Rhodium-Platinum Thermocouples as Precision Temperature Sensors

By D. F. Carter
National Physical Laboratory, Teddington, Middlesex

and P. H. Wells
Johnson Matthey Metals Limited, London

The standard of accuracy of all platinum: rhodium-platinum thermocouples produced by Johnson Matthey Metals Limited is extremely high. However, individual thermocouples for special purposes can be supplied to even higher standards of accuracy following their precision calibration by the National Physical Laboratory.

The choice of the platinum: 10 per cent rhodium-platinum thermocouple as the instrument for defining or reproducing that part of the International Practical Temperature Scale lying between the freezing point of antimony (630.74°C) and the freezing point of gold (1064.43°C) is mainly attributable to the remarkable accuracy and stability of this thermocouple at elevated temperatures. Furthermore the smooth e.m.f.-temperature relationship enables very accurate reference tables to be constructed (1), thus permitting interpolation with a high degree of confidence. Today this is also true of the platinum: 13 per cent rhodium-platinum thermocouple, which is if anything more stable and has a higher output at a given temperature. For this reason the platinum: 13 per cent rhodium-platinum thermocouple may well become the preferred combination for temperature measurement up to about 1500°C.

The stability and reproducibility of both thermocouples is very dependent on the purity and consistency of the platinum limb. Many years of experience coupled with strict quality control and inspection techniques have enabled Johnson Matthey Metals to achieve a standard accuracy of $\pm$1°C from 0°C to 1100°C on randomly matched batches.

For the most precise temperature measurement the National Physical Laboratory, on request, will calibrate individual thermocouples of both types to an accuracy of $\pm$0.3°C over the range 0 to 1100°C and the results are presented as a report. These calibrated thermocouples are used as standards in the calibration of other thermocouples, and Johnson Matthey Metals Limited are called upon regularly to supply them both to national standardising laboratories and to industrial concerns where extremely precise temperature control is necessary. One such thermocouple is shown in Fig. 1.

The calibration of platinum: 10 and 13 per cent rhodium-platinum thermocouples is one service of the Measurement Group of the National Physical Laboratory. The most precise calibration of an individual thermocouple amounts, in effect, to determining by how much it differs from the appropriate reference table. This is achieved by measuring the thermocouple e.m.f. values at a series of precisely known temperatures and comparing them with the corresponding e.m.f. values given in the reference table for the same temperatures. A smooth curve of difference derived from and linking these measurement points enables interpolation between the calibration temperatures to be obtained by difference from the reference table. In practice the measurements are obtained by adopting the procedures and methods con-

Fig. 1 A typical Johnson Matthey Metals high accuracy thermocouple in its foam-lined case after calibration at the National Physical Laboratory. With it is its N.P.L. report. The thermocouple is mounted in a one-piece insulator 400 mm long in order to retain its strain-free calibrated condition

tained in the recommendations of the International Practical Temperature Scale of 1968 (IPTS–68).

Procedure for Assembly and Calibration

The process of assembly of a thermocouple is as follows. Immediately on receipt at N.P.L. the thermocouple wires are annealed electrically, the platinum limb at 1100°C and the alloy limb at 1450°C. The wires are then threaded through a rigid and continuous twin-bore alumina insulator about 400 mm long. The hot junction is made by welding the wires together in an oxy-gas flame. While in this form the thermocouple is annealed again at 1100°C to eliminate the effect on thermal e.m.f. of any cold work or strain introduced during assembly.

The significance of the continuous length of rigid insulator lies in the desirability of maintaining the wires in a strain-free and uncontaminated condition. If these conditions do not prevail in any parts of the wire where considerable temperature gradients may occur then the thermocouple is likely to generate spurious e.m.f.s to the detriment of the calibration. It should be remarked here that subsequent use of the thermocouple at temperatures significantly above 1100°C can lead to changes in its behaviour which invalidate the high-accuracy calibration.

At the cold end of the thermocouple the reference junction is formed by winding a pure copper wire around each limb and then placing the four suitably insulated wires in a close-fitting glass tube, which is maintained with adequate immersion in a melting ice and water mixture at 0°C.

