The Stability of Metal-sheathed Platinum Thermocouples

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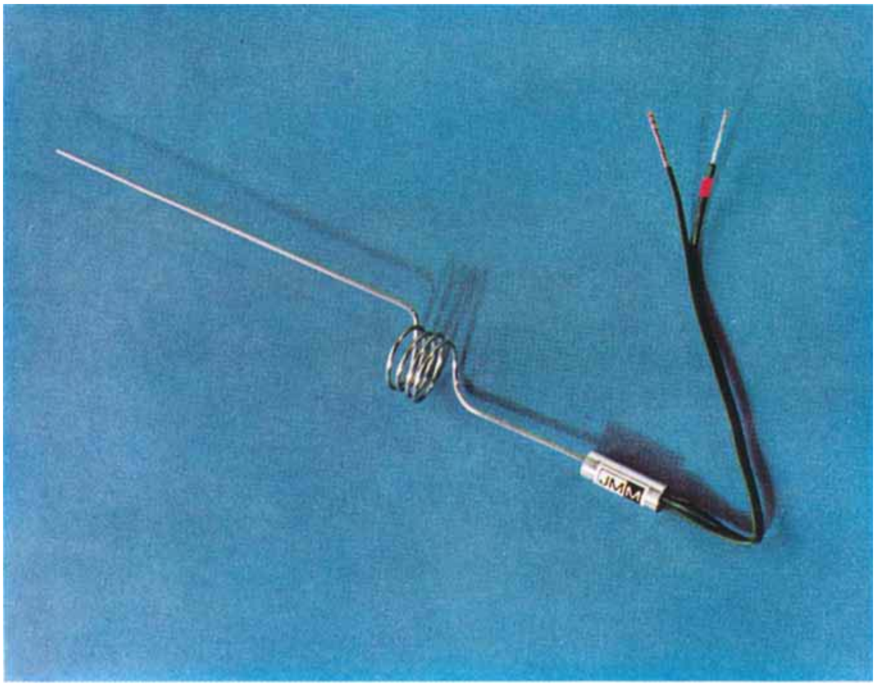
The instability sometimes encountered in metal-sheathed noble metal thermocouples used for long periods at temperatures above 1300°C is attributable to the presence within the sheath of mixed platinum and rhodium oxide vapours from which the pure platinum limb can take up rhodium. Such instability can be avoided by removing residual air from the sheath and substituting an inert gas before the assembly is hermetically sealed. Couples sheathed and sealed up in this way have thermoelectric stabilities comparable to those of the normal unsheathed thermocouple where natural convection prevents the accumulation of dangerous concentrations of rhodium oxide vapour. In the absence of oxygen, the deleterious effects of rhodium metal vapour migration upon the thermoelectric output of these devices can be reduced to negligible levels by suitably selecting the alloys from which the thermocouple and its sheath are constructed. This article is based upon a paper presented to the Fifth Symposium on Temperature, Its Measurement and Control in Science and Industry, held last month in Washington, D.C.

The platinum: rhodium-platinum thermocouple provides a reliable and precise means of temperature measurement in the range 1000 to 1500°C, and in many applications useful lives of thousands of hours can be obtained from alumina-insulated alumina-sheathed devices. Under more arduous industrial conditions, however, the metal-sheathed versions, being more robust and resistant to mechanical and thermal damage, have steadily gained in popularity.

The earliest forms of metal-clad thermocouple, although representing a considerable engineering advance over their refractory-sheathed counterparts, tended to be thermoelectrically less stable. Freeman (1) conducted a detailed examination of a variety of metal-sheathed noble metal thermocouples, and observed thermoelectric drifts equivalent to approximately 150°C over a 500-hour period at 1426°C. The major cause of this deterioration was shown to be transfer of rhodium, from both the sheath and the positive thermoelement, to the negative limb of the thermocouple. Rhodium was detected in pure platinum limbs at positions well removed from the hot junction, a situation consistent with the hypothesis that metal transfer was taking place through the vapour phase. The present work discusses these transport processes in greater detail and shows that they can be so reduced that the metal-clad device rivals in stability the more conventional arrangements.

