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PROBLEMS OF INVESTIGATING THERMOELECTRODE ALLOYS, STABLE TO OXIDATION UP TO 2000°C

by

I. A. Aleksakhin, I. R. Lepin, et al.

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PROBLEMS OF INVESTIGATING THERMOELECTRODE ALLOYS, STABLE TO OXIDATION UP TO 2000°C

By: I. A. Aleksakhin, I. R. Lepin, et al.

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ABSTRACT: The possibility of developing a thermocouple capable of measuring temperatures up to 2000°C in oxidizing media and in air was studied. Only alloys based on Ir are suitable for such thermocouples. A review is given on work done on the development of high-temperature thermocouples performing in oxidizing media. The thermocouple Ir-60Rh/Ir, suitable for measuring temperatures up to 2000°C for 10-20 hrs. in air was the best of the known thermocouples. Data for heat resistance, phase compn. of Ir alloys, and properties of pure metals indicate that good thermoelectric properties and high stability can be found in alloys of Ir with Rh, Pt, Pd, and Au. Alloys of Ir with nonnoble metals, and complex alloys based on Ir can also be used. 40 references. English translation: 21 pages.

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PROBLEMS OF INVESTIGATING THERMOELECTRODE ALLOYS, STABLE TO OXIDATION UP TO 2000°C

I. A. Aleksakhin, I. R. Lepin, G. B. Lapp, and B. K. Bragin

The development of science and technology at present requires the application and measurement of continuously higher temperatures. The solved problem appears to be measurement of high temperatures in a vacuum and in a neutral and reduced atmosphere. Under these conditions can be used thermocouples of high melting base metals: tungsten, molybdenum, tantalum, rhenium, and their alloys. But in an oxidizing medium, including air, these metals are inapplicable because of rapid oxidation and disintegration of the thermoelectrodes caused by it. The most stable to oxidation appear to be, as is known, noble metals.

For example the widely known platinum-rhodium-platinum rhodium thermocouple can be applied up to 1600°C, and a platinum rhodium-platinum rhodium thermocouple (30 and 6% rhodium) - up to 1800°C. The limit of their application is due substantially to the melting point.

Considering that above 2000° only iridium, ruthenium and osmium melt, it can be concluded that the sole metal which can be utilized in this case as a base of thermoelectrode alloys appears to be iridium. Ruthenium and osmium are brittle metals and cannot be processed into wire.

Known thermocouples of iridium and its alloys

The first thermocouples of iridium and its alloys were already known in 1909 (1, 2). These were iridium thermocouples - an alloy of iridium and 10% ruthenium (Ir/Ir10Ru) and a thermocouple introduced somewhat later - iridium alloy with 10% rhodium-iridium (Ir10Rh/Ir). Hoffmann characterizes both thermocouples as brittle (1, 3); this pertains especially to the electrode with 10% ruthenium. Thermoelectrodes Ir10Rh and Ir10Ru, according to Feussner (4) can be processed into wire only at a temperature of "white heat", but in this case it is difficult to obtain a wire of identical lengthwise cross-section. The stability of the thermoelectromotive force (thermo-emf) of an Ir/Ir10Ru thermocouple is evidently, very poor, because the author points out the necessity of frequency recalibration of this thermocouple because of the burning out of the ruthenium. The thermo-emf developed by both thermocouples is extremely low and constitutes for the Ir/Ir10Ru thermocouple 4.6 mV, and for the Ir10Rh/Ir thermocouple 3.5 mV at 2000°C. Their sensitivity in an area of high temperatures is low and constitutes 1.5 and 0.5 mV/deg, respectively (Fig. 1).

It is remarkable that iridium in an Ir/Ir10Ru thermocouple appears to be a positive electrode and an Ir10Rh/Ir thermocouple - a negative electrode. This gave the possibility, having combined electrodes of iridium-rhodium and iridium-ruthenium alloys, to obtain an Ir10Rh/Ir10Ru thermocouple with a thermo-emf reaching 11 mV at 2000°C (3). Although its sensitivity is still lower than the sensitivity of the known platinum-rhodium-platinum (Pt10Rh/Pt) thermocouple, practically two-fold in comparison with the sensitivity of other iridium thermocouples it is quite high (Fig. 1). Unfortunately, the Ir10Rh/Ir10Ru thermocouple has serious inherent deficiencies: brittleness of electrodes, poor machineability into wire, instability of thermo-emf because of the buring up of the ruthenium from a negative electrode.

A serious step forward was made thanks to Feussner's investigations (4, 5), he established that iridium alloys with a rhodium content of more than 10% are relatively easily processed into wire. Feussner proposed two thermocouples: Ir30Rh/Ir and Ir60Rh/Ir (4), of which he gave preference to the Ir60Rh thermocouple. The fact is that the properties of Ir30Rh and Ir60Rh electrodes are approximately identical, but the latter in a couple with iridium develops a much higher thermo-emf - about 11 mV at 2000°C (Fig. 1). Losses of iridium-rhodium alloys as a result of oxidation and evaporation according to Feussner are considerably less than losses of pure iridium. Feussner (5), considers that frequent recalibration of the Ir60Rh/Ir thermocouple is not required.

