

METAL FILAMENTS FOR HIGH-TEMPERATURE FABRICS

**E.H. Newton
D.E. Johnson
J.L. Sienczyk**

Arthur D. Little, Inc.

ABSTRACT

Tensile, ductile, and creep properties of selected superalloy and refractory metal filaments were measured up to 2200°F. Filament diameters ranged from 0.5 to 5.0 mils, using such materials as Rene' 41, Inconel 702, molybdenum, and tungsten.

Many methods were investigated for applying and testing very thin (approx. 0.1 mil) coatings to protect refractory metal filaments from oxidation up to 2200°F. These methods included vapor deposition, electrodeposition, electroless plating, diffusion coating, and hot dipping, as well as combinations of these.

Development work was carried out on techniques for producing fine metal filaments without the use of a diamond die. The most promising of these involved electroforming of nickel on a continuous helical mandrel.

I. SUMMARY

The purposes of this program are to 1) determine the mechanical and oxidation behavior of metal filaments for use in high-temperature fabrics, 2) develop protective coating for fine refractory metal fibers, and 3) develop new techniques for forming fine filaments.

As a group, 0.5 to 2.0 mil filaments of the nickel-base precipitation-hardened alloys exhibited the highest tensile strength between 1500°F and 2200°F, ranging from 14,000-23,000 psi at the latter temperature. In general, the cobalt-base alloys had lower high-temperature tensile strength, the iron-base alloys had the lowest strengths.

Unfortunately, all of the high strength superalloys exhibited low break elongation at high temperature and were especially brittle after cooling to room temperature.

All of the fine superalloy filaments appeared to be in the plastic flow region at 1800°F and above; consequently, in all the alloys tested, extremely high creep rates were observed.

Filaments drawn from tungsten, molybdenum, and alloys of these with rhenium have shown extremely high tensile strength, on the order of 200,000-300,000 psi at 2000°F, when tested in an argon atmosphere. Break elongation at high temperature varied from 1.9 to 5.6%, the same order of magnitude as the superalloys. Preliminary experiments indicated that tungsten filaments have no significant creep at 2000°F.

A wide variety of oxidation resistant coatings and methods of applying them to 1.0 mil refractory metal wires have been investigated. The only one showing any promise to date is a hot-dip tin-aluminum coating which has protected a 1 mil tungsten filament from oxidation in air at 2000°F up to 23 minutes.

Three methods for forming fine metallic filaments without the use of diamond dies have been investigated. Two of these, cold drawing over a ceramic pin and vapor deposition, were demonstrated in principle but would require an extensive development program to achieve a practical process.

The third of these wire forming techniques, electrodeposition on a selectively stopped-off helical mandrel, has shown the most promise. Nickel filaments, 1.4 x 8 mils cross-section, made on such a mandrel have shown room temperature tensile strengths of 100,000 psi and break elongations of 1.5%.

II. INTRODUCTION

The objectives of this program were to develop data on the use of metal filaments in high-temperature fabrics primarily for expandable structure in outer-space and re-entry deceleration devices. No attempt was made to direct this research toward any particular end use, although a typical re-entry condition from orbital velocity was used as a guide for evaluating filament performance.

A fabric employed in a deceleration parachute should have the flexibility typical of textiles, but because of the high re-entry velocities, it should have extremely low porosity. For metals to meet these requirements, they would have to have diameters on the order of 0.5 mils. Very little data on the high-temperature properties of fine filaments were available previous to this study.

The two basic groups of metals considered were the oxidation resistant superalloys and the refractory metals. In addition, it was necessary to investigate possible oxidation resistant coatings for the refractory metal filaments; because of the extremely fine filament diameters, such coatings should be on the order of 0.05 to 0.10 mils.

Metal filaments of the diameters required are made by drawing through diamond dies, an extremely expensive process when measured in terms of pounds of wire (roughly \$800-\$1500/lb). This was, therefore, a strong incentive for developing a less expensive method; some work along this line is reported herein.

III. HIGH-TEMPERATURE ALLOY WIRES

Considerable information has been published in recent years on the oxidation behavior and high-temperature mechanical properties of the group of alloy compositions known as superalloys in the form of sheet, rod and heavy wire. However, very little has been published heretofore on the properties of these alloys in the form of very fine wire filaments, of the order of 1-mil diameter and smaller. In this program, fine wires made from 15 high-temperature alloys have been evaluated for their high-temperature behavior. The nominal composition of these 15 alloys are shown in Table I.

A. SHORT-TERM HIGH-TEMPERATURE TENSILE STRENGTH

The room temperature and short-term high-temperature ultimate tensile strength of 31 fine wire filaments made from the 15 superalloys noted above is shown in Table II. Short-term in this case means the filament reached the test temperature in 20 seconds and was held at that temperature for 40 seconds before applying the load. In preliminary tests, it was found that the tensile strength increased with increasing strain rate up to a crosshead speed on the Instron Tensile Tester of 2 inches per minute. Above 2 inches per minute, the tensile strength was essentially constant. Since the reproducibility of results was found to be best at 2 inches per minute, most of our testing was carried out at this crosshead speed. The heated portion of the wire was estimated to be 1.25 inches which corresponded to a strain rate of 1.6 inches per inch per minute.

The high-temperature tensile strength of 1-mil diameter filaments drawn from alloys of the same general composition were noted to group together; the mean values for each group plotted in Figure 1. As one might expect, the nickel-base precipitation-hardened superalloys have higher hot tensile strengths than any of the other alloys tested (Curve 1). Hastelloy B tensile strength is at a somewhat lower level, and it drops off markedly between 2000 and 2200°F (Curve 2). Curves 3 and 4 are quite similar; they cross near 1800°F, and the nickel-base precipitation-hardened alloys containing no molybdenum or cobalt appear slightly stronger than the cobalt-base alloys above this temperature. Curve 5 indicates that the presence of iron in A-286 and Hastelloy X wires and the lack of precipitation-hardening elements in the latter renders both alloys significantly weaker at high temperature than most of the other alloys tested.

Ten of the above alloys were available in less than 1-mil diameter filaments, ranging from 0.5 to 0.65 mils. The short-term high-temperature tensile strength of these finer wires was in about the same relative order as the 1-mil wires. A more useful comparison might take into account the average strength of the wires exposed to the three highest test temperatures, 1800, 2000, and 2200°F. In this temperature region, the slopes of the tensile-temperature curves have begun to level off and the inclusions of three values tends to level out any inconsistencies in an individual reading. A comparison of the sums of the short-term ultimate tensile strengths of 1-mil and smaller diameter wires at 1800, 2000, and 2200°F is shown in Table III.

TABLE I
NOMINAL COMPOSITION OF ALLOY WIRES

Element, Weight Percent

Alloy	Ni	Co	Cr	Mo	W	Ti	Al	Fe	C	Si	Mn	B	Other
Udimet 700	53	17.5	15.0	5.0	--	3.5	4.25	1.0	0.15*	--	--	0.10*	
Udimet 500	50	16.5	17.5	4.0	--	3.0	2.75	4.0*	0.15*	0.75*	0.75*	.008*	
Rene' 41	49	11.0	19.0	10.0	--	3.1	1.5	5.0*	0.1*	0.5*	0.5*	.007	
M-252	54	10.0	19.0	10.0	--	2.5	0.75	2.0	0.1*	0.7	1.0	.005	
Waspalloy	55	13.5	19.5	4.3	--	3.0	1.25	2.0*	.05	0.75*	0.5*	--	
Hastelloy B	60	2.5*	1.0*	28.0	--	--	--	5.5	.05*	1.0*	1.0*	--	V-0.4*
HS-25	10.0	49	20.0	--	15.0	--	--	3.0*	0.10	1.0*	1.5	--	
Elgiloy	15	40.0	20.0	7.0	--	--	--	15.0	0.15	--	2.0	--	Be-.04
Inconel 702	77	--	15.5	--	--	0.6	3.3	2.0*	0.1*	0.7*	1.0*	--	
Hastelloy X	46	1.5	22.0	9.0	0.6	--	--	18.5	0.1	1.0*	1.0*	--	
A-286	26.0	--	15.5	1.25	--	1.95	0.20	52	0.05	0.95	1.35	--	V-0.30
Karma	73	--	20	--	--	--	3.5	3.0*	0.02*	--	0.2*	--	
Nichrome V	76	--	20	--	--	--	--	3.0*	0.02*	--	0.2*	--	
Chromel R	73	--	20	--	--	--	3.0	3.0*	0.05*	0.5*	--	--	
Nimonic (STAP)**	74	--	20	--	--	3.5	1.9	--	--	--	--	--	

* Maximum

** STAP = Stabilized Precipitate

TABLE II
SHORT-TIME ULTIMATE TENSILE STRENGTH (At Temperature) OF ALLOY WIRES
(Held at Temperature 40 Seconds Before Testing, Crosshead Speed 2"/Min.)

Wire No.	Alloy	Diameter, Mils	Tensile Strength, $\text{psi} \times 10^{-3}$				
			Room	1500	1800	2000	2200
1	Udimet 700	1.0	219	156	85	31	16
2	Udimet 700	0.65	338	292	90	36	23
3	Udimet 500	1.0	182	137	88	28	18
4	Udimet 500	0.6	162	144	69	26	17
5	M-252	1.0	192	133	67	35	23
6	M-252	0.65	165	120	58	30	17
7	Waspalloy	1.0	197	135	67	24	16
8	Waspalloy	0.6	174	127	61	23	14
9	Hastelloy B	1.0	211	148	53	23	5
10	Hastelloy B	0.6	195	132	67	29	5
11	A-286	0.95	117	79	28	17	10
12	HS-25	1.0	267	138	21	15	20
13	Hastelloy X	0.9	153	90	24	12	13
14	Rene' 41	0.5	206	155	61	27	23
15	Rene' 41	1.0	174	132	78	28	18
16	Rene' 41	2.0	182	129	87	27	18
17	Elgiloy	0.5	229	120	40	21	17
18	Elgiloy	1.0	203	116	44	18	16
19	Elgiloy	2.0	212	126	38	26	19
20	Inconel 702	1.0	138	90	39	25	20
21	Inconel 702	2.0	130	85	38	20	13
22	Chromel R	0.5	120	56	30	24	19
23	Chromel R	1.5	168	83	41	20	15
24	Karma (as drawn)	0.5	359	103	36	28	--
25	Karma (HT @ 1200°F)	0.5	377	103	36	28	--
26	Karma (annealed)	1.0	173	100	38	21	19

(cont'd on next page)

TABLE II (Cont'd)

<u>Wire No.</u>	<u>Alloy</u>	<u>Diameter, Mils</u>	<u>Temperature °F</u>				
			<u>Room</u>	<u>1500</u>	<u>1800</u>	<u>2000</u>	<u>2200</u>
27	Nichrome V (as drawn)	0.5	303	75	33	22	18
28	Nichrome V (HT @ 1200°F)	0.5	292	75	33	22	18
29	Nimonic (STAP) (annealed)	1.4	157	--	--	--	16
30	Nimonic (STAP) (annealed)	2.0	145	89	36	21	12
31	Nimonic (STAP) (as drawn)	2.0	241	91	30	17	11

