APEX-365

Calibration of Rhenium - Molybdenum and Rhenium - Tungsten Thermocouples to 4000 °F

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GENERAL ELECTRIC
ATOMIC PRODUCTS DIVISION
AIRCRAFT NUCLEAR PROPULSION DEPARTMENT

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TID-4500 (13th Ed., Rev)
UC-80 Reactors – General

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Applied Materials
Research Sub-Section

April 30, 1958

United States Air Force — Contract No. AF 33(038)-21102
United States Atomic Energy Commission — Contract No. AT (11-1)-171

GENERAL ELECTRIC
ATOMIC PRODUCTS DIVISION
AIRCRAFT NUCLEAR PROPULSION DEPARTMENT
CINCINNATI 15, OHIO

Published by
Technical Publications Sub-Section
April 30, 1958

Abstract

Calibration curves to 4000°F have been established for rhenium-molybdenum and rhenium-tungsten thermocouples in vacuum, hydrogen, or inert atmospheres. The practical application of rhenium-molybdenum thermocouples is limited to measurements up to 3200°F. Rhenium-tungsten thermocouples, however, measure temperatures up to and apparently higher than 4000°F.

Introduction

The need for materials that are suitable for thermoelectric applications has increased because of accelerated programs in the research of high-temperature materials and the limitations of existing thermocouples. For example, a thermocouple that is reliable for the measurement of temperatures to 4000°F in reducing or neutral atmospheres would be especially useful for determining melting points, controlling furnace temperatures, and studying phase diagrams.

In the past the measurement of high temperatures by means other than the optical pyrometer method has been the subject of extensive research. Platinum thermocouples, which are useful for temperatures to about 2600°F, are unstable in hydrogen and are generally satisfactory only in oxidizing atmospheres. Chromel-Alumel thermocouples have a temperature limitation of about 2000°F. Tungsten-molybdenum and tungsten-iridium thermocouples are limited because the tungsten-molybdenum combination has a low thermal emf and becomes brittle upon temperature cycling and because iridium is extremely brittle and is very scarce.

In the selection of a suitable thermocouple material a survey was made of metals known to have high melting points. Rhenium was of particular interest because of its strength and ductility. In addition, it was available in the form of commercial wire products. For these reasons initial efforts were concentrated on a study of rhenium in combination with other high-temperature metals.

Rhenium was suggested as a replacement for rhodium in platinum-rhodium thermocouples nearly thirty years ago, and a limited amount of work has been reported in European literature. Recently, investigations of rhenium have been conducted at Battelle Memorial Institute under the auspices of the United States Air Force.* As a result of this work rhenium combined with platinum was found to be a promising material for thermocouples. Furthermore, it was found that rhenium combined with molybdenum or tungsten could possibly be used for very-high-temperature applications. The studies at Battelle provided a basis for extended investigation of rhenium-molybdenum and rhenium-tungsten thermocouples at General Electric.

Thermocouples composed of these materials were found to have the following advantages:†

1. High thermoelectric potential.
2. High thermoelectric power.
3. Very high melting point of all components in the rhenium-tungsten and rhenium-molybdenum thermocouples.
4. Chemical stability in neutral or reducing atmospheres for rhenium-tungsten or rhenium-molybdenum thermocouples.
5. Ductility for rhenium or rhenium-alloy legs of thermocouples after temperature cycling.

*WADC Technical Report 56-319, "A Survey of the Literature on Rhenium," C. T. Sims, et.al., Battelle Memorial Institute, ASTIA Document No. AD 110596, June 1956.

†Ibid.

A series of calibration experiments has been conducted at ANPD to test the performance of rhenium-molybdenum and rhenium-tungsten thermocouples in hydrogen, vacuum, or inert atmospheres at high temperatures. In the first set of experiments a calibration curve was established to 3200°F, and in the second group the curve was extended to 4000°F. The following discussion of thermocouple studies includes a description of materials and procedures and a review of results for both sets of experiments.

Experimental Procedure

The objective of the initial investigation was to calibrate rhenium-molybdenum and rhenium-tungsten thermocouples with sufficient accuracy to permit their use in instrumentation. Experiments were also conducted to determine the effect, if any, of continuous temperature cycling in neutral or reducing atmospheres.