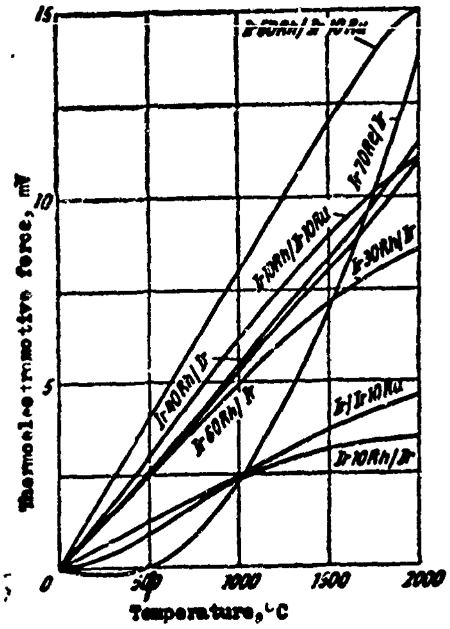

Fig. 1. Thermo-emf of thermocouples of iridium and its alloys (by a combination of literature data).

Also known is an Ir60Rh/Ir10Ru (2, 6) thermocouple, which develops maximum thermo-emf of the iridium thermocouples - about 15 mV at 2000°C (Fig. 1). But the Ir10Ru electrode, offering the possibility of increasing the thermo-emf of the thermocouple, simultaneously makes it unstable because of the above mentioned burn up of the ruthenium.

The advisability of selecting an alloy with 60% rhodium as the positive electrode of the Ir60Rh/Ir thermocouple was doubted by Carter (7), who proposed to replace it with an alloy with 40% rhodium. Carter assumes that at high temperatures, from the iridium-rhodium alloy primarily the iridium will burn out as a result of which the composition of the alloy will change, becoming enriched with rhodium (see Fig. 2). The thermo-emf in this case will at first rise somewhat (to a composition of 50% rhodium), then somewhat decrease (to a compoisition of 60% rhodium). The stability of the thermo-emf will in this case appear, according to Carter's opinion, satisfactory. The thermo-emf of an Ir40Rh/Ir thermocouple is about 11.5 mV at 2000°C (Fig. 1), which is approximately equal to the thermo-emf of an Ir60Rh/Ir thermocouple.

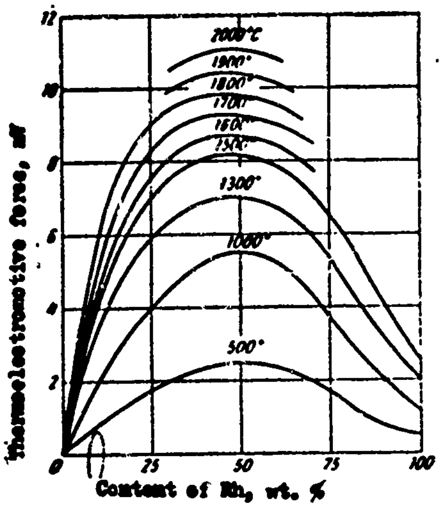

Fig. 2. Thermo-emf of alloys of the iridium-rhodium system with respect to iridium (in conjunction with literature data).
Numbers on the curves designate the temperature of measuring thermo-emf (cold junctions -0°).

Haase and Schneider proposed a thermocouple of rhenium alloy with 30% iridium coupled with pure iridium (8). The thermo-emf of this thermocouple (Ir70Re/Ir) is relatively high - about 14 mV at 2000°C (Fig. 1). The thermocouple is distinguished by a quite high sensitivity at high temperatures - about 15 μV/deg - and very low thermo-emf values - from 0 to 600°C. But it is necessary to expect that rhenium alloy with 30% iridium will be extremely unstable in an oxidizing medium at high temperatures. In this respect the Ir70Re/Ir thermocouple evidently has no substantial advantages over the much cheaper and widely known tungsten-iridium thermocouple (9), which can work only in neutral atmosphere and in vacuum.

Thus, of the existing thermocouples, as the best should be acknowledged the thermocouple consisting of the iridium-rhodium alloy (40 or 60% of rhodium) coupled with iridium. The question of what rhodium concentration - 40 or 60% - is more preferable remains open. Data confirming the opinion by Carter about the advantageous burning out of iridium from an iridium-rhodium alloy (7) are unavailable. On the other hand, data obtained by us at the Sverdlovsk branch of the All-Union Scientific Research Institute for Metrology confirm the rise of thermo-emf in iridium alloy with 60% rhodium after calcination at high temperatures, which can only be explained by a rise in iridium concentration due to primary burn up of rhodium.