The calibration begins with measurements of thermal e.m.f. at the freezing point of gold (1064.43°C), followed by the freezing point of silver (961.93°C). Figures 2 and 3 illustrate the apparatus, the most notable features being the nickel block to promote the uniform temperature zone enveloping the ingot, and the graphite lid, crucible and re-entrant tube which safeguard the metal against risks of oxidation and contamination. The protected thermocouple is placed in the

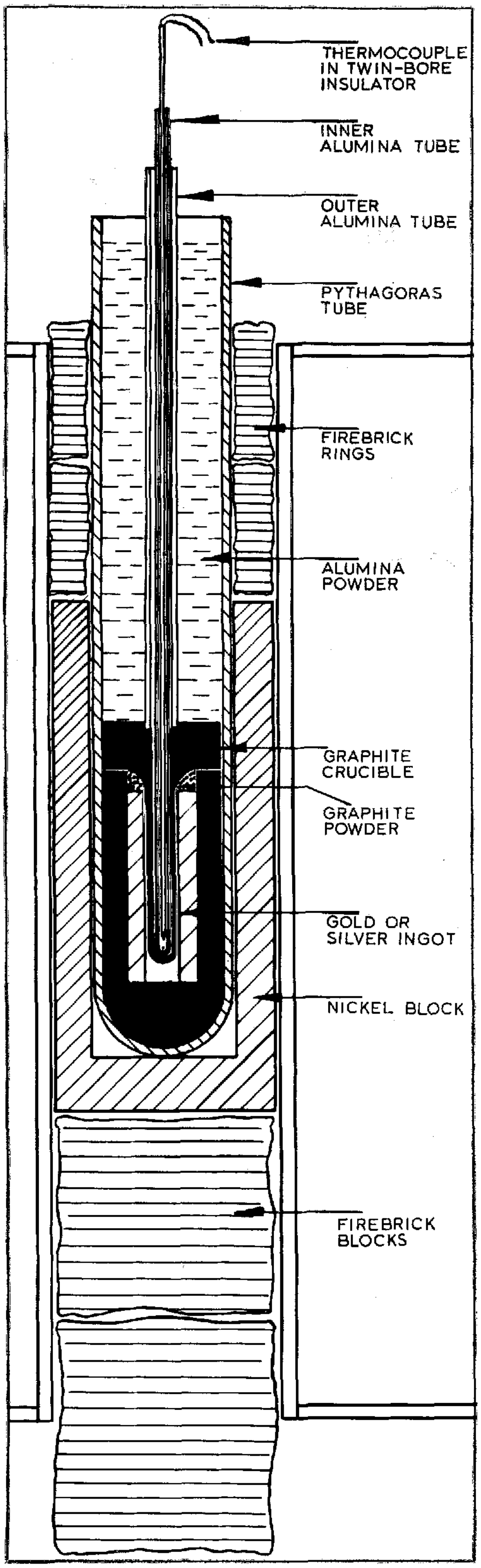


Fig. 2 Section through the N.P.L. apparatus for the calibration of platinum: rhodium-platinum thermocouples at the freezing points of gold and silver

graphite re-entrant tube and the ingot is melted. It is then cooled slowly and as it freezes a cooling curve of e.m.f. against time is plotted. The freezing point value is taken to be that corresponding to the plateau or level part of the curve. By controlling the cooling rate the plateau is readily sustained for a half hour or more, signifying that the equilibrium state is obtained. That the immersion of the thermocouple is sufficient to preclude thermal losses by conduction along the wires is demonstrated during the freeze by varying the immersion depth by about one centimetre, when the measured e.m.f. should not change by more than one microvolt.

The freezing point temperature is taken to be precisely that ascribed to the pure metal and requires that the purity of the metal, as supplied by the manufacturer, is compatible with the limits of accuracy imposed on the measurements. In this case a purity of 99.999 per cent is used, leading to a depression of the freezing point which is not likely to exceed a few millidegrees Celsius.

The calibration is continued in a uniform-temperature enclosure, available in the form of a stirred-liquid bath of concentric design and proven performance. This apparatus is shown in Fig. 4. The inner tube of the bath is about 7.5 cm in diameter and 65 cm deep, and under working conditions is constantly filling with a stirred liquid whose temperature is nominally uniform throughout. The liquid is a commercially available mixture of potassium nitrate and sodium nitrite salts, which is molten and usable in the bath from about 160°C to 630°C. [Some very real dangers attend the use of these mixtures: see H.M.S.O. Booklet No. 27, 1964, "Precautions in the Use of Nitrate Salt Baths".]

