



3 4456 0515421 2

cy .1

# NEW PLATINUM-RHODIUM-TUNGSTEN ALLOYS FOR SPACE ISOTOPIC HEAT SOURCES

H. Inouye  
C. T. Liu  
R. G. Donnelly

OAK RIDGE NATIONAL LABORATORY  
CENTRAL RESEARCH LIBRARY  
DOCUMENT COLLECTION

## **LIBRARY LOAN COPY**

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this  
document, send in name with document  
and the library will arrange a loan.

UCN-7969  
(3-67)



# OAK RIDGE NATIONAL LABORATORY

OPERATED BY UNION CARBIDE CORPORATION • FOR THE U.S. ATOMIC ENERGY COMMISSION

Printed in the United States of America. Available from  
National Technical Information Service  
U.S. Department of Commerce  
5285 Port Royal Road, Springfield, Virginia 22151  
Price: Printed Copy \$3.00; Microfiche \$0.95

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ORNL-4813  
UC-33 — Propulsion Systems  
and Energy Conversion

Contract No. W-7405-eng-26

METALS AND CERAMICS DIVISION

NEW PLATINUM-RHODIUM-TUNGSTEN ALLOYS FOR SPACE ISOTOPIC HEAT SOURCES

H. Inouye, C. T. Liu, and R. G. Donnelly

SEPTEMBER 1972

OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37830  
operated by  
UNION CARBIDE CORPORATION  
for the  
U.S. ATOMIC ENERGY COMMISSION

LOCKHEED MARTIN ENERGY RESEARCH LIBRARIES



3 4456 0515421 2



## CONTENTS

	<u>Page</u>
Abstract . . . . .	1
Introduction . . . . .	1
Fabrication . . . . .	2
Melting and Casting . . . . .	2
Sheet Fabrication . . . . .	3
Physical and Mechanical Properties . . . . .	5
Density, Melting Point, and Resistivity . . . . .	5
Recrystallization and Grain Growth Behavior . . . . .	7
Tensile Properties . . . . .	11
Oxidation Characteristics in Air . . . . .	19
Weldability . . . . .	23
Compatibility with T-111, Molybdenum, and Tungsten . . . . .	23
Compatibility with Low-Pressure Oxygen . . . . .	25
Summary . . . . .	27
Future Plans and Recommendations . . . . .	29
Acknowledgment . . . . .	29



## NEW PLATINUM-RHODIUM-TUNGSTEN ALLOYS FOR SPACE ISOTOPIC HEAT SOURCES

H. Inouye, C. T. Liu, and R. G. Donnelly

### ABSTRACT

New platinum alloys were developed as possible encapsulating materials in space isotopic heat sources. Alloys containing 26–30% Rh, 6–10% W, 0–1.0% Hf, and 0–0.5% Ti (by weight) are only slightly less oxidation resistant than platinum up to 1200°C, have higher tensile strengths than TZM or Pt–30% Rh at all temperatures, and are as strong as iridium but somewhat weaker than T-111 at 1316°C. Limited results suggest that these new alloys are readily fabricable, are compatible with heat source environments to at least 1100°C, and possess the highest toughness and post-impact oxidation resistance of all candidate alloys.

---

### INTRODUCTION

The heat source in a current thermoelectric generator for space power consists of  $^{238}\text{PuO}_2$  fuel encapsulated in successive layers of Mo–46% Re, Ta–10% W, T-111, and a noble metal cladding of Pt–30% Rh. In this design one alloy compensates for the shortcomings of another because no single alloy of current manufacture can reliably meet the safety requirements of launch aborts, normal service for several years, aerodynamic heating on reentry, earth impact at about 300 fps, and postimpact oxidation resistance.

The objective of this investigation was to develop alloys with optimum combinations of strength at high temperature, melting points of 2000°C or higher, good fabricability, compatibility with the heat source environment, and oxidation resistance. The ultimate goal is to replace multilayered fuel encapsulation with a single alloy cladding that will meet the performance, safety, and reliability requirements of current and future space isotopic heat sources. This report summarizes the properties of a family of new platinum alloys containing Rh, W, Hf, and Ti in terms of the above requirements.

## FABRICATION

## Melting and Casting

Platinum sheet 0.010 and 0.020 in. thick was arc melted several times under argon with previously electron-beam-melted rhodium and hydrogen-annealed tungsten powder to produce homogeneous buttons of 200 to 450 g. Hafnium and titanium additions, when desired, were also added during this step. The arc-melted buttons were then electron-beam melted and drop cast<sup>1</sup> into rectangular cross-section ingots with hot tops (Fig. 1). This method of producing ingots was selected mainly because it was convenient to our operation and produced an ingot structure and shape suitable for fabrication.

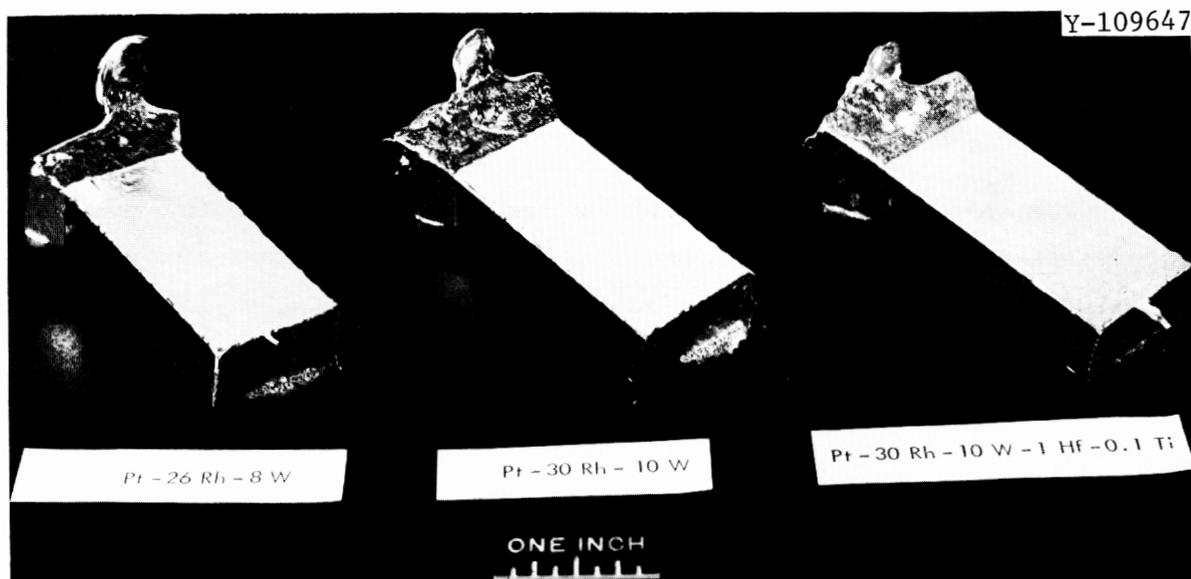


Fig. 1. One-Pound Ingots Prepared by Electron-Beam Melting and Drop Casting.

Although the vendor's analysis showed purity levels greater than 99.8% for the alloying elements, it was necessary to remove an excessive amount of gases from the rhodium melt stock by electron-beam melting

<sup>1</sup>C. W. Dean and R. E. McDonald, *High-Purity Shape Casting with an Electron-Beam Furnace*, ORNL-TM-1935 (October 1967).

before alloying. Failure to do so caused excessive splattering on melting the charge and resulted in porosity in the cast ingots. The use of powder improved dissolution of tungsten and thus minimized its segregation in the alloy. Homogenization of the alloys by arc melting before electron-beam melting reduced the vaporization losses of the noble metals.

Chemical analyses of selected ingots showed tungsten contents slightly above and rhodium contents slightly below the nominal composition. These deviations can be attributed to vaporization losses during electron-beam melting. The reported compositions are the nominal weight percentages.

#### Sheet Fabrication

After the hot top was removed, the as-cast ingots were hot rolled in air between 1000 and 1250°C to a thickness of about 0.100 in., with 5- to 10-min reheats between passes. After the surfaces were scalped to remove contamination and grinding out any edge cracks, the hot-rolled sheets were pickled in aqua regia and then vacuum annealed. Cold rolling to sheet was accomplished with intermediate vacuum anneals after about 30% reduction in thickness. The need for vacuum annealing has not yet been established, but it was used in this case because equipment was available.

In general, the difficulty of producing sound sheet increased with the tungsten content. At the 6 and 8% W levels no cracking was encountered, although some edge cracking was observed at 10% W (Fig. 2). The 12% W alloys were not fabricable.

To illustrate the fabricability, 0.030-in.-thick sheet of Pt-30 Rh-8 W-0.2 Hf-0.1 Ti (wt %) was cut into 2-in.-diam blanks, annealed, and deep drawn into a 1 1/4-in.-diam hemisphere at room temperature with two intermediate anneals at 1200°C (Fig. 3). The drawability of the alloy, although adequate, is significantly lower than that of Pt-30% Rh, which may be similarly formed in a single draw.

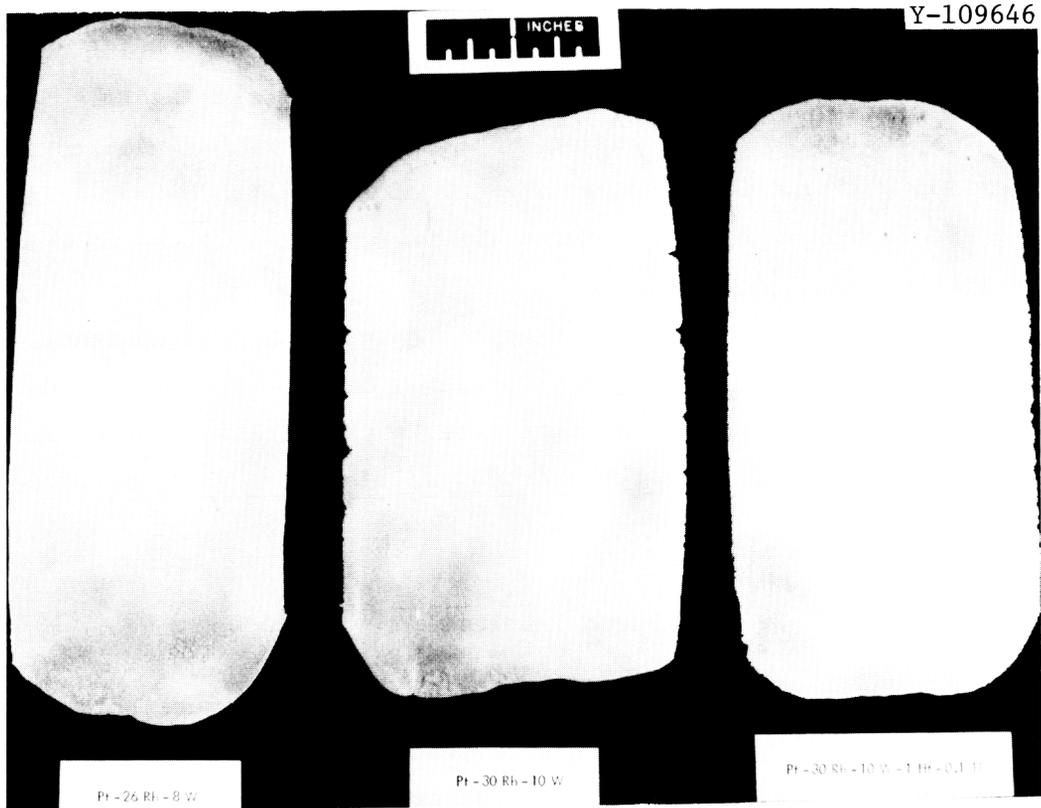


Fig. 2. Sheet Pt-Rh-W Hot Rolled to 0.040 in.