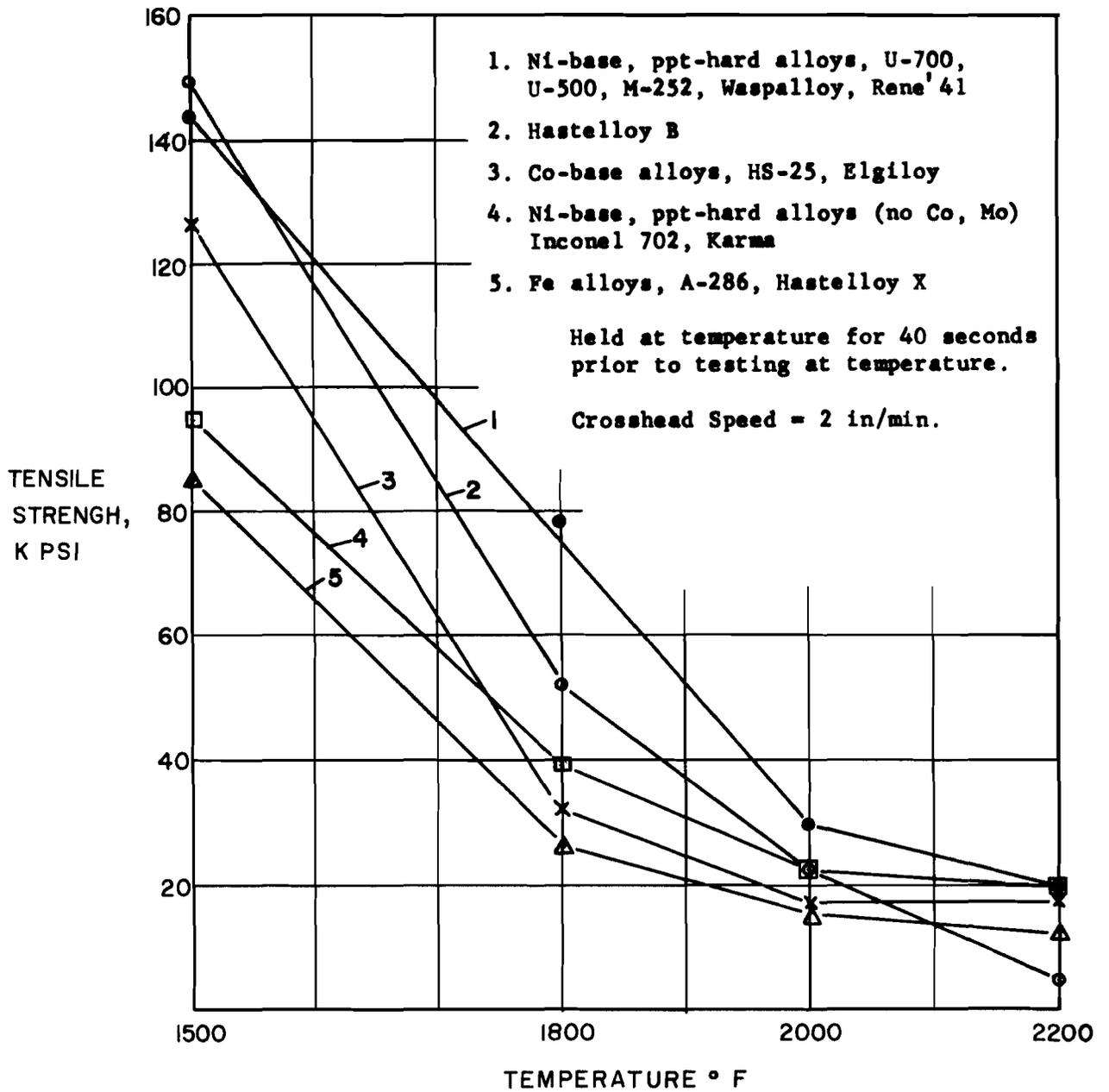


FIGURE I Short Time High Temperature Tensile Tests of One Mil Diameter Superalloy Wires

TABLE III

COMPARISON OF TENSILE STRENGTHS OF ALLOY WIRES FROM 1800-2200°F

<u>1 Mil Wires</u>		<u>0.5-0.65 Mil Wires</u>	
<u>Alloy</u>	<u>Sum of UTS, psi x 10⁻³ @ 1800, 2000, 2200°F</u>	<u>Alloy</u>	<u>Sum of UTS, psi x 10⁻³ @ 1800, 2000, 2200°F</u>
Udimet 500	134	Udimet 700	149
Udimet 700	132	Udimet 500	112
M-252	125	Rene' 41	111
Rene' 41	124	M-252	105
Waspalloy	107	Hastelloy B	101
Inconel 702	84	Waspalloy	98
Hastelloy B	81	Elgiloy	78
Elgiloy	78	Chromel R	73
Karma (annealed)	78	Nichrome V	73
HS-25	56		
A-286	55		
Hastelloy X	49		

The conclusions derived from Table III, with a few exceptions, are in general agreement with those arrived at from Figure I.

Of the five nickel-base titanium-aluminum precipitation-hardened alloys containing molybdenum and cobalt, U-500 and U-700 appear somewhat stronger than the others, probably because of their greater titanium and aluminum content. Actually the differences among the first four alloys listed are not too great, and any of these probably can be used interchangeably as far as high-temperature strength is concerned. Waspalloy has a lower Ti + Al + Mo + Co content and appears slightly weaker. It may be a fortuitous correlation, but the high-temperature strength ratings of these five alloys are in the same order as the sum of their Ti + Al + Mo + Co content.

B. DUCTILITY AT HIGH TEMPERATURE

The percent elongation is normally calculated from the irreversible extension of the wire, as recorded on the Instron Tensile Test Chart, and from the original length of the wire. At room temperature, we used a 6-inch length of wire on all samples except on some early tests with Rene' 41 and Elgiloy where a 2-inch length was employed. At higher temperatures, the exact length of wire that was heated to the test temperature in our platinum furnace was not accurately known. Our best estimate was 1.25 inches and this length was used in all calculations of percent elongation at 1500-2200°F. If there was any error, it is most likely to be on the high side (too long) and any corrections would increase the estimated percent elongation over those presented here. A complete listing of the comparative percent elongation of all the alloy wires we have tested is given in Table IV.

The change in ductility of small diameter superalloy wires is not a smooth function of temperature, and maximum and minimum are frequently observed. At 2000-2200°F, very few of the finest wires have appreciable ductility and the ductility decreases with decreasing wire diameter. Among the five alloy wires with the greatest high-temperature strength (U-700, U-500, M-252, Waspalloy, and Rene' 41), Rene' 41 appears somewhat more ductile than the four, the 1-mil wire having 8 percent elongation at 2000°F and 6.6 percent at 2200°F.

Among the more ductile 1-mil or finer wires at 2000-2200°F are Hastelloy X, HS-25, Inconel 702, Karma, and Elgiloy. In particular, Hastelloy X retains considerable ductility even at 2200°F, 17.6 percent. Unfortunately, this alloy is near the bottom of the list in high-temperature tensile strength, 13,000 psi at 2200°F. The reason for the abrupt drop in ductility and increase in tensile strength of HS-25 from 2000 to 2200°F remains to be explained. One-mil Inconel 702 and Karma are very similar in high-temperature tensile strength and ductility, and possibly may represent the best compromise in these properties among all the alloy wires tested to date.

C. EFFECTS OF HEATING FINE-WIRE FILAMENTS IN AIR UP TO 10 MINUTES

The high-temperature tensile strength and elongation values noted in the previous sections are for very short time periods, and the effect of holding the metal filament at temperature is not apparent from these tests. All of the

TABLE IV
COMPARATIVE DUCTILITY OF ALLOY WIRES

Percent Elongation in 1.25 Inches at High Temperature;
In 6 Inches at Room Temperature

(Held at Temperature 40 Seconds Before Testing, Crosshead Speed 2"/Min.)

<u>Wire No.</u>	<u>Alloy</u>	<u>Diameter, Mils</u>	<u>Room</u>	<u>1500</u>	<u>1800</u>	<u>2000</u>	<u>2200</u>
1	Udimet 700	1.0	15.5	5.4	3.4	3.3	1.7
2	Udimet 700	0.65	1.1	7.2	3.9	2.6	1.7
3	Udimet 500	1.0	12.3	23.2	3.6	3.3	2.1
4	Udimet 500	0.6	2.5	7.7	3.1	2.2	2.3
5	M-252	1.0	18.8	20.6	5.0	5.1	2.9
6	M-252	0.65	4.3	5.6	4.4	3.7	1.4
7	Waspalloy	1.0	19.7	12.5	7.7	7.1	2.2
8	Waspalloy	0.6	10.0	10.4	2.9	2.3	1.4
9	Hastelloy B	1.0	13.1	5.8	7.3	4.6	1.0
10	Hastelloy B	0.6	8.4	3.8	2.9	1.4	0.6
11	A-286	0.95	1.0	3.6	6.7	3.4	1.4
12	HS-25	1.0	1.4	10.1	34.3	23.5	2.4
13	Hastelloy X	0.9	6.5	7.5	23.2	32.8	17.6
14	Rene' 41*	0.5	15.7	6.0	6.9	3.2	3.0
15	Rene' 41*	1.0	26.0	36.0	5.6	8.0	6.6
16	Rene' 41*	2.0	31.2	29.6	7.2	13.2	8.2
17	Elgiloy*	0.5	11.0	6.7	9.9	8.8	2.3
18	Elgiloy*	1.0	28.9	11.6	10.2	17.8	2.5
19	Elgiloy*	2.0	28.6	4.0	21.6	11.6	2.0
20	Inconel 702	1.0	12.6	9.3	7.9	8.2	8.3
21	Inconel 702	2.0	20.2	19.7	9.3	12.7	9.7
22	Chromel R	0.5	11.8	9.8	11.2	2.2	1.8
23	Chromel R	1.5	18.7	20.3	12.2	8.5	10.4

* Room temperature elongation done on 2-inch samples.

(cont'd on next page)

TABLE IV (Cont'd)

<u>Wire No.</u>	<u>Alloy</u>	<u>Diameter, Mils</u>	<u>Temperature °F</u>				
			<u>Room</u>	<u>1500</u>	<u>1800</u>	<u>2000</u>	<u>2200</u>
24	Karma (as drawn)	0.5	2.1	8.9	9.3	5.1	--
25	Karma (HT @ 1200°F)	0.5	1.7	8.9	7.4	3.9	--
26	Karma (annealed)	1.0	13.9	8.0	14.7	17.0	6.5
27	Nichrome V (as drawn)	0.5	1.7	8.6	8.6	5.4	2.6
28	Nichrome V (HT @ 1200°F)	0.5	1.8	7.8	8.3	5.9	3.3
29	Nimonic (STAP) (annealed)	1.4	5.0	--	--	--	7.2
30	Nimonic (STAP) (annealed)	2.0	7.8	5.8	7.4	8.4	5.1
31	Nimonic (STAP) (as drawn)	2.0	1.4	7.2	10.5	10.2	14.8

high-temperature alloys are quite oxidation resistant and for applications where the thickness of the metal is above 5 mils, the loss of metal due to oxidation is not a serious problem. With metal filaments having diameters less than 1-mil, however, the growth of any oxide layer and penetration of oxygen or oxides may be of serious consequence to the integrity of the filament. Although most of our work has been directed toward relatively short-term high-temperature evaluation of fine metal wires, some tests were carried out after exposing the wires to high temperature up to 10 minutes.

1. Oxidation Rate

Figure 2 shows the oxidation rate of 1-mil Elgiloy, Rene' 41, and Inconel 702 wires on exposure to static air at 1500 to 2000° F up to 10 minutes' time. Rene' 41 is oxidized faster than Inconel 702 over the whole temperature range; Elgiloy has the highest oxidation rate of the three at 1500° F, is intermediate between Rene' 41 and Inconel 702 at 1800° F, and is the lowest of the group at 2000° F. These three alloys are representative of three of the groups of alloys shown in Figure 1.

The following trends were apparent as a result of the oxidation tests:

1. The oxide film on these wires grows most rapidly in the first minute, increases at a reduced rate from 1 to 5 minutes, and levels off between 5 and 10 minutes.
2. The rate of oxide growth (average absolute penetration depth) is greater with increasing wire diameter.
3. The rate of oxide growth is greater with increasing temperature.

The oxidation rates shown in Figure 2 are expressed as the increase in weight in micrograms per square centimeter due to the formation of an adherent oxide layer. The increase in weight is directly proportional to the metal lost and to the absolute penetration into the wire. The percent loss in the cross-sectional area was computed for each time, temperature, and wire size so as to give an indication of the possible weakening of these wires due to loss of metal.