Analogous data were obtained by Rudnitskiy (10), who tested an Ir60Rh/Ir thermocouple in aluminum oxide and beryllium oxide tubes and detected a rise in thermo-emf of the thermocouple in a ceramic of aluminum oxide. Considering the fine stability of thermo-emf of pure iridium, the change in thermo-emf of the thermocouple should be attributed to the change in composition of the iridium-rhodium electrode toward decreasing rhodium concentration. In a beryllium oxide ceramic after the initial rise in thermo-emf Rudnitskiy detected a drop in thermo-emf. But it is necessary to hold back from any definite conclusions relative to the mechanism of changes in thermo-emf because we also have data about the aggressive effect of beryllium oxide on platinum and platinum-rhodium alloys.

TABLE 1.

Thermoelectromotive Force of a Thermocouple of Iridium-Rhodium Alloy with 60% Rhodium-Iridium (Ir60Rh/Ir) According to Blackburn & Caldwell (14)

°C	Thermoelectromotive force, mV (cold junctions – 0°C)										°C
	0	10	20	30	40	50	60	70	80	90	
0	0,000	0,032	0,064	0,098	0,134	0,170	0,206	0,245	0,284	0,324	0
100	0,365	0,406	0,449	0,492	0,536	0,581	0,627	0,674	0,722	0,770	100
200	0,818	0,868	0,917	0,968	1,019	1,070	1,122	1,174	1,227	1,280	200
300	1,334	1,388	1,443	1,498	1,553	1,608	1,664	1,720	1,776	1,832	300
400	1,889	1,946	2,003	2,060	2,118	2,175	2,233	2,291	2,348	2,406	400
500	2,464	2,522	2,580	2,639	2,697	2,755	2,814	2,872	2,930	2,989	500
600	3,047	3,106	3,164	3,222	3,280	3,339	3,397	3,455	3,513	3,571	600
700	3,628	3,686	3,744	3,801	3,859	3,916	3,973	4,030	4,086	4,143	700
800	4,199	4,256	4,312	4,368	4,424	4,480	4,537	4,593	4,618	4,703	800
900	4,759	4,815	4,870	4,425	4,980	5,035	5,090	5,144	5,199	5,254	900
1000	5,308	5,362	5,417	5,471	5,525	5,580	5,634	5,688	5,742	5,796	1000
1100	5,850	5,904	5,958	6,012	6,066	6,120	6,173	6,227	6,280	6,334	1000
1200	6,388	6,441	6,493	6,548	6,601	6,654	6,708	6,761	6,815	6,869	1200
1300	6,922	6,976	7,029	7,082	7,136	7,190	7,244	7,298	7,352	7,407	1300
1400	7,461	7,516	7,571	7,626	7,681	7,736	7,791	7,847	7,902	7,957	1400
1500	8,013	8,070	8,127	8,183	8,241	8,298	8,356	8,413	8,470	8,526	1500
1600	8,583	8,640	6,697	8,754	8,811	8,868	8,925	8,983	9,040	9,098	1600
1700	9,156	9,914	9,272	9,331	9,390	9,449	9,508	9,567	9,627	9,686	1700
1800	9,745	9,805	9,866	9,926	9,987	10,048	10,108	10,169	10,230	10,292	1800
1900	10,355	10,417	10,480	10,543	10,606	10,670	10,735	10,800	10,865	10,930	1900
2000	10,995	11,061	11,126	11,192	11,258	11,324	11,389	11,455	11,521	11,588	2000
2100	11,654										2100

One of the reasons for the preference given abroad to the Ir60Rh/Ir thermocouple appears to be, evidently, the lower cost and lower specific weight of rhodium in comparison with iridium (2).

It should be mentioned that about the Ir40Rh/Ir thermocouple, very little data have been published (7, 11), while thermocouple Ir60Rh/Ir has been repeatedly investigated from the viewpoint of physical metallurgy as well as metrology. A thorough calibration of the Ir60Rh/Ir thermocouple up to 2000°C was made by Droms and Dahl (12), as well as by Rudnitskiy and Tyurin (13). Much work in compiling calibration tables for thermocouples (see Table 1) was carried out by Blackburn and Caldwell (14).

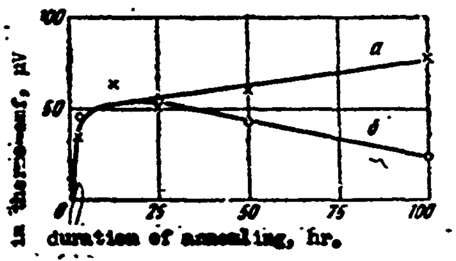

Fig. 3. Change in thermo-emf of the Ir60Rh/Ir thermocouple at 1800°C according to Rudnitskiy (10). a - in an Al_2O_3 ceramic with a TiO_2 admixture; b - in a BeO ceramics.

All these data, as well as the data of Rudnitskiy (10), are in excellent conformity with each other. The initial calibration of thermocouple Ir60Rh/Ir given by Feussner, inventor of this thermocouple (4), became obsolete, as well as its much later numbers (5) (the latter to a lesser degree).