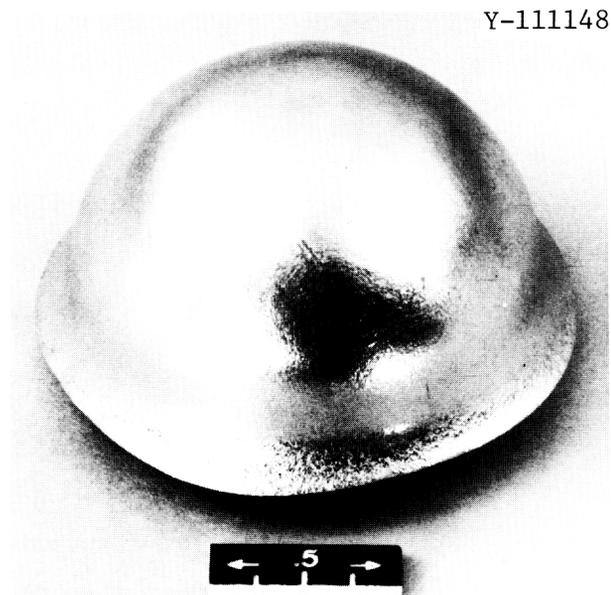


Fig. 3. Hemisphere of Pt-30 Rh-8 W-0.25 Hf-0.1 Ti (wt %) Cold Drawn from 2-in.-diam  $\times$  0.03-in.-thick Disk with Two Intermediate Anneals at 1200°C.

## PHYSICAL AND MECHANICAL PROPERTIES

## Density, Melting Point, and Resistivity

The densities of Pt-30% Rh-6% W and Pt-30% Rh-10% W were determined by a water-immersion method. An increase in the tungsten content from 6 to 10% lowers the density from 18.4 to 17.7 g/cm<sup>3</sup>.

Needle-shaped specimens were heated to the estimated melting points for 10 min in vacuum by radiation from an inductively heated tungsten susceptor. Temperatures were measured with a calibrated optical pyrometer sighted on a blackbody hole in the bottom cover of the susceptor. Melting points were established by examining a series of metallographic specimens heated to successively higher temperatures in increments of 20°C for evidence of grain boundary melting. The results listed in Table 1 establish a solidus temperature of 1980°C for Pt-30% Rh-6% W and 2060°C for the Pt-30% Rh-10% W alloy. The melting points for the corresponding platinum-tungsten binary alloys<sup>2</sup> are also listed to show that the melting points of both the platinum and the Pt-30% Rh base increase at an average rate of about 13°C for a 1% increase in the tungsten content.

The difference in the melting points of the platinum-tungsten binary and the Pt-30% Rh-W alloys remains at an approximately constant value of 130 to 150°C due to the rhodium.<sup>3</sup> This relationship was used as the basis for developing alloys with melting points of about 2000°C. Using the platinum-tungsten phase diagram in Fig. 4 as a guide, one sees that the Pt-30% Rh-W alloys can have melting points over 2460°C by increasing the tungsten content. This feature suggests that tungsten could be used in conjunction with the alloys, because any interdiffusion between them increases the melting point of the noble metal alloy.

---

<sup>2</sup>M. Hansen, "Platinum-Tungsten System," *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, p. 1146.

<sup>3</sup>M. Hansen, "The Platinum-Rhodium System," *ibid.*, p. 1137.

Table 1. Melting Points of Pt-30% Rh and Platinum as a Function of Tungsten Content

Tungsten Content (wt %)	Melting Point, °C	
	Pt-W <sup>a</sup>	Pt-Rh-W
0	1769	1930 <sup>b</sup>
6	1849	1980
8	1876	2000
10	1910	2060

<sup>a</sup>M. Hansen, "Platinum-Tungsten System," *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, p. 1146.

<sup>b</sup>M. Hansen, "The Platinum-Rhodium System," *ibid.*, p. 1137.

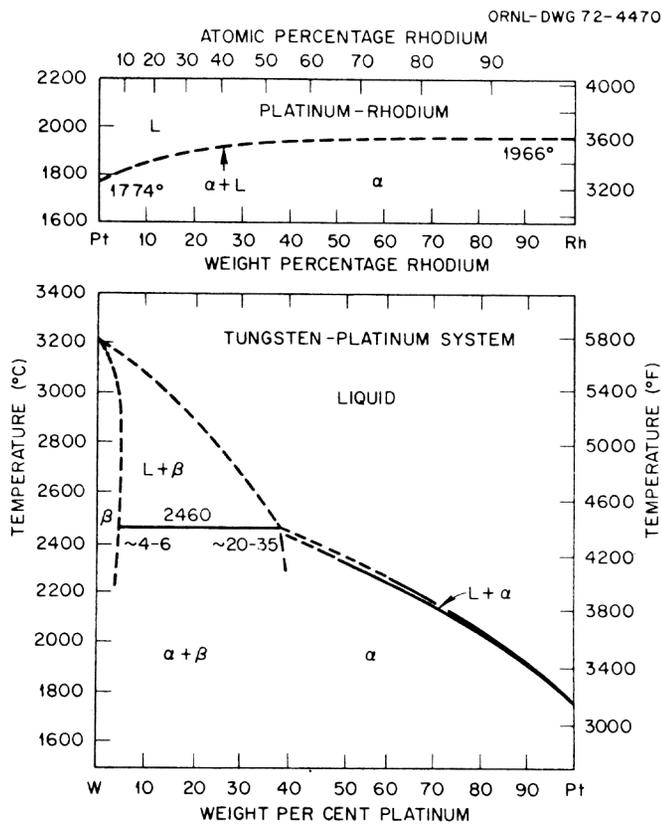


Fig. 4. The Platinum-Rhodium and Platinum-Tungsten Systems. (Based on M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, pp. 1137 and 1146.)

The electrical resistivity ( $\rho$ ) of Pt-30% Rh-6% W was measured<sup>4</sup> from 23 to 1100°C. The  $\rho$  values may be represented to  $\pm 0.2\%$  by the equation:

$$\rho \text{ (in } \mu\Omega\text{-cm)} = 40.8079 + 0.01855 t + 0.171497 \times 10^{-5} t^2, t \text{ in } ^\circ\text{C} .$$

Table 2 lists values for the temperature coefficient of electrical resistivity,  $\frac{1}{\rho} \frac{d\rho}{dt}$ , obtained from this equation.

Table 2. Electrical Resistivity ( $\rho$ ) of Pt-30% Rh-6% W<sup>a</sup>

t (°C)	$\rho$ ( $\mu\Omega\text{-cm}$ )	$\frac{1}{\rho} \frac{d\rho}{dt} \times 10^4$ (°C <sup>-1</sup> )
0	40.81	4.54
200	44.59	4.29
400	48.50	4.07
600	52.55	3.87
800	56.74	3.69
1000	61.07	3.52
1200	65.54	3.37
1400	70.14	3.24

<sup>a</sup>Based on  $\rho = 40.8079 + 0.01855 t + 0.0171497 \times 10^{-5} t^2$  .

#### Recrystallization and Grain Growth Behavior

Sheet specimens of several experimental alloys were cold rolled 35% in thickness and heat treated 1 hr at temperatures between 400 and 1500°C

<sup>4</sup>D. L. McElroy, Metals and Ceramics Division, Oak Ridge National Laboratory, private communication, Dec. 9, 1971.

under vacuum to determine the recrystallization temperature, softening behavior, and bend ductility. Figure 5 shows the effect of the heat treating temperature on the microhardness of four alloys. Typically, the as-rolled hardness increased after the 400°C heat treatment, then steadily decreased with increasing temperature. Above 1000°C the hardness dropped sharply to values between 200 and 300 DPH. Metallographic examination shows no recrystallization in the Pt-Rh-W ternary alloys at 980°C but complete recrystallization and a single-phased structure at 1050°C, as shown in Fig. 6. The recrystallized grains grow slowly until temperatures approach 1400°C. The recrystallization temperature of the alloy modified with hafnium and titanium was 1200°C. This alloy is also single phased (Fig. 7). Grain growth for this alloy was not serious below 1500 to 1600°C. The cold-rolled and heat-treated specimens in Fig. 5 were also subjected to a 90° free bend to determine the effect of the heat treatment on the ductility. All specimens, including the as-rolled specimens, were ductile, but cracks were observed in specimens heat treated at 400 and 600°C.

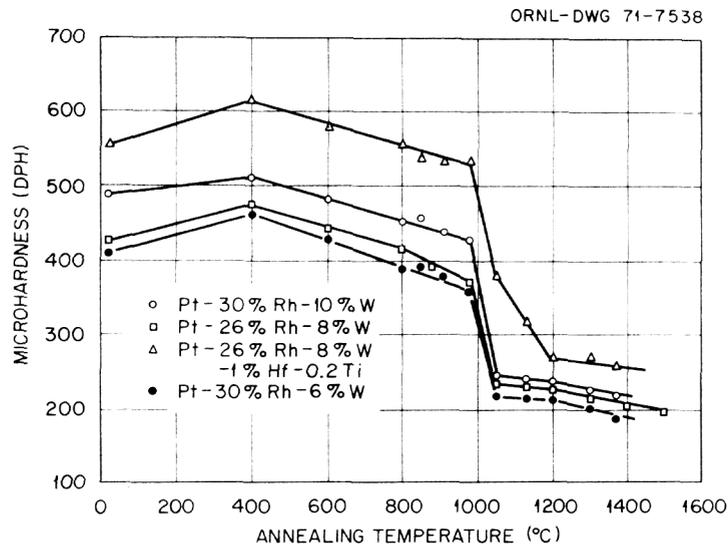


Fig. 5. Effect of 1-hr Heat Treatment on Hardness of Alloys Cold Rolled to 35% Reduction.