In this medium the thermocouple is protected by a pyrex glass sheath and is calibrated by measuring its e.m.f. at a series of known

Fig. 3 Calibration of thermocouples at N.P.L. includes plotting the thermal arrest at the freezing point of silver. The cold junctions are held in the flask of melting ice at 0°C. The use of a reversing switch eliminates the effect of stray e.m.f.s in the measuring system

Fig. 4 Simultaneous comparison at N.P.L. of temperature measurement by means of a platinum resistance thermometer and a.c. double bridge with the thermal e.m.f. of a J.M.M. thermocouple under test in a stirred-liquid salt bath

and steady temperatures—generally 200, 400 and 600°C. The bath temperature is controlled electrically and is determined by reference to a standard platinum resistance thermometer used in conjunction with an a.c. double bridge having inductively-coupled ratio arms. As a secondary standard instrument the resistance thermometer is itself calibrated by the N.P.L. Measurement Group in terms of IPTS-68 and is capable of measuring temperature to an accuracy of a few millidegrees Celsius.

Throughout the tests the e.m.f. measurements are effected by means of a precision vernier potentiometer or by a digital voltmeter of comparable discrimination and as a normal precaution against the effects of stray thermal e.m.f.s a reversing switch is included in the measuring system.

The calibration is concluded with the compilation of a table recording the e.m.f. output of the thermocouple quoted to the nearest microvolt for a series of nominal temperatures covering the range. Provided that the performance of the thermocouple has been satisfactory the calibration is given an accuracy of ±0.3°C.

Sensitive devices like these thermocouples call for special care in manufacture, in carriage and in use. Johnson Matthey Metals have recently introduced a foam-lined case, shown in Fig. 1, in which each thermocouple is sent to the National Physical Laboratory for calibration. On return from N.P.L. each thermocouple is despatched in its case, together with its N.P.L. calibration report, from Johnson Matthey direct to the customer, thereby ensuring that its accuracy is not impaired in transit by cold work induced by handling during transfer from one case to another. Thereafter the life of the calibration is finite, of course, and the rate of change from calibration will depend upon the frequency and conditions of use.

Reference

1 T. J. Quinn and T. R. D. Chandler, *Platinum Metals Rev.*, 1972, **16**, (1), 2–9

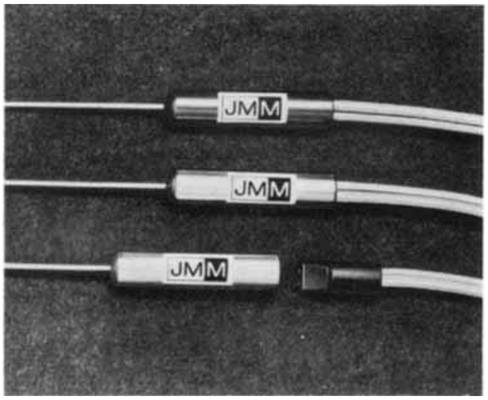
Connectors for Metal Clad Thermocouples

PLUG-IN END CAPS FOR COMPENSATING LEADS

A new type of end connector recently developed by Johnson Matthey Metals Limited enables the compensating lead to be disconnected from the thermocouple, so making thermocouple replacement simpler. The new unit makes it possible to connect one lead in turn to any number of thermocouples, thus saving on the number of leads and temperature recording instruments.

Housed within the anodised aluminium case are gold plated pins and sockets, to which are soldered the thermocouple wires and the compensating cable respectively. The assembly is then encapsulated in nylon to form a two-piece connector, each half bearing corresponding flats to ensure correct polarity with every connection.

These end connectors satisfactorily withstand operating temperatures of up to 100°C, the normal working temperature of the compensating lead. At this temperature stray e.m.f.s at the pin and socket junctions are negligible and do not affect output of the thermocouple.



Colour coding of the aluminium cases easily identifies thermocouples; red denotes platinum: 13 per cent rhodium-platinum, gold denotes platinum: 10 per cent rhodium-platinum, and silver or neutral colour other combinations (5 per cent Rh-Pt : 20 per cent Rh-Pt, 6 per cent Rh-Pt : 30 per cent Rh-Pt, Pallador).