

NRL Report 6236

A Study of the Instability of Noble Metal Thermocouples in Vacuum

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Chemistry Division*

May 10, 1965



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

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Thermoelectric instabilities of noble metal thermocouples and individual thermoelements (platinum, rhodium, iridium, and platinum-rhodium and iridium-rhodium alloys) have been studied in vacuum in the temperature range 800° to 1600°C. These studies are an extension of previous work performed in oxidizing and neutral atmospheres. As in that work, the principal source of instability was found to be contamination of the thermoelements by iron impurities from ceramic protection tubes. Iron contamination had a maximum effect on instability in Pt and the alloys but was less important for Ir and Rh. Thermocouple errors associated with this contamination in vacuum were compared with the previous data in air and argon, and the instabilities in vacuum were found to be comparable with those found in argon. The instabilities found for couples in argon and vacuum environments were of much greater magnitude than those found in air.

Criteria have been set forth for the use of noble element thermocouples. Important among these are the use of low-iron-content sheathing and large-diameter elements.

INTRODUCTION

In the measurement of thermal properties at temperatures from 1000° to 2000°C, thermocouples appear to offer the most promise for precise temperature determinations over extended periods of time. However, the reliability of even the common Le Chatelier thermocouple could not be predicted prior to recent investigations in this field (1).

Previous investigations at this Laboratory, involving platinum, rhodium, platinum-rhodium alloys, iridium, and iridium-50% rhodium, showed that contamination from iron in alumina sheathing was the major factor contributing to instability in both oxidizing and neutral atmospheres. Due to a lack of information concerning the behavior of noble metal couples in vacuum, another study was initiated to provide sufficient data to allow prediction of the reliability of noble metal couples in vacuum.

The instability (change in emf output with time) of a thermocouple at constant immersion is normally associated with compositional changes in the thermal gradient zone of each element. These changes may result from contamination by furnace atmosphere or ceramic protection tubes, from exchange of alloying elements at the welded

junction, or from preferential volatilization of an impurity (metal or oxide) from the alloy leg. Time, temperature, atmosphere, wire size, and geometry effects may also influence the magnitude of a compositional change which contributes to the instability.

In this study and the previous one (1), when thermocouples were given positive protection from furnace environment, impurities in ceramic protection tubes were found to be the principal source of contamination contributing to instability at high temperatures. Contamination tests in both investigations were confined to alumina insulation because of the availability and prevalent use of this material.

EXPERIMENTAL METHOD

The methods employed for the instability studies were discussed in detail in the previous article (1). The procedure may be described briefly as follows: A sheathed thermocouple or thermoelement was inserted into a firing furnace at a predetermined temperature and immersion depth and heated for a specified time. Upon removal from the furnace, each individual test leg was joined to a reference wire of the same material, and the junction was pulled into a constant temperature furnace for measuring stability (Fig. 1). Measurements were then made of the

NRL Problem C05-08; Project ONR-RR-007-01-46-5400. This is an interim report; work is continuing. Manuscript submitted December 12, 1964.

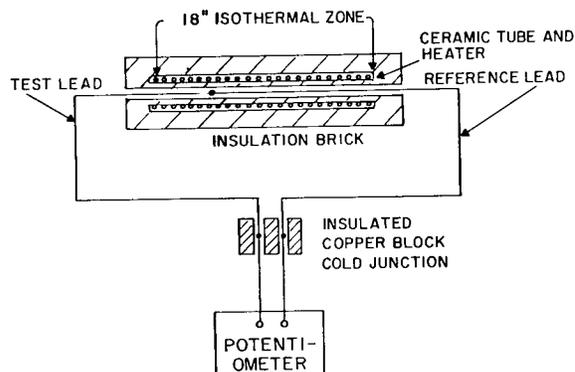


Fig. 1 - Stability furnace

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 the original junction. If the test wire and reference wire were identical before heat treatment, observed readings represented actual deviations in the thermoelectric force of the test wire for a temperature difference of 835°C (temperature difference between the constant-temperature furnace and room). Unheated portions of a test wire were also compared to the reference standard, and any thermoelectric potential between the two, generated by a chemical or physical inhomogeneity, was readily detectable. In practice, unheated test wires and reference wires from the same lot generally were identical for the noble metal thermoelements within $\pm 2 \mu\text{v}$. Iridium, Rh, and Ir-50%Rh thermoelements, however, showed variations of approximately $\pm 20 \mu\text{v}$.

