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1. Introduction

1.1 Physical and chemical properties of platinum

Platinum is a white – grayish metal with brilliant luster. It is harder than gold and copper, platinum has also the valuable quality that it is often before melting so that it can be welded. Platinum and rhodium do not volatilize appreciably at 900 °C but at 1300 °C volatilization can be detected. The high melting temperature, and the fact that platinum is not affected by air and strong acids, enables it to be used in the manufacture of temperature measuring sensors like platinum resistance thermometers and thermocouple. Platinum has nearly the same coefficient of expansion as glass, and platinum wires can be fused in glass so as to make gas-tight joints. This property makes it possible to prepare platinum. Resistance thermometers in glass outer sheath Platinum are also a good conductor of electricity which makes it suitable for making of temperature sensors.

The platinum indium allay (90:10) is used for making the prototype kilogram from 1889 to 1960 the same alloy was used to make the international prototype meter bar.

The physical properties of Pt which makes it suitable for thermometric sensors are given in table (1).

| Physical properties                  | Value       |
|--------------------------------------|-------------|
| Density in g/cm³                     | 21.45       |
| Melting point °C                     | 1768.30     |
| Molar heat capacity in J mol⁻¹ K⁻¹   | 25.86       |
| Thermal conductivity W m⁻¹ K⁻¹       | 71.6        |
| Thermal expiation at 25°C µm m⁻¹ K⁻¹ | 8.80        |
| Tensile strength Mpa                 | 125.24      |
| Electrical resistivity at 20°C n Ω.m | 105.        |
| Temperature coefficient of electrical resistance from 20 to 100°C | 0.003925 |

Table 1. The physical properties of Platinum
1.2 Thermoelectric phenomena

A thermocouple consists of two dissimilar conductors or thermo-elements joined to form a circuit. T. J. Seebeck (1822) first discovered that a thermocouple would produce a current in a closed circuit when one junction is at a different temperature from the other \(^{(1)}\). The emf that produced the current is refereed to as the thermocouple emf or as the Seebeck voltage \(E\) and its temperature derivative \(dE/dT\) is known as the thermoelectric power or Seebeck coefficient \(S\). The one conductor \(A\) is said to be positive with respect to the other \(B\), if current would flow from \(A\) to \(B\) at the cooler of the two junctions as shown in figure (1).

![Fig. 1. A typical thermocouple](image)

1.3 Mechanism of thermoelectricity

The purpose of this introduction is to show how the thermopower of metals and alloys depends so critically upon the composition, homogeneity and state of anneal of the material.

The origin of thermoelectricity in a metal can be demonstrated using the simple free-electron gas model of the conduction process. We can imagine a metal to be made up of a rigid lattice of atoms between which can move free electrons driven by electric, magnetic or thermal gradient in the conductor happen to be present. As a result of the temperature gradient in the conductor, the electrons at the hot end diffuse towards the cold end. The excess of electrons thereby produced at the cold end leads to a potential gradient being established at the same time. The negative charge at the cold end builds up until a state of dynamic equilibrium is established between the number of electrons having relatively high velocity, diffusing towards the cold end of the conductor driven by the temperature gradient and the number of electrons having relatively low velocity, diffusing towards the hot end of conductor driven by the electric potential gradient. This electric potential gradient arises whenever a temperature gradient exists in a conductor and is known as the thermoelectric emf. It follows that no thermoelectric emf can be present in the absence of a temperature gradient.

It is evident that the mechanism of electron scattering must play an important role in thermoelectricity. The electrons having a higher velocity would be scattered through smaller angles by the lattice atoms than those having a lower velocity; in this case an enhanced negative thermoelectric emf would develop. In other words the mean free path of the electron would depend upon its kinetic energy.
The complexity of the electron energy vs. scattering relations leads to the thermoelectric emf in different metals being very different from one another. Were they the same in all metals and alloys, then we would not be able to make use of it for temperature measurement, since the thermocouple is a device in which the difference between the thermoelectric emf in the two arms of the thermocouple gives an indication of the temperature difference between the hot and cold ends of the wires. The difference in emf is known as Seebeck effect.

