NRL Report 6231

Instability of Refractory Metal Thermocouples

B. E. Walker, Jr., C. T. Ewing, and R. R. Miller

Inorganic and Nuclear Chemistry Branch
Chemistry Division

March 26, 1965

U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

CONTENTS

Instability of Refractory Metal Thermocouples

B. E. WALKER, JR., C. T. EWING, AND R. R. MILLER

Inorganic and Nuclear Chemistry Branch
Chemistry Division

Thermoelectric instabilities of some refractory metal thermocouples have been studied in the temperature range 1000° to 2000°C under vacuum and neutral atmospheres. The sources of instability were found to be complex, involving contamination from ceramic protection tubes and furnace environments, preferential volatilization, and various thermal anomalies such as recrystallization and phase changes in the refractory thermoelements. Refractory thermocouples and thermoelements were studied under a variety of conditions, and emf changes associated with each were noted. Recommendations were made for the selection and application of these thermocouples to attain maximum thermoelectric stability.

INTRODUCTION

This Laboratory is engaged in high-temperature property investigations extending above 2000°C. For precise temperature measurements over extended periods, thermocouples appear to offer the most promise if material compatibility is within acceptable limits. Prior to recent investigations (1), however, the reliability of even the common LeChatelier couple could not be predicted above 1000°C from available data. Refractory metal thermocouples are relatively new, and thermal emf *vs* temperature relationships for most combinations are provisional or tentative. Consequently, it seems logical to study stability shifts in these materials and their compatibility before the emf *vs* temperature curves for various combinations are standardized.

The instability (change in emf output with time) of a thermocouple at constant immersion is normally associated with compositional or other changes in the thermal gradient zone of each element. These changes may result from contamination by furnace atmosphere and ceramic protection tubes, from exchange of alloying elements at welded junctions, from preferential volatilization of one metal (or oxide) from an alloy leg, or from temperature-induced transitions in the thermoelements. The magnitude of the changes which contribute to instability may also be influenced by time, temperature, atmosphere, wire size, and other geometry effects.

NRL Problem C05-08; ONR RR-007-01-46-5400. This is an interim report; work is continuing. Manuscript submitted December 3, 1964.

Since refractory metals, in general, readily oxidize in air, the present investigation has been restricted to inert atmosphere and vacuum. The ultimate purpose of these studies is to find a reliable thermocouple for use above 2500°C; therefore, only refractory materials with melting points exceeding 2500°C were considered. These included W, Re, Ta, Mo, and several alloys of these metals. The current phase of the instability study extends to approximately 2000°C.

In searching the literature for suitable refractory metal couples for high temperature application, information on ductility, thermoelectric output, material compatibility, chemical homogeneity, and thermoelectric stability was found to be restricted and contradictory. In the case of stability, contradiction has often resulted from a lack of control over factors such as immersion depth, environmental contamination, and chemical inhomogeneities in the thermoelements. The purpose of this investigation was to study factors which influence the stability of refractory metal thermocouples and to develop criteria for the selection and application of these couples.

EXPERIMENTAL METHOD

The methods employed for the stability studies were discussed in detail in a previous article (1). Briefly, the procedure was as follows: Well-sheathed thermocouples were fired in a furnace at a predetermined temperature and immersion depth for a specified time. Bare thermoelements were fired by passing electric current through them for specific times and temperatures. Upon removal from the firing operation, each individual test leg was joined to a reference wire of the same material; and the junction was pulled into the stability furnace (Fig. 1), which was provided with a protective atmosphere. Measurements were then made of the potential (using a Rubicon Type B potentiometer in a shielded system) between the test wire and its reference at various positions along the test wire from its original junction or from a convenient point in the case of electrically fired wires. If the test wire and reference wire were identical before heat treatment, observed readings represented deviations in the thermoelectric force of the test wire for a temperature difference of 860°C (the difference in temperature between the stability furnace and room). Unheated sections of a test wire were always compared to the reference standard. Thus, any thermoelectric potential between the test wire and its reference, generated by chemical or physical inhomogeneity, was readily detectable. In practice, if unheated test wires and reference wires were taken from the same lot, they were generally identical within ±20 μV.

EXPERIMENTAL RESULTS

Instability Tests on Thermoelements of Refractory Metals and Alloys in Argon and Vacuum

Maximum thermoelectric changes at a temperature difference of 860°C for individual elements of W, Re, W-26% Re, Mo, Re-50% Mo, W-3% Re, and W-5% Re, sheathed in low-iron-content alumina and fired at about 1625°C in argon, or unsheathed and fired electrically at the same temperature, are shown graphically as a function of firing time in Figs. 2, 3, and 4. The bare wire tests provided a frame of reference, and permitted the instability associated with the sheathing to be separated from that associated with recrystallization or other internal changes in the refractory metals. Low-iron-content alumina insulators were used for sheathing tests because previous studies involving noble metal thermocouples indicated that iron was the main contaminant contributing to thermoelectric instability (1). Since the previous study also showed that instability resulting from contamination was a function of wire size, all tests were made with 20-mil-diameter wire. The furnaces used for the firing tests had isothermal zones of approximately 3 in., and the plotted changes for thermoelements fired in this manner represent the maximum observed deviation in the thermal emf at 860°C (relative to 0°C) for that portion of wire subjected to full firing temperature. For wires fired electrically, the plotted change represents the observed deviation in the thermal emf at 860°C for the full length of the wire (usually 18 to 24 in.).

The sign convention used in Fig. 2 and subsequent data follows the generally accepted form. The thermoelectric change is designated negative when a negative charge is generated at the cold end and is designated positive when generated at the hot end. When two legs are joined to form a thermocouple, this convention dictates that a positive change in emf (in the thermal gradient zone) of that leg attached to the negative post of the potentiometer will decrease the emf of the couple, while a positive change in the leg attached to the positive post will increase the emf of the couple.

Figure 2 shows the maximum instability changes at 860°C for W thermoelements as a function of firing times at 1625°C. These results include tests on bare wires and wires sheathed in alumina. The electrical firings were limited to 48 hr, because of the repeated failure of the W wires beyond this time as a result of burn-outs caused by the weight of the wire. The tests with W were made on wires from two different sources, but instability differences between the two were negligible.