It is probable that the thermo-emf of the thermocouple as well as others of its operating properties, strongly depend upon metal purity and processing technology. For example, a recently published thermo-emf table of many iridium-rhodium alloys (15) gives a thermo-emf of the Ir60Rh/Ir thermocouple somewhat below values according to other data.

The data on the stability of an Ir60Rh/Ir thermocouple and the stability of its thermo-emf are contradictory. Above there were already mentioned the Rudnitskiy data (10) on the stability of the thermo-emf in ceramic tubes of aluminum or beryllium oxide in an atmosphere of air. Changes in the thermo-emf constituted about 0.05 mV (100 h at 1800°C) and took place basically in the first 2-3 hours which, apparently, confirmed the incomplete calcination of thermoelectrodes and excellent, in essence, stability of the thermo-emf of the thermocouple (Fig. 3).

Our data on stability and weight losses of the electrodes of the Ir60Rh/Ir thermocouple in an atmosphere of air show that the changes in thermo-emf are great in the first hours of calcination and considerably smaller from then on (Fig. 4). This pertains to both electrodes, although the stability of iridium thermo-emf is sufficiently good (the change in thermo-emf is not more than 3 uV); the value of the thermo-emf change increases with annealing temperature. The obtained numbers are in excellent conformity with Rudnitskiy's data (10).

On the contrary, it is necessary to evaluate the electrodes from the viewpoint of stability in an oxidizing medium (in air) at high temperatures (Fig. 5). The Ir60Rh electrode appears to be more satisfactory; its weight loss per hour at 2000°C constitutes 5%, while the weight losses of pure iridium under the same conditions is 27%.

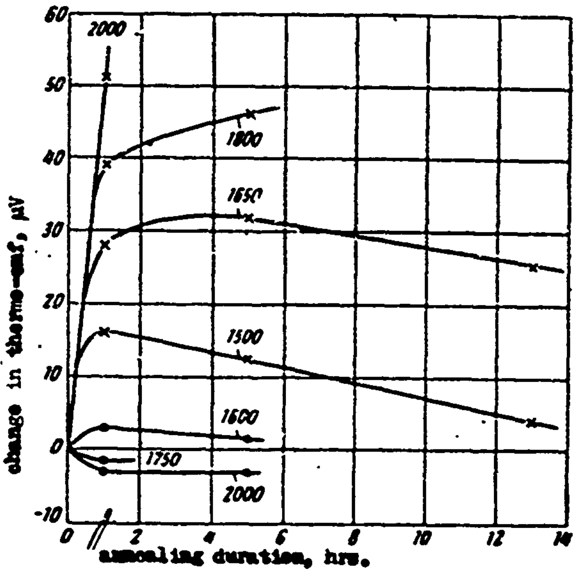

Fig. 4. Stability of thermo-emf of iridium and iridium alloy with 60% rhodium at isothermal exposures. The numbers on the curves designate the annealing temperature °C: -●-● -Ir; -x-x Ir60Rh.

At analogous tests in vacuum or in argon the weight losses of both electrodes are significant; consequently, the main role here is the oxidation of iridium and rhodium and the volatilization of the oxides.

Thus, pure iridium possesses excellent thermoelectric stability, but it oxidizes rapidly. An alloy of iridium with 60% rhodium is more stable to oxidation, but rapidly changes the thermo-emf value. Nonetheless, judging by Rudnitskiy's data (10), the Ir60Rh/Ir thermocouple can be used for a long time at 1800°C, a time of the order of 100 hrs. In other reports Rudnitskiy considers it possible to use this thermocouple in an oxidizing atmosphere up to 2300°C (16, 17) or to 2200°C (18), having in mind, evidently, short-term use.

Foreign authors, as a rule, give much lower maximum temperatures for the use of thermocouples: prolonged 2000°C and short-term 2100°C in oxidizing and reducing (?) atmospheres and in vacuum (19); 2000°C and short-term in air, prolonged in a vacuum or in a neutral atmosphere (15). According to Kostkovskiy's data (21), prolonged application of the Ir60Rh/Ir thermocouple is permitted up to 2100°C with an accuracy of 10°C in an inert atmosphere and only a short-term application in the air. Kostkovskiy reports, that in 50 hrs at 2000°C in an atmosphere with 2% oxygen the thermo-emf of the thermocouple changed slightly; in air the thermocouple became disintegrated at 2000°C within 12 hrs., but during that time there were practically no changes in thermo-emf.

Thus, it can be considered that the Ir60Rh/Ir thermocouple is appl [illegible]e, at least briefly for measurements at 2000°C in air. Its basic deficiencies appear to be great losses during the oxidation of the iridium electrode and instability in thermo-emf of the iridium-rhodium electrode in an oxidizing medium.