Mechanism of Metal Transfer

The magnitude of the metal transfer problem in the case of the early metal-sheathed thermocouples is clearly illustrated in Fig. 1, which presents the results of electron probe microanalyses made on the sheath and thermoelements of a 10 per cent rhodium-platinum-sheathed, magnesia-insulated platinum: 13 per cent rhodium-platinum thermocouple which was more than 200°C in error after use for



Metal-sheathed platinum alloy thermocouples possess high stability over long periods when residual air is removed from the sheath and is replaced by an inert gas before hermetic sealing. Versatile instruments of this type are produced by Johnson Matthey Metals

1400 hours at 1450°C. (These, and all subsequent results presented in this paper, refer to thermocouples having twin thermo-elements 0·30 mm diameter, enclosed within a sheath 1.5 mm outside diameter and 0.17 mm thick.) The curves show that a great deal of rhodium has migrated from the sheath and the positive limb to the pure platinum limb. Two important points emerge.

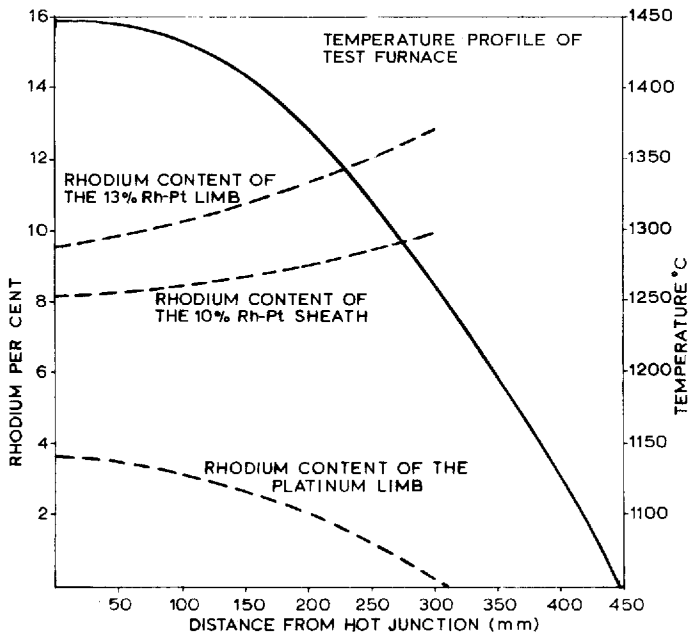


Fig. 1 Rhodium distribution in the sheath and limbs of a platinum : 13 per cent rhodium-platinum thermocouple clad with 10 per cent rhodium-platinum after immersion for 1400 hours at a hot junction temperature of 1450°C

First it is seen that little or no transfer has taken place in regions where the furnace temperature did not exceed 1200°C; used at or

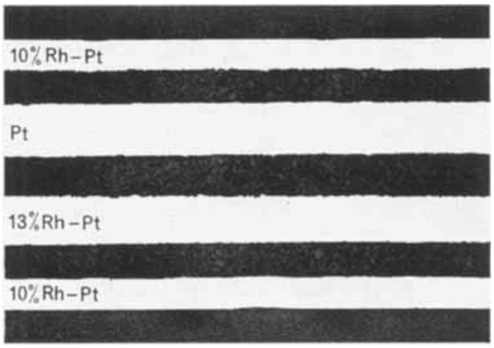


Fig. 2 A metallographic section taken through the heated zone of an unstable metal clad rhodium-platinum thermocouple after long-term exposure at 1450°C in air. The sheath and positive limb show clear signs of the erosion resulting from metal losses through the vapour phase

below this temperature the thermocouple would be expected to remain very stable. Secondly, when the results are considered in relation to the volumes of the two rhodium-bearing components, it becomes clear that the majority of the rhodium emanated from the outer sheath, rather than from the positive leg of the unit. The latter conclusion is of great practical importance when one comes to consider methods of minimising such effects.