It is obvious from Fig. 2 that a large part of the initial instability noted for W results from internal changes and can be eliminated by prefiring. Firing for periods of 0.1 to 1 hr on bare wires produced emf changes of approximately 110 μV, and 4 to 48 hr firings on bare and sheathed wires produced changes of approximately 150 μV. However, the wires emerge from firing tests in an extremely brittle condition. The additional change noted between 48 and 150 hr may be due to further internal changes in the wire or to sheathing contamination. Spectrographic analyses of samples fired for 120 hr did not reveal significant changes from the original wire, while samples fired for 240 and 360 hr showed contamination by nearly all constituents normally found in

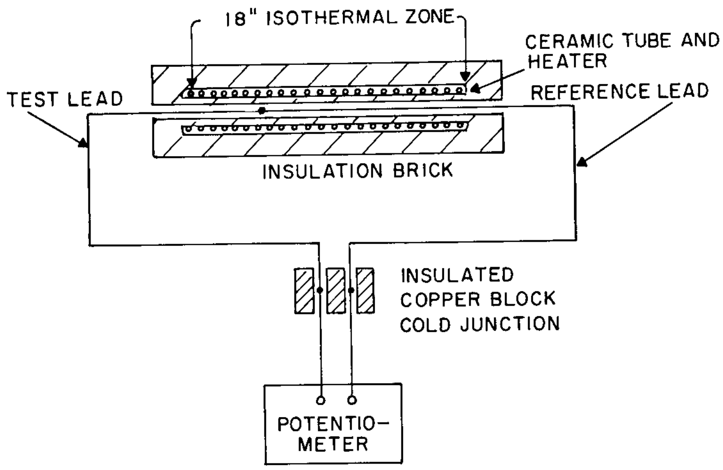

Fig. 1 — Stability measurement system

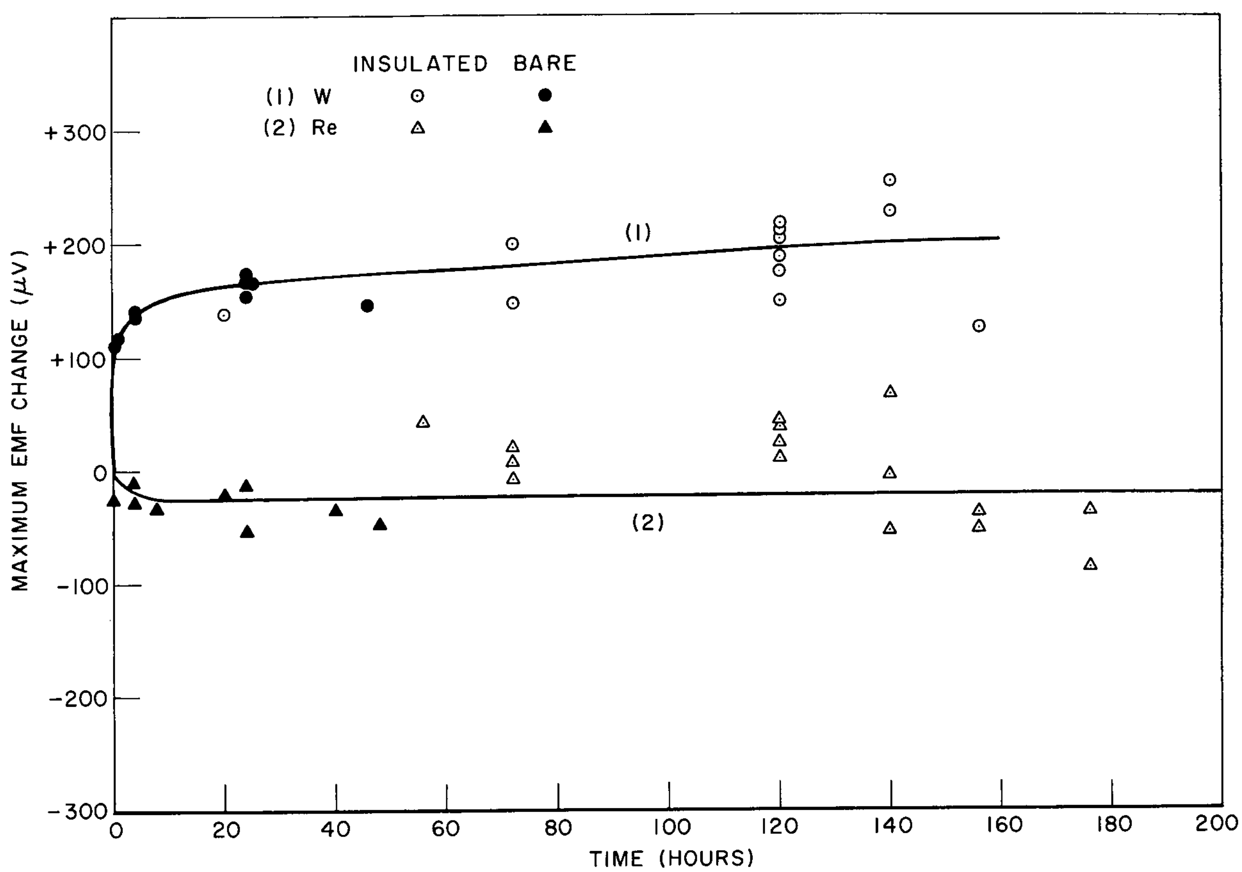

Fig. 2 — Maximum emf changes (μV) at 860°C for W and Re thermoelements fired bare and in alumina sheathing at 1625°C in argon atmosphere for various times

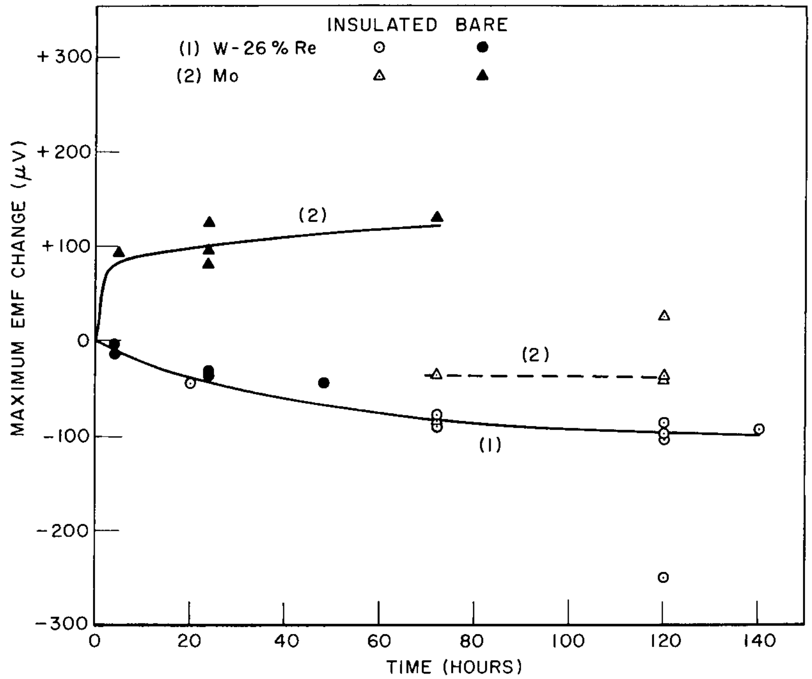

Fig. 3 — Maximum emf changes (μV) at 860°C for W-26%Re and Mo thermoelements fired bare and in alumina sheathing at 1625°C in argon atmosphere for various times