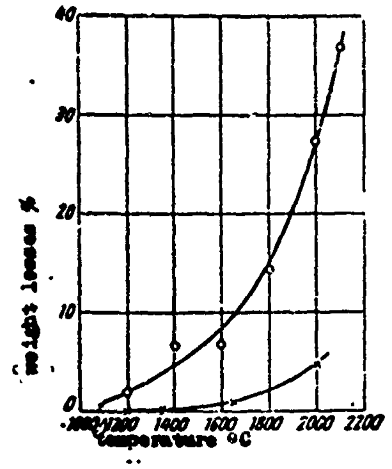

Fig. 5. Change in weight of iridium and iridium alloy with 60% rhodium after annealing with electric current in air in 1 h: -o-o-Ir; -x-x-Ir60Rh.

Thermal stability of iridium alloys

In connection with the deficiencies of the Ir60Rh/Ir thermocouples there naturally arises the question of the possibility of using other iridium alloys without the mentioned deficiencies.

Unfortunately, data are lacking about the thermal stability of iridium alloys, except for unsystematic data about the heat resistance of iridium, iridium-rhodium and iridium-ruthenium alloys mentioned in the previous chapter. These data can be briefly summarized as follows: stability to oxidation of iridium is increased by rhodium additives. Thus, the weight loss of the iridium alloy with 60% rhodium in one hour at 2000°C is 5.4 times less than pure iridium. But the composition of iridium-rhodium alloys does not remain constant in this case. So far it cannot be said with sufficient determination in what way the composition of iridium-rhodium alloys changes, but the very fact of a considerably greater change in thermo-emf of iridium-rhodium alloys (in comparison with pure iridium at high temperature exposures) appears to be indisputable, but highly undersirable.

Ruthenium additives, evidently decrease the thermal stability of iridium (2).

The effect of other noble metals has not been investigated. It is only possible to make certain assumptions, on the basis of properties of pure metals (see Table 2, Figs. 6 and 7).

Table 2.

Certain Properties of Noble Metals (22, 28,40)

Metal	Melting Point °C	Boiling Point °C	Vapor tension at 2000 °C mm Hg	Chemical formula of forming oxide	Heat of oxide formation kcal/mol.	Boiling Point of oxide °C
Ag	960,5	2212	300—750	Ag_2O	6,95	—
Au	1063,7	2530	60	—	—	—
Ru	2500	4900	0,0001	RuO_2	52,6	—
Rh	1966	4500	1	Rh_2O_3	21,7	—
Pd	1554	4000	1	PdO	20,4	—
Os	2700	5500	0,00001	OsO_4	93,6	130
Ir	2454	4800	0,0001	IrO_2	40,1	—
Pt	1760	4400	0,001	PtO	17	—

A common feature of all noble metals is the fact that at high temperatures on the surface no protective oxide films form. All noble metals reveal under these conditions weight losses, due to volatility of oxides, as well as evaporation of the nonoxidized metal.

Osmium is characteristic in this respect. In spite of the high melting and boiling points, osmium is absolutely unstable when heated in air. This is explained by the oxidation of osmium with the formation of osmium tetroxide, the melting point of which is 40°C, boiling point 130°C, as a result of which the surface of the metal is constantly exposed and subjected to the effect of oxygen. With respect to heat resistance of iridium/osmium alloys there are no data; by analogy with the influence of ruthenium in iridium-ruthenium alloys it can be assumed that additions of osmium will sharply deteriorate the heat stability of iridium.

Ruthenium is close in its properties to osmium, although more stable. At low temperatures, oxidation of ruthenium is accompanied by the formation of a protective film (22), but at high temperatures the oxides obviously melt and evaporate.

Palladium at low temperatures also forms an oxide film, but above 870°C palladium oxide is volatile. The relatively small weight losses of palladium, it is assumed, are explained by the greater solubility of oxygen in palladium (26).

The stability of iridium is considerably greater than the stability of osmium and ruthenium, but it is considerably worse (Figs. 6 and 7) than the stability of rhodium and platinum. The latter are the least volatile at high temperatures in an atmosphere, containing oxygen. Weight losses of rhodium and platinum are close in magnitude, whereby below 1300°C rhodium is more stable; above 1300°C - platinum is more stable (22). The heat resistance of iridium/rhodium alloys was discussed above; iridium/platinum alloys were investigated only for the part rich in platinum (27). From these data it follows, that heat resistance of platinum at 900°C is reduced by iridium additives there were investigated alloys with an iridium content up to 40 at %. This is fine, if we consider that the heat resistance of pure iridium is considerably lower than that of platinum; in this connection it is possible to raise the heat resistance of iridium by the addition of platinum.

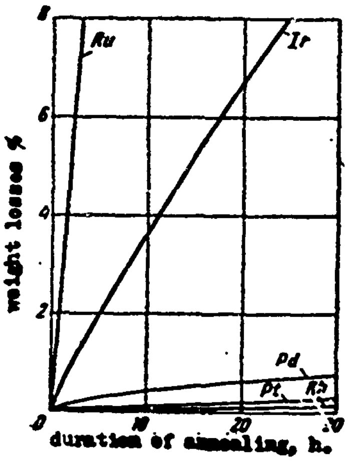

Fig. 6. Change in weight of platinum, rhodium, palladium, iridium, and ruthenium at a temperature of 1300°C in air according to Crookes (24).