The distribution of electric potential $E(T)$ in a pair of conductors of different materials A and B having a junction maintained at a temperature $T_2$ and having free ends both maintained at lower temperature $T_o$ is shown diagrammatically in figure (1) and (2). Both the junction and the free ends of the conductors are shown in regions of uniform temperature and both conductors pass through the same temperature gradient. $T_o$ permit measurements to be made of the thermoelectric potential difference between the free ends of A and B. A further pair of identical conductor C is attached at $T_o$ which lead to a detector at a temperature $T_1$.

$$S_{A(T)} = \frac{dE_{A(T)}}{dT} \quad \text{and} \quad S_{R(T)} = \frac{dE_{R(T)}}{dT}$$  \hspace{1cm} (1)

Analysis of the circuit in figure (2) now reduces to determining the thermoelectric effects for the three wires A and B for the thermocouple and C for the instrument leads. Clearly it is essential that any connections must be isothermal.

![Diagram of thermocouple measurement](image)

**Fig. 2. Model of thermocouple measurement**

The wires A, B and C should be kept as homogenous as possible by avoiding any chemical or mechanical treatment. The voltage $E$ produced by the circuit is the sum of three parts.

$$E = E_{A(T_2)} - E_{A(T_0)} + E_{C(T_2)} - E_{C(T_0)} + E_{R(T_2)} - E_{R(T_0)}$$  \hspace{1cm} (2)

Where for the wires A, B and C, $E_A$, $E_B$ and $E_C$ are the voltages for the end points at $T_2$ and $T_0$ which are the measurement and reference junction temperatures respectively.

From equation (2) it can be seen that the net contribution of the lead wires C is zero since they are both at the same temperatures $T_o$.

Under the above conditions the instrumentation for measuring a thermocouple voltage can be considered independent of the sensor. Also from equation (2) the voltage output from the pair of wires (A and B) is related to the difference between the thermoelectric effect for the...
wires A and B. It is common to consider only a relative Seebeck voltage \( E_{AB} \) and a relative Seebeck coefficient \( S_{AB} \) and equation (2) becomes;

\[
E = E_{AB(T_2)} - E_{AB(T_0)}
\]  

(3)

A simplification is made by choosing the reference temperature \( T_0 = 0 \) °C and setting \( E_{AB}(0 \) °C) = 0, equation (3) becomes.

\[
E = E_{AB(T_2)}
\]  

(4)

Equation (4) is the basic equation for thermocouple, which relates the voltage produced to the temperature being measured.

However, the equation is based on several assumptions. The assumptions made are:

- The reference junction is 0 °C.
- The relative Seebeck coefficient is known.
- There are isothermal conditions for instruments and connecting wires.
- There are isothermal conditions for measurement and reference junctions.
- There are homogeneous wires connecting measurement and reference junctions.

Note

Various metals and metal alloys have been developed for use in the construction of thermocouples. The thermocouple is classified by a letter code for the particular combination of metals used, for example a Type S thermocouple comprises of platinum and platinum 10% rhodium alloys. The current international standard for thermocouples is IEC 584.

Thermocouples have sensitivities from a few microvolts per degree C to a few 10’s of microvolt per degree C, varying with type and operating temperature. Sensitivities at 100 °C are shown in the table for various types.

| Type | Materials | Max. Temp. °C | Sensitivity (µV/°C) at 20 °C | Sensitivity (µV/°C) at 100 °C | Sensitivity (µV/°C) at 500 °C |
|------|-----------|--------------|-----------------------------|-----------------------------|-----------------------------|
| B    | Platinum 30% rhodium/platinum 30% rhodium | 1700          | 0                           | 0.9                         | 5.1                         |
| R    | Platinum 13% rhodium/platinum         | 1400          | 5.9                         | 7.5                         | 10.9                        |
| S    | Platinum 10% rhodium/platinum         | 1400          | 5.9                         | 7.4                         | 9.9                         |
| Au/Pt| Gold/Platinum                          | 1000          | 6.2                         | 8.1                         | 16.2                        |