Pure molybdenum and tungsten wire were readily available, and a quantity of 0.025-inch-diameter, high-purity rhenium wire was obtained. Chemical analyses of the basic materials used are shown in Table 1. Rhenium-molybdenum and rhenium-tungsten thermocouples were prepared by joining the component wires with inert arc welding. Platinum/platinum - 10 rhodium and Chromel-Alumel thermocouples were prepared as standards and calibrated. Double-bore beryllium oxide refractory sleeves were used to insulate that portion of the thermocouples that was in the hot zone of the furnace.

Calibration was carried out in high-temperature vacuum furnaces normally used for sintering. A cross section of the apparatus is shown in Figure 1. The junctions of a rhenium-molybdenum and rhenium-tungsten thermocouple were inserted into holes in a 2-inch-diameter molybdenum cylinder that was suspended in the hot zone of a high-temperature vacuum furnace by means of molybdenum rods. The thermocouple wires were brought out through rubber seals in the muffle cover.

In the first set of experiments a standardized platinum/platinum - 10 rhodium thermocouple was installed in a similar manner to measure reference temperatures, but this type of thermocouple proved to be unstable in vacuum. Therefore, the apparatus was modified to permit heating of the platinum thermocouple in a normal atmosphere while the rhenium thermocouples were heated in vacuum. The closed end of a heavy-wall aluminum oxide protection tube was inserted into the molybdenum cylinder and was sealed by a rubber stopper in the muffle cover. This arrangement proved adequate for isolating the platinum-rhodium reference thermocouple from the furnace atmosphere, and the aluminum oxide tube proved satisfactory for temperatures up to 3200^{o}F. The cold junctions of all thermocouples were maintained at 32^{o}F in an ice bath.

A vacuum of 5 microns was maintained in the furnace muffle while the temperature versus emf relationship for rhenium-molybdenum and rhenium-tungsten thermocouples was obtained up to 3000^{o}F; a high-precision Minneapolis-Honeywell Rubicon, using the platinum-rhodium standardized thermocouple, was used to measure temperatures. Chromel-Alumel thermocouples were calibrated to 2500^{o}F in the same manner. The accuracy of the reference temperatures was substantiated by recalibration of the standard platinum-rhodium thermocouple at the conclusion of the experiments. Above the range of platinum-rhodium thermocouples (3000^{o}F), temperatures were measured with a

TABLE 1

CHEMICAL ANALYSES OF MATERIALS USED FOR THERMOCOUPLE STUDIES

Elements	Rhenium, %	Molybdenum, %	Tungsten, %
Chromium	< 0.01	< 0.10	< 0.01
Nickel	< 0.01	< 0.10	< 0.01
Iron	< 0.1	< 0.10	< 0.1
Cobalt	< 0.01	< 0.01	< 0.01
Manganese	< 0.01	< 0.10	< 0.01
Boron	< 0.005	< 0.005	< 0.005
Lithium	< 0.005	< 0.005	< 0.005
Cadmium	< 0.005	< 0.01	< 0.005
Lead	< 0.005	< 0.005	< 0.005
Copper	-	< 0.01	-
Zirconium	-	< 0.005	-
Hafnium	-	< 0.005	-
Tantalum	< 0.01	-	< 0.01
Titanium	< 0.01	-	< 0.01
	Balance Rhenium	Balance Molybdenum	Balance Tungsten