To avoid contamination from the furnace environment and crosscontamination with adjacent wires, each test wire or thermocouple was individually protected by three alumina tubes—a test sheathing inside a closed-end tube of the same material, and an outer closed-end tube of high-purity alumina.

EXPERIMENTAL RESULTS

Instability of Pt, Rh, and Pt-Rh Thermoelements in Alumina in Vacuum

Thermoelectric changes measured at 860°C for individual elements of Pt, Rh, and Pt-Rh alloys, sheathed in McDanel AP35 and DeGussie AL23

and fired for 120 hr in vacuum, are shown graphically in Figs. 2 and 3. For each temperature and grade of alumina sheathing, maximum emf changes in the noble metals are plotted as a function of the percent Rh in the wires. The furnaces for the firing tests had isothermal zones of approximately 3 in., and the plotted change, in each case, represents the maximum observed deviation of the thermal emf at 860°C (relative to 0°C) for that portion of wire subjected to full firing temperature. All firing tests were conducted at pressures below 5×10^{-5} torr. Since instability was previously found to be a function of wire size, all tests were made with 20-mil wire. Test wires and reference wires were of the purest grade available.

The sign terminology used for the data in Figs. 2 and 3 and subsequent data follows the generally accepted usage. When a negative charge is generated at the cold end, the thermoelectric change is designated negative; and when a negative charge is generated at the hot end, the change is designated positive. 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 thermocouple.

The identification of iron impurities in alumina as the principal source of contamination leading to thermocouple instability in argon and air was fully established in the previous article (1). Evidence that iron is also the main contaminant in vacuum includes: (a) similarity of the instability changes in vacuum as shown in Figs. 2 and 3 with those found previously in an inert atmosphere, (b) correlation of the emf changes for a particular insulation with the vapor pressure of iron, (c) correlation of the emf changes with percent iron impurities in the alumina for a particular temperature, and (d) spectrographic analyses showing increased iron content in the test wires when significant emf changes were noted.

The emf changes indicated in Figs. 2 and 3 are only slightly less than those noted for wires fired in argon. This is as expected since the mechanism for iron migration to the thermoelements apparently depends on a reduction or decomposition of iron compounds in the alumina insulation

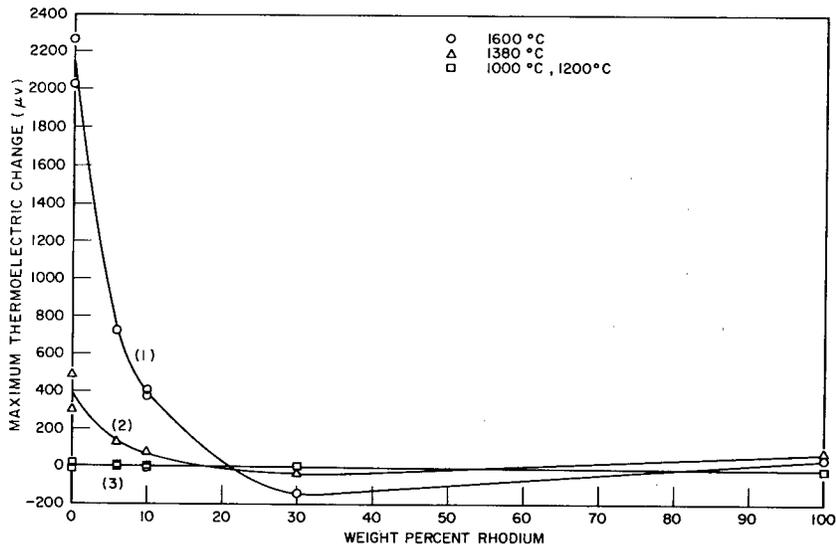


Fig. 2 — Maximum thermoelectric changes (μv) at 860°C for individual elements (20-mil diameter) of Pt, Rh, and Pt-Rh alloys, sheathed in McDanel AP35 insulation and fired for 120 hr in vacuum at the indicated temperature