Table 2. Noble metal thermocouple Sensitivities and Other Data

2. Noble metal thermocouples

In 1886, Le Chatelier discovered the platinum-10%rhodium vs. platinum thermocouple. Since that time, many investigators have made great contributions to the advancement of platinum group metals for temperature measurement, such as tungsten vs. iridium, palladium vs. platinum and gold vs. platinum etc.
In this series, the platinum–10%rhodium vs. platinum thermocouple is, from the scientific standpoint, the most important of all the thermocouples (base and noble metal) now employed. It was used to define the International Temperature Scale of 1948 (ITS-48) and the International Practical Temperature Scale of 1968 (IPTS-68) in the temperature range from the freezing point of antimony 630.5 °C to the melting point of gold 1063 °C on ITS-48 and 1064.43 °C on IPTS-68 (on ITS-90 the melting point of gold is 1064.18 °C). This thermocouple is noted for its high accuracy over a broad temperature ranges, its excellent mechanical and chemical properties and low electrical resistivity, it is readily obtained in uniform quality.

The work on the gold platinum thermocouples started at the National Institute of Standards and Technology (NIST) by the work of Roeser and Wensel (1). In 1987 McLaren and Murdock published a report (2) on the characteristics of Au/Pt thermocouple. His study had been undertaken to find a superior and practical sensor as an alternative to the standard Pt-10%Rh vs. Pt thermocouple for temperature measurements in the range (0 – 1000 °C). Subsequent to that study, Burns, Strouse and Mangum (3) undertook an investigation of such thermocouples to determine their feasibility to serve as rugged secondary reference thermometer at the 50 m °C level of uncertainty.

With the introduction of the International temperature Scale of 1990 (ITS-90) (4) emphasis shifted in 1990 to include the development of an ITS-90 based reference function to these thermocouples. Recently a reference function for Au/Pt thermocouples based on the ITS-90 was published by Gotoh et al (5) and by Burns, Strouse et al (6).

In the present investigation, the stability and reproducibility of Au/Pt thermocouples and of the Pt-10%Rh vs. Pt thermocouples have been carried out for comparison and to find the best mathematical formula for their calibration.

2.1 Assembly, annealing and stabilization of Pt-10%Rh vs. Pt thermocouple

Before any assembly began the Pt and Pt-10%Rh wires (0.5 mm diameter) were cleaned by boiling in distilled water followed in sequence by boiling in dilute nitric acid, distilled water, dilute hydrochloric acid, (approximately 2 N) and finally four times in distilled water (6). After drying in an oven in a dust free space the Pt and Pt-10%Rh wires, 120 cm long, were welded using a strongly oxidizing oxygen-natural gas flame to form the thermocouple junction. Surgical polyethylene gloves were worn during handling of the wires and thermocouple. The thermocouple was electrically annealed at 1100 °C using A.C for 1 hour. The purity of the clean, annealed platinum wires was within the requirements of the IPTS-68 relating to the emf output at the gold point and its relationship to that at the other two fixed points as will be shown in the results.

Twin bore recrystallized alumina (Al₂O₃), 60 cm long was used to electrically insulate the wires. This alumina sheath was boiled in aqua-regia and distilled water in the same manner as the wires to remove any metallic contaminations on the surface, then dried in an oven at approximately 100°C for some hours and then heated in a furnace to 1200°C in air for 24 hours. The free ends of the thermocouple were passed through the bores in the insulation tube, the wires were gently eased through the twin bores of the Al₂O₃ tube with the minimum amount of strain.
The completed thermocouple was stabilized by annealing in a furnace at which the temperature of the central 60 cm was at 1100 °C ± 10 °C. Cleaned single bore alumina tube was placed over the uninsulated wires and the thermocouple placed in a clean Al₂O₃ sheath and positioned so that the tip and the adjoining 60 cm lay in the furnace uniform zone at 1100 °C. After 8 hours of annealing the freezing point of silver was measured with the thermocouple after which it was replaced in the annealing furnace for a further 2 hours and then another freezing point of silver was determined. The two successive silver points agreed to better than 1 μV. Cleaned Plastic tubing was placed over the uninsulated wires and was placed in a glass dust free container and stored in a position free from vibration.

