total creep strain, percent	0.20	0	0.2	0.6	5.0	0.15	0.6	3.2
(a) A - As extruded, B-recrystallized 15 min at 4790F.								

TABLE 3.046 COMPRESSION CREEP OF W-0.3 HfC AT 4050 AND 4420F.

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