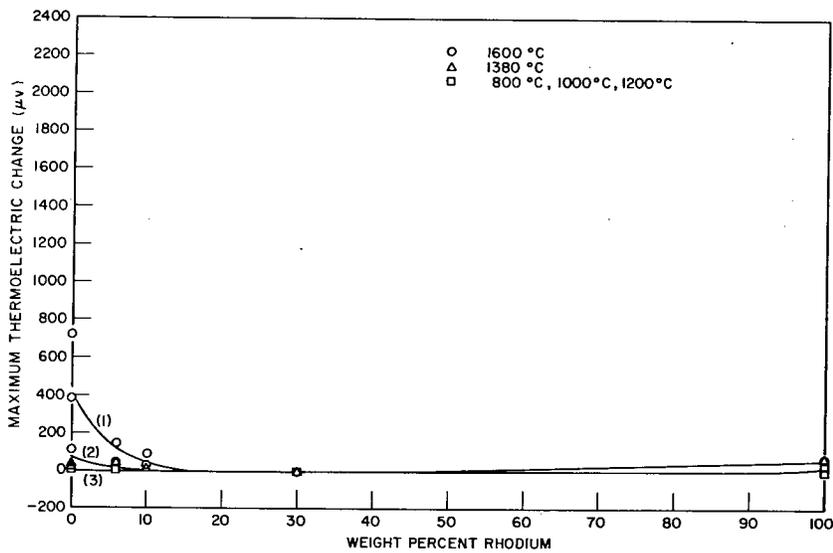


Fig. 3 — Maximum thermoelectric changes (μv) at 860°C for individual elements (20-mil diameter) of Pt, Rh, and Pt-Rh alloys, sheathed in DeGussit Al23 insulation and fired for 120 hr in vacuum at the indicated temperatures

and subsequent vaporization and diffusion into the noble metal wires. This would be expected to occur in either argon or vacuum.

Figures 2 and 3 also demonstrate the effect of contamination from alumina sheathing with varying iron contents (McDanel AP35 contains 0.07 wt-% iron, and DeGussit Al23, 0.03 wt-%

iron) and the influence of temperature on contamination and instability. The emf change due to iron contamination is maximum for pure Pt and falls in a well-defined manner as the proportion of Rh in the wire is increased at a particular temperature. The instability in the case of Rh is apparently in part the result of iron contamination, but

complete stabilization of this wire could not be achieved, and part of the emf change may result from internal changes in the Rh wire. The influence of temperature on contamination and instability is readily apparent. Above 1400°C, the noble metals exhibit significant emf changes in the low-iron-content alumina and gross changes in the alumina of higher iron content.

Preferential volatilization of Pt or Rh has been regarded by several investigators (2-6) as the governing factor contributing to instability of Pt-Rh thermocouples in vacuum, but this investigation revealed no evidence of significant volatilization. Iron contamination, when noble metals are sheathed in alumina, remains the dominant factor contributing to instabilities in all three environments—vacuum, argon, and air.

Instability of Ir and Ir-Rh Thermoelements in Argon and Vacuum

A few instability tests in argon were made on Ir and Ir-50%Rh thermoelements, with limited tests on Ir-40%Rh and Ir-60%Rh. Larger emf changes were noted for the 40 and 60% alloys. This is evident from Table 1, which shows the net instability changes (°C) at 860°C for Ir/Ir-Rh alloy thermocouples fired for 120 hr in argon at 1600°C in low-iron-content alumina. Consequently, the studies presented in vacuum were made involving only Ir and Ir-50%Rh thermoelements.