The percent loss of cross-sectional area on each alloy wire increases with decreasing wire diameter, even though the absolute oxidation rate decreases with decreasing diameter. The magnitude of the loss, however, is comparatively small - 0.2 to 3.6% for Elgiloy wires, 1.1 to 7.4% for Rene' 41 wires, and 0.08 to 3.8% for Inconel 702 wires. The higher values are for the finest wires held at 2000° F for 10 minutes. These figures indicate that the average loss of metal due to oxidation should not be a major cause for loss in strength of the wires at high temperature. On the other hand, if there is selective oxidation of the metal at grain boundaries or inclusions in the wire, a very small amount of oxidation could (and does) cause serious loss of strength and ductility.

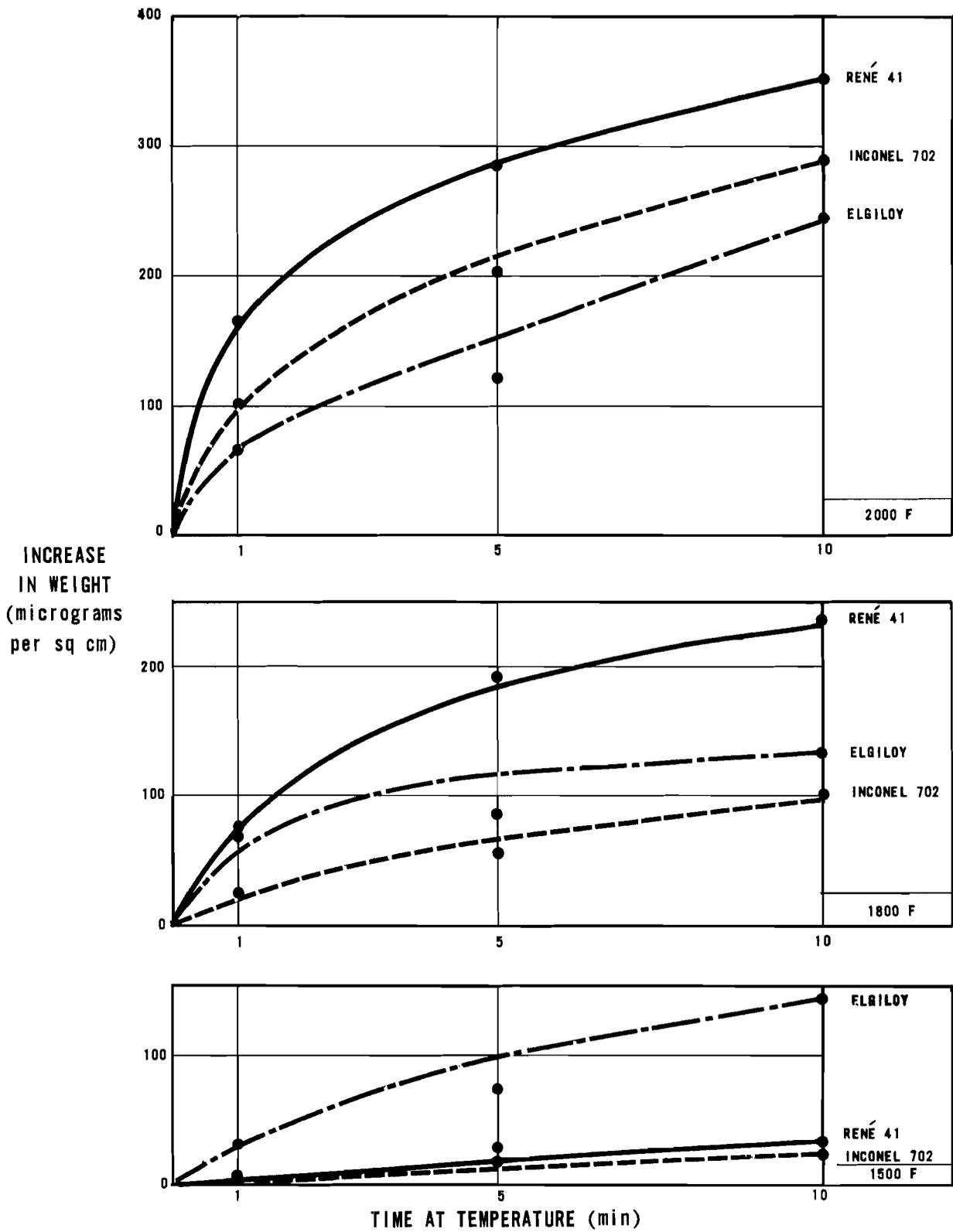


FIGURE 2

Comparison of Oxidation Rates of 1.0-Mil Elgiloy, René 41, and Inconel 702 Wires

2. Tensile Strength and Ductility at Temperature

Figure 3 shows the effect of exposure time in high-temperature air on the high-temperature tensile strength of 0.5-mil Rene' 41 and Elgiloy wires and of 1.0-mil Rene' 41 and Inconel 702 wires. The wires were held for the indicated times and temperatures in the high-temperature tensile test apparatus before a load was applied. There was no significant change in the tensile strength of any of the wires over a 10-minute period at 1500°F. At 1800°F, the tensile strength of 0.5- and 1.0-mil Rene' 41 wires decreased about 25% from 1 to 10 minutes, while the tensile strength of 0.5-mil Elgiloy and 1.0-mil Inconel 702 increased 15%. At 2000°F, the tensile strength of both sizes of Rene' 41 and 0.5-mil Elgiloy decreased about 50% over a 10-minute exposure time, while the Inconel 702 increased in strength 44% in the same time.

All of these wires are made from precipitation-hardened alloys that increase in hardness and tensile strength when heated to 1800-2000°F for a short time. On longer heating above 1800°F, the precipitate either dissolves or agglomerates, so that it loses its effectiveness; in any case, the alloy becomes weaker. These alloys are all quite oxidation resistant; oxide formation is not a significant cause for weakening of sections thicker than about 10 mils. The tensile strength of 0.5- to 1-mil wires can, however, be decreased significantly by very small amounts of oxide penetration. Over a 10-minute heating time, therefore, there are two opposing factors that affect tensile strength of these fine wires: weakening due to oxidation, and strengthening due to changes in the precipitated phases. With Rene' 41 wires at 1800 and 2000°F, it appears that the loss in strength due to oxidation exceeds any strengthening due to heat treatment. The reverse is true of Inconel 702 wires, which have been shown to be more oxidation-resistant than those of Rene' 41 or Elgiloy and indeed there is a net strengthening effect with time at 2000°F. The high-temperature behavior of 0.5-mil Elgiloy wires lies between that of Rene' 41 and Inconel 702, as does its oxidation behavior.

The high-temperature ductilities corresponding to the tensile strengths of the above four wires are shown in Figure 4. The percent elongation at 1500°F does not change significantly on any of these wires over a 10-minute heating period. At 1800 and 2000°F, the ductility decreases with increasing temperature and holding time. The 0.5-mil Elgiloy and Rene' 41 filaments in particular have lost most of their ductility in 10 minutes at 2000°F.

3. Room-Temperature Properties After Heating

The samples of wire used in the oxidation study were tested for tensile strength and percent elongation at room temperature before and after heating in static air. The results of tests on 1-mil wires are shown graphically in Figures 5 and 6.

The rapid drop in tensile strength on heating is especially marked at 1800 and 2000°F, and is more severe for the finer wires. The ductility decreases even more rapidly than the tensile strength, and all three alloy wires are extremely brittle after exposure to 2000°F air for 10 minutes.

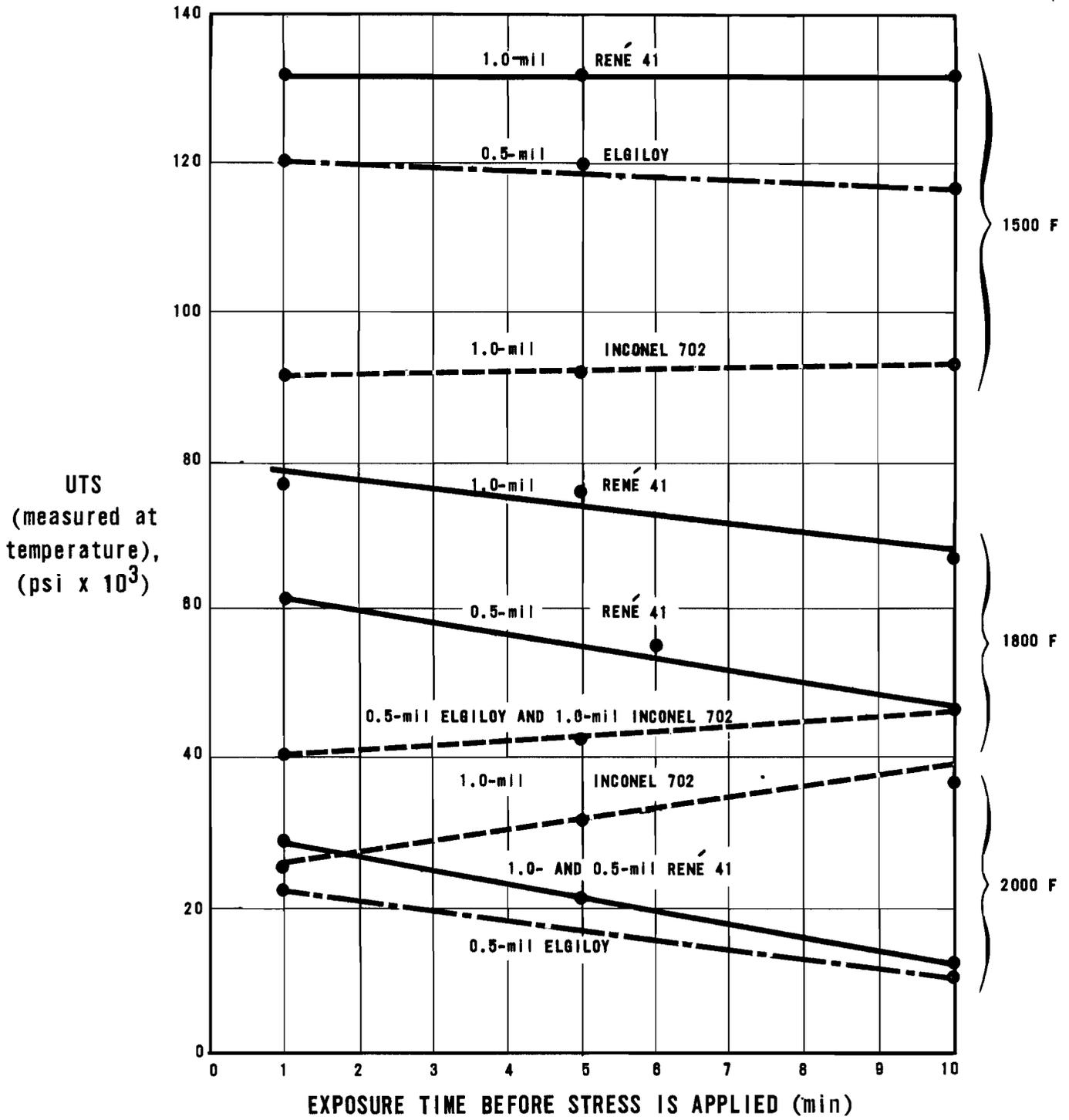


FIGURE 3

High-Temperature Tensile Strength of 0.5- and 1.0-Mil Wire as a Function of Exposure Time at Various Temperatures