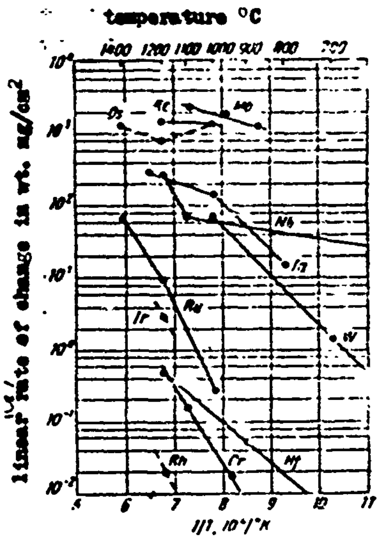

Fig. 7. Oxidation of refractory metals by Jaffey (25). Data for chromium, hafnium, tungsten, tantalum, and niobium - by overweight; for the remaining metals - by weight losses.

Gold is distinguished by a special characteristic. Up until now ther have been detected no signs of its reaction with oxygen at temperatures below the melting point of gold (27).

But since the temperature range of interest to us is considerably higher than the melting point of gold, it is possible to expect it to be less inert to oxygen; losses due to evaporation of gold at 2000°C are also substantial; vapor tension, as is evident from Table 2, constitutes 60 mm Hg.

Silver at high temperatures evaporates even more than gold. In addition, silver oxidizes noticeably already at 200°C. Evidently, its stability at 2000°C will be completely unsatisfactory because of oxidation as well as because of evaporation.

Raub and Plate cite interesting data on increasing the heat resistance of platinum by addition of gold, rhodium, and palladium (27). It can be assumed that the effect of these metals on the heat resistance of iridium is analogous to their effect on the heat resistance of palladium and, consequently, the heat resistance of iridium is also increased by the addition of gold, rhodium, and palladium. Although this is only an assumption, it does not contradict the above data and the characteristics of pure gold, rhodium, and palladium.

Thus, of the noble metals osmium and ruthenium are evidently undesirable as additives to iridium because they will reduce its heat resistance. Most likely, silver has an analogous effect. Gold, rhodium, palladium, and platinum in some measure or other increase the heat resistance of iridium.

Base metals possess a considerably greater affinity to oxygen than do the noble metals. They can improve the heat resistance of iridium only when the selective oxidation of the base metal produces a protective oxide film on the surface of the iridium alloy.

Unfortunately, there are no data on the heat resistance of iridium alloys with base metals; certain data on the properties of pure metals and their oxides are given in Table 3.

Analyzing the possible suitability of base metals for use as additives to iridium, it is necessary first of all to keep in mind that metals whose oxides melt at below 2000°C cannot improve the heat resistance of iridium. Such metals include vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, and cobalt. It is also undesirable to use metals with high vapor tension (manganese, chromium, and, in part, iron, cobalt, nickel, aluminum, and yttrium). Unfortunately, the vapor tension of hafnium is unknown to us; using its other characteristics (see Fig. 7) it can be tested as an addition to iridium for increasing its heat resistance. This also pertains to zirconium. Of interest for the investigation are also aluminum, nickel, yttrium, and tantalum, although at first glance they appear less desirable components of iridium alloys.

Table 3.

Certain Properties of Base High Melting and Heat Resistant Metals (22, 28, 40)

Metal	Melting Point °C	Boiling Point °C	Vapor tension at 2000 °C mm Hg	Chemical formula of forming oxide	Heat of oxide formation kcal/mol	Melting Point of oxide °C
Al	660.2	2327	4	Al_2O_3	403	2020
Y	1450	4600	1	Y_2O_3	440	2410
Zr	1855	3577	0.01	ZrO_2	258.1	2700
Hf	2222	5400	—	HfO_2	271.5	2812
V	1919	3400	0.1	V_2O_5	437	690
Nb	2469	3300	<0.00001	Nb_2O_5	463	1500
Ta	2996	5300	<0.001	Ta_2O_5	499.9	1900
Cr	1845	2500	100	Cr_2O_3	280	2000
Mo	2622	4800	<0.00003	MoO_3	180.4	795
W	3395	5930	0.00008	WO_3	195.7	1473
*Mn	1245	2027	630	Mn_3O_4	366	1650
Re	3180	5630	0.00001	Re_2O_7	297.5	350
Fe	1536	2828	7.6	Fe_2O_3	195.2	1565
Co	1490	3135	<7	CoO	57.9	1935
Ni	1455	2730	2.2	NiO	58	2090

Phase composition of iridium alloys

Besides heat resistance the phase composition and structure of the alloys are of equally important value. Thermoelectrode alloys, as is known, should be single-phase and shoult not experience conversions in the working temperature range, otherwise there is not maintained the need for an unequivocal dependence of thermo-emf upon temperature. Thermoelectrode alloys are used in the form of wire, while single-phase alloys, as a rule, are more easily machined by pressure than are alloys of complex phase composition.