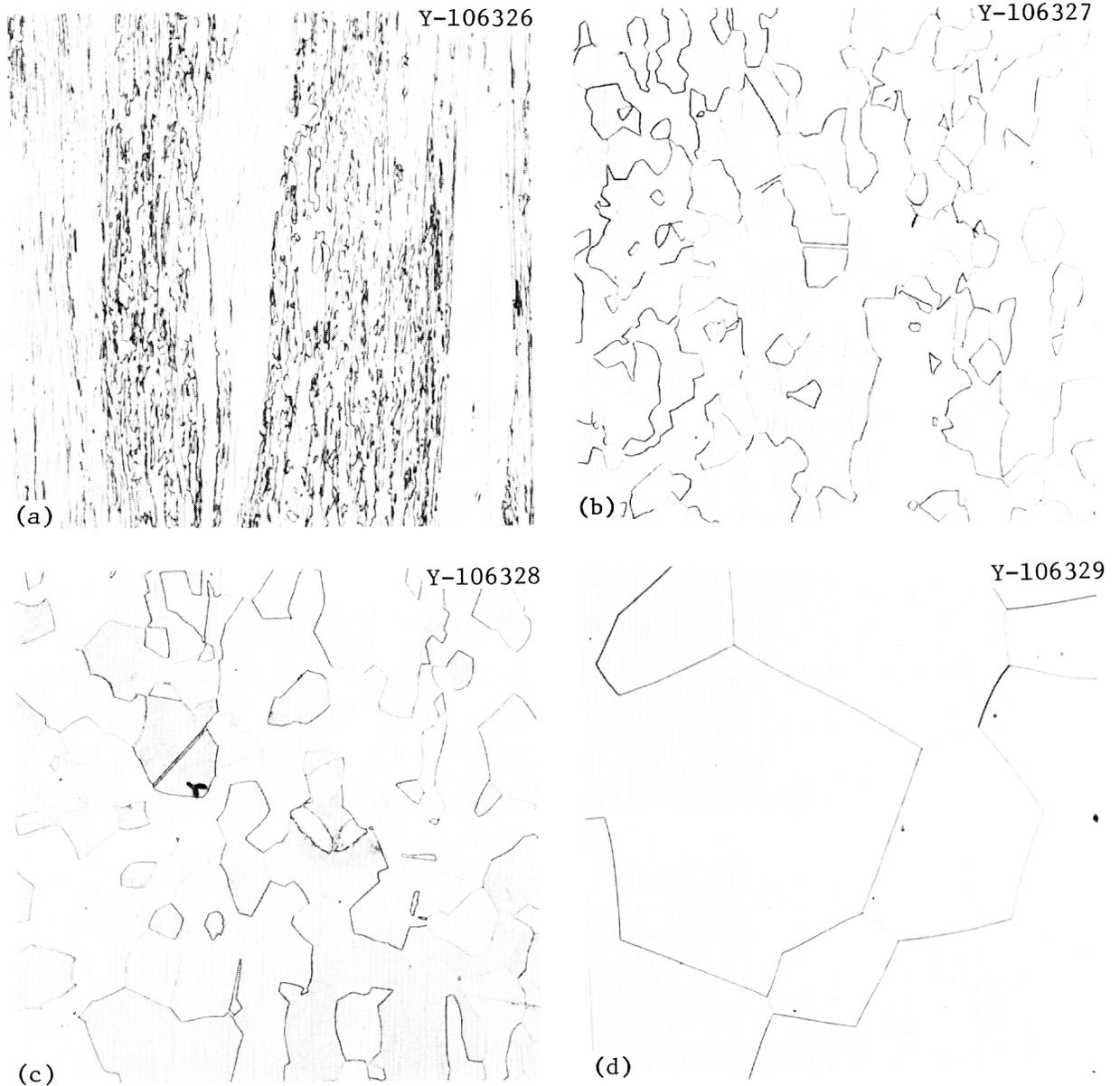


Fig. 6. Microstructures of Pt-26% Rh-8% W Alloy Cold Worked 35%, Followed by 1-hr Heat Treatment at (a) 980°C, (b) 1050°C, (c) 1200°C, and (d) 1400°C. Etchant: 80 parts H<sub>2</sub>O:20 parts HCl in saturated NaCl. Electrolytic etch 6 V ac for 1.5 min. 250×.

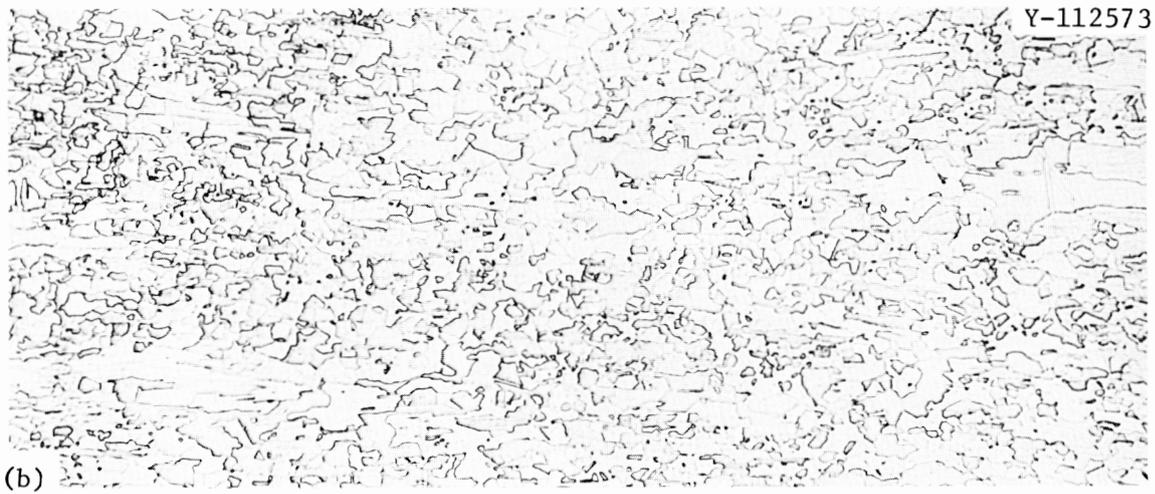


Fig. 7. Microstructure of Pt-26 Rh-8 W-1 Hf-0.2 Ti (wt %) Cold Rolled 35%, Heat Treated 1 hr at (a) 1050°C, (b) 1200°C, and (c) 1400°C. Etchant: 2 parts HNO<sub>3</sub>, 10 parts lactic acid, and 2 parts HF. 250×.

These results showed a steady increase in hardness as the tungsten content increased. Significant hardening at all temperatures resulted from hafnium and titanium additions. On the other hand, the recrystallization temperature of the Pt-Rh-W alloys was unaffected by the tungsten content but was raised about 150°C by the addition of hafnium and titanium. It should be noted that the hardnesses of the specimens heat treated at 400 and 600°C were higher than in the as-rolled condition. We believe that the increase in hardness and the propensity for cracking under these specific conditions are related to the segregation of substitutional impurities in the alloy, since other cold-worked platinum alloys also show an increase in hardness and brittleness when aged at low temperatures.<sup>5,6</sup>

#### Tensile Properties

Sheet tensile specimens with a gage section 0.125 in. wide × 1 in. long and 0.125-in.-diam pinholes were blanked from 0.020-in.-thick sheet. After the gage section was deburred, the specimen surfaces were polished on 400-A SiC paper, pickled in aqua regia, then heat treated in vacuum. Tensile specimens tested above room temperature were heated by radiation from an inductively heated tungsten susceptor under vacuum of less than 10<sup>-5</sup> torr. The vacuum environment was necessary to prevent oxidation of the susceptor and the Mo-0.5% Ti grips. A Pt vs Pt-10% Rh thermocouple centrally located on the specimen monitored the temperature. After a 5-min holding time at the test temperature tests were conducted on an Instron machine at a strain rate of 0.10/min.

The tensile properties of Pt-30% Rh and Pt-Rh-W alloys containing 6, 8, and 10% W are summarized in Table 3. In general, the strength increased with the tungsten level for both the stress relieved and

---

<sup>5</sup>R. W. Douglas et al., *High-Temperature Properties and Alloying Behavior of the Refractory Platinum-Group Metals*, NP-10939 (1961).

<sup>6</sup>E. P. Sadowski, "Stress-Rupture Properties of Some Platinum and Palladium Alloys," pp. 465-82 in *Refractory Metals and Alloys*, Vol. 11, ed. by M. Semchyshen and J. J. Harwood, Interscience, New York, 1961.

Table 3. Tensile Properties of the Platinum-Base Alloys

Alloy Composition (wt %)		Ultimate Tensile Strength, psi		Elongation, %	
Rh	W	Stress Relieved <sup>a</sup>	Recrystallized <sup>b</sup>	Stress Relieved <sup>a</sup>	Recrystallized <sup>b</sup>
<u>Room Temperature</u>					
30	0	76,000	63,000	42	43.8
30	6	169,000	112,000	15.7	26
26	8	171,000	142,000	15	16
30	10	194,000	118,000	12.5	14.5
<u>760°C (1400°F)</u>					
30	0	52,000	48,000	23	28.8
30	6	123,000	80,000	5.5	23.5
26	8	118,000	95,000	6.6	16
30	10	155,000	95,000	6.5	28
<u>1093°C (2000°F)</u>					
30	0	24,400	24,000	28	38
30	6	56,000	36,000	15	33.3
26	8	75,000	38,000	12	18
30	10	89,000	47,000	9	15.5
<u>1316°C (2400°F)</u>					
30	0	10,000	10,000	26.5	26.5
30	6	19,500	17,500	51.5	55
26	8	22,500	21,200	48	45
30	10	25,500	25,500	50.5	50.5

<sup>a</sup>Stress relieved 2 hr at 1000°C.

<sup>b</sup>Recrystallized 1 hr at 1200°C.

recrystallized conditions. Figure 8 shows the tensile data for stress-relieved alloys as a function of temperature. A minimum ductility of about 6% elongation is observed at 760°C; ductility increases to about 50% at 1316°C. Figure 9 is a plot of the tensile data for the same alloys recrystallized 1 hr at 1200°C. In this condition, the minimum ductility is about 15% at 760°C. The Pt-Rh-W alloys for either heat treatment are consistently less ductile than Pt-30% Rh up to about 1100°C. Above this temperature the ductility of the ternary alloys increases with

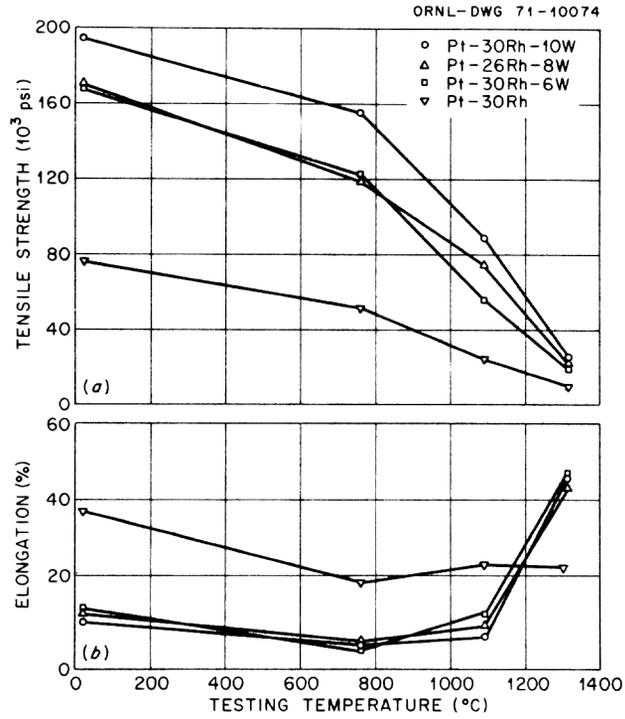


Fig. 8. Tensile Properties of Pt-Rh-W Alloys Stress Relieved 2 hr at  $1000^{\circ}$ C.