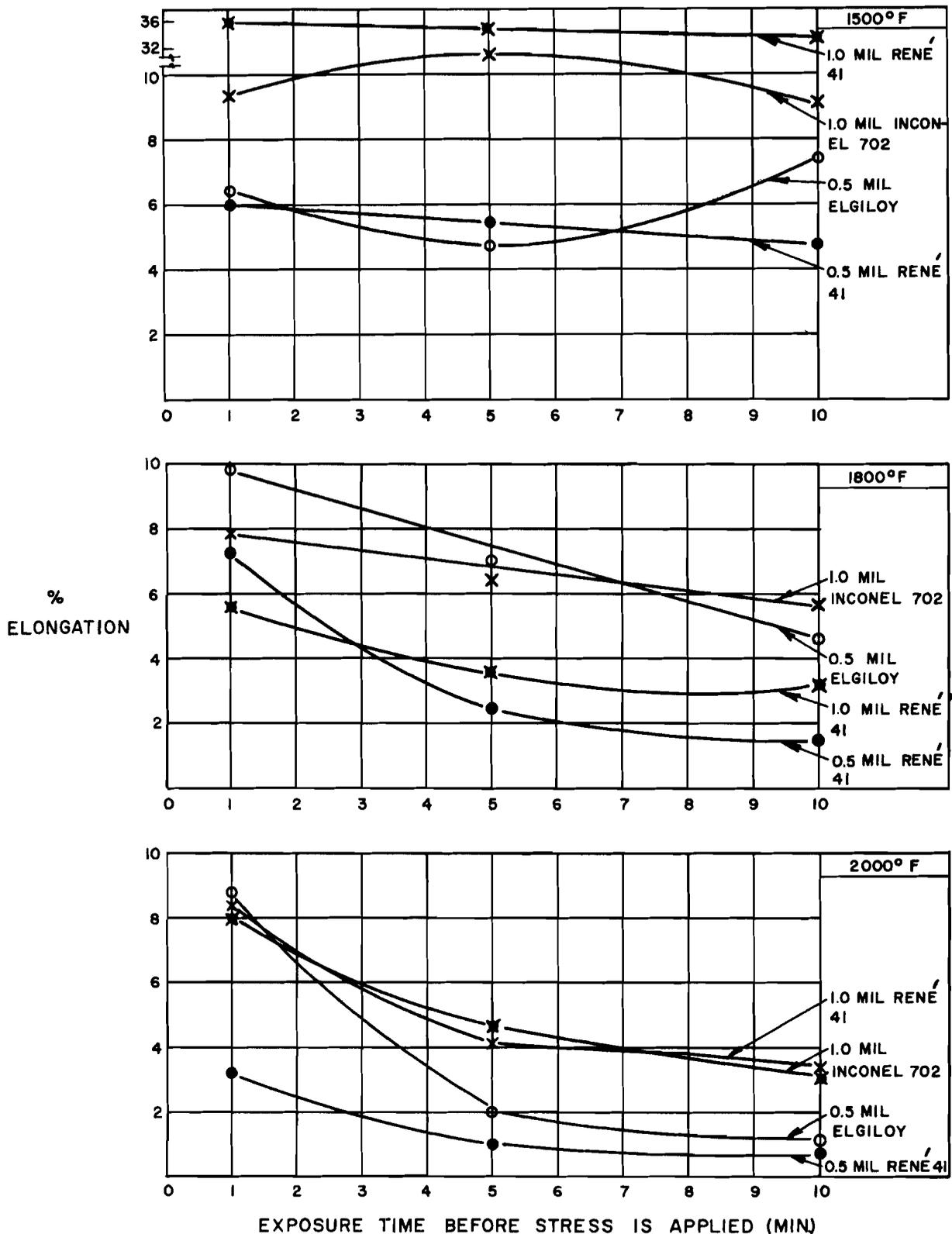


FIGURE 4 | High-Temperature Ductility of 0.5 and 1.0 Mil Wires after Heating in Air at 3 Temp.

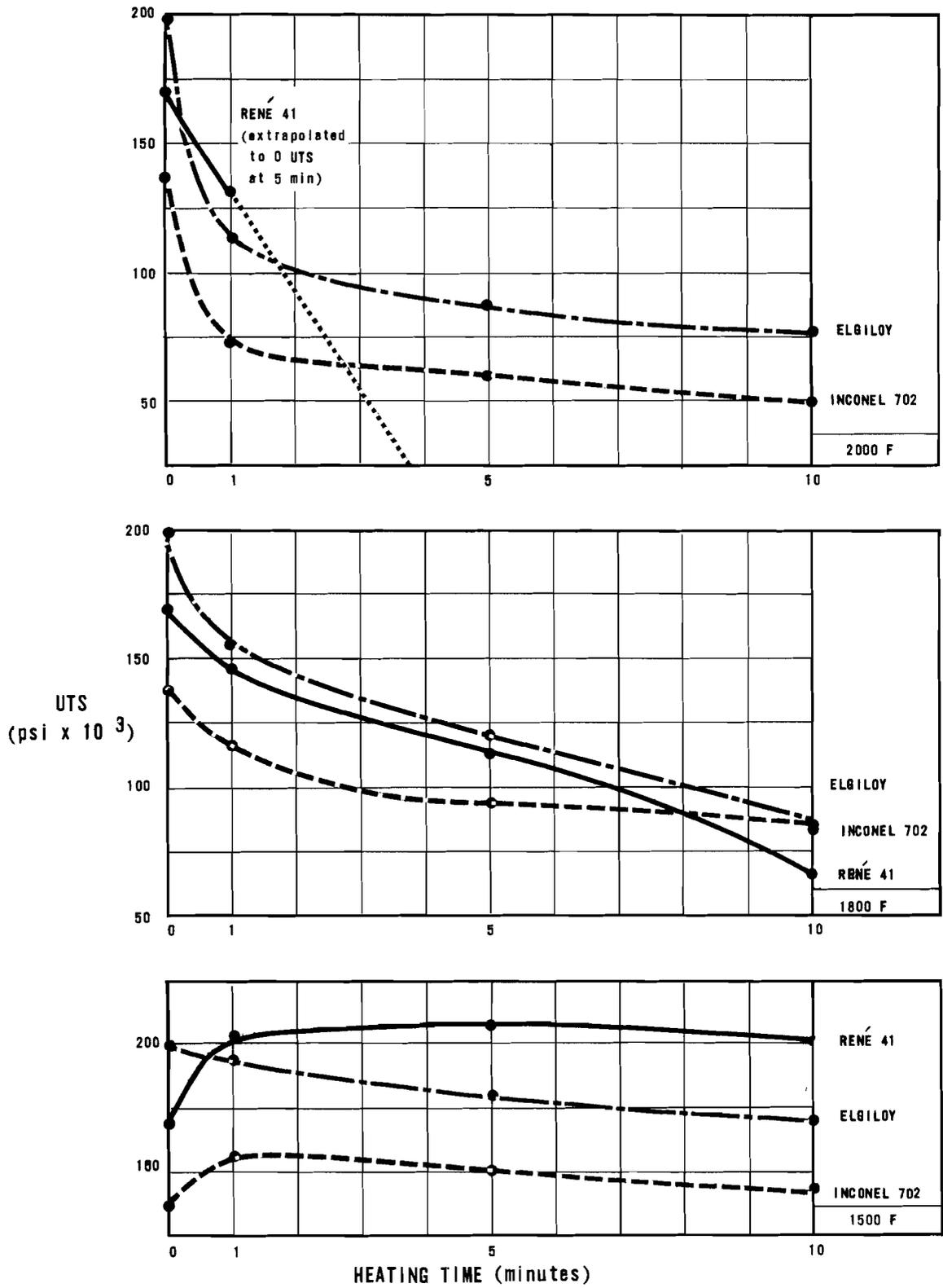


FIGURE 5 Comparison of Room-Temperature Tensile Strength of 1.0-Mil Wire after Heating in Static Air

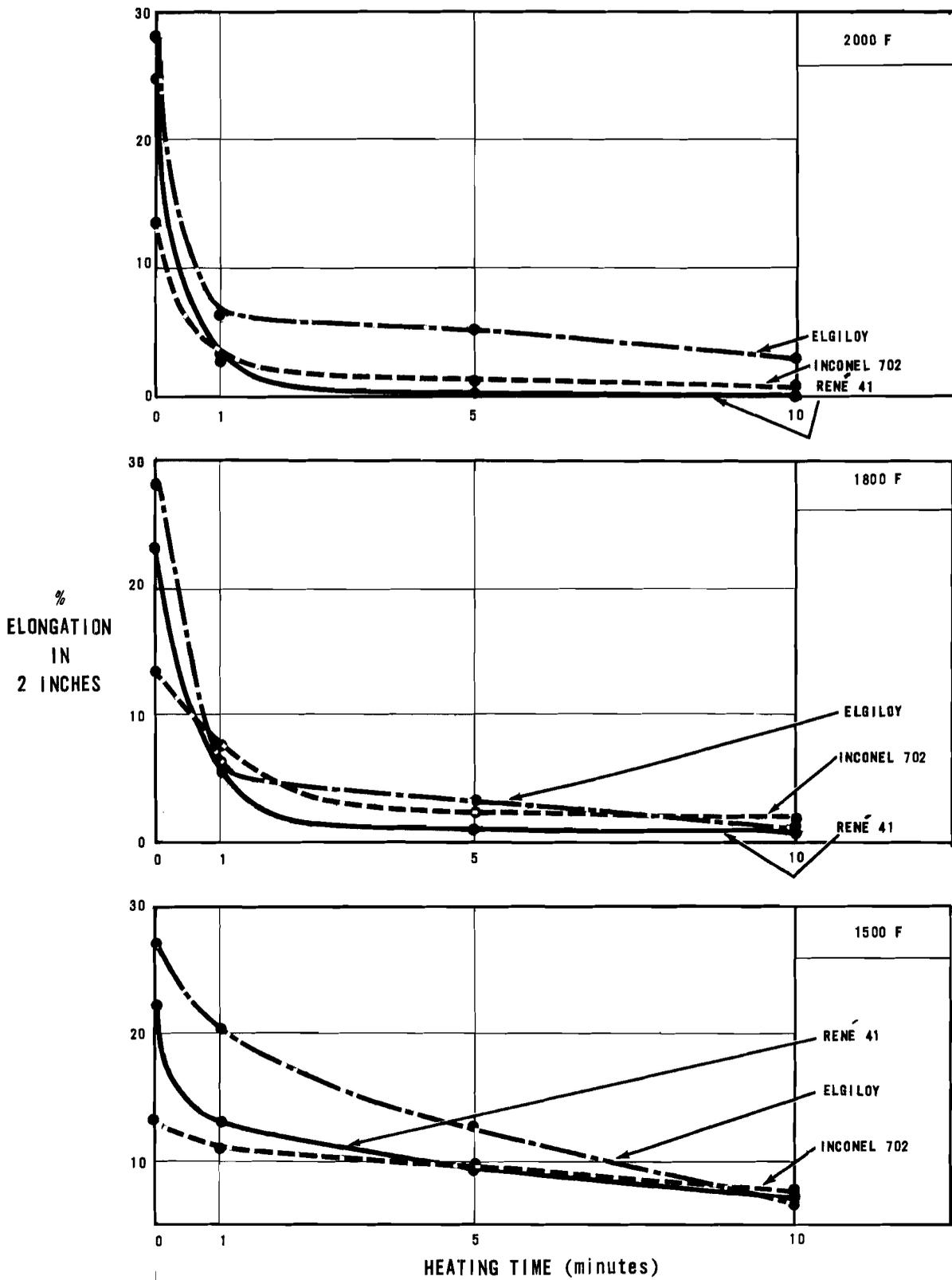


FIGURE 6 Comparison of Room-Temperature Ductility of 1.0-Mil Wires after Heating in Static Air

The loss in strength and ductility is probably due to both oxide penetration and changes in microstructure of the alloys rather than surface oxidation since the loss of cross-sectional area due to metal lost by oxidation is quite small. The drastic loss of ductility after heating and cooling indicates that a fabric made from these alloys would survive only one temperature cycle. If the brittleness is due to oxide penetration, protective coatings may be justified.

D. SHORT-TIME CREEP AT HIGH TEMPERATURE

Calculations of the elastic modulus made from the stress-strain curves of wire samples tested at high temperature show very low values which decrease as much as an order of magnitude from 1500 to 2000°F and which increase with increasing strain rate. This suggests that the behavior of the wires on stressing at high temperatures is one of plastic flow rather than reversible elastic strain over most of the stress-strain curve. Short-time creep measurements were, therefore, carried out in our 1½-inch platinum resistance furnace by hanging various weights on the wires and measuring the extension of the wires at intervals with a cathetometer. In making the creep calculations, the length of the heated zone was assumed to be 1½ inches. Some recent observations on oxidation of refractory metal wires in the furnace indicates that the assumed gauge length may be too high by a factor of 2 to 4 and thus our reported percent creep are too low by the same factor. These values are adequate for comparative purposes, however, and show the extremely high creep. The creep rupture data are not dependent on gauge length and are, therefore, quite accurate.