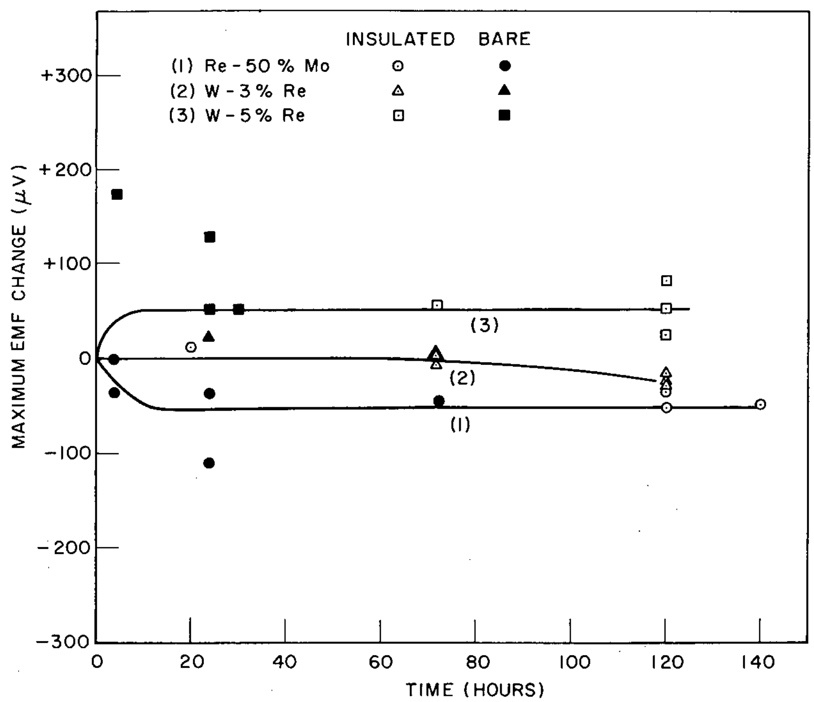

Fig. 4 — Maximum emf changes (μV) at 860°C for Re-50%Mo, W-3%Re, and W-5% Re thermoelements fired bare and in alumina sheathing at 1625°C in argon atmosphere for various times

alumina sheathing. The latter spectrographic studies were made on remaining portions of wire since several inches of the original wire had reacted to destruction. The higher oxides of many refractory metals are quite volatile, and the disappearance of their reaction products with alumina is not unexpected.

The instability changes for Re thermoelements, also shown in Fig. 2, were practically nil to 360 hr at a firing temperature of 1625°C. No contamination from alumina sheathing was evident, and the small change noted occurred in the first few minutes of heating. This initial shift apparently is due to internal changes. Electrical firings of Re in argon were also limited to 48 hr, since failure of the wire occurred beyond this time. The Re wires for the tests were from two different sources, but instability differences between the two were negligible.

The maximum emf changes at 860°C for W-26% Re thermoelements are shown in Fig. 3. The greatest change in emf occurs in the heating period up to 48 hr. The slight difference in emf between electrically fired wires after 48 hr of heating and sheathed wires after 140 hr indicates that most of the instability can be attributed to internal changes in the wires. In sheathed wires fired for 240 and 360 hr, extensive reaction with alumina was observed; therefore, a portion of the instability noted to 140 hr may be due to sheathing contamination, since impurities contained in alumina (principally Fe and Mg) are evident in spectrographic analyses of these samples. W-28% Re thermoelements (not shown in any of the figures) from another source were also tested in argon at 1625°C in alumina sheathing. These wires showed maximum emf changes of 200 μV after 20 hr firing and 500 μV after 120 hr. Spectrographic studies of these samples also revealed a strong pickup of Fe from the alumina sheathing. On the other hand, W-25% Re wires from a third source were found to have approximately the same instability changes for these test conditions as the W-26% Re thermoelements.

Instability data for Mo thermoelements are also shown in Fig. 3. The source of the small instability of Mo is apparently twofold, from reaction with alumina sheathing and from internal changes in the wire. Figure 3 demonstrates that in this case these mechanisms are competing. Unsheathed wires fired for intervals up to 72 hr at 1625°C indicate maximum instability of about 100 μV, whereas those fired in alumina sheathing for from 72 to 120 hr show changes of 50 μV in the opposite direction and give evidence of pickup of several constituents of alumina sheathing. As in the case of W elements, prefiring could remove that part of the instability resulting from internal changes, but at the cost of severe embrittlement.

Maximum instability changes for W-3% Re thermoelements are shown in Fig. 4. For firing times up to 120 hr, the instability of this alloy was practically negligible. However, another batch of the same type wire had an initial change of +400 μV in a few hours but no additional change for firing times extending to 120 hr. Neither spectrographic nor wet analyses of the two batches indicated any significant differences in composition, but small impurity differences may escape detection. It was found that prefiring the second lot of wire to 1625°C for 4 hr in argon removed practically all of this instability change. The wire, although somewhat embrittled, remained sufficiently ductile for further use.

Figure 4 also shows instability data for Re-50% Mo wires. The small instability of this material for intervals up to 140 hr firing is apparently due to internal changes in the wire, since no significant differences between bare and sheathed wires were observed. However, several results for longer term tests (240 and 360 hr) indicated gross changes (−1400 μV) and strong pickup of alumina constituents, particularly Al, Mg, and Fe.

Maximum emf changes at 860°C for W-5% Re wires (two lots from the same source) are also given in Fig. 4. Agreement of the instability data between the two lots was very good. Except for two tests, instability data for bare and sheathed wires were on the same curve. Consequently, the main source of instability of this material up to 120 hr is apparently internal changes in the wire.

Reproducible data for Ta thermoelements could not be determined with reasonable accuracy by the methods employed in the present investigation. Stability of this material could not be achieved, and continuous emf shifts of significant proportions were observed when wires were fired for several hours at 860°C. Although no practical evaluations of Ta were possible, some general observations were noted. Tantalum wires reacted to destruction in a matter of a few hr when fired in alumina sheathing in argon at 1625°C. Wires fired electrically in argon failed in a relatively short time and emerged from testing in an extremely brittle condition. Tantalum elements were successfully fired electrically for periods of 24 hr at 1625°C in vacuum and were more ductile than those fired in argon.