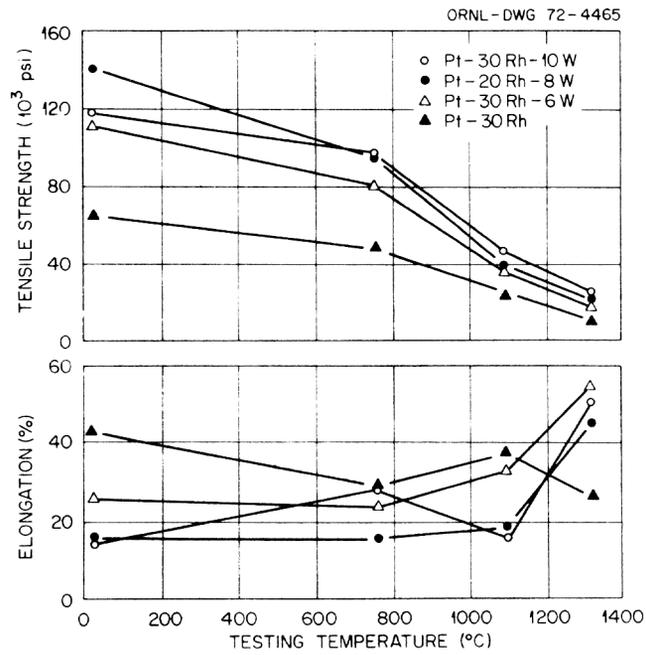


Fig. 9. Tensile Properties of Pt-Rh-W Alloys Annealed 1 hr at  $1200^{\circ}$ C.

temperature but that of the binary alloys decreases. Thus, tungsten significantly increases both the strength and the ductility and therefore the toughness of Pt-Rh alloys at 1316°C. Because ductility and strength normally vary in opposite directions, the observation for the Pt-Rh-W alloys is unique.

The tensile properties of the hafnium- and titanium-stabilized alloys and the ternary alloys are compared in Table 4. The stabilizing elements have no clear-cut effect on the ductility but do increase the tensile strength, especially at the highest test temperature.

Table 4. Tensile Properties of Hafnium- and Titanium-Stabilized Alloys Recrystallized 1 hr at 1200°C

Rh	Composition (wt %)			Test Temperature		Tensile Strength (psi)	Elongation (%)
	W	Hf	Ti	(°C)	(°F)		
30	6	0	0	Room		112,000	26.0
30	6	0.5	0.2			113,000	19.3
30	6	0	0	760	1400	80,000	23.3
30	6	0.5	0.2			81,000	27.5
30	6	0	0	1093	2000	36,000	33.3
30	6	0.5	0.2			42,200	28.1
30	6	0	0	1316	2400	17,500	55.0
30	6	0.5	0.2			23,500	44.3
26	8	0	0	Room		142,000	16.0
30	8	0.25	0.1			117,000	18.5
30	8	0.50	0.2			135,000	19.0
30	8	1.0	0.2			130,000	11.7
26	8	0	0	760	1400	95,000	16.0
30	8	0.25	0.1			84,000	28.0
30	8	0.50	0.2			91,000	24.3
30	8	1.0	0.2			108,000	26.3
26	8	0	0	1093	2000	38,000	18.0
30	8	0.25	0.1			40,000	15.8
30	8	0.50	0.2			44,500	12.5
30	8	1.0	0.2			52,000	24.1
26	8	0	0	1316	2400	21,200	45.0
30	8	0.25	0.1			21,600	52.0
30	8	0.50	0.2			25,000	44.5
30	8	1.0	0.2			27,700	54.5

Figures 10 and 11 compare the tensile properties of Pt-26% Rh-8% W and Pt-30% Rh-10% W with those reported<sup>7</sup> for recrystallized T-111, TZM, and Pt-30% Rh. The experimental alloys have higher tensile strengths than Pt-30% Rh and TZM at all temperatures but are weaker than T-111 above 1000°C. Above 1200°C, the Pt-Rh-W alloys are more ductile than the other alloys. All candidate alloys are compared further in Table 5 and Fig. 12. In terms of the toughness [defined as fracture strain  $\times$  (tensile strength + yield strength)/2] at 1316°C, the Pt-30 Rh-8 W-1.0 Hf-0.2 Ti (wt %) ranks first and is followed by T-111. Iridium<sup>8</sup> and TZM rank below the ternary Pt-Rh-W alloys. The high toughness of the platinum alloys at impact temperatures is derived from high ductility combined with yield strengths that exceed 80% of the ultimate tensile strength (Table 5).

<sup>7</sup>General Electric Company, *Multi-Hundred Watt Radioisotope Thermoelectric Generator Program*, GESP-7034 (March 1970).

<sup>8</sup>C. T. Liu, "Characterization of Iridium," *Fuels and Materials Development Program Quart. Progr. Rept. Mar. 31, 1972*, ORNL-TM-3797, pp. 289-290.

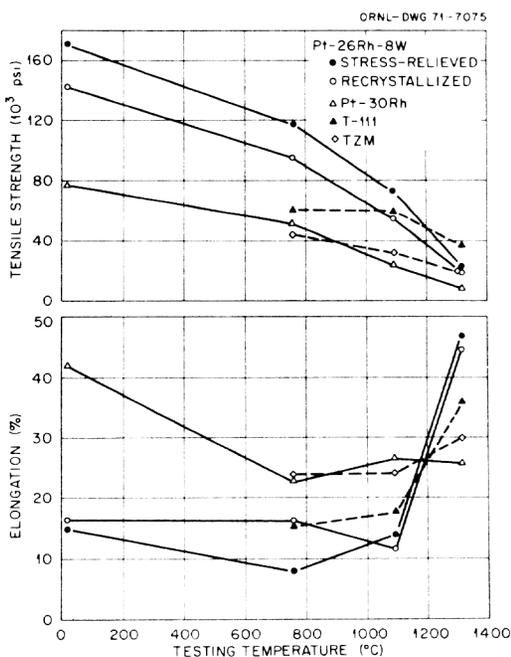


Fig. 10. Comparison of the Tensile Properties of Pt-26% Rh-8% W with Other Alloys.

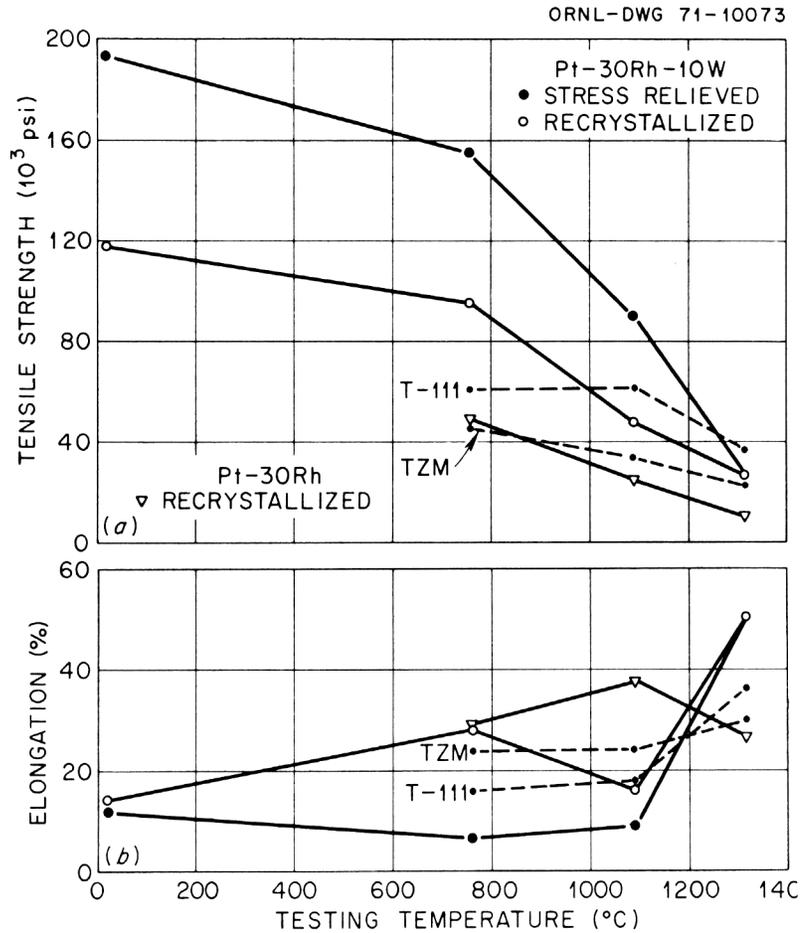


Fig. 11. Comparison of the Tensile Properties of Pt-30% Rh-10% W with Other Alloys.

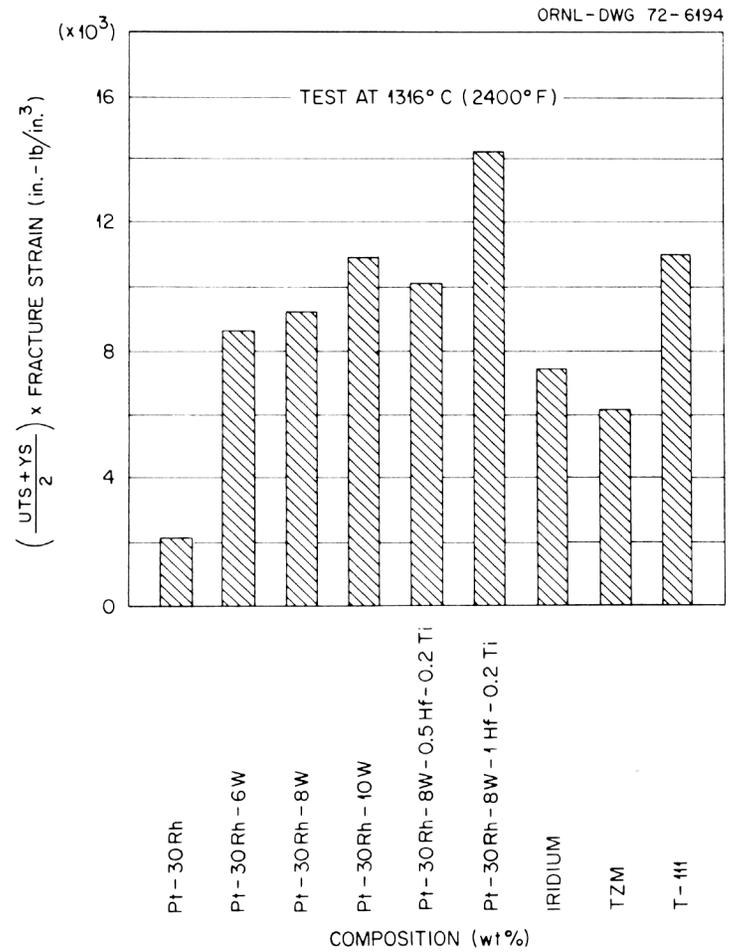


Fig. 12. Toughness of Cladding Alloys at 1316°C.