2.2 Assembly, annealing and stabilization of Au/Pt thermocouple

The wire used for preparing the Gold/Platinum thermocouples with diameter 0.5 mm and nominal purity 99.99% (7). The method of this thermocouple preparation followed the recommendations reported in the extensive investigation by McLaren and Murdock (2). Their study established the technique required to obtain measurements of the highest precision with the Au/Pt sensor, including the recommended heat treatments to obtain optimum stability and thermoelectric homogeneity, a stress relieving technique to minimize the tensile emf arising from differential thermal expansion of the Au and platinum elements and the immersion depths required to minimize the sensor conduction loss.

For annealing the gold wire, 120 cm long segment mounted in a 2 bore alumina insulating tubes, 1.2 mm bore and 3 mm in diameter and of total length 120 cm. The AL₂O₃ tubes were previously heated for 50 hours at 1000 °C. Then this assembly was heated in a 1.5 m long horizontal tube furnace for 10 hours at 1000 °C cooled over 3 hours to 450 °C held at 450 °C for 15 hours and then removed from the furnace.

For annealing the platinum wire an electric current was passed through the bare wire sufficient to heat it to 1300 °C, with this temperature sustained for 10 hours. Then the current was switched off and the wire was quenched in air. The electric current was then set to a value sufficient to heat the bare wire to 450 °C and this temperature was maintained for 1 hour to equilibrate the vacancies introduced by the annealing of the wire at 1300 °C. Again the current was switched off and the wire rapidly cooled in air so as not to oxidize the platinum. The annealed Pt and Au wires were assembled in a twin alumina bore (AL₂O₃) sheath of length 75 cm and 4.7 mm diameter. The two wires were joined by a stress relieving coil consisting of five turns of 0.13 mm diameter Au wire at the measuring junction, and given a 20 hour furnace anneal at 450 °C to relieve strain introduced by the assembly process.

The wires emerging from the alumina insulating tube were insulated with flexible Polyvinyl tubing to within about 5 cm of their ends. To complete the assembly of the thermocouple a pair of insulated Cu wires (0.4 mm in diameter) were soldered to the Au and Pt wires to form the reference junction.

2.2.1 Stress relieving coil

Due to the big differential thermal expansion of the Pt and Au wires, in Au/Pt thermocouples with regular hot junction a significant stress thermoelectro-motive force was observed and amounted to the equivalent of < 0.04 °C at the silver point. This stress – thermo emf can be eliminated (2) simply by welding a weak stress-relieving Pt or Au coil between Au and Pt...
elements to form a stress-relieved junction for the Au/Pt thermocouple. The stress-relieving coil deforms easily as the Pt and Au elements expand in the furnace gradients and cannot transport the differential expansion stress to the portion of the wires in the thermo-emf generating temperature gradient zones. Avoidance of the expansion stress allows an Au/Pt thermocouple to reveal its superior intrinsic thermoelectric homogeneity and to attain nearly the performance level expected of an ideal thermocouple with truly homogeneous.

Fig. 3. The stress relieving coil of Au/Pt thermocouple.

2.3 Thermocouple reference junction

A thermocouple used to measure temperature is from its nature a differential sensor, which actually measures the thermal emf, generated as a result of the difference of temperature between its two junctions. It follows then that the temperature of one of its junctions must be known if the measured emf is to be related to the temperature being measured, as was mentioned before. This junction is known variously as the cold, ice, or reference junction. The other is the measuring junction that often is called the hot junction. The reference junction refers to the electrical connection between the thermocouple and copper wires leading to the measuring instrument. The two thermocouple wires directly connected to a copper leads, this assembly can inserted in a Pyrex tube immersed in a bath of water ice slush at 0 °C. The ice bath illustrated in figure 4 was made in a large dewar flask with a clear plastic cover drilled to receive the Pyrex reference junction tubes.

Fig. 4. Ice bath for reference junction
Clear shaved ice and distilled water is used, and water-ice slush filled the dewar flask at all times during observations. This latter precaution is important in the use of an ice bath because the water at the bottom of a bath in which the ice is merely floating may be as high as 4°C, the temperature of maximum density of water. The Pyrex tubes are immersed, so deeply in the ice bath that further immersion caused no detectable change in the thermal emf. This depth is found to be from 15 to 20 cm depending on the diameter of the wires.

3. Calibration of thermocouples and data fitting methods

Calibration of thermocouples is sometimes necessary in order to confirm or establish the emf-to-temperature relationship for the device concerned.