From this viewpoint we will examine those iridium-base systems which, by reason of heat resistance, may be of interest for our purposes. Alloy systems with iridium have been little investigated; phase diagrams are known more or less thoroughly only for six binary systems (see Fig. 8), not considersing, of course, binary systems of iridium with metals, the -operties of which are unsatisfactory for our purposes. Ternary systems with um have not been investigated at all.

The iridium-silver system was investigated by Rudnitskiy and Polyakov (28). They detected in the system a limited solubility in the liquid state and a low (less than 1%) solubility of silver into iridium in the solid state.

The iridium-gold system was investigated by the same authors (29). They detected a limited solubility of components in the liquid state; the solubility of gold in solid iridium was estimated by the authors to be less than 2%. The hardness of iridium is somewhat increased by the addition of gold.

An iridium-palladium system was investigated by Raub and Plate (30). At high temperatures, in the system then was detected a continuous line of solid solutions; with a drop in temperature there was observed a solubility discontinuity in the solid state. The process of separating out the second phase takes place very slowly and is accompanied by hardening of the alloy. The solubility of palladium in iridium, determined by Raub and Plate, constitutes about 5% palladium at 600°C. The hardness of iridium is increased by the addition of palladium.

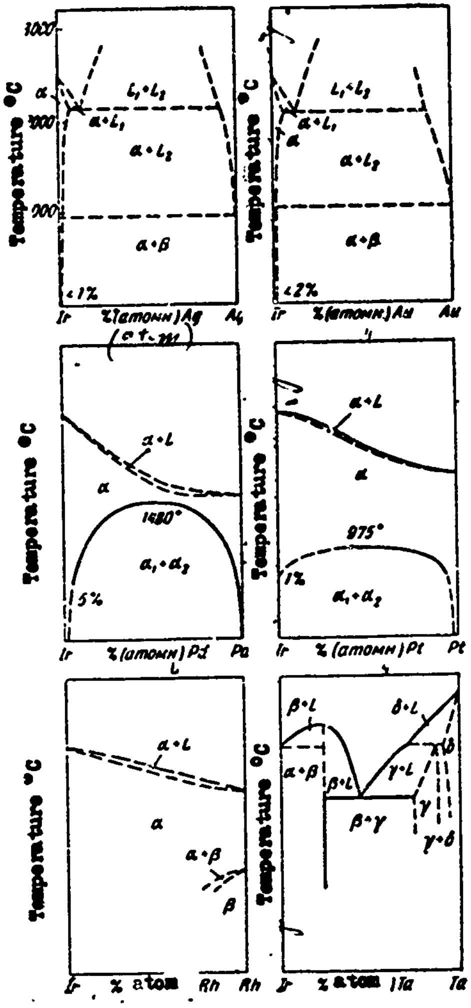

Fig. 8. Phase diagrams of iridium alloys.

An iridium-platinum system was investigated by the same authors (31). Earlier investigations (32) showed, that iridium-platinum alloys crystallize as a continuous line of solid solutions. Raub and Plate, having confirmed this assumption, discovered a solubility discontinuity in the solid state. The boundaries of the two, phase region, as mentioned by the authors, is difficult to determine accurately because of the very slow separation process; the solubility of platinum in iridium is assumed by Raub and Plate to be 1% at 700°C. Platinum practically does not increase the hardness of iridium and does not worsen its deformability.

The iridium-rhodium system has so far not been investigated. It is assumed that the components form a continuous line of solid solutions (32), because both have an identical (face-centered cubic) lattice and very similar atomic diameters. This is confirmed by thermo-emf data of the alloys.

System of iridium with base metals have been investigated to an even lesser degree. There exists a tentative phase diagram of the iridium-tantalum system (33), from which it is evident that tantalum practically does not dissolve in iridium in the solid state. It is known that yttrium with iridium form a Laves phase YIr_2 (34),

Table 4.

Thermo-emf of Iridium (cold junctions—0°C

Thermo-emf of iridium relative to platinum (36)						Absolute thermo-emf of iridium (37)		Thermo-emf of iridium relative to copper (12)		Thermo-emf of iridium relative to platinum*	
°C	E, mV	°C	E, mV	°C	E, mV	°C	micro/dg mV/deg	°C	E, mV	°C	E, mV
250	1,966	700	7,564	1150	15,462	—100	+1,8	37,8	—0,020	419,6	3,836
300	2,474	750	8,320	1200	16,482	0	+1,5	93,3	—0,080	630,5	6,731
350	3,002	800	9,116	1250	17,498	+100	+0,9	148,9	—0,175	1083,1	14,340
400	3,550	850	9,948	1300	18,580	200	+0,3	204,4	—0,305		
450	4,156	900	10,798	1350	19,662	300	—0,3	260,0	—0,470		
500	4,778	950	11,670	1400	20,766	400	—0,8				
550	5,424	1000	12,588	1450	21,904	500	—1,3				
600	6,102	1030	13,518	1500	23,056	600	—1,7				
650	6,810	1100	14,482								

* According to data by authors of the report.

and zirconium with iridium a Laves phase $ZrIr_2$ with a structure of the type $MgZn_2$ (35). The solubility of both metals in iridium is probably low.