Visible evidence indicating the presence of rhodium within the interfacial space was found when unstable thermocouples of this kind were sectioned for micro-examination. The originally pure white magnesia insulation invariably reddened visibly as the heat treatment was prolonged. The insulation in such devices was generally of poor quality, displaying many fissures and cracks, and provided, therefore, an indifferent barrier to metal vapours.

A longitudinal section taken through a high temperature zone of such a thermocouple is illustrated in Fig. 2. It is difficult to resolve the insulation clearly on this photograph, but the vapour loss erosion of the outer sheath and the positive leg on the surfaces closest to the pure platinum limb is very evident.

It is at first glance somewhat surprising that metal-sheathed thermocouples should behave in this way, in view of the generally excellent performance of their alumina-sheathed counterparts, which do not appear to suffer such significant composition changes.

The curves in Fig. 3, calculated in part from Alcock's thermodynamic data (2), show the vapour pressures of platinum, rhodium, and their oxides as a function of temperature in equilibrium with a 10 per cent rhodium-platinum surface in air, and help to explain in a quantitative way a number of the important practical observations which have been made on the behaviour of the rhodium-platinum alloys used for thermocouples. In the interesting temperature range the oxide vapour pressures are several orders of magnitude higher than the metal vapour pressures, which may, under oxidising conditions, be disregarded.

The curves show that for every atom of rhodium leaving the alloy surface, in air,

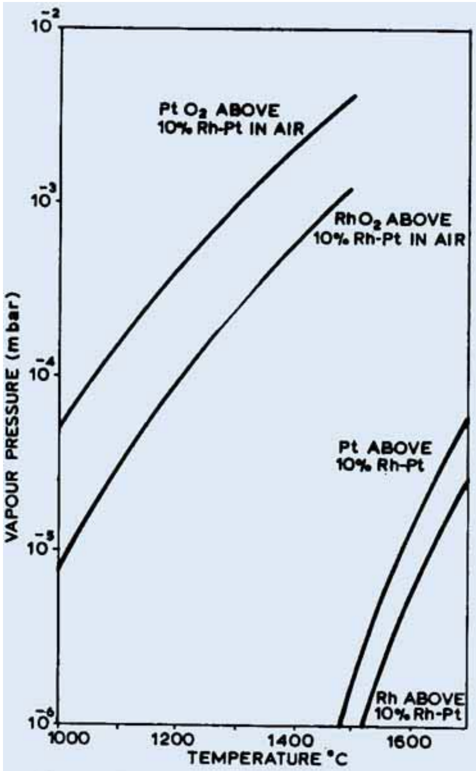


Fig. 3 The vapour pressures of rhodium, platinum, and their oxides above a 10 per cent rhodium-platinum surface in air as a function of temperature

approximately 5 atoms of platinum will evaporate. Thus the vapour will have the same composition as the alloy, and under conditions of free evaporation the composition of the positive leg of the rhodium-platinum thermocouple should not change significantly with time at temperature. Under vacuum conditions the metal vapour pressures become important, and the situation is rather less favourable, since the alloy limb will lose rhodium preferentially and this loss is perhaps the biggest source of instability in vacuo.

Configuration Effects

During conditions of free evaporation in air, therefore, an ideal situation exists in which neither leg of the platinum : rhodium-platinum thermocouple will alter significantly in composition. It is important to emphasise, however, that the geometry of the thermocouple system employed can, if unfavourable, alter this situation quite dramatically. Perhaps the closest approximation to the ideal arrangement is an 'in line' thermocouple, positioned in a furnace such that an air current passes from the platinum leg to the alloy leg, as shown in Fig. 4 (*a*). Under these conditions rhodium vapours from the positive element do not contact or react with the negative leg, which remains, therefore, as pure platinum. If the air flow is reversed, or if conditions do not allow completely free evaporation from the rhodium bearing limb, rhodium oxide may build up to reasonable concentrations above the pure platinum surface, and some instability may be observed.