The effect of temperature on the stability of refractory thermoelements in argon was studied by 24-hr electrical firings at various temperatures. The emf changes at 860°C for thermoelements fired in this manner at temperatures from 1000° to 2000°C are shown in Figs. 5, 6, 7. In varying degrees, the instability of these materials increased with increasing temperature. W, Re, Mo, and W-3% Re show fairly gradual increases, but rates for W-26% Re and Re-50% Mo increase more rapidly above 1600°C. The experimental data for W-5% Re were somewhat scattered; but, in general, the instability changes for this alloy were greater above 1600°C than for W-3% Re thermoelements.

All stability tests on refractory thermoelements in vacuum were conducted by electrical firing techniques. The data obtained, however, were found to be invalid beyond 24 hr (8 to 12 hr for Re) because of reaction between the thermoelements and small quantities of oil vapor from the diffusion pump. Metallographic examinations provided positive evidence of chemical reaction for the long-term vacuum-fired wires. The changes generated by this reaction ranged as high as 8000 μV (at 860°C) for refractory metal samples fired at 1625°C for 120 hr. A number of tests were made in an effort to eliminate the effect of the back-diffusion of the oil vapor. A chevron baffle system was regularly used between the test chamber and the diffusion pump; and for several tests with Re wire, liquid nitrogen was used as a trap coolant. Back-diffusion was not eliminated, however, as evidenced by a decreased but still significant reaction between Re wire and carbon. Limited tests with a vac-ion pump at 10^{-9} to 10^{-10} torr for several thermoelements produced instability changes of the same magnitude as those observed in comparable argon studies.

The contamination of refractory metals by carbon or oxygen in vacuums of 10^{-6} to 10^{-7} torr was also observed by Inouye (2) at 600° to 1200°C. He estimated the permissible pressures for noncontamination to be below 10^{-7} torr. Since these conditions could not be reached with present facilities, further tests in vacuum were discontinued.

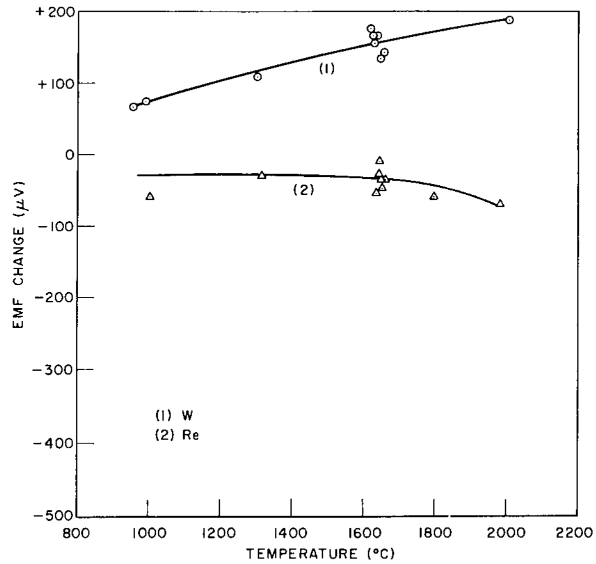

Fig. 5 — Emf changes (μV) at 860°C for W and Re thermoelements fired bare in argon for 24 hours at various temperatures

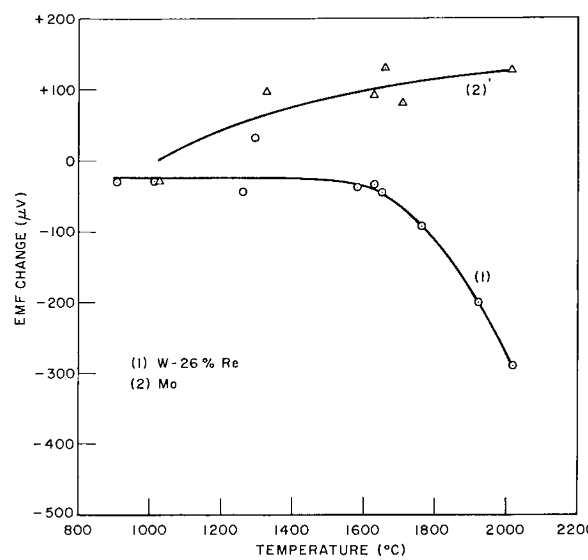

Fig. 6 — Emf changes (μV) at 860°C for W-26% Re and Mo thermoelements fired bare in argon for 24 hours at various temperatures

The limited tests in the vac-ion pump system and the shorter time vacuum tests at 1625°C in

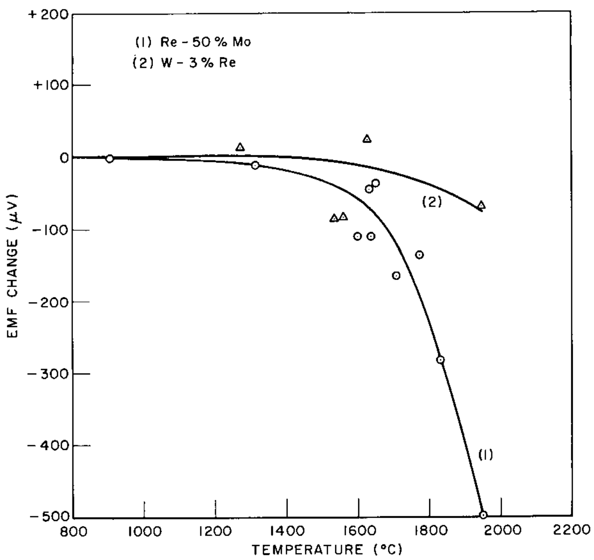

Fig. 7 — Emf changes (μV) at 860°C for Re-50% Mo and W-3% Re thermoelements fired bare in argon for 24 hours at various temperatures

the regular test chamber (up to 24 hr) indicate agreement with the instability data in argon atmospheres. This does not mean that instabilities of refractory metals fired in argon and vacuum will necessarily be in agreement for longer time periods.

Test wires and reference wires for all the argon and vacuum tests were of the highest grades available. However, the firing tests made in this investigation indicated that emf changes occurred in many of the wires in very short time intervals and appeared to be associated with recrystallization, volatilization of impurities, or other thermally induced changes. Prefiring appeared to be beneficial for some materials, but the majority became extremely fragile, with a consequent increase in the failure rate during use.