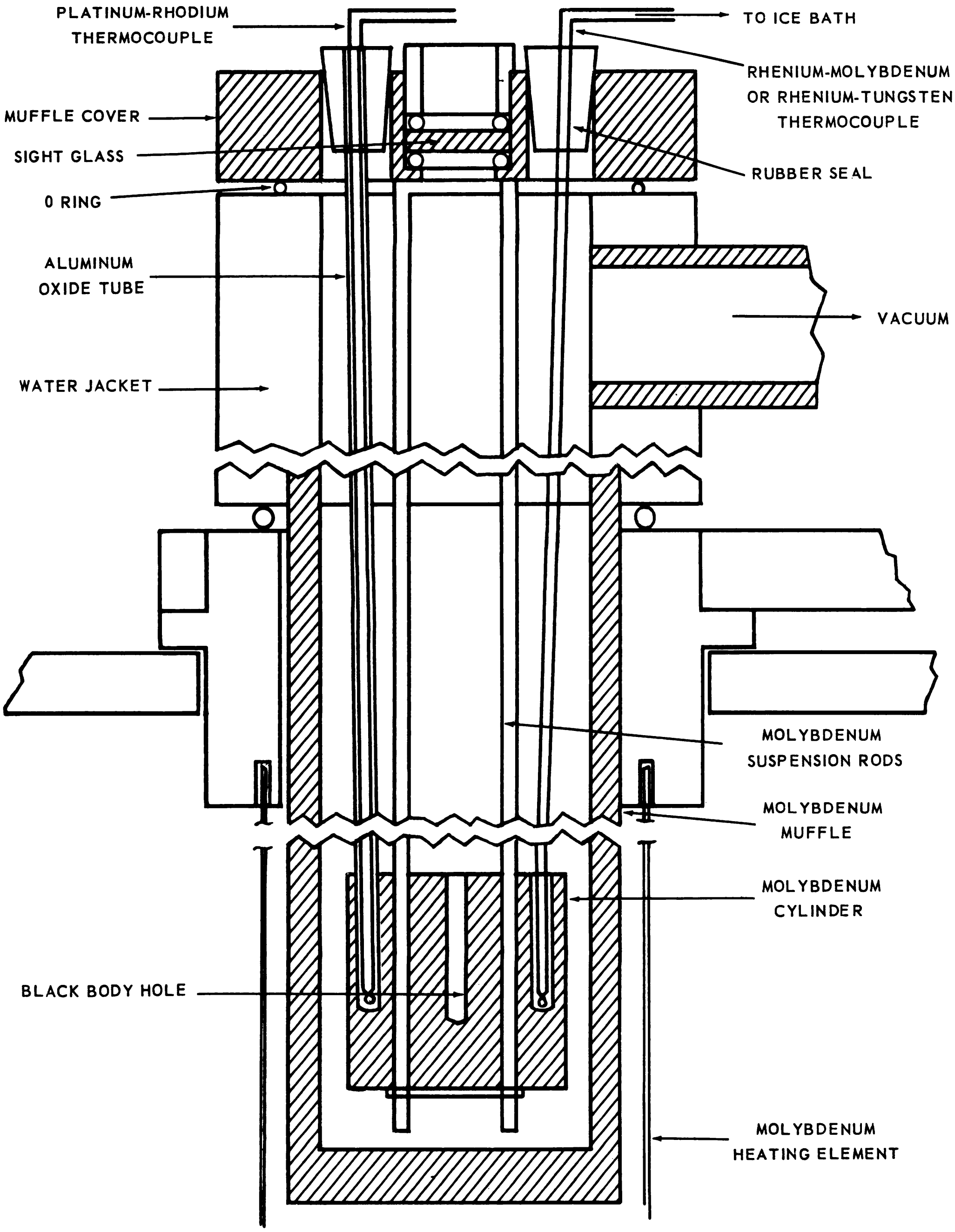

Fig. 1 – Thermocouple calibration apparatus

standardized optical pyrometer by sighting on a black-body hole in the molybdenum cylinder. This optical method was also used to make frequent checks of the reference thermocouple at lower temperatures.

After several preliminary calibration runs a second rhenium-molybdenum thermocouple was installed in the molybdenum cylinder adjacent to the original rhenium-molybdenum thermocouple. The thermal stability of rhenium thermocouples was proved by comparing the emf of the new thermocouple with the emf of the one that had been temperature-cycled several times. A possible source of error due to induced emf from the furnace heating element was eliminated by adequate filtering of the thermocouple input to the potentiometer. Filtering resulted also in faster instrument response.

Additional proof of the thermal stability of rhenium thermocouples was shown by comparing the emf of a new rhenium-molybdenum thermocouple operating in vacuum with that of another that had been temperature-cycled many times in a hydrogen atmosphere. The latter thermocouple had previously been installed in the furnace close to the heating element.

Results

Both rhenium-molybdenum and rhenium-tungsten thermocouples produced a high emf and exhibited good sensitivity to temperature change. The data for the calibration of these thermocouples are shown in Figure 2 and are compared with that for standard Chromel-Alumel and platinum-rhodium thermocouples in Figure 3. The emf values were considerably higher at particular temperatures than those reported at Battelle Memorial Institute, although the calibration curves were of similar slope. This variation in emf is attributed to the difference in the purity of rhenium wire.