If the thermocouple wires are allowed to lie parallel to each other in the conventional manner as in Fig. 4 (*b*), rhodium oxide vapour can come into contact and react with the pure platinum limb. Convection currents fortunately minimise the extent of such contamination, however, and in practical terms the instabilities so caused are of little significance. Rigid insulators, while acting as a barrier to gaseous transfer along much of their length, do encourage the formation of local oxide vapour concentrations where gaps exist, although the contamination induced in this way is local and not too severe.

Conditions are very different, however, when the thermocouple is surrounded with a tightly fitting, impermeable alumina sheath, the configuration shown in Fig. 4 (*d*). The atmosphere within this assembly is now completely stagnant, and the rhodium oxide vapour can exert very nearly its full equilibrium vapour pressure around the pure platinum wire. Contamination is inevitable, and such devices have shown a loss in output equivalent to about 40°C over a 100-day period at 1400°C. The rhodium distribution in a thermocouple which has deteriorated in this way is shown in Fig. 5. The peaks and troughs in the curves correspond to the gaps between the 75 mm long alumina insulators, and it is interesting to note that these solid insulators have afforded some considerable protection

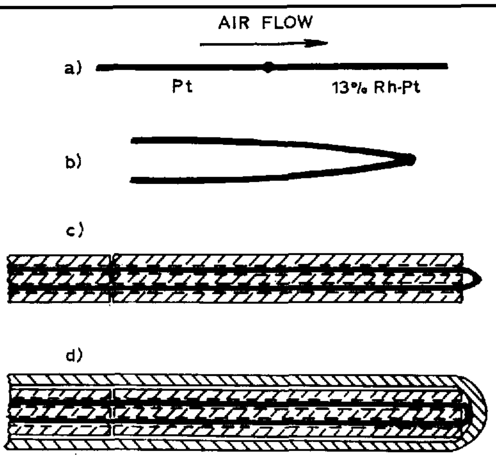


Fig. 4 Effect of thermocouple and insulant geometry upon stability.
(a) In line arrangement – no contamination of the negative limb.
(b) Parallel arrangement – some cross contamination, minimised by convection.
(c) Twin bore insulated – local cross contamination at insulator junctions.
(d) Fully sheathed – moderate to severe contamination of the platinum limb encouraged by stagnant atmosphere

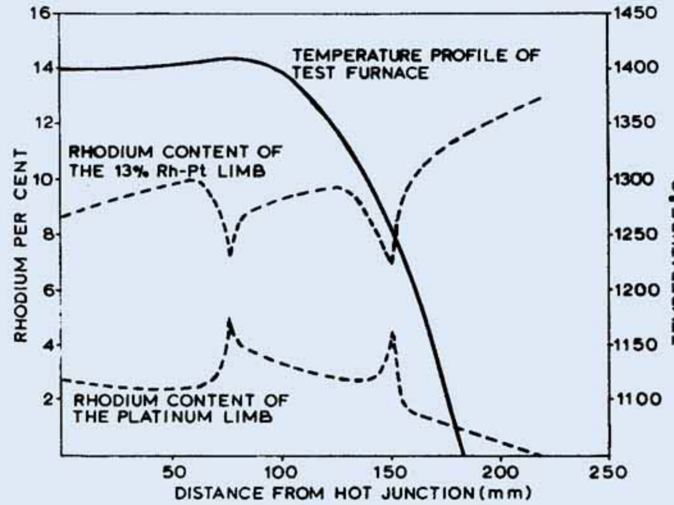


Fig. 5 Rhodium distribution in a twin-bore alumina-insulated thermocouple surrounded by a tightly fitting alumina sheath after 100 days at 1400°C

against contamination in other regions. The composition of the positive limb has changed in this instance, the equilibrium vapour concentrations above it having been disturbed by selective removal of rhodium at the adjacent pure platinum surface, causing more rhodium to evaporate in an attempt to redress the balance.

It is worth emphasising here that errors of this magnitude will only develop when the outer sheath is really tight fitting. The more normal loosely fitting outer sheath allows considerable convection to occur, thus avoiding contamination of the negative limbs.