There are no data about the iridium-hafnium system. Since hafnium appears to be a homolog of zirconium, whereby their atomic diameters are very close while the lattice is identical, it is difficult to expect a large region of solubility of hafnium in iridium.

Iridium-aluminum and iridium-nickel systems have not been investigated. The lattices of both metals face-centered cubic are the same as in iridium; the atomic diameter of aluminum is 5.1% higher, and that of nickel is 6.4% lower, than the atomic diameter of iridium. On the basis of this, we can assume the presence of a definite substantial region of solid solutions of aluminum as well as nickel in iridium.

Thus, as thermoelectrode alloys we can utilize alloys of the iridium-rhodium system. Other noble metals can apparently be added in small amounts: palladium - up to 5%, gold - up to 2%, platinum - up to

1%, silver - up to 0.5%. On the other hand, in iridium-palladium and iridium-platinum systems with a solubility continuity in the solid state it is possible, in connection with the difficulty of separating the second phase, that alloys with a somewhat greater content of admixtures will have a sufficiently constant thermo-emf. Single-phase alloys will be, probably, those of iridium with aluminum or nickel (in an amount on the order of 10%). In iridium/yttrium alloys, zirconium/hafnium alloys, nothing definite can be stated. Tantalum is unsuitable as a component of iridium-base thermoelectrode alloys, because there is no tantalum solubility in iridium in the solid state.

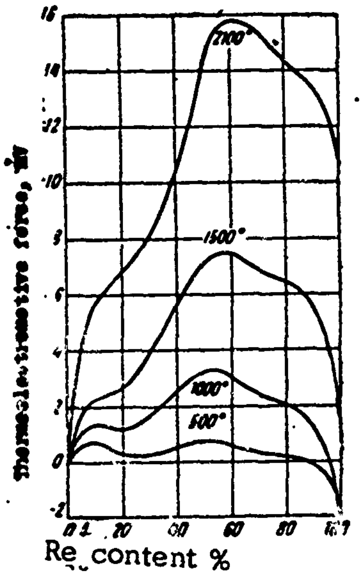

Fig. 9. Thermo-emf of alloys of iridium-rhenium system relative to iridium after Haase and Schneider (8). Numbers on the curves designate the temperature of measuring thermo-emf °C (cold junctions -0°).

Thermo-emf of iridium alloys

In conclusion we will introduce data about the thermo-emf of iridium alloys. Although this factor is not decisive during the selection of alloys for thermocouples, it is desirable that the alloys should develop a high thermo-emf which increases linearly with temperature. The thermo-emf of pure iridium has been determined in only a few reports (see Table 4), but the results of all these determinations coincide well.

Of the iridium alloys, the thermo-emf is known for iridium-rhodium, iridium-ruthenium and iridium-rhenium systems. For iridium-silver (28), iridium-gold (29), iridium-platinum (38), and iridium-palladium systems (39) the thermo-emf was investigated in the region of small iridium additions to the second component; therefore we will not cite them.

The thermo-emf of iridium-rhodium alloys was discussed above and is given in Fig. 2. In the iridium-ruthenium systems there was investigated only one alloy, containing 10% of ruthenium. Its thermo-emf relative to iridium is shown in Fig. 1. It should be mentioned that the noble metals (during alloying) change the thermo-emf of iridium relatively little.

The thermo-emf of alloys of the iridium-rhenium system is shown in Fig. 9. As has already been shown above, iridium-rhenium alloys cannot be used for thermoelectrodes operating in an oxidizing atmosphere, even though they develop a sufficiently high thermo-emf as do the other iridium alloys with base metals. For a rhenium-base solid solution the content of a thermo-emf maximum of about 40% iridium, is characteristic and for an iridium-base solid solution - about 5% rhenium.

Conclusions

1. At present we know of a number of thermocouples suitable for use in an oxidizing medium at a temperature of 2000°C; the best of these appears to be the thermocouple of iridium alloy with 60% rhodium coupled with pure iridium (Ir60Rh/Ir).

2. At 2000°C the Ir60Rh/Ir thermocouple allows us with sufficient accuracy to measure the temperature, at least briefly, for a period of 10-20 hrs. The factors limiting its service life appear to be: losses to oxidation and evaporation by the iridium electrode (within the limit of electrode destruction) and instability of the thermo-emf of the iridium-rhodium electrode due to a change in its composition in connection with selective oxidation and evaporation of one of the alloy components.

3. To increase the service life of an Ir60Rh/Ir thermocouple or to select other more stable alloys, it is necessary to investigate alloys of the iridium-rhodium, iridium-platinum, iridium-palladium and iridium-gold systems. It is possible that admixtures of certain base metals will exert a positive effect.

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