As shown in Figure 2 the emf generated by rhenium-molybdenum thermocouples levels off at about 3400°F. On the other hand, rhenium-tungsten thermocouples continue to show an increasing emf with temperature beyond 4000°F. The temperature limitation for their use appears to be about 5000°F where an eutectic in the system is formed.*

A comparison of the data from the calibration of the cycled thermocouple and the new rhenium-molybdenum thermocouple shows that temperature cycling had no effect upon thermoelectric properties. In addition, emf values for the rhenium-molybdenum thermocouple that was cycled in a hydrogen atmosphere agree exactly with those for the thermocouple cycled in vacuum.

The rhenium leg of all experimental thermocouples remained ductile after temperature cycling. Of particular significance was the excellent ductility of the rhenium-molybdenum thermocouple installed in the furnace and cycled many times in a hydrogen atmosphere.

The brittleness that is characteristic of tungsten and molybdenum following temperature cycling caused no difficulty. In fact, the molybdenum wires were surprisingly ductile and could be readily handled. However, brittleness will undoubtedly be a problem in this type of thermocouple when it is used in various applications that are subject to handling.

A solution to the problem may lie in the use of molybdenum-rhenium or tungsten-rhenium alloy wire. Recently published data on the ductility of such alloys are encouraging. For example, G. A. Geach and J. E. Hughes report that certain alloys of rhenium with tungsten or molybdenum are not subject to the recrystallization embrittlement that is characteristic of tungsten or molybdenum. † These alloys are apparently easily worked and could readily be drawn into fine wires. In view of this development additional studies are being conducted to determine the thermoelectric properties of these alloys and their possible use as thermocouple materials.

*WADC Technical Report 54-371, Supplement 1, "Investigation of Rhenium," C. T. Sims, et.al., Battelle Memorial Institute, ASTIA Document No. AD 97301, September 1956.

†G. A. Geach and J. E. Hughes, "The Alloys of Rhenium with Molybdenum or with Tungsten and Having Good High Temperature Properties," Plansu Proceedings 1955, Pergamon Press Ltd., London, 1956.