Table 5. Comparison of the Tensile Properties of Platinum-Base Alloys<sup>a</sup> with Iridium, TZM, and T-111 at 1316°C (2400°F)

Composition (wt %)	Strength, psi		Elongation (%)	Impact Capability <sup>b</sup> (in.-lb/in. <sup>3</sup> )
	Tensile	Yield		
Pt-30 Rh	10,000	5,800	26.5	2,100
Pt-30 Rh-6 W	17,500	13,800	55.0	8,600
Pt-30 Rh-8 W	22,500	15,900	48.0	9,200
Pt-30 Rh-10 W	25,500	17,800	50.5	10,900
Pt-30 Rh-8 W-0.5 Hf-0.2 Ti	25,000	20,300	44.5	10,100
Pt-30 Rh-8 W-1.0 Hf-0.2 Ti	27,700	24,000	55.0	14,200
Iridium <sup>c</sup>	26,000	13,100	38.0	7,400
TZM <sup>d</sup>	20,500	9,900	40.0	6,100
T-111 <sup>e</sup>	37,300	23,500	36.0	11,000

<sup>a</sup>0.020- to 0.025-in.-thick sheet recrystallized 1 hr at 1200°C, strain rate 0.1/min.

<sup>b</sup>(UTS + YS)(fracture strain)/2.

<sup>c</sup>0.020-in.-thick sheet recrystallized 1 hr at 1500°C, strain rate 0.1/min.

<sup>d</sup>J. A. Houck, *Physical and Mechanical Properties of Commercial Molybdenum-Base Alloys*, DMIC-140 (Nov. 30, 1960).

<sup>e</sup>Wah Chang Albany Corporation, *Columbium, Tantalum, and Tungsten Alloys Technical Information*, Vol. 3, pp. 89-96, Wah Chang Albany Corp., Albany, Oregon, January 1968.

Broken tensile specimens of Pt-26% Rh-8% W were examined with the scanning electron microscope to determine the fracture mode. Figure 13 shows the fractured surfaces after testing at room temperature, 760, 1093, and 1316°C. Failure appears to be transgranular at room temperature and ductile tearing at 760°C and above. The large voids in the specimen tested at 1316°C suggest that the cracks that nucleate as a result of deformation do not propagate but grow in the direction of strain. Figure 14 is the micrograph of a tensile specimen of another heat of the same composition tested at room temperature. Grain boundary

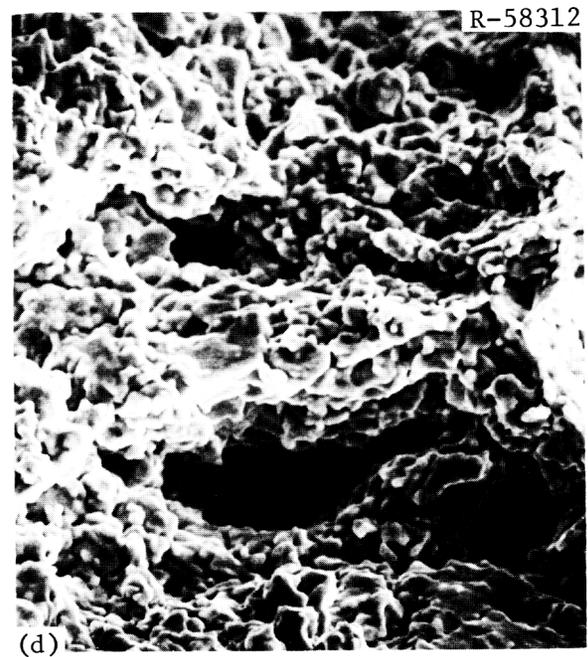
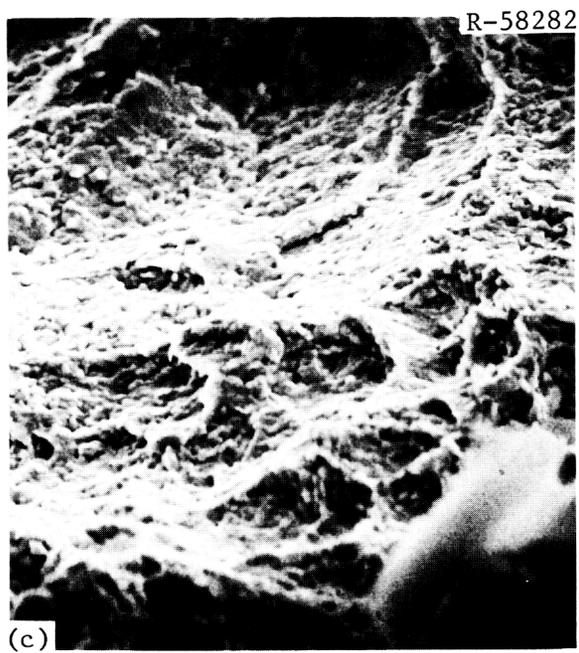
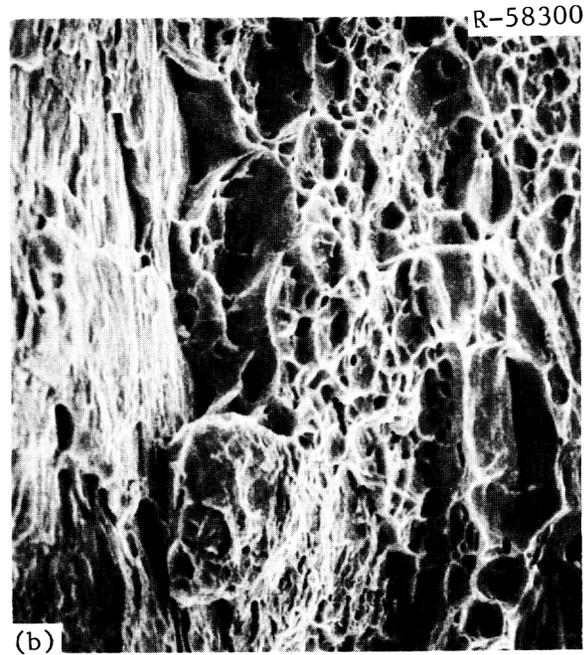


Fig. 13. Scanning Electron Micrographs of Fracture Surfaces of Tensile Specimens of Pt-26% Rh-8% W. (a) At room temperature, elongation = 16%; (b) at 760°C, elongation = 16%; (c) at 1093°C, elongation = 18%; and (d) at 1316°C, elongation = 45%. 2000 $\times$ .

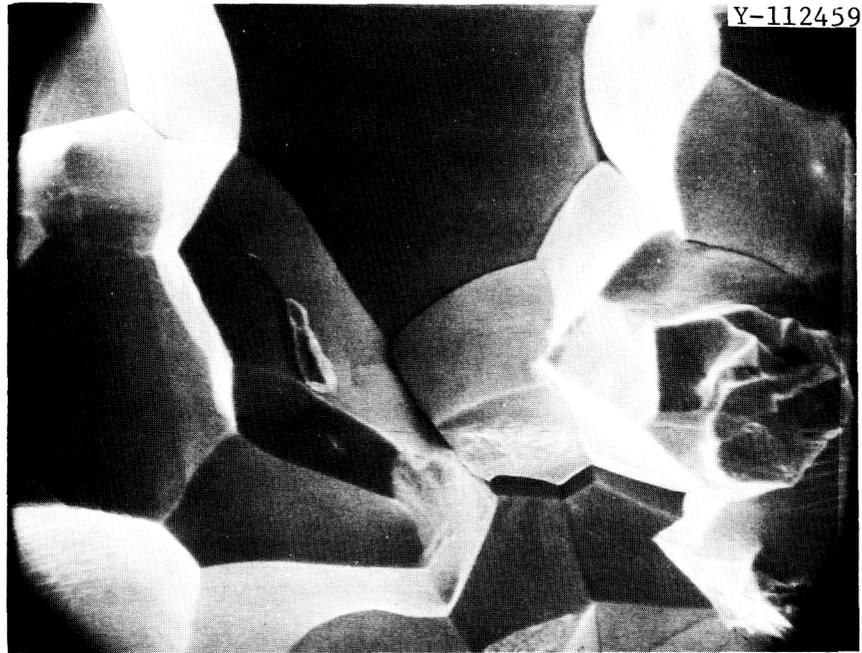


Fig. 14. Scanning Electron Micrograph of the Fracture Surface of Pt-26% Rh-8% W Embrittled by Contamination with Stainless Steel. 2000 $\times$ .

separation is the fracture mode. The elongation in this case was only about 2%, in contrast to the 16% elongation measured in the previous specimen. Iron, chromium, and nickel were detected on the grain boundaries by x-ray fluorescence. This brittle behavior has been seldom encountered and based on their concentration is attributed to contamination from stainless steel.

#### Oxidation Characteristics in Air

Rectangular sheet specimens 0.020 in. thick were polished through 2/0 paper, pickled in aqua regia, vacuum annealed, and then oxidized in static air for times to 200 hr. Since the thickness change on oxidation was less than 0.0001 in., the specimens were periodically removed from the furnace and weighed on an analytical balance with a sensitivity of  $10^{-6}$  g.

The weight changes as functions of time at 760, 1000, and 1200 $^{\circ}$ C are plotted in Fig. 15. In general, a transient period of decreasing reaction rate precedes a constant reaction rate. Typically the oxidation