If the alumina outer sheath of the aforementioned thermocouple is replaced with one of rhodium-platinum, this configuration represents, in essence, the metal-clad thermocouple. It is not too surprising, therefore, that metal transfer of the type shown in Fig. 1 can occur, particularly when the insulant layer is of poor quality and permeable to gases.

The Effect of Insulation Quality

It will be appreciated from the analysis of the vapour transport process made in the preceding paragraphs that the quality of the refractory insulation within the metal-clad thermocouple will have a considerable effect upon its long-term stability. In recent times considerable advances have been made in this direction, as a direct result of improved manufacturing processes. One interesting effect which was observed during the course

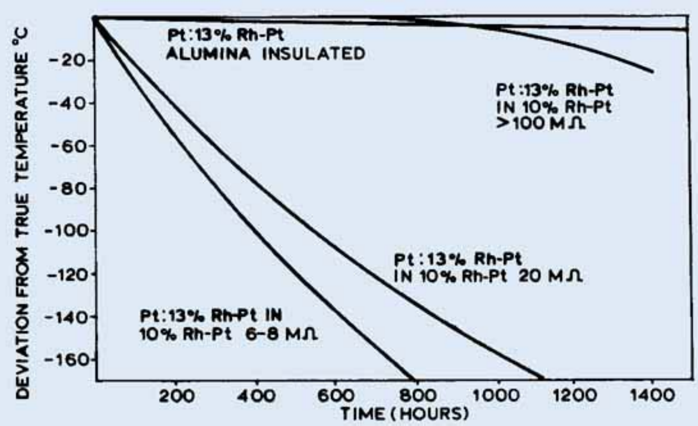


Fig. 6 The effect of room temperature insulation resistance upon the long-term performance of some magnesia-insulated metal-clad thermocouples at 1450°C in air

of development work on these devices is highlighted in Fig. 6, which compares the long-term performances of three 10 per cent rhodium-platinum-clad, magnesia-insulated, platinum : 13 per cent rhodium-platinum thermocouples in air at 1450°C. A conventional alumina-insulated thermocouple was employed as a reference. The three metal-clad thermocouples were identical in construction, but in two cases no particular precautions were taken to drive off absorbed water vapour from the magnesia insulators, with the result that the room temperature insulation resistance, measured between the sheath and one leg of the thermocouple, was low. These two thermocouples, which on insertion within the test furnace gave a signal equal to that of the standard, immediately drifted away from calibration at about 6°C per day. The high insulation resistance thermocouple, on the other hand, was in error by only 20°C after 1400 hours at temperature.

It was initially thought that water vapour was in some way aiding the transport of rhodium from the sheath to the platinum leg of the low insulation resistance couples. When all three thermocouples were sectioned for microexamination, however, it became clear that the magnesia insulation within the stable thermocouple had sintered to a dense, impervious mass which would have almost completely prevented gaseous transfer between the metallic components. The insulation within the unstable devices was highly cracked and porous, and provided no real barrier to vapour transport. It is now thought that the main effect of moisture is to alter the sintering characteristics of magnesia at high temperatures, making it more difficult to maintain a defect-free barrier.

Careful production procedures can, therefore, reduce the problem of cross-contamination in the metal-clad thermocouple. While it is possible to produce a substantially defect-free magnesia barrier during manufacture, however, there can be no guarantee that this ideal state of affairs will be maintained during service. Mechanical bending, although not detrimental to performance when applied to an unused thermocouple, can promote instability if the insulant has been partially sintered during previous use. A more permanent solution to the problem of vapour transfer, independent of the quality of the insulation, is obviously required.

Practical Solutions

The vapour pressure curves presented in Fig. 3 provide a clear indication of one approach whereby the deterioration of the clad thermocouple may be minimised. By removing all traces of oxygen from within the sheath the effective rhodium content of the interfacial atmosphere will be reduced by several orders of magnitude to a level dictated by the vapour pressure of rhodium metal above the alloys concerned. At first sight the difficulties involved in achieving this desirable objective would appear to be prohibitive. In real terms, however, little is gained by reducing the pressure within the sheath below about 0.7 mbar, at which stage the equilibrium vapour pressure of rhodium oxide above 10 per cent rhodium-platinum approximately equals the metal vapour pressure. Overall pressures of this order are not difficult to obtain by vacuum pumping, even when the thermocouple itself is fairly long and of small diameter. Standard glass to metal sealing techniques can be used with advantage for the final hermetic seal.