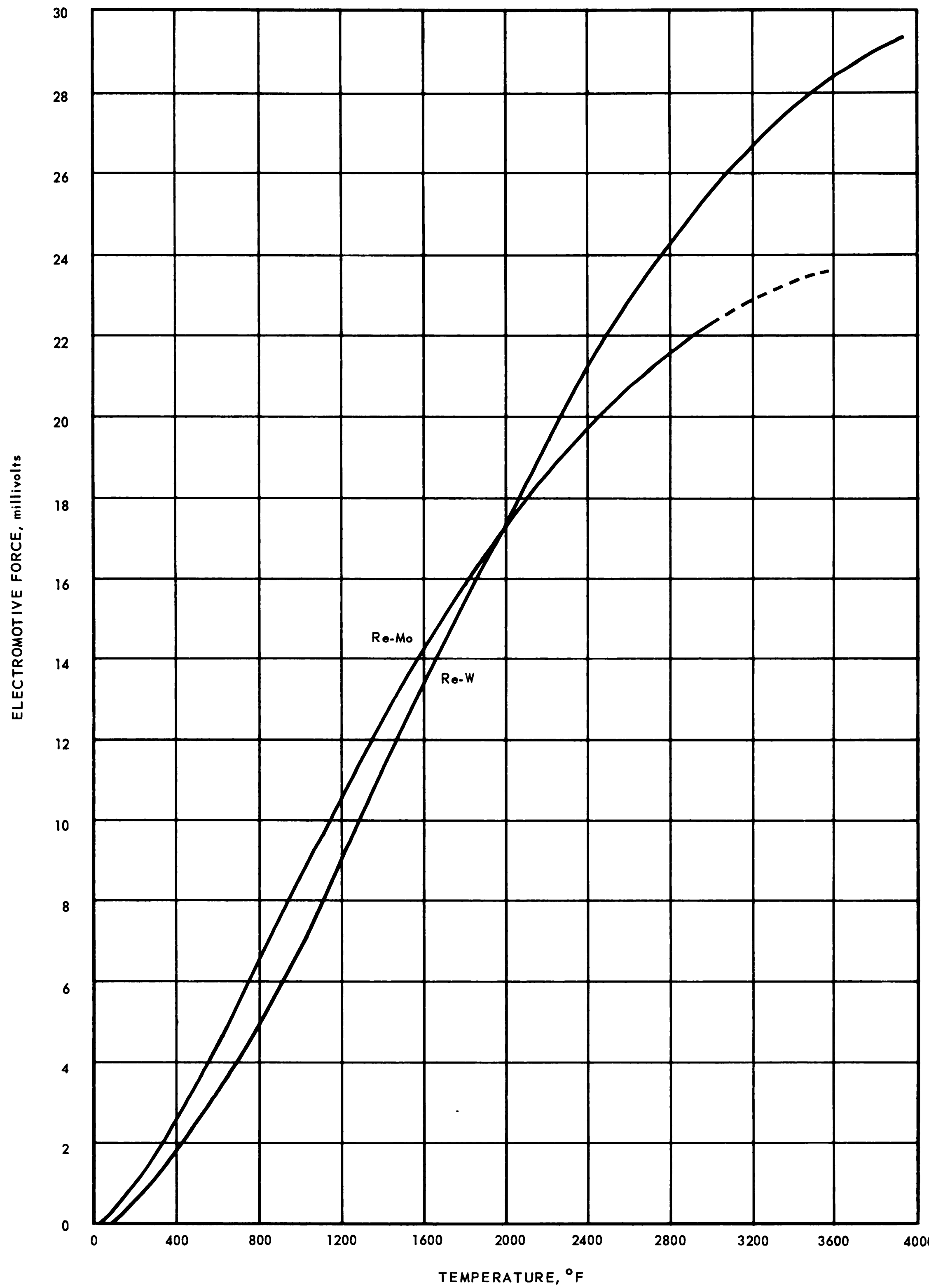

Fig. 2—Calibration of rhenium-molybdenum and rhenium-tungsten thermocouples to 4000°F