There are a number of ways of calibrating thermocouples. The emf of the thermocouple can be determined at a relatively small number of fixed points using special homogenous furnaces (Figure 5) and interpolation performed using agreed formulae or by considering the difference from a standard table. An alternative method is to compare the emf of the thermocouple being calibrated with that of the same type of standard thermocouple for a large number of temperatures and then fit a curve or algebraic relationship to the emf versus temperature data using a least squares method.

![Fig. 5. The schematic diagram of metal fixed point cell and its furnace](image)

Ideally a calibration should be traceable to the ITS-90. This can be achieved by a hierarchy of calibration activity between the end user and the national standards laboratory or accredited service. Calibration should be undertaken to a specified uncertainty and within a range of temperatures relevant to the application.

For calibration by comparison methods, a liquid bath can be used up to 600°C and a furnace, for higher temperatures up to a limit of about 1800°C (Figure 6). Fully automatic systems are commercially available that control a heater across a programmable temperature range and allow measurements to be taken from a calibrated temperature sensor and the thermocouple to be tested and provides the facility for the data to be logged in a data file.
Despite the extensive use of thermocouples in scientific and industrial measurements for over half a century, theoretical studies have not yielded an adequate basis for predicting the electromotive force vs. temperature (ET characteristic) curve. Hence thermocouple ET characteristics are based on laboratory measurements, the data being fitted to an approximating formula. The approximating formula is at best an educated guess.

Platinum-10%Rhodium/Platinum thermocouples which satisfy the criteria stated in the text of the International Practical Temperature Scale of 1968 (IPTS-68) are used to realize temperatures in the range 630.74 °C to 1064 °C. The calibration of these thermocouples at the freezing points of Sb, Ag and Au resolves the quadratic relationship.

\[ E = a + bt + ct^2 \]  

(5)

which defines temperature in this range. However the thermocouple is used over a much wider range of temperature approximately from 100 °C to 1400 °C and it is desirable that it should be calibrated at that range with a minimum of uncertainty. There are two methods of thermocouple calibration generally referred to as the fixed point and the intercomparison methods. In the former the thermocouple is calibrated at the freezing points of metals specified by the ITS-90 whilst in the latter the output of the thermocouple is measured at temperatures determined by a calibrated thermocouple or resistance thermometer. In general calibration at the fixed points is more accurate than calibration by the intercomparison method. However there is very limited information on the estimated uncertainty of calibration in the region of interpolation. Before a rigorous comparison of the uncertainty in thermocouple calibration by the two methods can be made, the error associated with interpolation between fixed points must be evaluated.
3.1 Methods of interpolation

Methods which can be used for interpolation between measured data have been stated in many texts. Data fitting is a technique for constructing a mathematical model that characterizes the data or providing a mathematical formula by which the data can be reproduced. An extensive discussion of data fitting is given in Hamming’s book\(^8\).

When the intervals between the measured values are not equal the two methods most commonly used are those in which a curve is fitted to the points using a least squares method and the Lagrangian method\(^9\). In forcing the curve to pass through the data points, Lagrangian method can introduce large deviations into the interpolation between the points. The least squares method consists of fitting a polynomial function to minimize the sum of the squares of the deviations of all data points from the polynomial curve. Functions of increasing powers are fitted and it is desired to find the lowest order curve, which gives a satisfactory fit. The criterion for satisfactory fit depends on the number of measured values. The most satisfactory criterion is to specify that the maximum deviation of the calibration points from the fitted curve should be less than the maximum uncertain associated with the calibration points. When a large number of calibration points are available, as the power of the fitted polynomial increases, the modulus of the maximum deviation of the calibration points from the fitted curve decreases rapidly at first and then becomes more nearly constant. The order of the polynomial one beyond which this modulus becomes nearly constant is the one chosen as a satisfactory fit.

Computer generated plots of emf vs. temperature can quickly reveal an adequate mathematical fitting of the approximating functions to the experimental data. Another method used specifically for the calibration of thermocouples is to draw a curve of the differences between the measured values and a smooth thermocouple reference table for example the IEC reference tables. In this method, which has been detailed by Roesser and Lonberger\(^10\), the difference between the measured values and the reference tables at the calibration points are determined, and smooth curve is fitted to these differences. The values of the difference curve are then added to the reference tables to give the final calibration table for the thermocouple. However any irregularities in the reference tables will produce irregularities in the calibration table.