Unfortunately, reducing the equilibrium rhodium content of the interfacial atmosphere in this way does not provide a complete answer to the problem since at the same time the blanketing effect of an interfacial gas is removed. It is necessary to go further, therefore, and to introduce a viscous inert gas, such as argon, within the interfacial space. Figure 7 highlights the advantages of this approach. The curves describe the long-term stability of 10 per cent rhodium-platinum-sheathed, magnesia-insulated thermocouples which were evacuated and subsequently back-filled with argon to pressures of 67 and 270 mbar. A conventional high

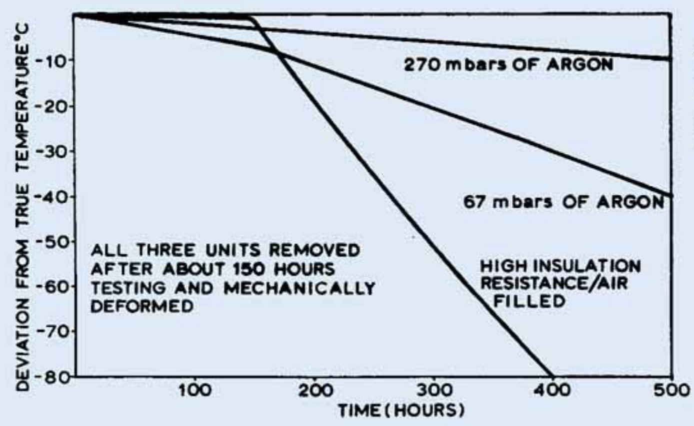


Fig. 7 The effect of interfacial atmosphere upon the stability and sensitivity to mechanical damage of metal-clad thermocouples operating at 1450°C in air

insulation resistance air-filled unit was included in the test bundle, which was heated in a furnace at a hot junction temperature of 1450°C. After 150 hours, during which period none of the thermocouples had deviated by more than a few degrees from their initial output, the bundle was removed from the furnace, and each thermocouple was deformed severely by bending in the heated zone. The bundle was then replaced in the test furnace, and the air-filled thermocouple immediately began to drift at an extremely rapid rate, due to the destruction of the formerly impervious magnesia barrier. Mechanical damage had no effect upon the subsequent performance of the thermocouple sealed at the higher pressure of argon. It initiated a slight, but nevertheless detectable increase in the rate of deterioration of the device sealed at 67 mbars, insufficient argon being present in this case to completely inhibit metal transfer across the interfacial space.

After 500 hours the thermocouple back-filled with 67 mbars of argon had drifted by the equivalent of 40°C. That back-filled to 270 mbars remained close to the alumina-sheathed reference, confirming the beneficial effects of argon as a blanket gas. In order to avoid problems associated with the development of high internal pressures when the thermocouple is at high temperatures, it is of course necessary to back-fill to a reduced pressure at room temperature, as described.

Having proceeded thus far the situation may be improved still further, if so desired, by suitable compositional adjustments to the sheath and thermo-elements. (3) It has been shown that the thermocouple sheath acts as the major source of rhodium during the high temperature exposure, and from the form of