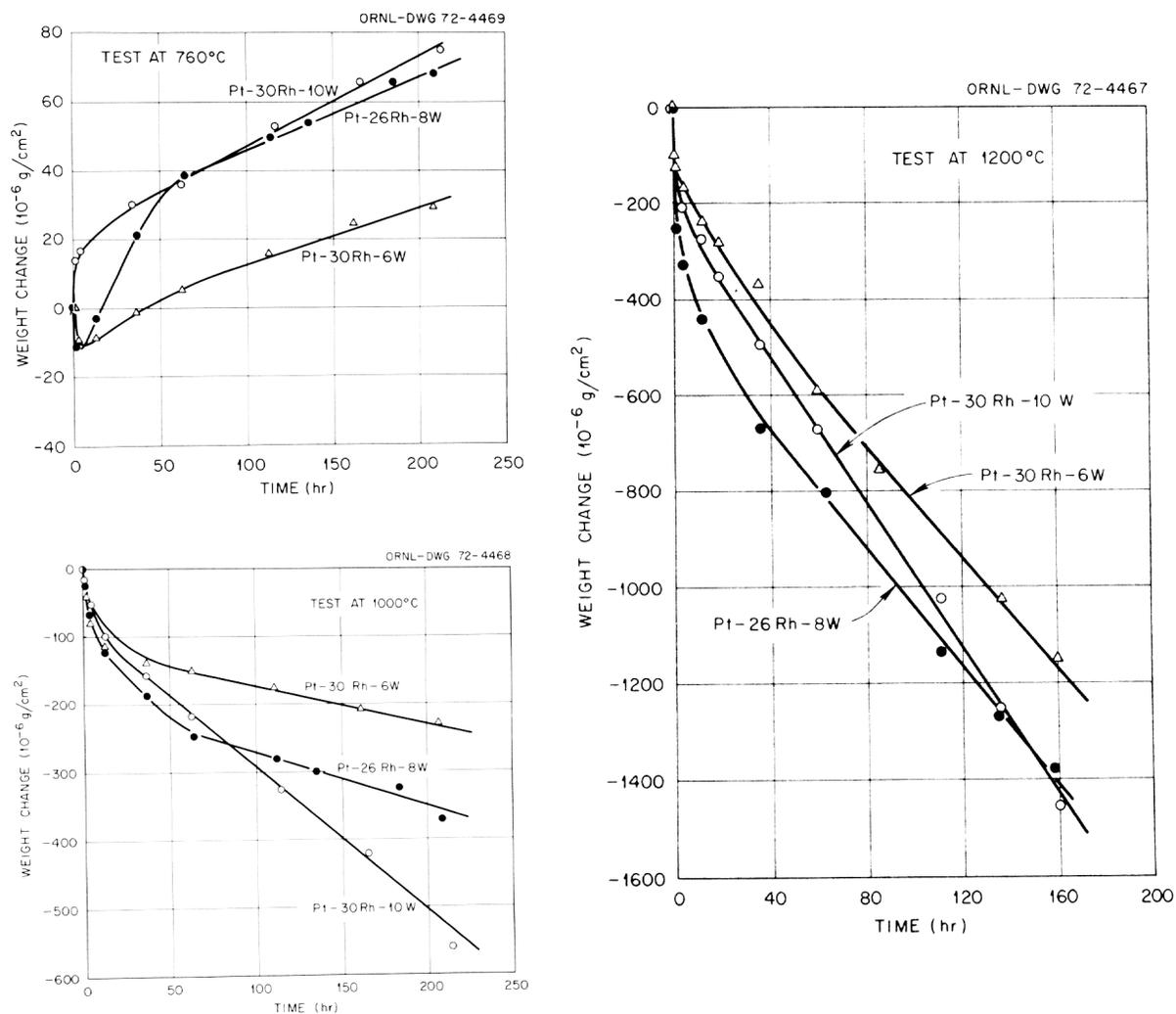


Fig. 15. Air Oxidation of Pt-Rh-W Alloys at 760, 1000, and 1200°C.

rates increase with the tungsten content. At 760°C the alloy specimens gained weight by the formation of adherent black oxides identified as  $W_2O_5$ ,  $Rh_2O_3$ , and  $RhO_2$ . At 1000 and 1200°C, however, the specimen lost weight, remained bright as initially prepared, and formed no visible oxide because the oxides are volatile.<sup>9</sup> The linear reaction rate constants for the experimental alloys were compared with literature data

<sup>9</sup>W. L. Phillips, Jr., *Trans. Am. Soc. Metals* 57: 33-37 (1964).

for molybdenum,<sup>10</sup> tantalum,<sup>10</sup> iridium,<sup>9</sup> and platinum.<sup>11</sup> As indicated in Table 6, the oxidation rates of Pt-Rh-W alloys are lower than those of molybdenum or tantalum by about five to six orders of magnitude, about two to three orders lower than iridium, but are higher than platinum by a factor of 2 to 10.

Table 6. Comparison of Air Oxidation Rate of Pt-Rh-W Alloys with Platinum and Refractory Metals

Composition (wt %)	Oxidation Rate, $\mu\text{g cm}^{-2} \text{hr}^{-1}$		
	1200°C	1000°C	760°C
Platinum	-2	-0.2	
Pt-30 Rh-6 W	-5.2	-0.5	+0.18
Pt-26 Rh-8 W	-6.0	-1.0	+0.20
Pt-30 Rh-10 W	-7.5	-2.2	+0.26
Pt-26 Rh-8 W-1 Hf-0.2 Ti	-6.7	-0.5	+0.20
Iridium	-800	-500	-200
Tantalum	+250,000	+150,000	+9,000
Molybdenum	-3,000,000	-1,500,000	-700,000

The microstructures of Pt-26% Rh-8% W after oxidation for 210 hr at 760 and 1000°C are shown in Fig. 16. Figure 17 shows the microstructure of Pt-30% Rh-10% W oxidized 159 hr at 1200°C. A zone at the surfaces consisting of fine grains less than about 1 mil thick is the only evidence of a reaction at 760°C. At 1000 and 1200°C oxidation results in grain boundary attack and the formation of porosity to a depth of 1 to 2 mils.

<sup>10</sup>R. I. Jaffee et al., "Rhenium and the Refractory Pt-Group Metals," pp. 383-464 in *Refractory Metals and Alloys*, Vol. 11, ed. by M. Semchyshen and J. J. Harwood, Interscience, New York, 1961.

<sup>11</sup>R. W. Douglas et al., *High-Temperature Properties and Alloying Behavior of the Refractory Platinum-Group Metals*, NP-10939 (1961).

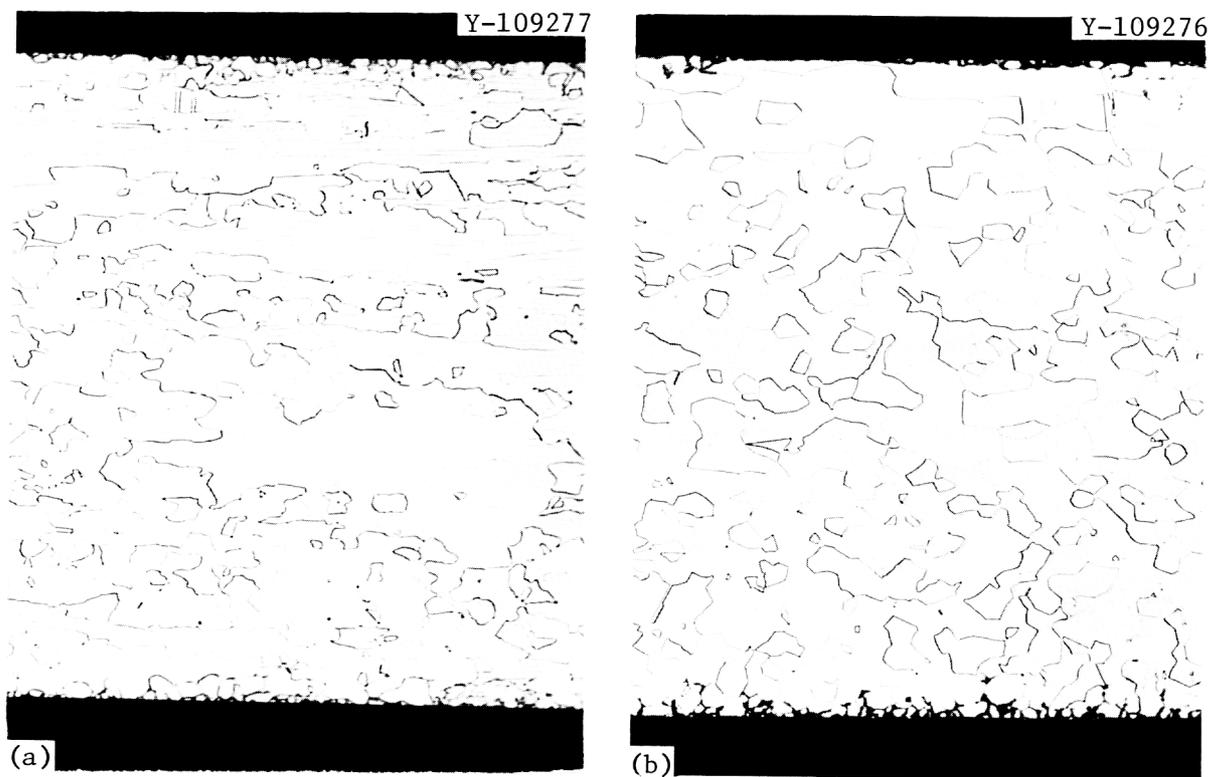


Fig. 16. Alloy Pt-26% Rh-8% W Oxidized 210 hr. Electrolytically etched at 6 V ac for 1.5 min in 80 parts H<sub>2</sub>O:20 parts HCl in saturated HCl. (a) Oxidized at 760°C; (b) at 1000°C. 150×.

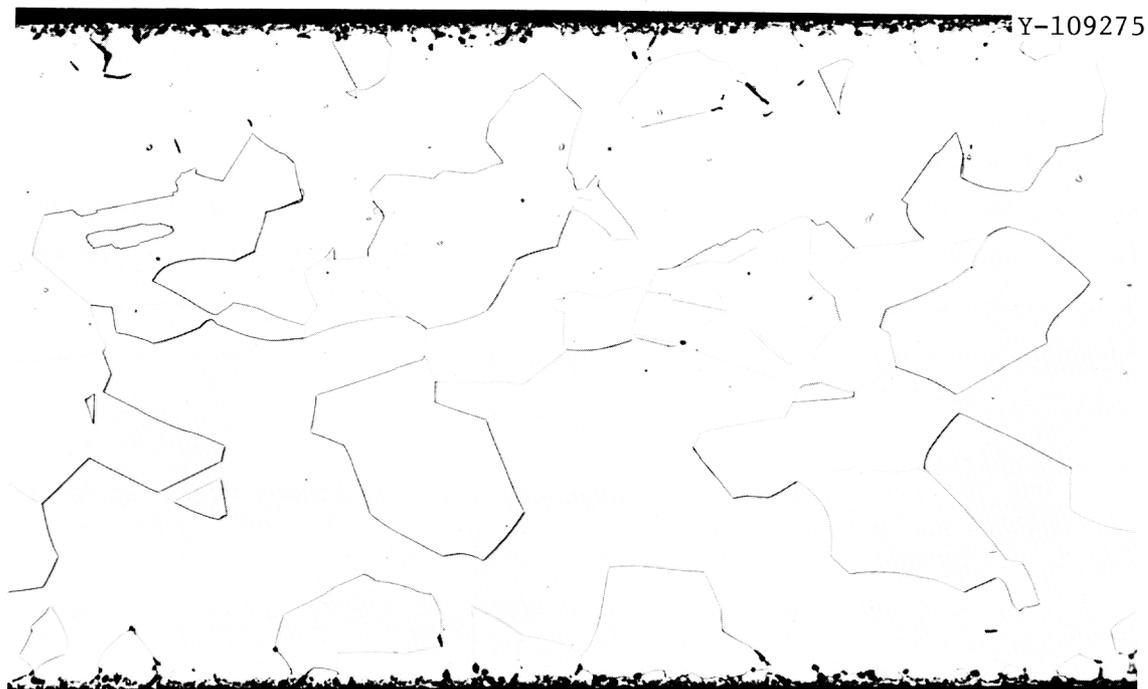


Fig. 17. Alloy Pt-30% Rh-10% W Oxidized 159 hr at 1200°C. Electrolytically etched at 6 V ac for 1.5 min in 80 parts H<sub>2</sub>O:20 parts HCl in saturated HCl. 150×.

## Weldability

Gas tungsten-arc welding was used to test the weldability of the Pt-26% Rh-8% W alloy. When examined by dye-penetrant and metallographic techniques, bead-on-plate welds showed no cracks as welded or after bending about 90°.