3.1.1 Interpolation by using the standard reference function

Standard reference functions play a very important role in thermocouple thermometry and lead to considerable savings in time and effort. A standard reference function represents the behavior of typical example of particular type of thermocouple. The calibration of an individual example of this type of thermocouple is thus reduced to determining the difference between its behavior and that of the standard embodied in the reference function. Provided that the original work which led to the reference function was well done and that the thermocouple conform to the IPTS criteria mentioned before. It will be found that the differences are very small. The number of the calibration points necessary to determine adequately the differences from the standard reference function will be correspondingly small and the whole process will be simple and economic.

Figure (7) shows differences from the standard reference function measured for a number of type R thermocouples. The differences from the table were measured (Coats 1978a) at the
freezing point of Zinc (≈419 °C), Silver (≈960 °C) and Gold (≈1064 °C). The accuracy of the measurement was estimated to be ±0.2 °C.

It is clear that a quadratic expression of the differences is perfectly adequate to give a calibration of each thermocouple within the limits of accuracy of measurement.

3.2 The reference functions for Au/Pt thermocouples

In that work Gotoh et al (5) established a reference function (reference table) for the Au/Pt thermocouple through the investigation of the emf-temperature relationship over the range 0-962 °C, with such a reference function calibration at a small number of fixed points to fit the deviation of particular Au/Pt thermocouple from the reference function should be sufficient to permit high precision temperature measurement over the full range 0-962 °C.

The thermocouples used in that project were initially annealed after annealing they were calibrated at the metal fixed points using the well developed techniques by McLaren and Murdock (11). The measurement sequence was indium, tin, zinc, antimony, Au-Cu eutectic (liquidus point) and silver. The emf was measured with a Keithley nanovoltmeter.

Next a comparison measurement was performed in the stirred bath beginning in the water bath from 25 to 75 °C followed by the oil bath from 75 to 300 °C and finally the nitrate salt bath from 300 to 494 °C. For intercomparison a high temperature platinum resistance thermometer HTSPT was used.

The emf temperature data were analyzed by fitting polynomials of various degrees by the method of least squares. The preferred equation relating emf in millivolts to 890(°C) is

\[
emf = \sum_{i=1}^{8} C_i (t_a)^i
\]

Where:

- \(c_1 = 6.0310705 \times 10^{-3}\)
- \(c_2 = 1.9377291 \times 10^{-5}\)
- \(c_3 = -2.2104563 \times 10^{-8}\)
- \(c_4 = 3.1103354 \times 10^{-11}\)
- \(c_5 = -3.5645621 \times 10^{-14}\)
- \(c_6 = 3.1611501 \times 10^{-17}\)
- \(c_7 = -1.7549464 \times 10^{-20}\)
- \(c_8 = 4.2602445 \times 10^{-24}\)
The above reference function provides emf in \( \mu V \) as a function of temperature in degrees Celsius to within \( \pm 10 \) mK from 0 to 962 \( ^\circ C \). The agreement between the intercomparison data and the fixed-point data was not as good as was expected by the authors.

3.3 The reference function for Pt-10%Rh vs. Pt thermocouple

In July 1990 the Comite Consultatif de Thermometrie requested its working group 2 to collaborate with national laboratories in the production of new reference tables and functions for the standard Pt-10% Rh vs. Pt thermocouples based on the International Temperature Scale of 1990 (ITS-90). Pursuant to this recommendation, eight national laboratories \(^{(1)}\) have obtained new data for Pt-10%Rh vs. Pt thermocouples. The thermoelectric voltages of those thermocouples have been measured as a function of \( t(90) \) in the range -50 \( ^\circ C \) to 1070 \( ^\circ C \) with temperatures obtained from standard platinum resistance thermometer that were calibrated in accordance with the ITS-90 to 962 \( ^\circ C \) and extrapolated to 1070 \( ^\circ C \). In addition the thermoelectric voltage of the thermocouples has been determined at various thermoelectric fixed points. From the results of these measurements, polynomials giving the thermoelectric voltage as a function of \( t(90) \) have been developed.