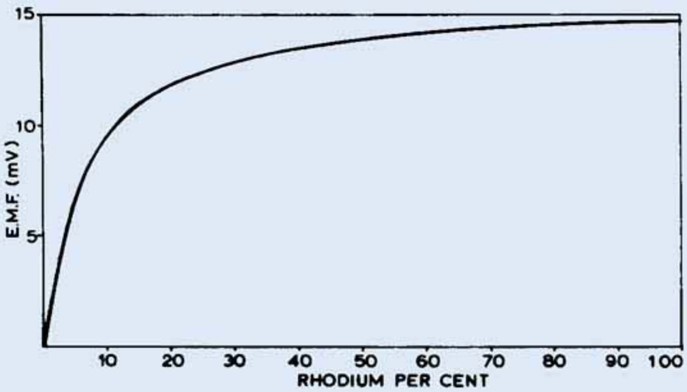


Fig. 8 The e.m.f. of rhodium-platinum alloys against platinum at 1000°C

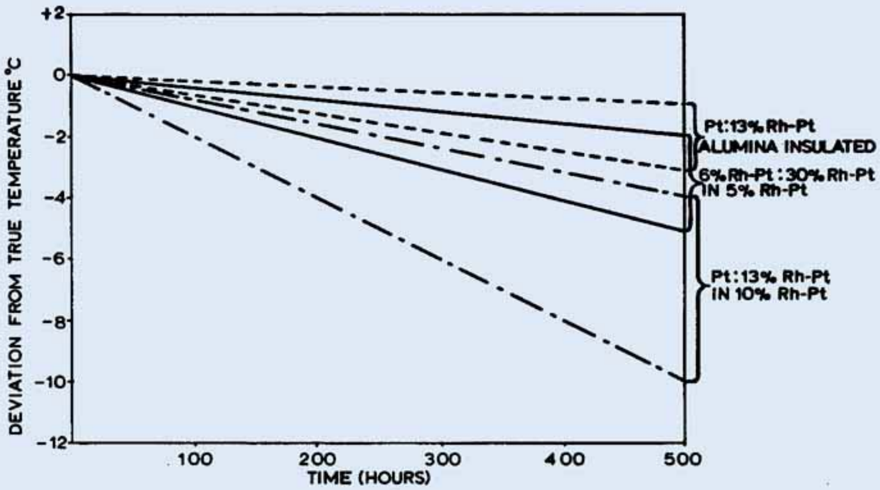


Fig. 9 Drift characteristics of argon-filled magnesia-insulated metal-sheathed thermocouples compared to those of alumina-insulated alumina-sheathed thermocouples at 1450°C in air

the e.m.f. composition curve, shown in Fig. 8, it is clear that even small preferential losses of rhodium from the 10 per cent rhodium-platinum sheath or 13 per cent rhodium-platinum positive leg will have a significant effect upon the output of the thermocouple.

This situation may be ameliorated by using the 6 per cent rhodium-platinum: 30 per cent rhodium-platinum combination. Minor losses of rhodium from the positive limb have little effect on the thermal e.m.f. and by surrounding the assembly with a 5 per cent rhodium-platinum sheath, changes in the more composition-sensitive negative limb are mostly avoided.

This thermocouple configuration has been examined, and its performance over periods up to 1000 hours at 1450°C has proved to be equal to that of a platinum:13 per cent rhodium-platinum thermocouple insulated and sheathed with recrystallised alumina.

Conclusions

The initial sections of this paper described possible disadvantages of the metal-clad thermocouple configuration concerning long-term stability. In practice, however, since the manufacturer does have the opportunity to control the environmental conditions under which the thermocouple will operate in service, the ability of these units to provide, round the thermoelements, a "micro-atmosphere" conducive to stability for long periods must be considered as a great advantage.

It can be concluded that the variations in stability reported for conventional, air-filled, metal-sheathed units have been due to variations in the permeability of the insulant employed, and therefore in its ability to interfere with the passage of metal and oxide vapours. The performance of the argon-filled units is not affected by insulant quality.

The long-term performances to be expected from metal-clad thermocouples operating at 1450°C in air when modified according to the principles outlined in this paper are presented in Fig. 9. The scatter bands shown must be regarded as tentative at the present time, until the results of further stability trials at present under way become available. It is clear, however, that the utility of these units has been considerably extended over that of existing devices.

References

1 R. J. Freeman, Temperature, Its Measurement and Control in Science and Industry, (Reinhold Publishing Corporation), 1962, **3**, (2), 201
2 C. B. Alcock and G. W. Hooper, *Proc. Roy. Soc.*, 1960, **254**, 557
3 Johnson Matthey, *British Patent Appl.* 24409/69