The maximum emf changes at 860°C for Ir wires fired at several temperatures in various environments and grades of alumina are summarized in Table 2. Previous experiments (1) indicated that Ir and Ir-50%Rh thermoelements were contaminated by iron to about the same degree as the Pt metals in air and argon, but the instability changes due to contamination were

different. This was also found to be true in the current vacuum studies. Internal changes in Ir wire, due to loss of impurities, oxidation, or other effects appear to be the source of instability in this material. These emf changes are apparently independent of temperature, atmosphere, and alumina sheathing from approximately 1000° to 1700°C. The instability changes were noted for both unannealed wires and for wires annealed at 1900°C for 1 min. Time is a slight factor because no change is evident after firing for 24 hr at 1400°C, for example; but the change, which amounts to only 30 to 50 μ v, is almost complete after about 90 hr, and further heat treatment to 240 hr produces very little additional change. The lack of effect by iron contamination from the sheathing is understandable since the thermoelectric forces for both iron and Ir are of the same magnitude.

Table 3 summarizes data on Ir-50%Rh wire fired in air, argon, and vacuum. For this alloy, there are apparently competing mechanisms causing emf changes. Internal changes and contamination were both found to have an effect on this material in air and argon (1); and the effect in vacuum was found to be similar. Internal instability changes of nearly the same magnitude noted for Ir were observed for the Ir-50%Rh alloy when iron contamination was not a factor. However, when iron contamination occurs, the instability changes are greater in magnitude (though not nearly as large as noted in the Pt-Rh systems) and opposite in sign. Consequently, iron contamination may become the dominant factor at higher temperature in argon and vacuum; but at lower temperatures and in air, internal changes determine the instability of this material.

TABLE I
Instability Changes (°C) at 860°C for Ir/Ir-Rh Alloy Thermocouples Fired for 120 Hours in Argon at 1600°C in DeGussit Al23 Alumina Sheathing

Thermocouple Pair	Net Instability Change (°C) at 860°C, after Firing at Constant Immersion
Ir/Ir-50%Rh	-1
Ir/Ir-40%Rh	+6
Ir/Ir-60%Rh	+8

TABLE 2
Maximum emf Changes (μv) at 860°C for Ir Wires
(20-mil Diameter) Fired at Indicated Temperatures and Times,
in Various Alumina Sheathings and Atmospheres

Insulation	Firing Temp. (°C)	Atm.	Max. emf (μv) at 860°C Generated by Firing for 120 and 240 hr	
			120 hr	240 hr
DeGussit Al23	1387	Vac.	+37	—
DeGussit Al23	1590	Vac.	+50	—
McDanel AP35	1206	Vac.	+33	—
McDanel AP35	1387	Vac.	+33	+40
McDanel AP35	1590	Vac.	+37	+48
DeGussit Al23	1373	Argon	+34	—
DeGussit Al23	1577	Argon	+53	—
DeGussit Al23	1605	Argon	+54	—
DeGussit Al23	1632	Argon	+47	—
DeGussit Al23	1647	Argon	+56	—
McDanel AP35	1373	Argon	+36	+33
DeGussit Al23	1380	Air	+28	—
DeGussit Al23	1730	Air	+39	—
McDanel AP35	1380	Air	+39	—

TABLE 3
Maximum emf Changes (μv) at 860°C for Ir-50% Rh Wires
(20-mil Diameter) Fired at Indicated Temperatures and Times
in Various Insulators and Atmospheres

Insulation	Firing Temp. (°C)	Atm.	Max. emf (μv) at 860°C Generated by Firing for 120 and 240 hr	
			120 hr	240 hr
DeGussit Al23	1387	Vac.	+60	—
DeGussit Al23	1590	Vac.	+50	—
McDanel AP35	1206	Vac.	+62	—
McDanel AP35	1387	Vac.	-58	-120
McDanel AP35	1590	Vac.	-145	-303
DeGussit Al23	1373	Argon	+35	—
DeGussit Al23	1577	Argon	-10	—
DeGussit Al23	1632	Argon	-155	-320
DeGussit Al23	1647	Argon	-210	—
McDanel AP35	1373	Argon	-13	—
DeGussit Al23	1380	Air	+96	—
DeGussit Al23	1730	Air	+98	—
McDanel AP35	1380	Air	+105	+60