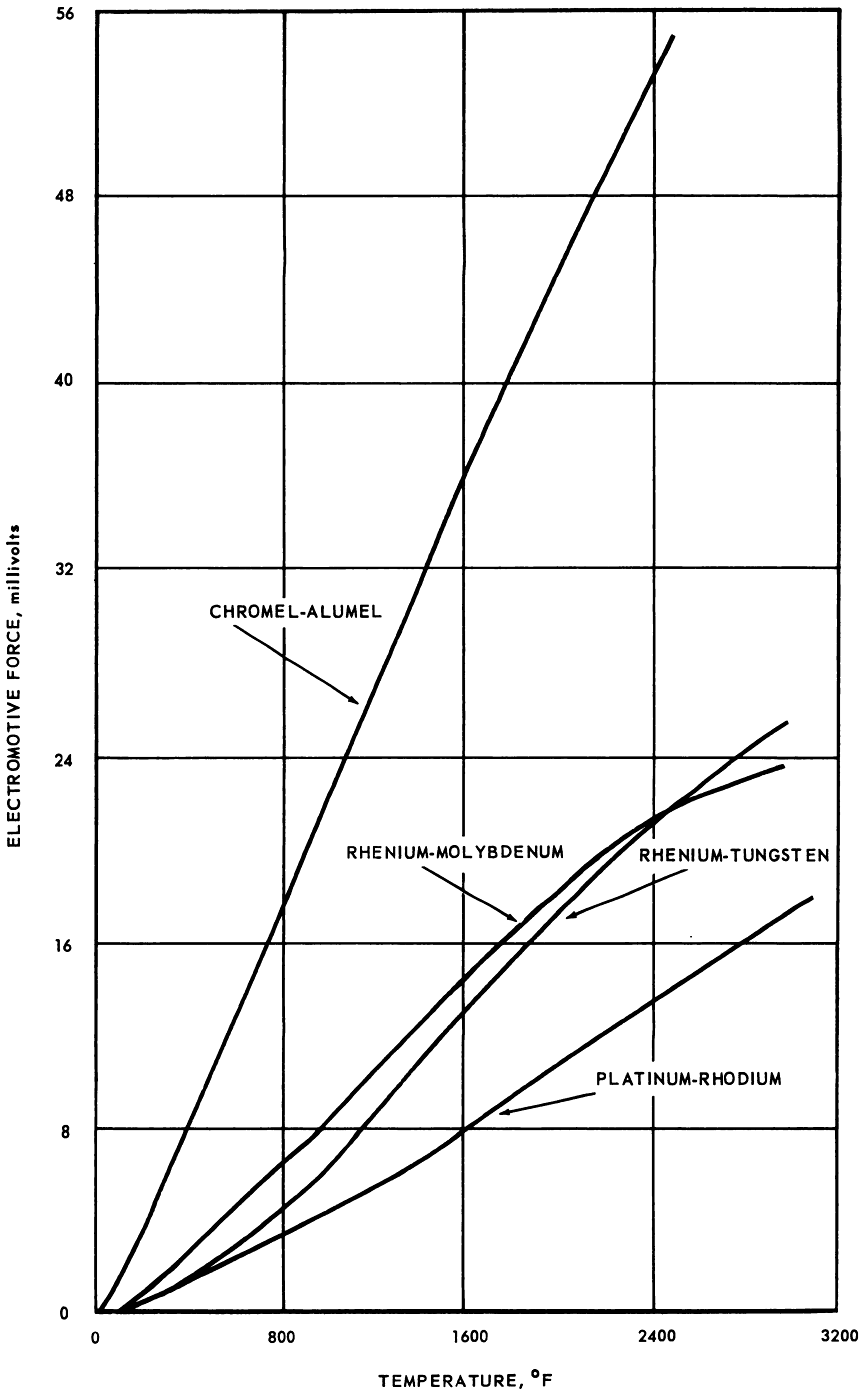

Fig. 3 – Calibration of rhenium and standard thermocouples to 3200°F

Conclusions

1. Rhenium thermocouples have been established as reliable for measuring temperatures to $4000^{\circ}F$ in vacuum, hydrogen, or inert atmospheres.
2. Rhenium-tungsten thermocouples have been calibrated to $4000^{\circ}F$ with an accuracy of 0.1 millivolt.
3. Rhenium-molybdenum thermocouples are useful only to $3200^{\circ}F$ because of limitations in thermoelectric power.
4. Rhenium-tungsten thermocouples are useful for measurements from room temperature to $4000^{\circ}F$, and the only limitation to their use appears to be an eutectic occurring in the system at about $5000^{\circ}F$.

At this time rhenium-molybdenum and rhenium-tungsten thermocouples have been used extensively for accurate temperature control of equipment in melting, sintering, and other heat-treating activities. In addition, they have been used for thermal-analysis studies and have proved to be extremely sensitive for determining thermal arrests in cooling cycles.

As a result of extensive uses of rhenium-molybdenum thermocouples and of subsequent calibration of a considerable number of these thermocouples, accurate emf values as a function of temperature were established to $2700^{\circ}F$. These data are listed in Table 2. Studies will be continued in which similar data will be presented both for rhenium-molybdenum and rhenium-tungsten thermocouples at higher temperatures. Calibrations to $5000^{\circ}F$ for rhenium-tungsten thermocouples will also be conducted when problems in constructing high-temperature furnaces are resolved.

In addition, a series of workable alloys of rhenium-molybdenum and rhenium-tungsten is being fabricated into 0.025-inch-diameter wire. This alloy wire in combination with unalloyed rhenium, molybdenum, or tungsten will be used in developmental thermocouples. If one of these alloy combinations proves to have favorable thermoelectric properties, an extremely ductile thermocouple will be available.