Figure 7 is a plot of a typical set of data for creep versus time for different applied loads. It is from such data that all other data are derived.

Figure 8 is a Larson-Muller plot for Rene' 41, Elgiloy, and Inconel 702. This plot gives stress vs. "P", where "P" is a function of time and temperature for rupture at the stated stress. As some of the data were obtained by extrapolation of the creep-rupture curves, the results are preliminary. As an example, the line for Inconel 702 crosses over the Rene' 41 line at stress = 21,000 psi and $P = 66$. This can be interpreted in two ways: (1) Above a design stress of 21,000 psi, Rene' 41 will always give better time-temperature results to rupture, or (2) for values of temperature and time that give "P" values above 66 in the equation $P = T(30 + \log t)10^{-3}$, Inconel 702 is better than Rene' 41. Thus, for an operating temperature of 1800°F (2260°R): $66 = 2260(30 + \log t)10^{-3}$, and $t = 0.16$ hour = 9½ minutes; for operation over 9½ minutes at 1800°F, Inconel 702 is better, and below 9½ minutes, Rene' 41 is better.

The relative performance of different alloys can perhaps be seen more readily when data is plotted as in Figure 9. This chart gives less information than does the Larson-Muller plot but requires less data for each alloy, so that two other alloys are also presented for comparison. Two parameters are given: Time to rupture at 1500°F, and time lapsed for 5% creep at 2000°F. As can be seen from the data, at 1500°F the Rene' 41 has the highest creep rupture strength, where at 2000°F the Inconel 702 has the highest (best) stress-time relationship for 5% creep.

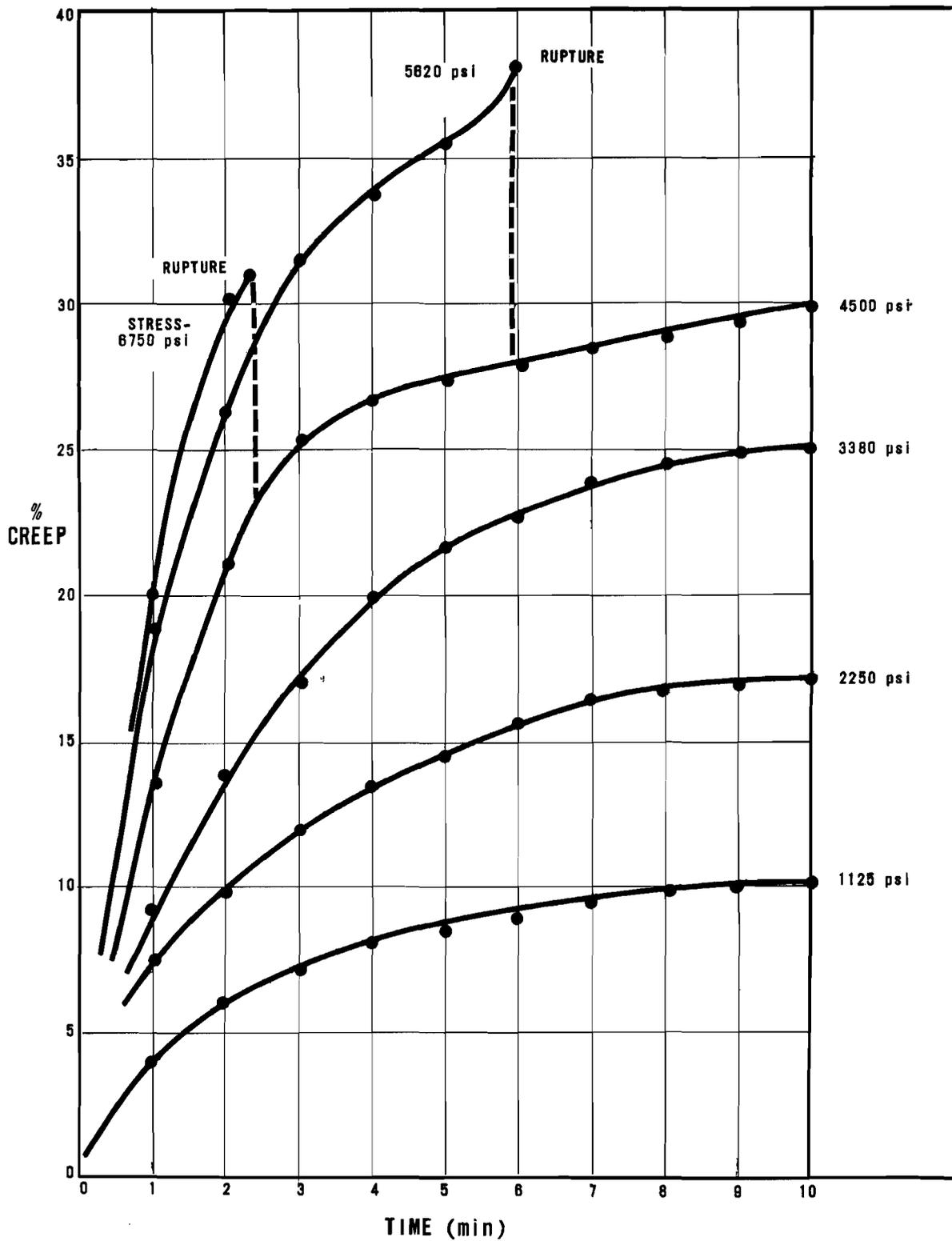


FIGURE 7

Creep of 0.5-Mil René 41 Wire at 2000 F
(Linear Plot)