Instability of Refractory Metal Thermocouples in Argon

It was noted by Chaussain (3) and by the authors in previous work (1) that the thermal emf change caused by contamination in noble metal thermoelements was linear with temperature, regardless of the degree of contamination. Therefore, the thermoelectric power α expressed in μV/°C generated by a given emf instability should have the same value at any temperature. In the present investigation, the emf changes induced in refractory metals were apparently more complex, involving contamination from sheathing, loss or gain of impurities, internal changes in the thermoelements, and combinations of these. Consequently, the changes were not necessarily linear with temperature, and α was usually not constant with temperature. Figure 8 illustrates the behavior of the thermoelectric power α with respect to temperature for typical specimens of thermoelements studied in the present investigation.

Wires were generally tested for instability by comparison with references at 860°C, and the thermoelectric power was measured along the length of each thermocouple leg. In order to determine the temperature data shown in Fig. 8, several electrically fired wires of each material with different instability changes were measured by the same referee technique (1) at several temperatures to 1430°C. This data revealed that the thermoelectric power for different instability changes of the same refractory metal varied with temperature in a similar manner and in approximate ratio to the degree of change at 860°C. Consequently, the thermoelectric force measurements at 860°C in the stability furnace system on any thermoelement, regardless of the degree of the change at 860°C, could be adjusted to any desired temperature. By additional measurements of the temperature gradients along the wires at any predetermined temperature of the firing furnace, it was possible to calculate the net emf change in microvolts for a given thermocouple when fully immersed by graphically integrating the following equation over the affected lengths of both legs:

$$\Delta E = \int_{t_1}^{t_2} (\alpha_x{}^+ - \alpha_x{}^-)\, dt. \qquad (1)$$

In Eq. (1), ΔE is the net emf change of the thermocouple reading, t is the temperature (°C) of both legs in the gradient zone at a distance x from the junction, $\alpha_x{}^+$ is the thermoelectric power of the emf change for the leg attached to the positive pole of the potentiometer at a distance x from the junction, and $\alpha_x{}^-$ is the thermoelectric power of the emf change for the leg attached to the negative pole of the potentiometer at a distance x from the junction.

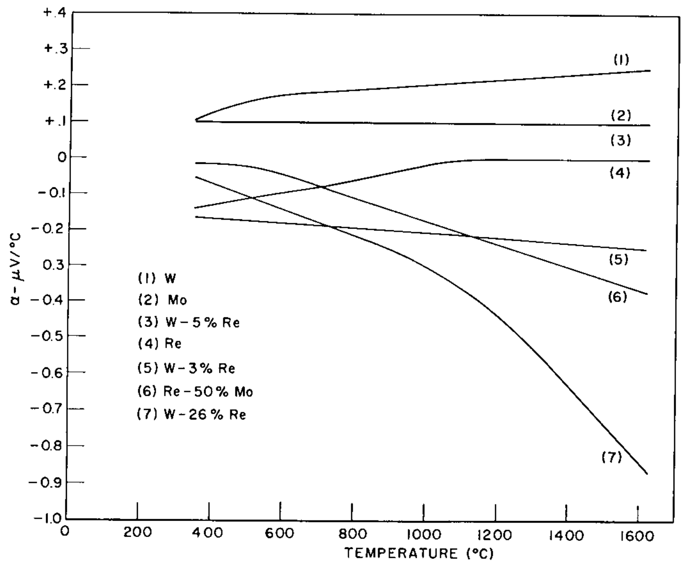

Fig. 8 — Variation of thermoelectric power of changes ($\alpha - \mu V/°C$) for individual thermoelements as a function of temperature.

Comparisons of the instabilities of several thermocouple pairs, sheathed in low-iron-content alumina and fired in argon at approximately 1625°C for various lengths of time, are presented in Table 1. Instability figures represent an average of two or more experimental values from tests at the same conditions. The net emf change of each thermocouple at 860°, 1200°, and 1625°C was calculated by the integration procedure outlined, after firing at constant immersion under specified conditions. Since the temperature error of a couple pair is determined by the induced deviation in degrees, integrated microvolt changes were converted to corresponding temperatures in degrees centigrade. The maximum changes at the various temperatures for each thermocouple are also given in Table 1 to illustrate the error which could be generated by decreasing the immersion after firing. The estimated net instabilities at 1200° and 1625°C were computed to provide a better comparison between the various couples, since several of these (W/Mo, Re/W-26% Re, and Re-50%Mo/W-26%Re) have no practical use below 1000°C. This is illustrated in Fig. 9, which given the emf versus temperature relationships (4-6) for most of the couples shown in Table 1 (a number of W-3% Re and W-5% Re combinations with other metals are not shown because of close proximity to emf values of the corresponding W combinations).

Since the stability tests permitted a measurement of the distribution and magnitude of emf changes in the individual couple wires as a function of distance from the couple weld, junction effects could be distinguished from other effects and studied independently. Stability experiments were made for individual thermoelements and for welded combinations after firing at 1600° to 1650°C in argon. Any transfer of metal from one leg to the other by diffusion or vaporization could contribute to thermocouple instability. However, the distribution and magnitude of emf changes in individually fired wires and in those fired in joined combination were identical in most cases. No junction effects for the various couple combinations were detected beyond 1 to 2 in. from the welded junction.

The influence of wire size on the instability changes of the refractory couples was not studied. A previous investigation (1) indicated that this was an important factor when contamination occurred; therefore, all tests shown in Table 1 were made on 20-mil wire. Geometry factors, involving wire, sheathing, contact areas, and the influence of these on the degree of instability and movement of contamination along the wires, are probably quite complex. Even the standard practice of using 12-in. sheathing with 1/32-in. bore did not prevent an influence of geometry and time on the distribution of change along the

TABLE 1
Instability Changes (°C) at Constant Immersion and Maximum Δt Which Could Be Generated by Reducing Immersion for Indicated Temperatures and Firing Times at 1625°C in Argon for Various Refractory Metal Thermocouples