TABLE 2

THERMOELECTRIC EMF VERSUS TEMPERATURE FOR RHENIUM-MOLYBDENUM THERMOCOUPLES

Temperature, °F	0	100	200	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000	2100	2200	2300	2400	2500	2600
	Emf, millivolts																										
0	-	0.345	0.999	1.760	2.598	3.510	4.453	5.434	6.442	7.433	8.420	9.428	10.409	11.362	12.312	13.256	14.116	14.971	15.765	16.536	17.263	17.967	18.587	19.169	19.703	20.198	20.668
5	-	0.371	1.032	1.800	2.642	3.557	4.500	5.481	6.491	7.482	8.470	9.478	10.457	11.411	12.358	13.299	14.159	15.011	15.803	16.573	17.298	17.998	18.618	19.198	19.728	20.222	20.691
10	-	0.400	1.069	1.839	2.686	3.604	4.548	5.530	6.540	7.531	8.521	9.528	10.505	11.460	12.404	13.342	14.202	15.051	15.842	16.609	17.333	18.029	18.649	19.226	19.753	20.246	20.714
15	-	0.428	1.102	1.879	2.731	3.652	4.597	5.579	6.590	7.581	8.571	9.577	10.552	11.508	12.450	13.385	14.245	15.091	15.880	16.646	17.368	18.060	18.680	19.253	19.778	20.270	20.737
20	-	0.457	1.140	1.919	2.777	3.700	4.645	5.629	6.640	7.630	8.622	9.627	10.599	11.556	12.496	13.428	14.288	15.130	15.918	16.682	17.403	18.091	18.710	19.280	19.803	20.294	20.760
25	-	0.488	1.173	1.960	2.822	3.748	4.695	5.681	6.690	7.679	8.673	9.676	10.647	11.604	12.542	13.471	14.331	15.170	15.957	16.718	17.438	18.122	18.740	19.307	19.828	20.318	20.783
30	-	0.520	1.214	2.001	2.867	3.797	4.745	5.732	6.740	7.727	8.724	9.727	10.693	11.652	12.588	13.514	14.374	15.209	15.995	16.754	17.473	18.153	18.770	19.335	19.853	20.342	20.806
35	-	0.553	1.250	2.042	2.911	3.845	4.796	5.783	6.790	7.776	8.776	9.777	10.740	11.700	12.636	13.557	14.417	15.248	16.034	16.791	17.508	18.184	18.799	19.363	19.878	20.366	20.829
40	-	0.587	1.291	2.084	2.955	3.892	4.844	5.833	6.840	7.824	8.826	9.826	10.788	11.748	12.684	13.600	14.460	15.287	16.072	16.827	17.543	18.215	18.828	19.390	19.903	20.390	20.852
45	-	0.620	1.330	2.127	3.000	3.939	4.892	5.885	6.890	7.873	8.876	9.873	10.836	11.796	12.730	13.643	14.503	15.327	16.110	16.863	17.578	18.246	18.856	19.417	19.928	20.414	20.875
50	-	0.653	1.370	2.171	3.045	3.985	4.940	5.937	6.939	7.922	8.926	9.923	10.883	11.844	12.777	13.686	14.546	15.367	16.149	16.900	17.613	18.277	18.884	19.444	19.953	20.436	20.898
55	-	0.691	1.406	2.215	3.090	4.032	4.988	5.989	6.989	7.971	8.976	9.972	10.931	11.891	12.824	13.729	14.589	15.407	16.188	16.936	17.648	18.308	18.912	19.471	19.978	20.460	20.921
60	-	0.728	1.444	2.259	3.136	4.080	5.036	6.040	7.039	8.020	9.026	10.020	10.980	11.938	12.871	13.772	14.631	15.447	16.226	16.973	17.683	18.339	18.940	19.497	20.003	20.483	20.944
65	-	0.761	1.482	2.302	3.180	4.127	5.085	6.091	7.089	8.068	9.076	10.069	11.028	11.984	12.918	13.815	14.673	15.486	16.265	17.010	17.718	18.370	18.968	19.523	20.028	20.506	20.967
70	-	0.799	1.521	2.346	3.225	4.175	5.135	6.140	7.138	8.118	9.127	10.119	11.075	12.031	12.966	13.858	14.715	15.526	16.304	17.047	17.753	18.401	18.996	19.549	20.053	20.530	20.990
75	-	0.831	1.560	2.388	3.273	4.221	5.186	6.192	7.189	8.169	9.177	10.168	11.123	12.078	13.014	13.901	14.758	15.566	16.343	17.083	17.788	18.432	19.025	19.577	20.078	20.553	21.012
80	0.236	0.869	1.601	2.429	3.320	4.268	5.236	6.243	7.237	8.218	9.228	10.217	11.170	12.124	13.061	13.944	14.800	15.605	16.382	17.119	17.827	18.463	19.054	19.603	20.102	20.576	21.034
85	0.262	0.902	1.642	2.470	3.367	4.314	5.286	6.294	7.285	8.268	9.278	10.265	11.218	12.171	13.107	13.987	14.843	15.645	16.420	17.155	17.862	18.494	19.082	19.629	20.126	20.599	21.056
90	0.290	0.934	1.682	2.513	3.415	4.360	5.337	6.344	7.335	8.319	9.328	10.313	11.265	12.219	13.154	14.030	14.886	15.684	16.459	17.192	17.898	18.525	19.111	19.654	20.150	20.622	21.078
95	0.317	0.968	1.721	2.555	3.462	4.406	5.385	6.393	7.384	8.370	9.378	10.361	11.314	12.266	13.210	14.073	14.929	15.724	16.498	17.226	17.933	18.556	19.140	19.679	20.174	20.645	21.100
100	0.345	0.999	1.760	2.598	3.510	4.453	5.434	6.442	7.433	8.420	9.428	10.409	11.362	12.312	13.256	14.116	14.971	15.765	16.536	17.263	17.967	18.587	19.169	19.703	20.198	20.668	21.122

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