Instability Tests of Noble Metal Thermocouples in Vacuum and Comparison of Results with Data in Air and Argon

It was noted by Chaussain (7) in reference to silicon and verified by the authors in reference to iron (1) that the thermal emf change caused by contamination was linearly proportional to temperature; and, therefore, the thermoelectric power α ($\mu\text{v}/^\circ\text{C}$) generated by a given degree of contamination should have the same value at any temperature. The stability test used in this investigation measured α along the length of each couple leg. By additional measurements of the temperature gradients along the wires at any predetermined temperature of the firing furnace, it was convenient to calculate the net emf change in microvolts for a given thermocouple, when fully immersed, by integrating the following equation over the contaminated lengths of both legs:

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

where ΔE is the net emf change of the thermocouple reading, t is the temperature of both legs in the gradient zone at a distance x from the junction, α_x^+ is the thermoelectric power of the contamination for the leg attached to the positive pole of the potentiometer at a distance x from the junction, and α_x^- is the thermoelectric power of the contamination for the leg attached to the negative pole of the potentiometer at a distance x from the junction.

Comparisons of the instabilities of several thermocouple pairs, sheathed in McDanel AP35 (0.07 wt-% iron) or DeGussit Al23 (0.03 wt-% iron) and fired for 120 hr in vacuum, are presented in Table 4. The net emf change of each couple was calculated using the procedure outlined above at the reduced temperature of 860°C after firing at constant immersion under specified conditions. Integrated microvolt changes were converted to corresponding changes in degrees centigrade. The maximum change for each thermocouple at the reduced temperature of 860°C is also presented to illustrate the error which could be generated by decreasing the immersion after firing. If the thermoelectric power ($\mu\text{v}/^\circ\text{C}$) of a given contamination is assumed to be constant with changes in temperature, the maximum

change in microvolt units will be approximately proportional to temperature and can be estimated for other temperatures.

The effectiveness of the integration procedure for calculating net changes at constant immersion was established by a standard referee technique. Since the observed and calculated values for the vacuum experiments are in reasonable agreement, as indicated in Table 4, this integration procedure was adopted for the majority of the tests in preference to the more time-consuming referee technique. The data shown in Table 5 were compiled by this method.

Since the instability tests permitted a measurement of the distribution and magnitude of emf changes in the individual thermoelements as a function of distance from the thermocouple weld, junction effects could be distinguished from contamination effects and studied independently. Transfer of a metal (or oxide) from one leg to the other by vaporization or diffusion could contribute to the instability of a couple. Both individual elements and welded combinations were fired in vacuum over the temperature range 800° to 1600°C. The distribution and magnitude of emf changes, however, were normally identical for individually fired wires and welded combinations; no junction effects for the various thermocouples were detected beyond 1 in. from the welded junctions.

The influence of time on the contamination of thermocouples in vacuum was investigated to a limited degree. The results agreed with the more extensive studies made in the neutral atmosphere investigation, which revealed that the effect of contamination was linear with time up to 216 hr (1). This influence of time on contamination is in accordance with similarities in instability noted for thermocouples fired in alumina sheathing in argon and vacuum environments.

Table 5 illustrates the behavior of several noble metal thermocouples as a function of firing temperature, insulation purity, and atmosphere. Maximum instabilities which could be generated by reducing the immersion of these couples are approximately five to eight times the net instabilities shown. Under minimum conditions of iron contamination, the order of decreasing thermocouple reliability in all three environments for the Pt-Rh series is Pt-6% Rh/Pt-30% Rh, Pt/Rh, and Pt/Pt-10% Rh. The Ir/Ir-50% Rh couple

TABLE 4
Instability Changes (°C) for Various Thermocouple Pairs Fired
in Vacuum as a Function of Temperature and Immersion in
McDanel AP35 and DeGussit Al23 Alumina Insulation