### Compatibility with T-111, Molybdenum, and Tungsten

The extent of interface reactions of Pt-Rh-W alloys with T-111, molybdenum, and tungsten was measured by metallography and hardness tests to determine their mutual compatibility. Noble metal couples metallurgically bonded with molybdenum or tungsten were prepared by chemically vapor coating sheet specimens. Couples of noble metals with T-111 were prepared by mating polished surfaces. Each combination was isothermally exposed for 1000 hr between 900 and 1300°C under vacuum of about  $10^{-8}$  torr and in separate furnaces to exclude all other environmental effects. Heat pulses to 1649°C (3000°F) for 10 min in a vacuum-induction furnace simulated reentry heating.

Table 7 summarizes the compatibility data for Pt-Rh-W with T-111. The results show that interface melting occurred during the heat pulse at 1704°C (3100°F) in the Pt-Rh-W/T-111 couple. Interface melting was not observed at 1649°C (3000°F) in the Pt-Rh-W/T-111 couple but did occur in the Pt-30% Rh/T-111 couple. Thus, alloying Pt-30% Rh with tungsten increases the reentry temperature limit by about 50°C. Interface reactions were not observed at 900 or 1200°C for times to 1000 hr.

The interactions of Pt-26% Rh-8% W with molybdenum or tungsten (Table 8) are characterized by the formation of a reaction zone whose thickness increases with the test temperature. The 10-min heat pulses at 1600°C had only a small effect on the extent of the reactions. The hardness of the reaction zone approached DPH values of about 800. Void formation, cracking, or interface melting was not observed.

Table 7. Compatibility of Pt-30% Rh and Pt-Rh-W Alloys with T-111

Composition (wt %)		Temperature		Time (min)	Reaction Zone Thickness ( $\mu\text{m}$ )	Remarks
Rh	W	( $^{\circ}\text{C}$ )	( $^{\circ}\text{F}$ )			
30	0	1593	2900 <sup>a</sup>	10	25	No interface melting
		1649	3000 <sup>a</sup>	10	62	Interface melting
30	9	1649	3000 <sup>a</sup>	10	5	No interface melting
		1704	3100 <sup>a</sup>	10	140	Interface melting
30	10	1704	3100 <sup>a</sup>	10	90	Interface melting
30	9	900	1652	60,000	0	No interaction
26	8	1200	2200	60,000 + 10	0	No interaction
		1600	2912 <sup>a</sup>			

<sup>a</sup>Simulates reentry heat pulse.

Table 8. Compatibility of Pt-26% Rh-8% W Alloy with Chemically Vapor Deposited Molybdenum and Tungsten

Heat Treatment		Reaction Zone Thickness ( $\mu\text{m}$ )	Hardness, DPH <sup>b</sup>		Remarks
Temperature ( $^{\circ}\text{C}$ )	Time <sup>a</sup>		Matrix	Reaction Zone	
			<u>Molybdenum</u>		
1600	10 min	0	219		No interaction
900	1000 hr	10	252		No interface melting
{	900	11	185		No interface melting
	1600				
1100	1000 hr	46	200	750	No interface melting
{	1100	35	203	730	No interface melting
	1600				
1200	1000 hr	100	217	600	No interface melting
{	1200	92	225	650	No interface melting
	1600				
1300	1000 hr	76	180	720	No interface melting

Table 8. (continued)

Heat Treatment		Reaction Zone Thickness ( $\mu\text{m}$ )	Hardness, DPH <sup>b</sup>		Remarks
Temperature ( $^{\circ}\text{C}$ )	Time <sup>a</sup>		Matrix	Reaction Zone	
{1300 1600	1000 hr 10 min	66	175	620	No interface melting
<u>Tungsten</u>					
1600	10 min	0	213		No interaction
900	1000 hr	11	304		No interface melting
1100	1000 hr	63	203	620	No interface melting
{1100 1600	1000 hr 10 min	67	213	799	No interface melting
1200	1000 hr	95	202	592	No interface melting
{1200 1600	1000 hr 10 min	95	210	782	No interface melting
1300	1000 hr	112	213	567	No interface melting
{1300 1600	1000 hr 10 min	114	206	770	No interface melting

<sup>a</sup>10-min exposure simulates reentry heating.

<sup>b</sup>The microhardness was measured by using a 100-g load.

#### Compatibility with Low-Pressure Oxygen

Tensile specimens of Pt-Rh-W and Pt-Rh-W-Hf-Ti alloys were exposed to a low partial pressure of oxygen because the environment in the heat source can be oxidizing. The tensile properties of 0.025-in.-thick sheet specimens of Pt-Rh-W alloys held 253 hr at 1100°C in  $1 \times 10^{-5}$  torr  $\text{O}_2$  are listed in Table 9. The oxygen-doped specimens show a reduction in the tensile strength at room temperature and at 825°C. A small reduction in the ductility was observed at room temperature, but no effect was apparent at 825°C. Table 10 compares the ductility of the hafnium- and titanium-modified alloys after a 1000-hr exposure to  $1 \times 10^{-5}$  torr  $\text{O}_2$  at 1000°C with the alloy in the recrystallized condition. In contrast to the results for the ternary alloys, the modified alloys suffered a

Table 9. Mechanical Properties of Pt-Rh-W Alloys after Oxygen Doping at 1100°C and  $1 \times 10^{-5}$  torr for 253 hr

Composition (wt %)		Condition	Elongation (%)	Ultimate Tensile Strength (psi)
Rh	W			
<u>Room Temperature</u>				
30	6	As recrystallized	26	112,000
		Doped	16.3	88,000
26	8	As recrystallized	20 <sup>a</sup>	115,000 <sup>a</sup>
		Doped	13.5	90,000
30	10	As recrystallized	14.5	118,000
		Doped	10	82,000
<u>825°C</u>				
30	6	As recrystallized	30 <sup>a</sup>	71,000 <sup>a</sup>
		Doped	31.5	52,000
26	8	As recrystallized	30 <sup>a</sup>	76,000
		Doped	30	54,000
30	10	As recrystallized	30 <sup>a</sup>	85,000 <sup>a</sup>
		Doped	31	66,000

<sup>a</sup>Value obtained from composition or temperature extrapolation.

Table 10. Tensile Ductility of Pt-30% Rh Alloys with Various Contents of W, Hf, and Ti after Oxygen Doping at 1000°C and  $1 \times 10^{-5}$  torr for 1000 hr

Composition, <sup>a</sup> wt %			Tensile Ductility, %			
			As Recrystallized		Doped	
W	Hf	Ti	Room Temperature	825°C	Room Temperature	825°C
6	0.5	0.2	19.3	30 <sup>b</sup>	8.7	21.3
8	0.25	0.1	18.5	30 <sup>b</sup>	10	22
8	0.5	0.2	19.3	30 <sup>b</sup>	7.3	16

<sup>a</sup>30% Rh, balance platinum.

<sup>b</sup>Estimated from temperature extrapolation.

ductility loss both at room temperature and at 825°C. The results further indicate that the degradation is independent of the tungsten content and is affected more by the presence of hafnium and titanium.

Reductions in both the room temperature strength and ductility have been reported for platinum-tungsten alloys after exposure to air at atmospheric pressure. The degradation is attributed to the enhanced diffusion of oxygen in platinum after the addition of tungsten.<sup>12</sup> Readily oxidizable alloying elements like Cr, Ti, Zr, and Al are furthermore reported to cause internal oxidation of platinum alloys.<sup>12,13</sup> Although both these processes are possible in the present alloys, the pure thermal effects near the recrystallization temperature and aging effects due to other impurities cannot be discounted yet. The degradation of the tensile properties, by whatever responsible mechanism, is not considered to be serious in this application in view of ductilities of 7 to 10% at room temperature and 16 to 30% at 825°C. Both T-111 and TZM are completely brittle under the same exposure conditions.<sup>14</sup>

#### SUMMARY

Materials of standard purity can be used to prepare Pt-Rh-W alloys having adequate ductility and fabricability at room temperature. Based on limited fabrication experience, special processing equipment, procedures, or protective heat treating environments are not required.

The Pt-Rh-W alloys are oxidation resistant to at least 1200°C. Whereas the oxidation resistance of tantalum and molybdenum alloys are expressed in terms of the recession rates of the surface in mils per hour, the dimensional changes in Pt-Rh-W alloys are too low to be measured in these units after 200 hr of oxidation at 1200°C. Moreover, the

---

<sup>12</sup>W. Betteridge and D. W. Rhys, "The High-Temperature Oxidation of Pt Metals and Their Alloys," pp. 186-92 in *First International Congress on Metallic Corrosion, 1961*, ed. by L. Kenworth, Butterworths, London, 1962.

<sup>13</sup>J. C. Chaston, *Platinum Metals Review* 15(4): 122-28 (October 1971).

<sup>14</sup>C. T. Liu, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1971*, ORNL-TM-3550, pp. 224-34.

oxidation rate of iridium is about two orders of magnitude higher than these alloys, as shown in Fig. 18. Because oxidation resistance can be considered to be equivalent to post-impact fuel containment capabilities, it is apparent that the platinum alloys are superior to the other candidate claddings.

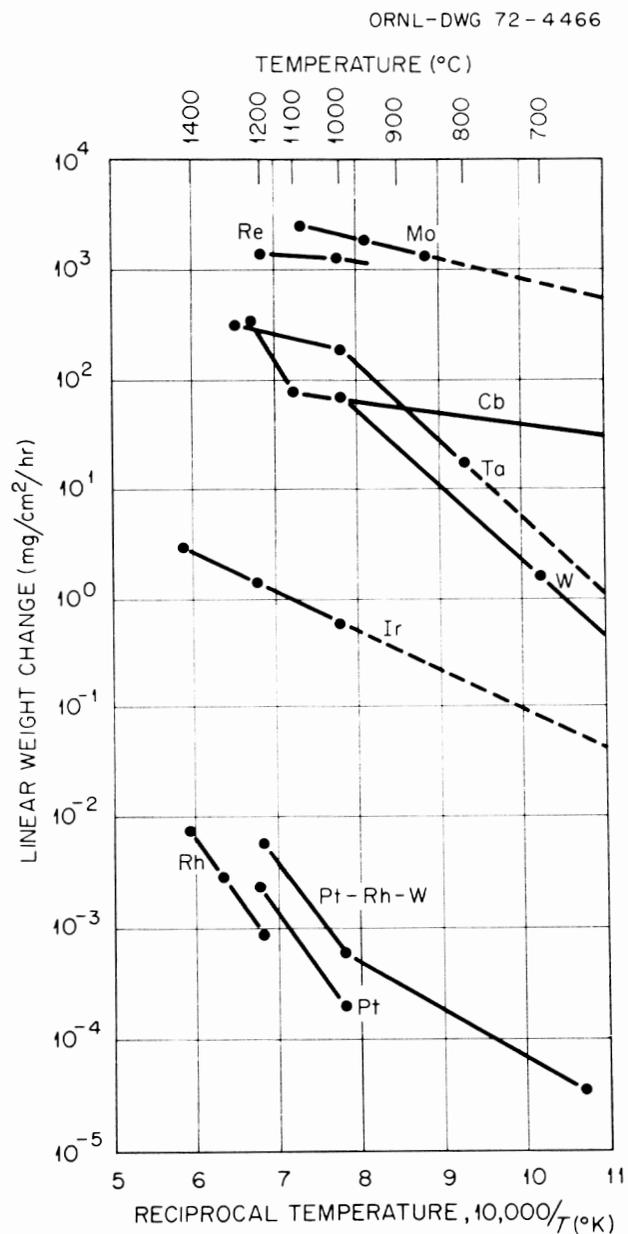


Fig. 18. Air Oxidation of Refractory and Noble Metals. Based on R. I. Jaffee et al., "Rhenium and the Refractory Pt-Group Metals," pp. 383-464 in *Refractory Metals and Alloys*, Vol. 11, ed. by M. Semchyshen and J. J. Harwood, Interscience, New York, 1961.