The new reference function for the Pt-10% Rh vs. Pt thermocouples for the temperature range from -50 to 1064.18 \( ^\circ C \) is of the form

\[
E = \sum_{i=1}^{8} a_i (t_{90})^i
\]

where \( t(90) \) is in degree Celsius and \( E \) is in microvolts. The coefficients of equation for the temperature range -50\( ^\circ C \) to 1064.18 \( ^\circ C \) are;

\[
a_1=5.40313308631, \quad a_5=-3.31465196389X10^{-21},
\]
\[
a_2=1.25934289740X10^{-2}, \quad a_6=2.55744251786X10^{-2},
\]
\[
a_3=-2.3247796869X10^{-5}, \quad a_7=-1.25068871393X10^{-17},
\]
\[
a_4=3.22028825036X10^{-8}, \quad a_8=2.71443176145X10^{-21}.
\]

The eight laboratories involved in this study are:

- National Institute of Standards and Technology NIST, USA,
- Istituto di Metrologia G. Colonnetti IMGC, Italy,
- Korea Research Institute of Standards and Science KRISS, Korea,
- National Physical Laboratory NPL, UK,
- National Research Laboratory of Metrology NRLM, Japan,
- Mendeleyev Institute for Metrology VNIIM, Russia,
- Van Swinden Laboratorium VSL, Netherlands,
- And Shanghai Institute of Process Automation Instrumentation SIPAI, China.

4. Factors affecting the calibration constancy and reproducibility of Pt-10%Rh vs. Pt thermocouples

4.1 The effect of temperature gradient on annealed thermocouples

Stabilizing the gradient and the Seebeck coefficient can minimize the thermocouple drift. If the impurity concentration, (homogeneity) along the wires is reasonably uniform over the
section of wires that are to be subjected to the main gradient, then as the average Seebeck coefficient is constant along the wire, the thermal emf generated will depend only upon the temperature difference and will be independent of the temperature gradient as the junction is displaced along the ingot. If on the other hand the impurity distribution is not uniform within the gradient zone then there should, obviously, be measurable gradient dependence.

4.2 The effect of soaking thermocouples in a high temperature gradient

The most likely reason why annealed thermocouples are unstable when introduced into a temperature gradient is that while uniform temperature homogenize impurities within the wire during annealing, temperature gradients induce segregation of impurities.

When a thermocouple wire is annealed, it is subjected to a uniform high temperature. If there are impurity concentration gradients within the wire they gradually disperse by diffusion as the wire approaches a stable thermodynamic equilibrium state. As the rate of approach to homogeneity depends on the mobility of impurities and as this mobility increases with increasing temperature, the higher the annealing temperature the faster the thermocouple wire will reach its annealed state. If however, an annealed thermocouple wire is inserted into a temperature gradient region then the temperature gradient will induce thermal diffusion of impurities. Thermal diffusion will cause segregation of impurities until a steady state is reached in which the flow induced by the temperature gradient is in balance with that induced by the gradient of concentration.

Due to the relatively low mobilities in the solid state, especially at lower temperatures (T ≤ 1000 °C), such diffusion process take a very long time to reach the steady state and hence thermoelectric stability. In the present study the thermocouples are gradient stabilized in the Ag furnace. They remained stable in all other fixed point furnaces because, although the temperature gradient was altered, the temperatures were also lowered thus lowering the mobility to low enough values that the altered gradients could not cause major impurity rearrangement within the short duration of our measurements. Such impurity gradient accumulation by thermal diffusion was reported by Darling and Selman (13). According to their findings a Pt vs. Pt-13%Rh thermocouple was used to monitor a temperature set at 625 °C. After several years of use the Pt-13%Rh wire showed a measurable depleted Rh concentration in certain sections of the wire exposed to high temperature and an increased Rh concentration towards the colder parts of the wire. Soaking the wire at a uniform temperature of 1200 °C the accumulated Rh concentration gradients dissipated (a tendency towards thermodynamic equilibrium) restoring the generated emf to its original value.