Insulation	Couple Pair	Firing Temp. (°C)	Net Instability Change (°C) at 860°C after Firing at Constant Immersion for 120 hr		Maximum Instability Changes (°C) at 860°C Which Could Be Generated by Decreasing Immersion after Firing 120 hr	
			Obs.*	Calc.		
McDanel AP35	Pt/Pt-10%Rh	1010	0	< 0.2	< 0.2	
		1205	-1	< 0.5	-1	
		1380	-4	-6	-36	
	Pt/Rh	1595	-23	-38	-159	
		1010	0	< 0.2	-1	
		1205	-1	< 0.5	-2	
	Pt-6%Rh/Pt-30%Rh	1385	-4	-2	-12	
		1590	—	-29	-106	
		1010	0	0	< 0.5	
	Ir/Ir-50%Rh	1200	-1	< 0.5	-1	
		1385	-5	-4	-20	
		1590	—	-29	-104	
	DeGussit Al23	Pt/Pt-10%Rh	1205	+1	+3	+5
			1385	0	+2	-6
			1590	-5	-9	-26
Pt/Rh		800	0	< 0.2	< 0.2	
		1000	0	< 0.2	< 0.2	
		1200	0	< 0.5	< 0.5	
Pt-6%Rh/Pt-30%Rh		1380	0	< 0.5	-2	
		1595	-5	-4	-18	
		800	0	< 0.5	< 1	
Ir/Ir-50%Rh		1000	0	< 0.5	< 1	
		1200	0	< 0.5	< 1	
		1380	+3	+1	+3	
Pt/Rh		1595	-7	-5	-20	
		800	0	< 0.2	< 0.5	
		1000	0	< 0.2	< 1	
	1200	0	< 0.5	< 1		
	1380	0	-1	-6		
	1595	-2	-2	-12		
Ir/Ir-50%Rh	1385	+1	+3	+4		
	1590	0	+4	+6		

*Observed values taken from optical pyrometer comparisons.

TABLE 5
 Net Instability Changes (°C) at 860°C for Several Noble Metal Thermocouples (20-mil diameter) Fired for 120 Hours at Indicated Temperatures in McDanel AP35 and DeGussit Al23 Alumina Sheathing in Various Environments

Insulation	Couple Pair	Firing Temp. (°C)	Net Instability Changes (°C)		
			Air	Argon	Vac.
DeGussit Al23	Pt/Pt-10%Rh	1000	0	0	0
		1200	0	0	0
		1380	0	0	0
		1600	-1	-11	-4
	Pt/Rh	1000	0	0	0
		1200	0	0	0
		1380	0	0	+1
		1600	—	—	-5
	Pt-6%Rh/Pt-30%Rh	1000	0	0	0
		1200	0	0	0
		1380	0	0	-1
		1600	0	-7	-2
	Ir/Ir-50%Rh	1000	—	—	—
		1200	+2	+2	+3
		1380	+2	0	+3
		1600	+4	-2	+4
McDanel AP35	Pt/Pt-10%Rh	1000	0	0	0
		1200	0	—	0
		1380	0	-10	-6
		1600	—	—	-38
	Pt/Rh	1000	0	0	0
		1200	0	0	0
		1380	-1	-2	-2
		1600	—	—	-29
	Pt-6%Rh/Pt-30%Rh	1000	0	0	0
		1200	0	—	0
		1380	0	-4	-4
		1600	—	—	-29
	Ir/Ir-50%Rh	1000	—	—	—
		1200	+2	+2	+3
		1380	+2	-1	+2
		1600	—	—	-9

appears to be more reliable than any of the Pt-Rh couples in argon or vacuum at higher temperatures under minimum iron contamination, but the internal changes associated with these thermoelements make this couple less reliable in air and at lower temperatures in argon and vacuum. When gross iron contamination is a factor, the Ir/Ir-50%Rh couple is more resistant to changes than any of the Pt-Rh series thermocouples, and the Pt/Rh couple is slightly more stable than the Pt-6%Rh/Pt-30%Rh combination. Interpolation of the data on Pt-Rh thermoelements (Fig. 2), and the data on Rh indicates that a Rh/Pt-20%Rh couple would be more reliable than the previously discussed Pt/Rh combinations when iron contamination is a factor, and only slightly less stable than the Ir/Ir-50%Rh thermocouple.