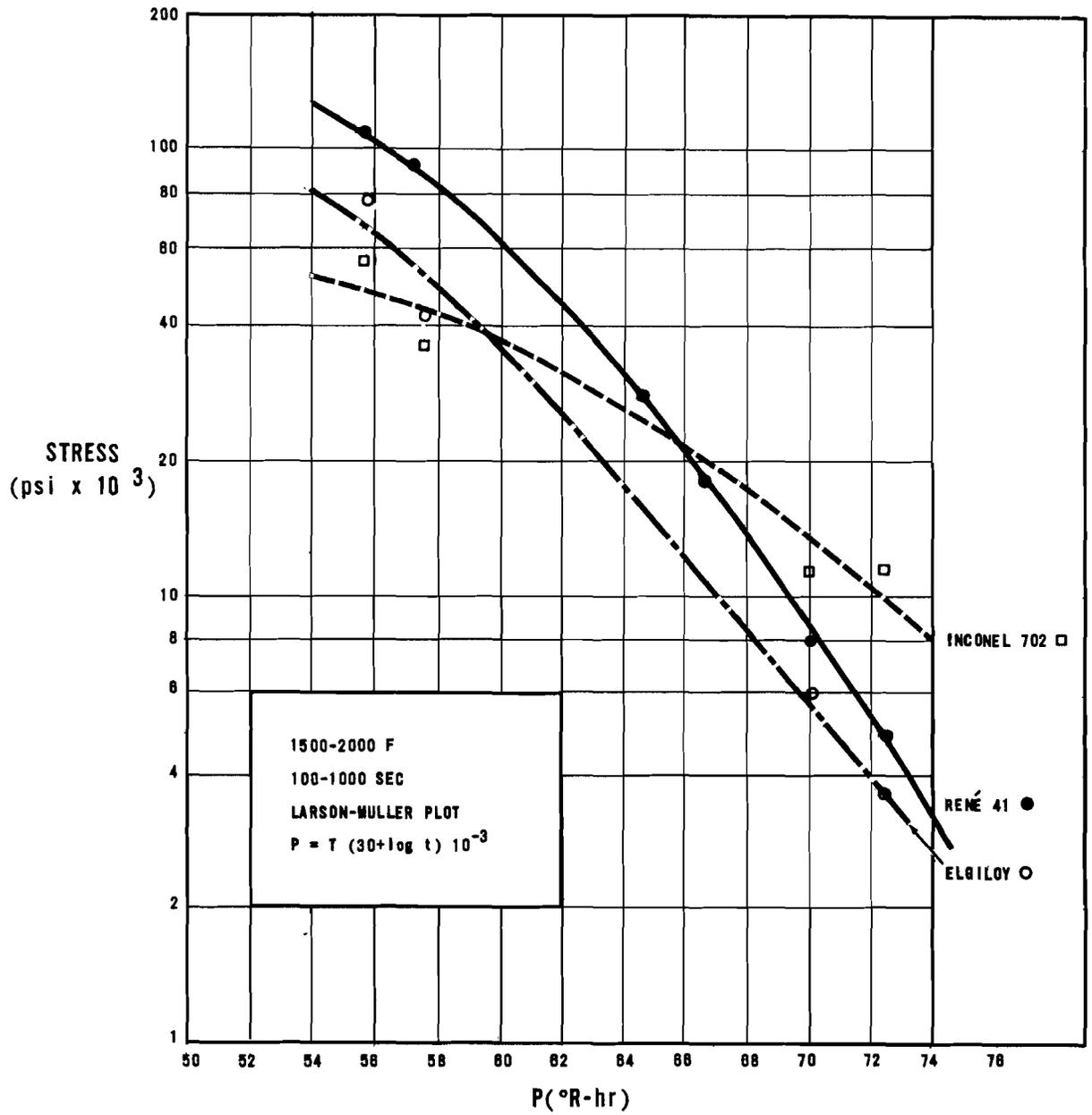


FIGURE 8

Stress Rupture of 1.0-Mil Superalloy Wires

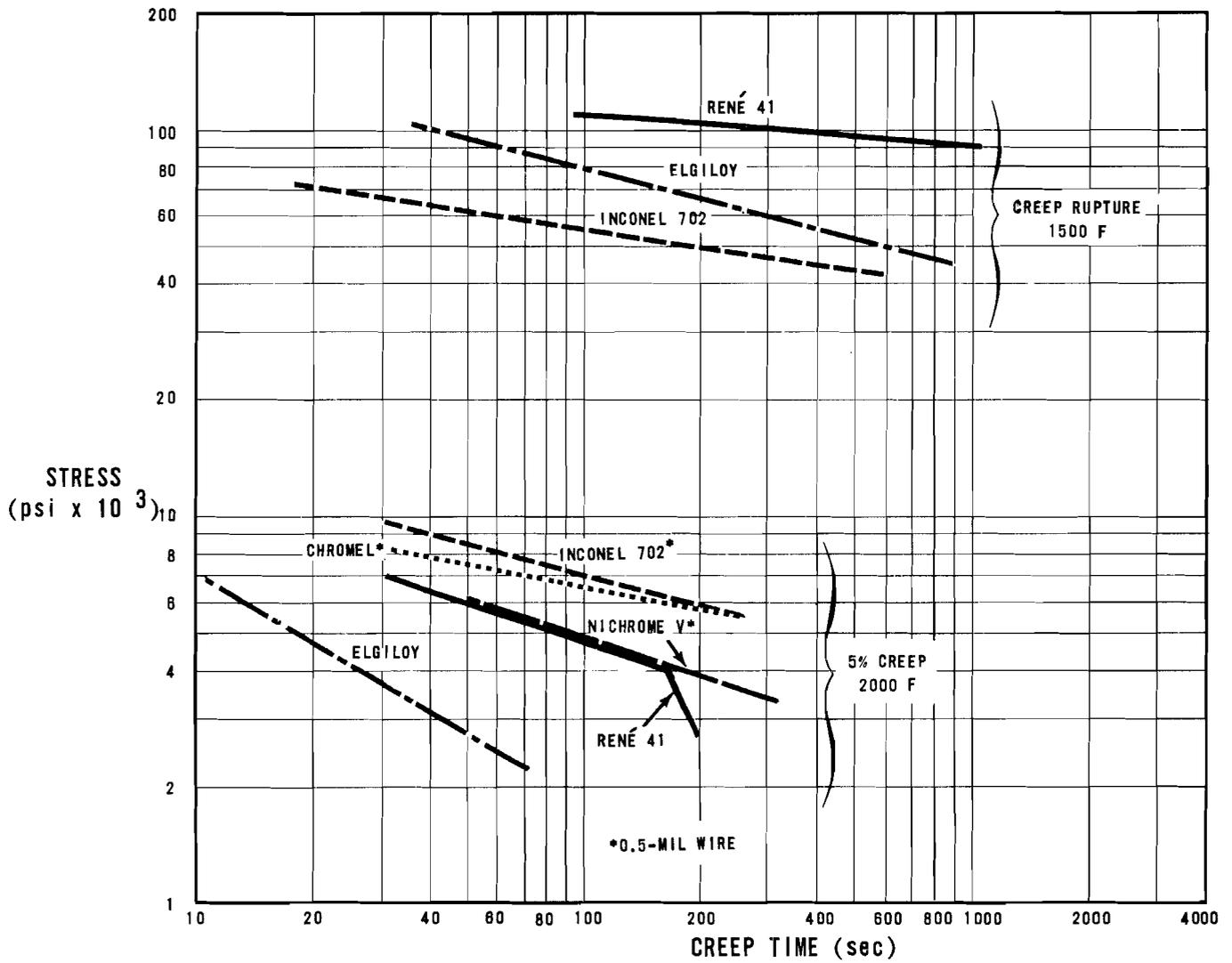


FIGURE 9

Comparison of 5% Creep and Creep Rupture Data for 1.0-Mil Superalloy Wires

Figure 10 shows the effect of wire diameter on stress rupture time for 0.5- to 10-mil Rene'41 wires. For comparison, published creep rupture data for Rene'41 sheet is also shown. It can be seen that for a given unit stress, a 0.5-mil filament has only one-third the creep rupture time of a 2-mil filament. Also, for a given time to rupture, a direct linear relationship was found to exist between wire diameter and stress required to cause rupture. Thus, it appears that the relative effect of a given surface defect or oxidation penetration rises with decreasing diameter wire. It is possible that fine filaments, bunched into yarns and woven into a fabric, would not exhibit this effect to such a marked degree because of the decreased effective length of the filaments; i.e., a break in a filament would invalidate a filament over only a very short portion of its length, on the order of 10-100 yarn diameters. This effect would be expected only in the fabrics, not in the bunched yarns, because the low twist used would not effectively transmit tensile forces from one filament to another.

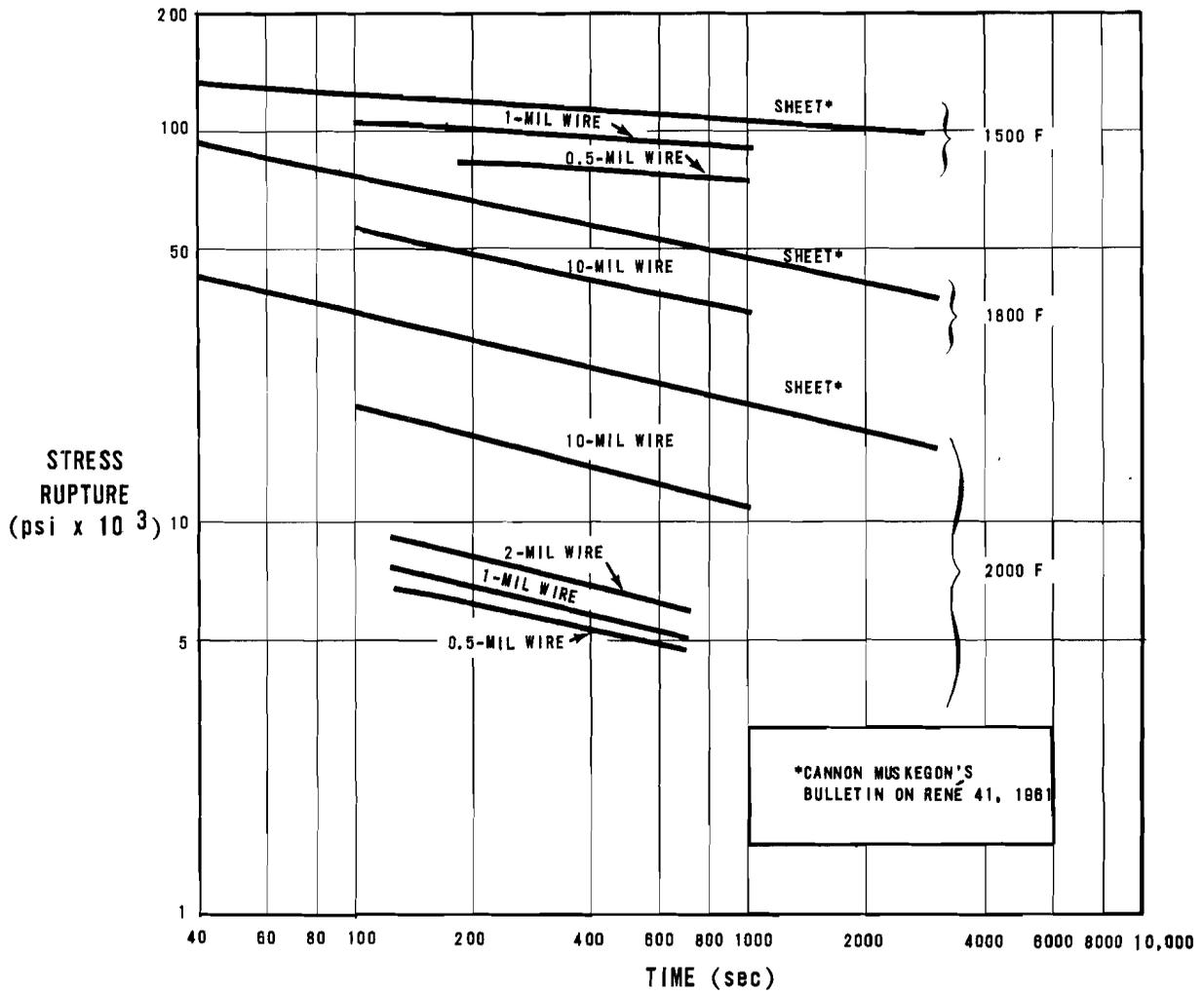


FIGURE 10

Stress Rupture of René 41

IV. REFRACTORY METAL WIRES

A. SHORT-TERM HIGH-TEMPERATURE TENSILE STRENGTH

The oxidation-resistant superalloy wires discussed in the previous section have been considered for use in fabrics that will withstand temperatures up to 2000°F. Above 2000°F, the tensile strength of these superalloys is extremely low, and one must consider the refractory metals and alloys for any application requiring even a moderate stress level.

The short-time high-temperature tensile strengths of 1-mil diameter refractory metal wires were tested in our platinum resistance furnace in a pure argon atmosphere. Five metal and alloy compositions were evaluated: pure tungsten, pure molybdenum, KW molybdenum, 26% rhenium-tungsten, and 50% rhenium-molybdenum. All the wires were in the as-drawn condition. The KW molybdenum (sold by General Electric Company) contains small amounts of an additive that inhibits the recrystallization of the metal at high temperature and thereby reduces the brittleness of the wire. The rhenium-tungsten and rhenium-molybdenum alloy wires were recently developed by Hoskins Manufacturing Company for use as high-temperature thermocouples.* These alloys are reported to have greater room-temperature ductility than pure tungsten or molybdenum after being heated to very high temperatures. The results of these tests are shown in Figure 11.

The superiority of the 26% rhenium-tungsten alloy wire over pure tungsten and the molybdenum alloys in high-temperature tensile strength is quite evident. An inspection of the slopes of these curves indicates that this superiority will be even greater beyond 2000°F. A 0.7-mil diameter wire of the same alloy had a tensile strength of 330,000 psi at 2000°F.

Even though the density of the refractory metals is from 25% to 150% greater than the superalloys, their much greater strength at high temperatures places them in a favorable strength-to-weight ratio. Numerous comparisons of the strength-to-weight ratios of superalloys and refractory metals in bulk, sheet, bar, and rod forms, have been published in recent months. These studies **,*** have shown the superiority of some of the superalloys up to about 1700°F and of the refractory metals above 1700°F.

Figure 12 compares the strength-to-weight ratios of 1-mil wires of Rene 41, Inconel 702, tungsten, molybdenum, KW molybdenum, 26% rhenium-tungsten, and 50% rhenium-molybdenum. Contrary to comparisons of bulk material **,*** the molybdenum wires had a higher strength-to-weight ratio than the superalloy wires from room temperature to 2000°F, while the 26% rhenium-tungsten and the

*Port, J.; *Materials in Design Engineering*, 51, 140 (June 1960)

**Grobeck, D.W. (editor), *Metals for Supersonic Aircraft and Missiles*, ASM, Cleveland, Ohio, 1958, Appendix 4, p. 388.

***Jaffee, R.I., and Maykuth, D.J., "Refractory Materials - Part II High-Temperature Behavior," *Aero/Space Eng.* 19, 39 (July 1960).

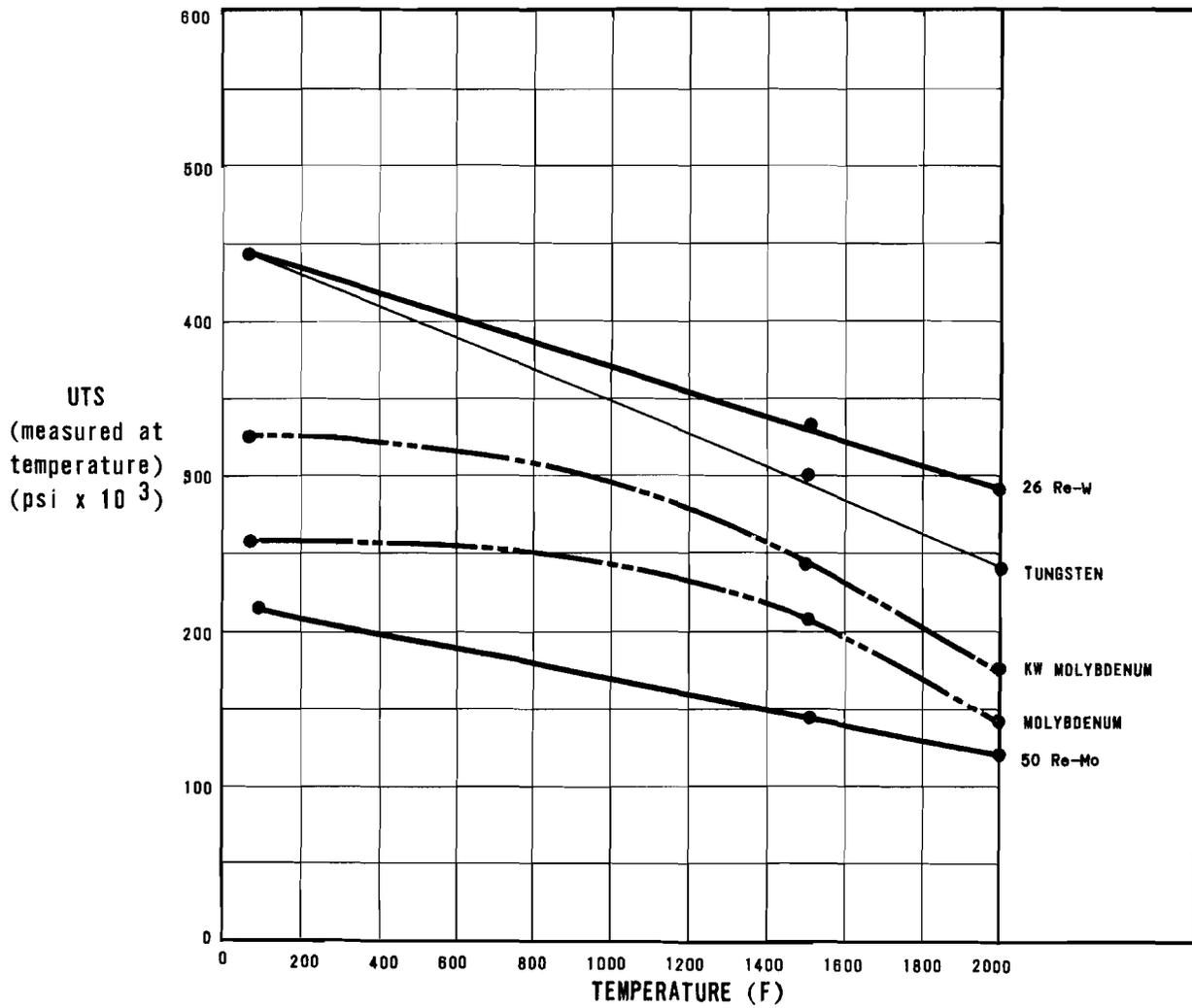


FIGURE 11

High-Temperature Tensile Strength of 1-Mil Molybdenum and Tungsten Wires in Argon Atmosphere