4.3 Factors affecting the calibration constancy and life of Pt-10%Rh vs. Pt thermocouples

The platinum vs. platinum rhodium thermocouple consists of a positive element of platinum 10 % rhodium and a negative element of platinum. The platinum from which the negative element is prepared is the purest metal produced commercially. This high purity is necessary in order to prevent unpredictable thermoelectric effects caused by impurities. Contamination of the pure platinum leg in service is perhaps the main reason for loss of calibration. In respect to the platinum vs. platinum 10 % rhodium couples, the following also may limit the life or constancy of calibration;
1. Diffusion of rhodium from the bead into the Platinum.
2. Volatilization of the Platinum or Rhodium.
3. Contamination of the thermocouple.

All of these are temperature dependent. The second is also dependent on the atmosphere in which the thermocouple is used. The third is dependent on the nature of the insulating and protection tubes and the atmosphere in which the thermocouple is used. These will be discussed in the following.

Diffusion of rhodium increases with the temperature and the time during which the thermocouple is exposed to the temperature. Its effect is negligible (14) if the furnace temperature is uniform, and if there is sufficient depth of uniform temperature, as then the zone containing the diffused rhodium acts only as a connector between the legs of the thermocouple and so does not interfere with the indications of the thermocouple. Should the diffused zone enter a region of non-uniform temperature, the result would be to reduce the emf output of the thermocouple, thus making the indicated temperature lower than the true temperature of the furnace. Diffusion of rhodium into the platinum leg may also occur by volatilization from platinum-rhodium wire and deposition on to the platinum. This only significantly occurs at temperatures over 1200°C. Its occurrence can be detected by an examination of the twin bore insulating tube, where small metallic crystals will be seen.

The loss of platinum and rhodium in air or oxidizing atmospheres is higher than in vacuum. This has been attributed to the formation of volatile oxides. The rate of volatilization depends upon the temperature, percent oxygen, and the velocity of the gas stream over the metal surface.

Contamination of a thermocouple is by far the easiest method of shortening its life. Should any metals (solid, liquid or vapour) come into contact with the thermocouple, alloying will take place and this will change the emf of the thermocouple and render it unfit for further use. Furnace gases or chemical fumes, particularly those carrying sulfur compounds may cause embrittlement of the wires in addition to affecting the emf output. It is very difficult to predict how long a couple may last. So many factors are involved in this type of an evaluation that a standard answer cannot be given. Some experimental results show that volatilization appears to be the main problem.

5. General conclusion

- Temperature sensors constructed from high-purity noble metals exhibit the highest degree of interchangeability and stability in comparison to all other artifact thermometers.
- The Au/Pt thermocouple should be considered as a suitable and challenging alternative to the high temperature platinum resistance thermometers HTSPRT for many precise temperature measurements in the range from 660 °C to 950°C. The HTSPRT, however, is expensive about (10,000 US $) and fragile and requires either a DC resistance comparator bridge (60,000 US$) or an AC resistance comparator (50,000 US$) to measure electrical resistance. In contrast, a normal Au/Pt thermocouple with 170 cm long, 0.5 mm diameter thermo-element, has a material value of (1000 US$) and requires only a superior digital Nanovoltmeter (≈3000 US$) to measure the thermo-emf.
The Au/Pt thermocouple, following suitable high temperature preparatory annealing, is also capable of repeatability of few mK at the Ag point and the uncertainties in temperature measurements arising from the intrinsic thermoelectric inhomogeneity along the Au and Pt wires can be reduce to 10 or 20 mK.

Further on the basis of cost, simplicity of construction, ruggedness and reconstruction of damaged thermo-elements by re-annealing and re-assembly procedures.

- Au/Pt thermocouple should be given serious considerations as a superior replacement for the standard Pt-10% Rh vs. Pt thermocouple in the temperature range from 0 to 1000 °C and as a worthy alternative to the high temperature platinum resistance thermometer in the range 500 °C to 1000 °C in the future International Temperature Scale.
- Following careful annealing of Au and Pt wires forming the thermocouple to stabilize their thermopower for sustained exposure to high temperature, the Au/Pt thermocouple has distinct advantages over the standard Pt-10%Rh vs. Pt thermocouple for temperature measurements up to 1000 °C. Substituting Au element for the Pt 10%Rh element in the standard thermocouple eliminates the thermoelectrically degrading effect on the thermopower of the Pt-10% Rh element.

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