Couple Pair	Temp. (°C)	Δt (°C) for Various Heating Times At 1625°C					
		20 Hr		72 Hr		120 Hr	
		Constant Immersion	Max Δt	Constant Immersion	Max Δt	Constant Immersion	Max Δt
W/Re	860	+ 4	+ 9	+ 4	+10	+ 5	+10
	1200	+10	+16	+11	+21	+13	+21
	1625	+20	+29	+23	+41	+27	+41
W-3%Re/Re	860			0	0	0	− 1
	1200			0	0	0	− 5
	1625			0	0	− 1	− 8
W-5%Re/Re	860			+ 1	+ 3	+ 1	+ 2
	1200			+ 2	+ 8	+ 2	+ 5
	1625			+ 3	+13	+ 4	+ 9
W/W-26%Re	860	+ 4	+ 9	+ 5	+14	+ 6	+15
	1200	+11	+18	+13	+29	+16	+34
	1625	+25	+34	+32	+55	+41	+66
W-3%Re/W-26%Re	860			+ 1	+ 4	+ 2	+ 5
	1200			+ 4	+18	+ 6	+14
	1625			+18	+30	+24	+36
W-5%Re/W-26%Re	860			+ 2	+ 6	+ 3	+ 4
	1200			+ 6	+22	+ 9	+26
	1625			+27	+51	+37	+63
Mo/W-26%Re	860			0	+ 1	+ 2	+ 5
	1200			+ 3	+10	+ 7	+18
	1625			+25	+32	+39	+57
Re-50%Mo/W-26%Re	860	+10	+20			+11	+26
	1200	+24	+41			+23	+59
	1625	+59	+71			+83	+104
W/Mo	860			−57	−152	−54	−131
	1200			+42	+88	+42	+78
	1625			+38	+83	+40	+70
W-3%Re/Mo	860					+ 4	+12
	1200					− 2	−10
	1625					− 2	− 3
W-5%Re/Mo	860					− 8	−18
	1200					+ 6	+25
	1625					+ 5	+22
Re/W-26%Re	860	− 4	−11	− 9	−43	−16	−57
	1200	+10	+20	+12	+41	+20	+56
	1625	+23	+28	+31	+52	+43	+71
Re/Re-50%Mo	860	+29	+52			−10	−85
	1200	−10	−11			+13	+43
	1625	− 7	− 9			+10	+43

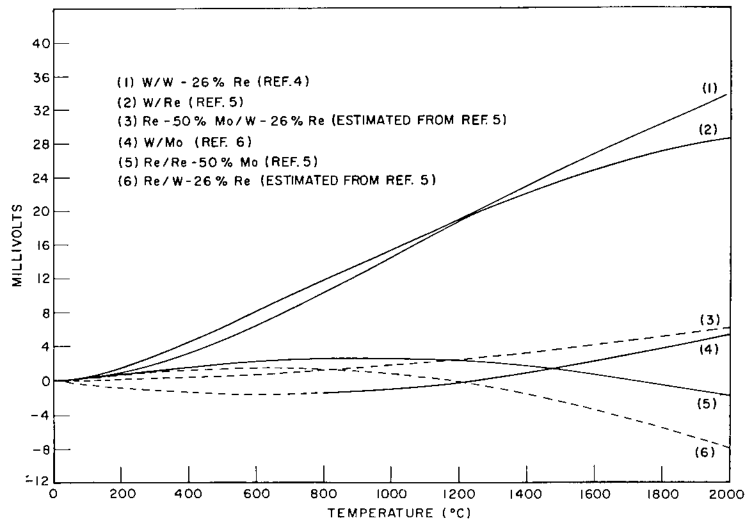

Fig. 9 — Thermal emf (mV) *vs* temperature data for several refractory metal thermocouples

various wires. This is evident in Table 1 by the lack of uniformity in the ratio of maximum change to net change at constant immersion. The fact that other factors were usually contributing to the emf shifts at the same time made it difficult to study the influence of geometry.

The major portion of the instability changes noted for W/Re thermocouples in Table 1 occurs in less than 1 hr and is due almost entirely to the W thermoelement. Up to 150 hr, most of the change is the result of recrystallization or other internal change in the thermoelement. Beyond this time, reaction with the alumina sheathing proceeds rapidly. Prefiring would reduce the initial change noted in this couple, but as pointed out previously, at the cost of severe embrittlement to the W thermoelement.

The instability of the W/Re thermocouple system is reduced significantly by the substitution of W alloy legs containing 3% to 5% Re for the pure W. Although the results shown in Table 1 indicate that W-3%Re/Re thermocouples are very stable, a second batch of W-3% Re wire was found to have an initial change of about 400 μV after less than 4 hr heating at 1625°C. However, further change with increased time did not occur; consequently, prefiring of this second batch would remove virtually all of its instability. The alloy thermoelements are considerably more ductile than W, and embrittlement is not as serious a problem as with W.

For thermocouples formed by combining W, W-3% Re, W-5% Re, or Re with W-26% Re, the major source of instability is due to the W-26% Re thermoelement. The thermoelectric power of the instability for this element (Fig. 8) increases rapidly with increase in temperature. Consequently, the increase of the net instability with temperature (Table 1) for couples combined with W-26% Re is unusually high.

The thermoelectric power of the instability of a Re-50% Mo thermoelement also increases quite rapidly with temperature (Fig. 8) but not as fast as that of W-26% Re. Although the observed instability changes for both of these alloys are in the same direction, the increasing divergence of their thermoelectric powers with increasing temperature and the low emf versus temperature curve for the couple contribute to a rather sharp increase in the instability of the Re-50%Mo/W-26%Re thermocouple with increase in temperature.

The W-25% Re wires were not studied as extensively as the W-26% Re thermoelements. However, the instability and the thermoelectric power of the instability for W-25% Re were found to be somewhat lower than those observed for W-26% Re (Figs. 3 and 8), especially at temperatures above 1200°C. It was pointed out in a previous section that W-26% Re wire was more stable than W-28% Re wire (from another source). Consequently, part of the instability of these

W-25% to 28% Re alloys may be a result of alloying and fabrication techniques. As manufacturing processes become more uniform, these alloys should become more reliable for thermocouple use.

For W/Mo couples, most of the instability is attributable to W. Molybdenum thermoelements react with alumina sheathing, producing a thermoelectric power of contamination in the opposite direction to that produced by internal changes in the wire (Fig. 3), and the overall result is a fairly stable thermoelement to 140 hr. After 140 to 150 hr, however, the reaction proceeds more rapidly and Mo thermoelements react to destruction.

While couples composed of Mo thermoelements combined with W-3% Re or W-5% Re appear to offer more promise for stability up to 150 hr than some of the other refractory couples, severe embrittlement of Mo wires remains a major problem, though not as critical as in the case of W. This factor, combined with a lower melting point (2610°C) and the subsequent lower temperature limit of operation, makes the use of Mo thermoelements less attractive than other refractory metals.

Re/Re-50%Mo thermocouples give indication of usefulness. The Re leg is quite stable, and the alloy leg seems to offer more stability than the corresponding couple with W-26% Re. The thermoelectric output of this couple is rather low in the temperature range 860° to 1625°C but increases considerably at higher temperatures. Consequently, for use above 2000°C, this couple may prove to be quite satisfactory.

Although some of the instability changes shown for the refractory metal thermocouples in Table 1 may appear to be rather large, the net change (at constant immersion) for the couple (Re-50% Mo/W-26%Re) showing the largest deviation after firing for 120 hr at 1625°C in argon is only 5%. The instability changes of the remainder of the couples for the same conditions are all less than 3%, and many are below 1/2%. At this stage of development of refractory metal couples, the uncertainties in the thermal emf output is greater than the latter percentage.