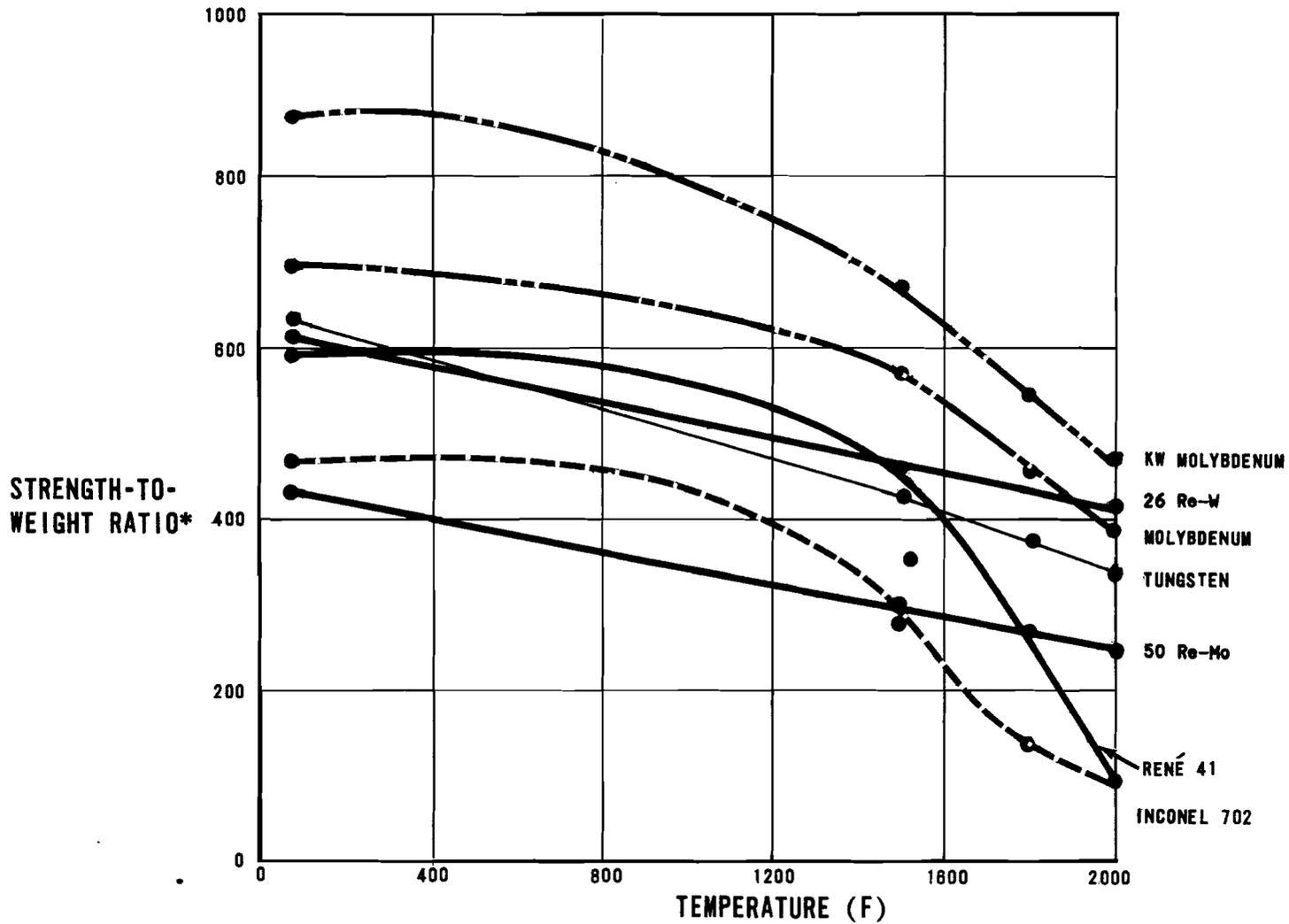


FIGURE 12

Strength-to-Weight Ratio of 1.0-Mil Superalloy and Refractory Metal Wires

*TENSILE STRENGTH (psi) $\times 10^{-3}$
DENSITY (lb/cu in.)

pure tungsten wire was superior above 1500-1600°F. This behavior is the result of the very high room-temperature strengths of the as-drawn refractory metal wires. Extrapolation of the curves seems to indicate the superiority of the 26% rhenium-tungsten wire in strength-to-weight ratio over the other four wires tested beyond 2000°F. Annealed molybdenum wires have not been tested as yet, but since they have about one-half the room temperature tensile strength of as-drawn wires, their strength-to-weight ratio will probably exceed that of the superalloy wires only above 1700°F.

B. DUCTILITY AT HIGH TEMPERATURE

The ductility of these 1-mil refractory metal and alloy wires does not change as uniformly with increasing temperature as does their tensile strength. The calculated values shown below for percent elongation are based on 15-inch samples at room temperature and 1.25-inch samples at high temperature. The absolute percent elongation at high temperature may be in error, because the length of the maximum heated zone is not known accurately. However, we believe comparisons of elongations at a given temperature are valid.

Elongation (1-Mil Wires, Argon Atmosphere)

<u>Test Temperature</u>	<u>Molybdenum</u>	<u>KW Molybdenum</u>	<u>50% Rhenium-Molybdenum</u>	<u>Tungsten</u>	<u>26% Rhenium-Tungsten</u>
Room Temp.	1.5%	1.5%	0.6%	1.9%	1.4%
1500F	4.6%	5.5%	2.0%	5.0%	5.1%
2000F	2.9%	5.5%	1.9%	3.8%	5.6%

The high-temperature ductility of the KW molybdenum wires is somewhat better than that of pure molybdenum and is probably the result of the "doping" material added to the KW to inhibit recrystallization. The rhenium-molybdenum alloy in the massive form is known to have lower high-temperature ductility than pure molybdenum, and the same is true of these fine wires. The ductility of the rhenium-tungsten alloy wires is better than that of pure tungsten only at the highest test temperature, 2000F. The room-temperature ductility of these wires after heating has not been evaluated as yet.

C. CREEP AT HIGH TEMPERATURE

Investigation of the creep behavior of refractory metal filaments at high temperature in an inert atmosphere has just begun. Preliminary data show no discernible creep of a 1-mil tungsten wire in 45 minutes at 2000°F with a load of 55,000 psi.

D. OXIDATION-RESISTANT COATINGS FOR REFRACTORY METAL WIRES

Molybdenum metal oxidizes readily at 480°F and above; tungsten at 570°F and higher. At 1470°F and above, oxides of both metals are quite volatile, and

oxidation-resistant impervious coatings must be applied to them to prevent catastrophic oxidation. The thickness of a coating, which is directly related to its porosity, has long been considered the most important single parameter in evaluating it, whether the coating is designed to provide protection to the basis metal from corrosive aqueous environments or from high-temperature oxidation.

Even though pore-free, the thickness of a metal coating on molybdenum or tungsten is of primary importance at high temperatures because of the likelihood of rapid diffusion of coating-metal atoms into the wire and of basis-metal atoms into the coating, where they may be oxidized. Since in this study we are looking at wires in the 0.5-1.0 mil range for the sake of flexibility, the present investigation was necessarily limited to very thin coatings, and the difficulty of obtaining pore-free films has been magnified tremendously. A number of coating materials and techniques for applying them to fine molybdenum and tungsten wires have been evaluated.

1. Electrodeposited and Electroless Plated Coatings

Coatings were applied by conventional cleaning, activating and plating sequences on 16-inch lengths of 1-mil pregold plated (as supplied by General Electric or Sylvania) molybdenum and tungsten wires and on bare 1-mil molybdenum wires. The thicknesses of the coatings ranged from .01 to .28 mils. The following metals and combinations of metals were applied:

Single Metals

Nickel
Two Types of Chromium,
Bright and High Temp.
Gold
Platinum
Palladium
Rhodium
Electroless Nickel (E. Ni)
Electroless Palladium (E. Pd)

Duplex Coatings

Chrome & Nickel
E. Ni & Chrome
E. Ni & Rhodium
Nickel & E. Ni
E. Ni & E. Pd

Triple Coatings

Ni-Cr-Ni
E.Ni-Cr-Rh
Ni-E.Ni-Cr

Quadruple Coating

Ni-E.Ni-Cr-Rh

The coatings were evaluated by exposing the wire to 2000^oF air with and without a weight hanging on wire. The time necessary to burn up the wire or for the wire to break was compared with a control wire with no coating.

Almost all these coatings provided some protection, but generally the wire had either failed in 60 seconds or the wire was so brittle by this time that it broke on handling. The best coating was a composite of nickel-electroless nickel and chromium on 1-mil molybdenum which lasted 4 minutes in one test. Other samples only lasted 45 to 60 seconds.

In the present state of the art, the protection of 1-mil or smaller refractory metal wires from oxidation in 2000°F air with .05 to 0.10-mil thick electrodeposited or electroless plated coatings does not appear feasible.

2. Vapor Phase Coatings

Several 16-inch lengths of 1-mil molybdenum wire were coated by the vapor phase coating method. Chromium was deposited from di-cumene chromium, nickel from nickel carbonyl, and silicon from silicon tetrachloride. Combinations of chromium-nickel were also deposited and diffused together by heating in argon.

None of the chromium vapor deposits in the thickness range of 0.05 to 0.25-mil significantly improved the oxidation behavior of 1-mil molybdenum wire at 2000°F. Chromium deposits were also made on 2-mil nickel-clad molybdenum wire. Some improvement was obtained on a sample that was given a 5-minute diffusion treatment after coating but not enough to be of interest.

Nickel was applied by vapor deposition from nickel carbonyl. The thicknesses varied from 0.3 to 1.2 mil. The heated zones on some of the nickel-plated wires that had been exposed for 30 minutes in the platinum furnace without failure were inspected at 1000X. They were covered with a greenish-yellow amorphous coating that could be scraped off easily, leaving the bare molybdenum wire. Presumably, the coating was an adherent mixture of nickel and molybdenum oxides that inhibited further oxidation and volatilization of the molybdenum. None of the nickel coated wires broke after 30 minutes at 2000°F with the standard 0.18-gram weight used in most of the tests (equivalent to only 510 psi on the 1-mil wire). With a 10-gram weight, the wires with thinner nickel coatings broke within one minute, probably because the composite oxide layer was gradually fractured due to creep of the partially oxidized wire.

Composite coatings of chromium-nickel were applied by vapor deposition. The chromium was deposited first; the plating chamber was then swept free of the di-cumene chromium plating with pure argon, and nickel was applied over the chromium by nickel carbonyl gas plating. In two experiments the composite coating was given diffusion heat treatment. The composite coatings were considerably more protective than single deposits of chromium or nickel. However, it appears that a minimum total thickness of 0.5 mil is needed for 5-minute protection. All of these wires were very brittle and broke easily on bending.

One attempt was made to produce a siliconized diffusion coating on molybdenum wire by the hydrogen reduction of silicon tetrachloride. The coating resembled metallic silicon, and it is doubtful if much molybdenum disilicide was formed. Although the coating improved the oxidation resistance of the molybdenum wire somewhat, it was far from adequate since it lasted only 51 seconds in 2000°F air.

