Improved Metal Sheathed Thermocouples

HIGH STABILITY AT HIGH TEMPERATURES

Long-term calibration changes of rhodium-platinum thermocouples operating close to their maximum service temperatures are attributable to rhodium migration from the positive to the negative limb. In the metal-clad thermocouple described here the effects of this phenomenon are considerably reduced by balancing the rhodium content of the sheath and of the thermocouple wires.

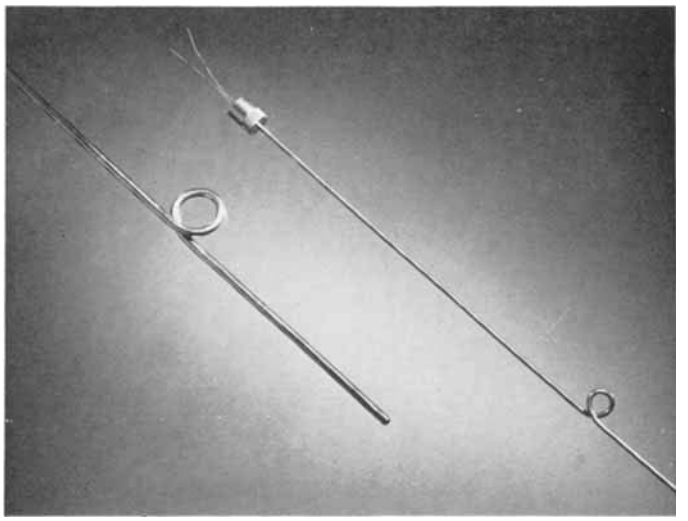
Industrial temperature measurement in the range 1000° to 1500°C is largely dependent upon the use of rhodium-platinum thermocouples, and it is difficult to envisage an alternative measuring device of comparable reliability and precision. The factors that affect the stability of noble metal couples have been carefully studied for many years and it has been established that, provided external contamination is avoided, a slow migration of rhodium from the positive to the negative limb accounts for the gradual deterioration in thermoelectric behaviour that occurs at high temperatures.

Rhodium is transferred by a vapour phase reaction involving the volatile oxide of rhodium. The standard type of noble metal thermocouple has a fairly loosely fitting refractory sheath, and the natural convection and ventilation that occur in air at high temperatures generally prevent the accumulation of serious concentrations of rhodium oxide within the assembly. Different conditions exist within metal-sheathed thermocouple assemblies, however, which are hermetically sealed, so that mixed platinum/rhodium oxide vapours can build up to pressures commensurate with the oxygen partial pressure within the sheath. From these saturated oxide vapours the pure platinum limb can take up rhodium, and the view has sometimes been expressed that metal-clad thermocouples, although robust and resistant to mechanical damage, must inevitably be less stable than those which are well ventilated.

This view is valid only if the sealed sheath contains air at atmospheric pressure. By filling the sheath with an inert gas, oxide vapour pressures are correspondingly reduced and rhodium migration via the oxide phase is therefore virtually eliminated.

When extreme stability is required, however, metallic vapour pressures must also be considered. Any harmful effects caused by rhodium metal vapour migration can then be reduced to negligible levels by suitably selecting the alloys from which the thermocouple and its sheath are constructed (1). Very satisfactory results are obtained when the 6 per cent rhodium-platinum versus 30 per cent rhodium-platinum thermocouple is insulated with magnesia and sealed within a 5 per cent rhodium-platinum sheath from which air has been removed. With this arrangement the vapour pressure of rhodium in equilibrium with the sheath alloy is, at any temperature, lower than that which is in equilibrium with either of the thermocouple wires. Any rhodium vapour generated by the couple wire is immediately dissolved by the sheath, which, because of its considerably greater volume, is capable of acting as a rhodium 'getter' for prolonged periods. The net effect of rhodium migration is a slow and gradual fall in the rhodium content of the 30 per cent rhodium-platinum wire which,

Metal-sheathed mineral-insulated platinum thermocouples provide flexibility with resistance to thermal shock as well as accuracy and reliability over long periods. Even greater stability has now been achieved in a new type of construction.



however, has little effect upon the thermoelectric power of the couple.

A sheathed thermocouple of this sort was recently tested at 1450°C by the Atomic Energy Research Establishment, Harwell (2). Tests were made in air, and the indicated temperatures were compared to those given by a 20/40 rhodium-platinum thermocouple of simple bare wire construction which was inserted into the furnace about once every 24 hours. The results obtained over a 30-day period of test showed no steady drift in calibration and only slight random variations (in general less than 1°C) between the temperature indications of the two thermocouples. Slight grain growth of the sheath alloy near the hot junction was the only visible evidence of deterioration.

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References

1 Johnson Matthey, Br. Pat. Appln No. 24409/69
2 P. J. Skelton, Stability Test on Pt 6 per cent Rh v Pt 30 per cent Rh Thermocouple with Pt 5 per cent Rh Sheath, R.R.D. Dev. Rep. 54, January 30th, 1969

Disposal of Radioactive Wastes

STABILITY OF PLATINUM CRUCIBLES EXPOSED TO MOLTEN GLASS

The disposal of radioactive waste material from atomic reactors presents many problems and the U.S. Atomic Energy Commission therefore is developing methods of concentrating liquid residues and converting them to stable solid glass, as has been reported previously in this journal (1).

Platinum and its alloys are used widely in the glass industry because of their resistance to corrosion by the constituents of glass. This property has led naturally to their use in two methods for the fixation of radioactive residues in glass. These are the spray calciner process of the Pacific Northwest Laboratory and the continuous phosphate glass process of the Brookhaven National Laboratory.

E. J. Tuthill, G. Strickland and G. G. Weth, from Brookhaven, have now reported on the comparative merits of platinum and its alloys as crucibles in the latter process, together with long-term studies of the creep of platinum and of its corrosion resistance (2).

A bench-scale platinum crucible 3 inches diameter and 10 inches high with a 40 mil wall withstood 300 thermal cycles to 1200°C with only slight distortion and less than 4 microns transgranular corrosion over 1000 hours' exposure. A pilot plant vessel 8 inches diameter and 24 inches high supported by a platinum flange and ceramic baseplate has operated for 1400 hours at 1250°C, the glass-making temperature.

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1 *Platinum Metals Rev.*, 1965, **9**, (3), 89
2 *Ind. Eng. Chem., Process Des.Dev.*, 1969, **8**, (1), 36