Precision Temperature Measurements with Platinum Thermocouples

EFFECT OF LOW-TEMPERATURE OXIDATION OF THE PLATINUM-RHODIUM ELEMENT

The Ottawa laboratories of the Physics Division of the National Research Council of Canada are internationally recognised for the work there of E. H. McLaren and E. G. Murdock in developing furnaces and freezing point cells for standardising thermocouples at the freezing points of pure metals.

With this equipment, melts in graphite crucibles 4 mm in diameter and up to 25 cm long can be maintained at the freezing point for 9 hours or more, the crucible being surrounded by a metal block controlled by heaters to keep it at a degree or so below the melting point.

Thus equipped, the authors have recently carried out an unusually extensive study of the reliability of the platinum: 10 per cent rhodium-platinum thermocouple for measuring temperatures with a precision of at least 0.1°C. The results are published (1) in a report of four volumes, of which the first two only appear at present to be available in the U.K.; but their general conclusions are clearly stated and warrant attention.

They make it clear from the beginning that they are concerned only with temperature measurements that may require accuracies of 0.001 to 0.1°C. For the bulk of industrial or scientific work, in which precisions of ± 1°C are all that are required, they concede that thermocouples provide the quickest, simplest, and cheapest method of measuring high temperatures. But they show that in precision thermometry the platinum:platinum-rhodium couple may have inherent uncertainties.

These stem from the essential qualification, often over-looked, that the e.m.f. generated depends on the temperature difference between the hot and cold junctions only if the two conductors are, and remain, electrically homogeneous throughout their length.

Ensuring Uniformity

It is thus first necessary to ensure that the elements are initially uniform throughout their full length. The generally accepted practice is to electrically anneal the couples at 1300°C in air for 1 to 10 hours and to cool in air. This is said to drive dislocation-recovery processes to near completion, evaporate any rhodium oxide on the rhodium alloy element, and possibly remove trace impurities as oxides. However, it is shown that the treatment leaves a high concentration of quenched-in vacancies, which will be annealed out to differing degrees along the length of the couple when it is put into use. It is therefore considered that the couple should be annealed for one hour at 450°C and, after sheathing, that the assembly be given a recovery and equilibrium anneal at 450°C overnight.

The most serious cause of inhomogeneity which has been identified is attributed to oxidation of the platinum-rhodium element along that portion which is exposed to air in the temperature range 500 to 900°C. The wires visibly blacken, and it is suggested that they undergo internal oxidation. The magnitude of the degradation effect due to oxidation may amount to several microvolts when measuring high temperatures.

Finally a small enhancement of the thermoelectric e.m.f. has been found as a consequence of unidentified changes along the portion of the alloy element exposed to temperatures from 160 to 450°C. There is a hint that this effect might be due to an ordering in the alloy lattice—though there is no evidence that such an atomic rearrangement has ever been found.

The report describes the results of hundreds of experiments using the freezing point cells for indium, tin, zinc, lead, silver and copper. In the first two volumes alone about 560 experimental curves are reproduced in 83 graphs, using both normal couples and specially constructed ones in which spiralled lengths of thinner wire were incorporated to allow one or other or both of the leads to be withdrawn without moving the junction itself. Measurements are recorded of the changes in temperature as a couple was inserted into the thermocouple well of the freezing ingot and later withdrawn; and the curves serve as a measure of the couple's behaviour. The effects of prior heat treatments of the couple wires in various atmospheres either in the range 160 to 500°C or at 800°C on the readings at the indium, tin, antimony, and copper points are recorded. The text is repetitious and many of the curves are identified by coded abbreviations, but the results of the experimental work are most comprehensively set out and there can be no doubting their authenticity.

Oxidation of Rhodium

The most interesting feature disclosed in these tests concerns the preferential oxidation of rhodium on the alloy wires at 500 to 900°C. At high temperatures, above about 1200°C, it is well established that the vapour pressures of the volatile oxides, PtO_2 and RhO_2, formed in air are very nearly equal. The composition of the deposits condensed beside the windings of a standard furnace operating at high temperatures is found to be almost exactly the same as that of the 10 per cent rhodium-platinum alloy of which the wires are constructed. At the lower temperatures, however, the conditions are most unusual. In the temperature range 500 to 900°C, PtO_2 exists in the vapour phase but RhO_2 is a solid. Thus, while PtO_2 is in the process of escaping from the surface, perhaps especially from the crystal boundaries, solid RhO_2 is forming and being left behind. This action may well lead to an accumulation of RhO_2 at the crystal boundaries, producing an appearance of internal oxidation. The changes proceed very slowly. The only direct evidence so far appears to be in a photomicrograph reproduced by Darling, Selman and Rushforth (2) showing shallow oxidation at the grain boundaries in a 13 per cent rhodium-platinum alloy thermocouple wire after operation in air in a creep laboratory for about five years (40,000 hours) at about 400°C. The oxide penetration amounts to about half a thousandth of an inch, and this led to a reduced output from the thermocouple equivalent to about 2°C.

McLaren and Murdock suggest that the change in e.m.f. associated with the blackening of the rhodium-platinum alloy elements at 800°C is attributable to a reduction in the amount of rhodium in solid solution in the affected region. This ignores any consideration of the amount of platinum lost by volatilisation, and it seems likely that the effect must be more complicated and affected by the presence of the solid RhO_2 particles.

Whatever the explanation, however, of both the low-temperature effects, there is no questioning of the thoroughness with which instability in platinum: 10 per cent rhodium-platinum thermocouples has been studied in this report—even if the first two parts alone are considered. The author's findings will provide valuable data which will undoubtedly be considered very carefully when next the International Temperature Scale comes up for revision and may influence the argument for replacing the thermocouple by the platinum resistance thermometer for defining the scale in the range from 600 to 1064°C.

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References

1 E. H. McLaren and E. G. Murdock, "The Properties of Pt/PtRh Thermocouples for Thermometry in the Range 0-1100°C". Part I. Basic Measurements with Standard Thermocouples. Part II. Effect of Heat Treatment on Standard Thermocouples. 1979, Ottawa, National Research Council Canada. (APH-2213/NRCC 17408)

2 A. S. Darling, G. L. Selman and R. Rushforth, *Platinum Met. Rev.*, 1971, **15**, (1), 16