DISCUSSION

The results of this study cannot be fully compared with the work of other investigators. The difficulty in comparison of the data is the result of short time periods of testing, lack of information on gradient zones and immersions during firing and calibration experiments, insufficient data on environmental conditions, and limited experimentation. For the Pt-Rh couples fired in vacuum, the negative changes observed in the emf due to contamination are consistent with the findings of McQuillan (2), Metcalfe (3), Svec (5), and Dwyer and Klamut (8). However, most of these investigators concluded that vaporization of Pt or Rh was responsible for the instability of Pt-Rh couples, whereas no evidence was found in this study to indicate that volatilization or diffusion of either metal was a significant factor in the observed instabilities.

Although no directly applicable experiments were conducted, the information gained from the air, argon, and vacuum experiments provides some basis for speculation on the instability of noble metals in reducing atmospheres. The mechanism of iron contamination from alumina sheathing in oxidizing and neutral atmospheres appears to involve the reduction or decomposition of iron compounds present as impurities. McQuillan (2), Bennett (9), Ehringer (10), and Darling (6) noted the reduction of silica in the presence of sulfur or other reducing agents and its subsequent reaction with and effect on Pt.

Consequently, it seems probable that the transfer of iron from the alumina to noble metal couples would be greatly accelerated under reducing atmospheres. In addition, silica, which is present in even greater amounts than iron in alumina, would also tend to be reduced, thus providing further thermocouple contamination. The possibility that contamination could become significant in shorter times and at lower temperatures than those noted for thermocouples in oxidizing and neutral atmospheres may be a reasonable expectation.

CRITERIA FOR THE USE OF NOBLE METAL THERMOCOUPLES AT HIGH TEMPERATURES

1. The emf instability of a noble metal thermocouple generally results from compositional changes in the thermal gradient zone of one or both elements. When Pt-Rh series thermocouples are used for extended periods at temperatures between 1000° and 1700°C in oxidizing, neutral, or vacuum atmospheres, compositional changes result mainly from a contamination by ceramic protection tubes. Contributing effects from the preferential volatilization of one metal (or oxide) from alloy legs or the exchange of alloying elements at welded junctions have been shown to be very small. With alumina sheathing, the principal impurity contributing to this instability has been identified as iron. In vacuum or neutral atmosphere, the instability generated by iron contamination is at least one order of magnitude greater than corresponding changes in an oxidizing atmosphere. When Pt-Rh thermocouples are used in neutral or vacuum atmospheres above 1000°C, or in air above 1200°C, a protective sheathing of very low iron content is required.

2. The instabilities of Pt-Rh couples, resulting from contamination by iron in an oxidizing atmosphere (to 1400°C), were found to be independent of wire size; and the distribution of contaminant along each element is a single function of temperature. In vacuum and neutral atmospheres, however, both the degree and the distribution of contamination were influenced by wire size, temperature, firing time, and other geometry effects. Therefore, large-diameter elements are advisable for maximum stability in neutral atmospheres and in vacuum.

3. The instability of thermocouples in the Pt-Rh series, sheathed in alumina and heated for extended periods, increases rapidly in the 1000° to 1700°C temperature range. In general, instability also increases with decreasing Rh content in the thermoelements.

4. Instability of a pure Rh thermoelement was found to result mainly from internal changes which occur in Rh, and only a small part was due to iron contamination. Thermocouples with pure Rh in one leg can be more reliable than other Pt-Rh combinations for conditions of gross iron contamination but will be less reliable if iron contamination is not a factor. Therefore, the advisability of using thermocouples with pure Rh in one leg (Pt/Rh and Rh/Pt-20%Rh) is dependent on the iron content of the sheathing and the firing temperature.