Miscellaneous Studies

Nearly all of the wires studied in the present work were subjected to bend tests after the thermoelectric measurements were completed. This was done by securing the wire on two flat sections, hinged 1/2 in. apart, and observing the point of breakage on a protractor dial. Good ductility was assumed if a wire survived five cycles of bends forward and backward. The purpose of these tests was to determine if any relationship existed between ductility and firing. Neither firing time nor temperature from 1000° to 2000°C could be related directly to the ductility. However, a correlation between ductility and emf instability for a particular material was found. In general, for each refractory thermoelement, ductility decreased with increasing thermal emf instability. This relationship was found to hold regardless of whether the emf instability was a result of insulation contamination, loss or gain of impurities, or internal changes in the wire.

Cold-working tests with fired and unfired wires produced thermal emf shifts in some of the wires. For example, W-26% Re fired at 1650°C in argon or vacuum for 24 hr exhibited emf changes ($\approx$ 40 to 50 μV) due to cold working, whereas unfired wires did not. Re-50% Mo wires fired in argon at 1650°C showed similar changes when cold worked, whereas untreated wires and those fired in vacuum showed no changes. Rhenium wires unfired or fired in argon, showed no emf change due to cold working. Unfired W also was not affected by cold working. Fired W wires were too brittle to check for this effect.

The results of the above tests, combined with the thermoelectric data, demonstrate the complexity of instability in refractory thermoelements. In varying degrees, firing temperature, time, environment, and cold working all have the effect of increasing the instability of these thermoelements.

DISCUSSION

In recent years an increasing amount of work has been performed on refractory metal thermocouples. Most of the studies involved testing the emf output of various combinations, with only a few devoted to the practical use and reliability of these couples. Consequently, comparison of the results of this study with other investigations must be quite limited.

Fanciullo (7) reported on the instability of several refractory thermocouples which had been tested in argon for periods up to 5000 hr in swaged alumina sheathing. Since the work was done at firing temperatures below 1100°C, only rough comparisons can be made with the present studies, which were conducted mainly at 1625°C. However, his results, which indicated a greater stability for W-3%Re/W-25%Re couples as compared to W-5%Re/W-26%Re couples, and for the latter as compared to W/W-26%Re thermocouples, are consistent with present data. Fanciullo also reported that Mo/W-26%Re couples showed rather good stability at 1100°C; and this, too, is consistent with the present results.

Kuether and Lachman (8,9), investigating W/Re couples fired up to 2300°C in hydrogen and 1400°C in vacuum for various cycling periods totaling about 20 hr, found that this couple showed changes of +35°C in hydrogen at 1000°C and no change at 1100°C in vacuum. The findings are roughly comparable with those found in the current study in argon.

Lachman (10) reported some results for unsheathed W/W-26%Re and W-5%Re/W-26%Re thermocouples in hydrogen and argon atmospheres up to 2300°C. He concluded that the instability results in each environment were essentially the same. For variable cycling periods totaling about 5 hr up to 1600°C in hydrogen, he noted a change of approximately +2°C at 800°C and 1100°C for W/W-26%Re couples and +1°C at 800°C and 1100°C for W-5%Re/W-26%Re thermocouples. These results are in agreement with the present studies in argon. Some drift studies in flowing argon were also made by Lachman on a W/W-26%Re couple at approximately 1000°C for 500 hr and 2200°C for 100 hr, and these data indicate net instability changes of less than 1/2% at these respective temperatures. The current studies are in agreement (up to 140 hr) with his instability changes at 1000°C, but indicate an instability of approximately 2.5% at 1625°C. In view of the different methods employed in the instability studies, possible differences in the thermoelements, and differences in sheathing (unsheathed versus alumina sheathed), the overall agreement of the data is quite reasonable.

In studies on W/Re thermocouples, Thomas (11) observed changes ranging from +3° to +7°C at 1100°C for sheathed couples cycled for 5 hr in helium between 1100° and 2000°C. These results are also in agreement with the present investigation. Furthermore, Thomas found that the emf produced by W/Re couples at a specific temperature was highly dependent on the lot of material and the degree of heat treatment, and these findings are also compatible with the results of the present study.

Lakh, Stadnyk, and Kuz'ma (12) observed instability changes, ranging from +1% to +4%, at 1400° and 1800°C for several W-Re alloy couples (W-5%Re/W-20%Re, W-10%Re/W-20%Re, and W-15%Re/W-20%Re) fired at these temperatures in vacuum, argon, and hydrogen for various time intervals up to 400 hr. Instability drifts of approximately ±1% for temperatures of 1200° to 1450°C for W/W-26%Re and W-5%Re/W-26% Re thermocouples fired in high vacuums (10^{-6} to 10^{-8} torr) for times up to 1000 hr were noted by Hendricks and McElroy (13). The results and conclusions of these investigators also compare favorably with those found in the present studies, despite differences in samples and investigative procedures.

Although most of the instability data in this report can only be compared qualitatively with that of other investigators, the results are generally in agreement. Inconsistencies are believed to result from differences in methods of investigation, limited information on gradient zones and immersions during the firing and calibration experiments, and variations in firing times, environments, and temperatures.

CRITERIA FOR THE USE OF REFRACTORY METAL THERMOCOUPLES AT HIGH TEMPERATURES

1. The emf instability for refractory metal thermocouples results from compositional or other internal changes along the thermal gradient zone of one or both elements. These changes are complex and may be caused by contamination from ceramic protection tubes, internal anomalies in the wires (recrystallization or phase changes), and gain or loss of small amounts of impurities. Some factors which contribute to instability, such as the exchange of alloying elements at welded junctions or preferential volatilization of one metal (or oxide) from alloy legs, were generally found to be of small significance. For couples sheathed in high-purity alumina, the contaminating effect is not too pronounced at 1625°C for 150 hr in argon; but after that time, reaction between the

alumina and most of the refractory metals (except Re) proceeds rapidly (reaction of Ta thermoelements with alumina sheathing occurs in a matter of a few hours). Consequently, when refractory metal thermocouples are used for extended periods above 1500°C, an unsheathed couple gives maximum reliability; but high-purity alumina sheathing may be used for a limited time.

2. Most of the refractory metal wires exhibited some internal changes, which may include transitions from unstable to stable crystalline forms. Prefiring can eliminate some of the instability changes noted for W, Mo, Re, and the alloy wires. However, W and Mo elements become severely embrittled by prefiring. Addition of 3% or 5% Re to W seems to improve stability and retention of ductility. Prefiring of these alloys, as well as the W-26% Re (or W-25% Re) and Re-50% Mo, is advantageous. There is some loss of ductility, and subsequent handling after heat treatment should be held to a minimum.