The strength of Pt-Rh-W alloys increases with the tungsten content. Above about 1100°C tungsten significantly increases the ductility. Because strength is normally obtained by sacrificing ductility, this behavior is unique and fortuitous. Hafnium and titanium additions further strengthen the ternary alloy base, increase the recrystallization temperature, and inhibit grain growth. The high temperature strength and toughness of the platinum alloys are comparable to T-111 and are greater than those of TZM and unalloyed iridium. The high toughness of the platinum alloys at impact temperatures is derived from their high ductilities combined with yield strengths that exceed 80% of the ultimate tensile strength. The present alloys appear to be compatible with T-111, molybdenum, tungsten, and low-pressure oxygen.

Whereas the melting point and the strength of the platinum alloys increase with the tungsten content, so does the oxidation rate and the difficulty of fabrication. A limiting tungsten level of 12% is dictated by fabricability. The recommended composition that represents trade-offs between the above properties is 8 wt % W as in Pt-26% Rh-8% W.

#### FUTURE PLANS AND RECOMMENDATIONS

Near-future program plans include detailed characterization of one or two experimental alloys. Included in these studies are more extensive fabrication studies, scale-up problems, welding, and compatibility. In view of the improvements over other alloys, it is recommended that a comprehensive study on the compatibility between the platinum alloys and potential isotopic fuels be initiated.

#### ACKNOWLEDGMENT

Preparation of experimental alloys was carried out in the Casting and Forming Technology facilities of the Metals and Ceramics Division.



ORNL-4813  
 UC-33 - Propulsion Systems  
 and Energy Conversion

INTERNAL DISTRIBUTION  
 (206 copies)

(2)	Central Research Library	E. L. Long, Jr.
	ORNL - Y-12 Technical Library	A. L. Lotts
	Document Reference Section	T. S. Lundy
(116)	Laboratory Records Department	W. R. Martin
	Laboratory Records, ORNL RC	R. W. McClung
	ORNL Patent Office	H. E. McCoy, Jr.
	G. M. Adamson, Jr.	R. E. McDonald
	D. J. Bostock (Y-12)	D. L. McElroy
	G. E. Boyd	J. R. McGuffey
	T. A. Butler	C. J. McHargue
	J. L. Cadden (Y-12)	R. E. McHenry
	J. M. Case (Y-12)	(20) P. Patriarca
	F. L. Culler, Jr.	R. A. Robinson
	J. E. Cunningham	A. F. Rupp
	J. H. DeVan	A. C. Schaffhauser
	J. R. DiStefano	R. W. Schaich
	W. H. Dodson (Y-12)	J. L. Scott
(10)	R. G. Donnelly	G. M. Slaughter
	J. H. Erwin	D. A. Sundberg
	J. H. Frye, Jr.	W. H. Thompson, Jr. (Y-12)
	J. H. Gillette	D. B. Trauger
	R. F. Hibbs	A. M. Weinberg
(3)	M. R. Hill	J. R. Weir, Jr.
(10)	H. Inouye	J. W. Yaggi (Y-12)
	E. Lamb	W. Kohn (Consultant)
	C. T. Liu	G. V. Smith (Consultant)

EXTERNAL DISTRIBUTION  
 (272 copies)

AEC ALBUQUERQUE OPERATIONS OFFICE, P.O. Box 5400, Albuquerque, NM 87115

D. Ofte

AEC DAYTON AREA OFFICE, P.O. Box 66, Miamisburg, OH 45342

D. D. Davis

AEC DIVISION OF APPLIED TECHNOLOGY, Washington, DC 20545

E. E. Fowler  
 W. S. Holman  
 J. N. Maddox  
 R. W. Shivers

## AEC DIVISION OF REACTOR DEVELOPMENT AND TECHNOLOGY, Washington, DC 20545

E. E. Kintner  
M. Shaw  
J. M. Simmons  
E. E. Sinclair  
A. Van Echo  
C. E. Weber

## AEC DIVISION OF SPACE NUCLEAR SYSTEMS, Washington, DC 20545

R. E. Anderson  
R. T. Carpenter  
G. P. Dix  
D. S. Gabriel  
N. Goldenberg  
H. Jaffe  
W. K. Kern  
A. P. Litman  
G. A. Newby  
F. Schulman  
F. C. Schwenk  
C. O. Tarr

## AEC OAK RIDGE OPERATIONS, P.O. Box E, Oak Ridge, TN 37830

R. J. Hart  
Patent Office  
Research and Technical Support Division

AEC-RDT SITE REPRESENTATIVES, Oak Ridge National Laboratory, P.O. Box X,  
Oak Ridge, TN 37830

D. F. Cope  
D. C. Davis, Jr.

## AEC SAVANNAH RIVER OPERATIONS OFFICE, P.O. Box A, Aiken, SC 29801

F. E. Kruesi

## AIR FORCE MATERIALS LABORATORY, Wright-Patterson Air Force Base, OH 45433

L. N. Hjelm  
I. Perlmutter

## AIR FORCE SYSTEMS COMMAND (SCIZM), Andrews Air Force Base, MD 20331

G. R. Crane

AIR FORCE WEAPONS LABORATORY, Kirtland Air Force Base, Albuquerque, NM  
87117

A. Noonan  
M. MacWilliams  
G. L. Zigler

ARGONNE NATIONAL LABORATORY, 9700 S. Cass Avenue, Argonne, IL 60439

P. G. Shewmon

ATOMICS INTERNATIONAL, P.O. Box 309, Canoga Park, CA 91304

H. Pearlman  
S. Siegel

BATTELLE MEMORIAL INSTITUTE, 505 King Avenue, Columbus, OH 43201

Defense Materials Information Center  
W. Pardue

BUREAU OF MINES, ALBANY METALLURGY RESEARCH CENTER, P.O. Box 70, Albany,  
OR 97321

Haruo Kato

DONALD W. DOUGLAS LABORATORIES, 2955 George Washington Way, Richland,  
WA 99352

D. Watrous

ENGELHARD MINERALS AND CHEMICALS CORPORATION, 497 Delaney Street, Newark,  
NJ 07105

H. Albert  
E. Zysk

GENERAL ELECTRIC COMPANY, SPACE DIVISION, ISOTOPE POWER SYSTEMS OPERATIONS,  
P.O. Box 8661, Philadelphia, PA 19101

J. A. Garate  
R. E. Schafer

GEORGE C. MARSHALL SPACE FLIGHT CENTER, Huntsville, AL 35812

W. Brooksbank  
R. J. Schwinghamer

GULF GENERAL ATOMIC, P.O. Box 608, San Diego, CA 92112

N. B. Elsner  
L. Yang

ISOTOPES, INC., NUCLEAR SYSTEMS DIVISION, 110 W. Timonium Road,  
Timonium, MD 21093

G. Linkous  
J. McGraw  
N. Strazza

JET PROPULSION LABORATORY, 4800 Oak Grove Drive, Pasadena, CA 91103

R. G. Ivanoff

JOHNS HOPKINS UNIVERSITY, Department of Mechanics, Baltimore, MD 21218

R. Fischell

LOS ALAMOS SCIENTIFIC LABORATORY, P.O. Box 1663, Los Alamos, NM 87544

R. D. Baker  
K. Cooper  
T. Keenan  
R. Mulford  
D. Pavone

MATHEY BISHOP, INC., Malvern, PA 19355

J. A. Bard

MONSANTO RESEARCH CORPORATION, MOUND LABORATORY, P.O. Box 32, Miamisburg,  
OH 45342

V. L. Avona  
W. T. Cave  
R. K. Flitcraft  
E. W. Johnson  
J. E. Selle  
W. H. Smith  
R. E. Vallée

NASA, AMES RESEARCH CENTER, Moffett Field, CA 94035

H. Nelson  
A. Wilbur

NASA, GODDARD SPACE FLIGHT CENTER, Greenbelt, MD 20770

J. Epstein

NASA HEADQUARTERS, CODE RN, 600 Independence Avenue, Washington, DC 20545

G. Deutsch  
T. B. Kerr

NASA, LANGLEY RESEARCH CENTER, Langley Station, Hampton, VA 23365

R. Brouns

NASA, LEWIS RESEARCH CENTER, 21000 Brookpark Road, Cleveland, OH 44135

G. M. Ault  
N. T. Saunders  
H. C. Slone

NASA, MANNED SPACECRAFT CENTER, Mail Code E-P5, Houston, TX 77058

T. W. Redding

NAVAL AIR SYSTEM COMMAND (AIR-52031B), Washington, DC 20360

I. Machlin

NAVAL UNDERSEA RESEARCH AND DEVELOPMENT CENTER, Technical Library,  
Code 133, San Diego, CA 92132

Commander

NAVY FACILITIES ENGINEERING COMMAND, Department of the Navy, Code 042,  
Washington, DC 20390

M. D. Starr

NAVY SPACE SYSTEMS ACTIVITY, Air Force Unit Post Office, Los Angeles,  
CA 90045 ATTN: R. V. Silverman, Code 40

Commanding Officer

PACIFIC NORTHWEST LABORATORY, P.O. Box 550, Richland, WA 99352

Director

RADIO CORPORATION OF AMERICA, AEC, Electronic Components and Devices,  
415 S. 5th Street, Harrison, NJ 07029

M. J. Hegarty

SANDIA CORPORATION, P.O. Box 5800, Albuquerque, NM 87115

J. R. Holland  
J. McDonald  
P. D. O'Brien

THERMO ELECTRON CORPORATION, 85 First Avenue, Waltham, MA 02154

L. Benker

TRW SYSTEMS, One Space Park, Redondo Beach, CA 90278

J. Blumenthal  
S. E. Bramer  
A. Hoffman  
I. Jones  
J. Ogren

UNION CARBIDE CORPORATION, 270 Park Avenue, New York, NY 10017

T. A. Nemzek  
J. A. Swartout

WESTINGHOUSE ASTRONUCLEAR LABORATORY, P.O. Box 10864, Pittsburgh, PA 15231

R. W. Buckman, Jr.  
D. C. Goldberg

(174) Given distribution as shown in TID-4500 under Propulsion Systems  
and Energy Conversion category (25 copies - NTIS)