5. While Ir and Ir-Rh alloy thermoelements show excellent resistance to instability resulting from contamination by iron, those tested appear to exhibit instability from internal changes in the wires. As with Rh, the reliability of thermocouples involving these materials is dependent on the degree of iron contamination to be expected. For conditions where gross contamination is expected in argon and vacuum, the Ir/Ir-50% Rh couple is potentially more reliable than any of the Pt-Rh couples.

6. If thermocouples are to be used under conditions where compositional changes in either element are expected, the depth of immersion should be maintained constant or increased if maximum stability is required.

7. If a couple is used under any condition which could lead to contamination, deviations from the original calibration may be expected; and the couple should be periodically checked for induced chemical inhomogeneity along its full length. This can be done by comparing the output of the suspect couple against an unused couple at varying depths of immersion in a long isothermal furnace.

8. The firing of thermoelements prior to calibration and use was found to be unnecessary for the wires used in this study. No positive conclusions regarding the necessity for pre-firing could be reached from the small sampling employed. Pre-firing could effect equalization of any physical or

chemical inhomogeneity in a wire and also aid in the removal of any volatile impurities. On the other hand, it should be noted that pre-firing did cause some recrystallization, which led to losses in mechanical strength and a reduction in useful life.

SUMMARY

The data on contamination and instability presented in this report and the preceding article (1) are by no means complete and definitive. Several factors limit the specific application of the data to practical problems. Variables such as geometry factors and purity were difficult to control. Trace impurities in the thermocouple insulation (or the thermoelements) were shown to be important, and variations in purity can be expected in different batches from the same source. However, the several criteria which have been drawn from the data should aid in the identification and control of many sources of error which are encountered when noble metal thermocouples are used above 1000°C.

ACKNOWLEDGMENT

The authors are indebted to Samuel A. Cress of the Metallurgy Division for spectrographic analyses of the thermocouple materials.

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1. ORIGINATING ACTIVITY <i>(Corporate author)</i> U.S. Naval Research Laboratory Washington, D.C. 20390		2 a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
		2 b. GROUP
3. REPORT TITLE A Study of the Instability of Noble Metal Thermocouples in Vacuum		
4. DESCRIPTIVE NOTES <i>(Type of report and inclusive dates)</i> An interim report on one phase of the problem.		
5. AUTHOR(S) <i>(Last name, first name, initial)</i> Walker, B. E., Ewing, C. T., and Miller, R. R.		
6. REPORT DATE May 10, 1965	7 a. TOTAL NO. OF PAGES 12	7 b. NO. OF REFS 10
8 a. CONTRACT OR GRANT NO. NRL Problem C05-08	9 a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6236	
b. PROJECT NO. ONR-RR-007-01-46-5400	9 b. OTHER REPORT NO(S) <i>(Any other numbers that may be assigned this report)</i>	
c.		
d.		
10. AVAILABILITY/LIMITATION NOTICES Unlimited availability Available at CFSTI—		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research)	
13. ABSTRACT <p>Thermoelectric instabilities of noble metal thermocouples and individual thermoelements (platinum, rhodium, iridium, and platinum-rhodium and iridium-rhodium alloys) have been studied in vacuum in the temperature range 800° to 1600°C. These studies are an extension of previous work performed in oxidizing and neutral atmospheres. As in that work, the principal source of instability was found to be contamination of the thermoelements by iron impurities from ceramic protection tubes. Iron contamination had a maximum effect on instability in Pt and the alloys but was less important for Ir and Rh. Thermocouple errors associated with this contamination in vacuum were compared with the previous data in air and argon, and the instabilities in vacuum were found to be comparable with those found in argon. The instabilities found for couples in argon and vacuum environments were of much greater magnitude than those found in air.</p> <p>Criteria have been set forth for the use of noble element thermocouples. Important among these are the use of low-iron-content sheathing and large-diameter elements.</p>		

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Noble metals Noble metal alloys Platinum Iridium Rhodium Thermoelectric instability Thermocouple sheathing contamination Vacuum Alumina sheathing						

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