3. Pure Re thermoelements sheathed in alumina were found to be very stable up to 360 hr at 1625°C in argon and remained quite ductile. This element appears to have the most promise for use at high temperatures.

4. Significant emf differences in various batches of the same wire were observed in some cases but were generally less than anticipated. Prefiring, when possible, may eliminate some of the effect of these inhomogeneities; but calibration of each lot seems advisable.

5. For high-temperature experiments in vacuum of longer than 24-hour duration, the use of a vac-ion pump or vacuum pressures below 10^{-7} torr is recommended when maximum reliability of refractory metal couples is sought. Vacuums of 10^{-6} torr are insufficient to prevent back-diffusion of vacuum pump oil which will react with the refractory metals at temperatures above 1000°C.

6. A relationship seems to exist between instability and ductility. For a particular thermoelement, increased instability is generally accompanied by increased embrittlement. Cold-working after firing has also been found to increase instability changes for several refractory metals and alloys. Consequently, couples of these materials should be subjected to a minimum of bending.

7. Tantalum was observed to have considerable instability at low temperatures. Since this instability appears to be associated with the reaction of Ta with impurities in the atmosphere, more positive protection of this thermoelement may improve its thermal stability. At present, it is not recommended for use in thermocouples.

8. Instabilities of refractory metal thermocouples, resulting from contamination or internal changes, were found to be influenced by temperature and certain geometry effects. Whereas instability changes for noble metal thermoelements (1) due to iron contamination were found to be linear with temperature, those noted for the refractory metals were not necessarily linear. Thermoelements of W-26% Re and Re-50% Mo, in particular, demonstrated rather marked increases in their effective instabilities with increasing temperature. Consequently, determination of the instability drift of a refractory metal couple at lower temperatures does not necessarily reflect proportional changes at higher temperature.

9. If refractory metal thermocouples are used under conditions where compositional or internal changes in either element may be expected, depth of immersion should be maintained constant or increased for maximum reliability.

10. For couples used in circumstances where contamination or other changes may be expected, the thermocouples should be periodically checked for induced inhomogenities along their full length. This can be done rather easily by comparing the output of the suspect couple against an unused one at varying depths of immersion in a long isothermal furnace.

11. For thermocouples sheathed in alumina and used at 1625°C for 120 hr in argon, the approximate order of decreasing reliability at this temperature is as follows:

a. W-3%Re/Re or W-5%Re/Re

b. W-3%Re/Mo or W-5%Re/Mo

c. Re/Re-50%Mo

d. W-3%Re/W-26%Re or W/Re

e. W/W-26%Re, W-5%Re/W-26%Re, Re/W-26%Re, Mo/W-26%Re or W/Mo

f. Re-50%Mo/W-26%Re

The data on contamination and other instability effects presented in this report are incomplete. Variables such as geometry parameters and purity were difficult to control. Trace impurities and the crystalline state of thermoelements were shown to be important, and variations in different batches of material from the same source can be expected. Trace impurities from environment and insulators were also shown to be significant. All these factors tend to limit the specific application of the data to practical problems. However, the several criteria which have been drawn from the data should help to identify and control many sources of error which may be encountered when refractory metal thermocouples are used at high temperatures.

ACKNOWLEDGMENTS

The authors are indebted to Samuel A. Cress of the Metallurgy Division for spectrographic analyses of thermocouple materials, Robert Seebold of the Optics Division for metallographic studies, and Dale D. Williams of the Chemistry Division for chemical analyses.

REFERENCES

1. Walker, B.E., Ewing, C.T., and Miller, R.R., *Rev. Sci. Instr.* **33(No. 10)**:1029 (1962)
2. Inouye, H., *Tech. Conf. on Applied Aspects of Refractory Metals,* Dec. 1963
3. Chaussain, M., *Foundry Trade J.* **91(No. 1823)**:147 (1951)
4. Hoskins Mfg. Co., Table Adopted Sept. 1961
5. Sims, C.T., Gaines, G.B., and Jaffee, R.I., *Rev. Sci. Instr.* **30(No. 2)**:112 (1959)
6. Morgan, F.H., and Danforth, W.E., *J. of Appl. Phys.* **21**:113 (Feb. 1950)
7. Fanciullo, S., "Thermocouple Development, Lithium-Cooled Reactor Experiment," PWAC-422 (Mar. 1964)
8. Lachman, J.C., and Kuether, F.W., *ISA J.* **7(No. 3)**:67 (1960)
9. Kuether, F.W., and Lachman, J.C., *ISA J.* **7(No. 4)**:66 (1960)
10. Lachman, J.C., *ISA Trans.,* **1(No. 4)**:340 (1962)
11. Thomas, D.B., *J. Res. NBS,* **67C(No. 4)**:337 (1963)
12. Lakh, V.I., Stadnyk, B.I., and Kuz'ma, Yu.B., *Teplofizika Vysokikh Temperatur,* **1(No. 2)**:299 (1963)
13. Hendricks, F.W., and McElroy, D.L., "High-Temperature High-Vacuum Thermocouple Drift Tests," ORNL-TM-883, Aug. 1964

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* U.S. Naval Research Laboratory Washington, D.C. 20390	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

Instability of Refractory Metal Thermocouples

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

An interim report on one phase of the problem.

5. AUTHOR(S) *(Last name, first name, initial)*

Walker, B.E., Jr., Ewing, C.T., and Miller, R.R.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 26, 1965	16	13

8a. CONTRACT OR GRANT NO. NRL Problem C05-08 b. PROJECT NO. RR-007-01-46-5400 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6231 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. AVAILABILITY/LIMITATION NOTICES

Unlimited Availability

Available at CFSTI—

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Dept. of the Navy (Office of Naval Research)

13. ABSTRACT

Thermoelectric instabilities of some refractory metal thermocouples have been studied in the temperature range 1000° to 2000°C under vacuum and neutral atmospheres. The sources of instability were found to be complex, involving contamination from ceramic protection tubes and furnace environments, preferential volatilization, and various thermal anomalies such as recrystallization and phase changes in the refractory thermoelements. Refractory thermocouples and thermoelements were studied under a variety of conditions, and emf changes associated with each were noted. Recommendations were made for the selection and application of these thermocouples to attain maximum thermoelectric stability.

DD FORM 1 JAN 64 1473

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Refractory metal thermocouples Thermocouple instability Stability furnace Prefiring						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2*a*. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2*b*. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7*a*. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7*b*. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8*a*. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8*b*, 8*c*, & 8*d*. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9*a*. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9*b*. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through
____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through
____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through
____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.