3. Clad Metal Coatings

Three clad refractory metal wires were obtained and evaluated. They were made by applying the cladding metal to a heavy wire or bar of molybdenum or tungsten and drawing the composite to size.

A 3-mil 38% platinum clad molybdenum wire and a 1-mil 24% platinum clad tungsten wire supplied by the Baker Platinum Division of Engelhard Industries, Inc. were tested in 2000°F air. The cladding on the molybdenum wire was 0.18 mils thick and .06 mils thick on the tungsten wire. Because of the thickness of the platinum claddings, these wires should have represented the ultimate in protective coatings, provided they were continuous. Unfortunately, this did not appear to be the case. In one test in which a 0.18-gram weight was used, the platinum seemed to be protecting the molybdenum very well. However, microscopic examination of the heated area showed that the weight was being suspended only by the platinum shell; all of the molybdenum had apparently distilled off through sub-microscopic pores and cracks in the cladding. A 5-gram load was sufficient to break the cladding after the molybdenum oxide had vaporized in about 2 minutes. A 3-mil bare molybdenum wire was not available as control, but it is probable that the clad wire would not last much longer than a control. There did not appear to be a metallurgical bond between the platinum and the molybdenum, since the cladding split off when the wire was heated suddenly in a gas flame. This was probably due to difference in coefficient of expansion of the two metals.

The 24% platinum-clad tungsten wire appeared quite badly scored under the microscope, and therefore it is not surprising that it had no better oxidation resistance than a bare tungsten control wire.

A 2-mil 15% nickel-clad molybdenum wire obtained from the General Electric Company (the nickel cladding was .09-mils thick) behaved in much the same manner as the 38% platinum-clad molybdenum wire. Figure 13, a photomicrograph of the broken area after the wire was exposed to 2000°F in the platinum furnace for 12.5 minutes, shows holes and cracks in the coating adjacent to the break. Obviously, the molybdenum oxidized and distilled out through the cracks, leaving behind a shell of nickel and nickel oxide.



FIGURE 13

2-Mil Diameter Ni Clad Mo Wire after 12 1/2
Minutes in 2000 F Air

4. Diffusion Coatings

The W-2 diffusion-type coating developed by the Chromalloy Corporation and the chromium diffusion coating of the Alloy Surfaces Company, Inc. were applied to 1-mil molybdenum wires by these companies. In both cases, a coating 0.1-0.2 mil thick was not sufficient to protect the wires for more than a few seconds in high-temperature air. Attempts to produce a thicker W-2 coating resulted in complete embrittlement of the wire.

5. Hot-Dip Coatings

The most promising coating to date is a hot-dip tin-aluminum coating originally developed for tantalum sheet by the Sylcor Division of Sylvania Electric Products, Inc.

Considerable work has been done on applying these hot-dip tin-aluminum coatings to various fine refractory metal wires. The best coating to date has been made in an 80 tin - 20 aluminum hot-dip melt on a 1-mil gold-plated tungsten wire. Samples of this wire with a 0.15-0.30 thick coating have withstood 16 to 23 minutes in air at 2000°F as compared with 13 seconds for an uncoated control wire.

V. ALTERNATE METHODS FOR FORMING FINE METAL FILAMENTS

A. COLD-DRAWING OVER A CERAMIC PIN

The expense of forming metal filaments by conventional cold-drawing techniques abruptly increases when the wire size approaches the 10-mil range, for at this point there is a change from carbide dies to diamond dies. In the 10-mil range, the diamond die itself is expensive because of its size, and as we go to smaller wires, the cost of drilling the ever-finer holes in the diamond becomes the predominant cost. At the 1-mil to $\frac{1}{2}$ -mil wire range, the length of wire per pound of metal processed becomes enormous, but so does the wear on the diamond dies.

One approach toward developing an inexpensive fine-wire process would be to start with wires in the 10-mil range made in the normal way with carbide dies. These wires would then be cold-drawn over a ceramic draw pin to localize the point of drawing, in a manner similar to that of the carbide or diamond die. The wires would then be annealed to increase the residual elongation before redrawing to a still finer size. This process, if successful, would not only have the advantage of eliminating the diamond die but would have the greater advantage of allowing the drawing of many filaments simultaneously, in contrast to the single-strand operation of the diamond die process.

Considerable effort was expended in developing equipment and techniques for cold drawing 10-mil wires of 304 stainless steel, Rene 41, nickel, and copper over a ceramic pin as outlined above. Although all of these wires have been drawn to smaller sizes by this process, the best results were obtained with stainless steel. A practical process has yet to be demonstrated, however, chiefly because of the increasing variability of wire diameter with each cold-drawing-annealing operation as shown in Figure 14.

B. ELECTROFORMING

One of the alternate approaches to conventional wire drawing of fine metal filaments considered in this investigation was the electroforming of metals or alloys on a mandrel so constructed that the deposit can be removed in a continuous filament as plating proceeds. While it may not be possible to produce a filament with a circular cross section by electroforming, rectangular or semi-circular cross sections are possible and may be acceptable for many applications.

The electroforming of thin metal sheets is a well-known process. For instance, the Chromium Corporation of America, Waterbury, Connecticut, will supply unsupported pore-free sheets of pure copper or nickel down to 0.02-mil thickness. These films are made by electrodepositing the metal from a purified plating bath onto a polished, chrome-plated cylindrical mandrel. After plating, the deposit is cut through along the axis of the cylinder and peeled off from the chromium plate, to which it does not adhere. Electroformed copper sheet, made by plating on a rotating drum, has long been an article of commerce.

Our first experiments in electroforming metal filaments were made by plating nickel into the metallized grooves or on the spaces between grooves of a plastic mandrel, i.e., a plastic phonograph record. This approach was abandoned because the extremely long and thin silver metallizing coating had too high a resistance to provide a uniform plating current density.

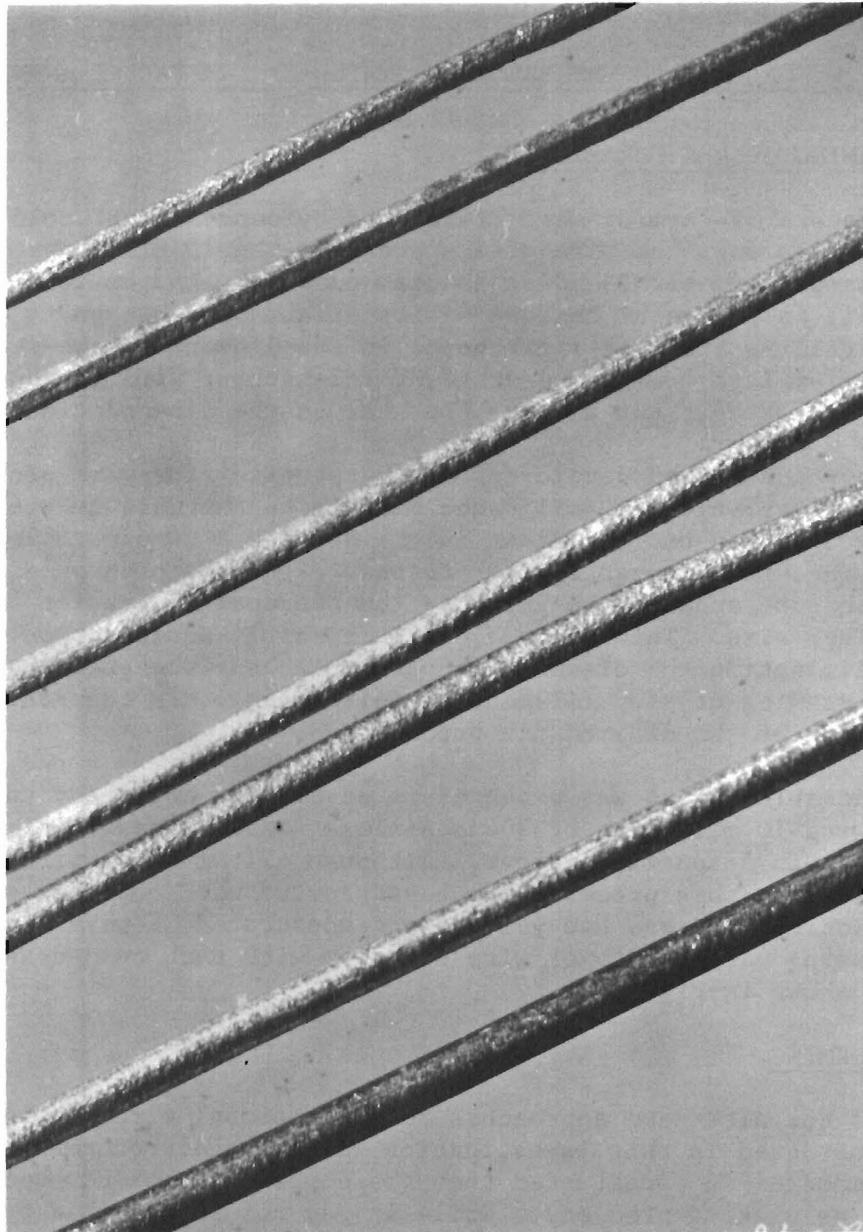


FIGURE 14 | 10-Mil Diameter 304 Stainless Steel Wire with Samples from Six Successive 20% Draws with Subsequent Annealing

Most of our electroforming experiments have been directed toward the deposition of nickel filaments on selectively stopped-off cylindrical helical mandrels. One of these mandrels was made from a copper pipe on which a continuous fine thread was cut. While the pipe was still in the lathe, an epoxy resin was applied in and over the threads. After the resin had hardened, the tops of the threads were exposed by machining away the resin, leaving resin in the grooves. Nickel was plated on the exposed groove tops and removed as a long continuous filament as shown in Figure 15.

Nickel filaments about 1.4 x 8 mils in dimensions were produced in the same way on another mandrel made from free-machining brass. These filaments had a room temperature tensile strength of 100,000 and an elongation of 1.5%.

Further work is in progress with mandrels from which 0.2 x 1.0 mil filaments can be made.

C. VAPOR DEPOSITION

Another method that we considered for producing fine metal filaments was the thermal decomposition of metal-organic compounds from the vapor state. The techniques and apparatus are similar to those used in coating refractory metal wires by vapor plating. The main difference between the two methods is the substrate on which the metal vapor is decomposed.

Two techniques for selectively decomposing nickel carbonyl to form thin filaments of nickel were investigated. In one series of tests, an india ink line was drawn on a strip of glass or polished aluminum; the strip was then placed in a glass tube 2 inches in diameter and 16 inches long, and a nickel carbonyl-argon plating gas mixture was passed through. An attempt was made to heat the black line selectively by radiant energy from a photoflood bulb or an infrared heating lamp. Although the black line was heated enough to decompose the nickel carbonyl on it, sufficient heat was also conducted into the substrate to deposit nickel along the edges of the line. Previous experience with this technique proved that selective deposition can be attained if the radiant energy is very great and of short duration, such as that produced by large flash bulbs. This type of heating is extremely inefficient and expensive, however, and further experiments with radiant heating were discontinued.

The second technique we tried was electric resistance heating of the surface on which deposition was desired. A fine line was drawn along the length of a 0.5-inch diameter glass tube with Du Pont conducting silver paint. After the paint was cured, the tube was positioned in the center of the larger plating tube through which a mixture of nickel carbonyl and argon was passed. Water flowing through the smaller glass tube cooled it as the painted line was heated from a direct-current source. This arrangement worked quite well, and a nickel filament was deposited selectively on the silver line in about two minutes. The filament could not be removed in one length, because local differences in the thickness and width of the silver line caused unequal heating and thus unequal deposition of nickel. Sections a few inches long were removed with a razor blade and tensile-tested. The strength of these strips (which measured approximately 0.2 x 20 mils) was very low--on the order of 1000psi--mostly because of wide variations in thickness.



FIGURE 15

Continuous Nickel Filament Electroformed
on Cylindrical Copper Mandrel

These experiments illustrate that the formation of fine metal filaments by vapor deposition is possible. The major advantage of this technique over the electroforming method is the speed with which vapor-deposited films may be deposited (up to 1 mil per minute in the case of nickel carbonyl plating).

