Platinum and the Refractory Oxides

IV – THE PERFORMANCE IN SERVICE OF PLATINUM THERMOCOUPLES

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The reactions between platinum and the refractory materials in contact with it, described in earlier articles in this series, account for many of the thermocouple failures that occur under practical industrial conditions. Reducing atmospheres accentuate such tendencies, although several factors usually co-operate to cause complete failure. This article examines the way in which platinum:rhodium-platinum thermocouples behave in service under both oxidising and reducing conditions and also in vacuum furnaces.

Above the melting point of gold, practical temperature measurements are made with platinum thermocouples which generally provide long and trouble-free service in this temperature region. Under specific conditions, however, environmental reactions can occur, and earlier articles in this series have attempted an analysis of some of the processes which can lead to thermocouple change and deterioration. Against the general background of satisfactory performance the reactions between platinum and the refractory oxides must be viewed in perspective, and it is important therefore to consider the industrial behaviour of thermocouples in relation to the results of the laboratory compatibility experiments previously described.

Oxidising and Reducing Conditions

Most platinum thermocouples are used in air and providing that both limbs are properly supported and protected against metallic and vapour contamination satisfactory performance can be obtained for very long periods at temperatures up to 1500°C. An indication of the stability which can be expected under such conditions is provided by Fig. 1, where the upper curve indicates the very slow departure from standard calibration of a platinum : 13 per cent rhodium-platinum thermocouple used horizontally in an electrical resistance furnace to which free access of air was available at 1450°C. The fall in EMF, as measured at regular intervals, was

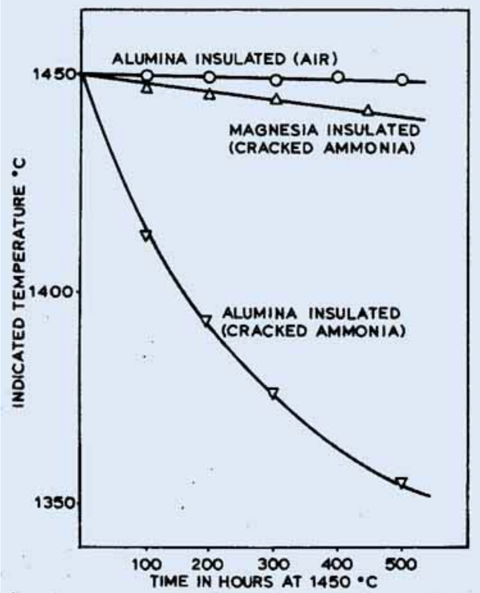

Fig. 1 The thermoelectric stabilities of platinum : 13 per cent rhodium-platinum thermocouples insulated with alumina in air and dissociated ammonia, and with magnesia in dissociated ammonia. The true hot junction temperature in each case was 1450°C.

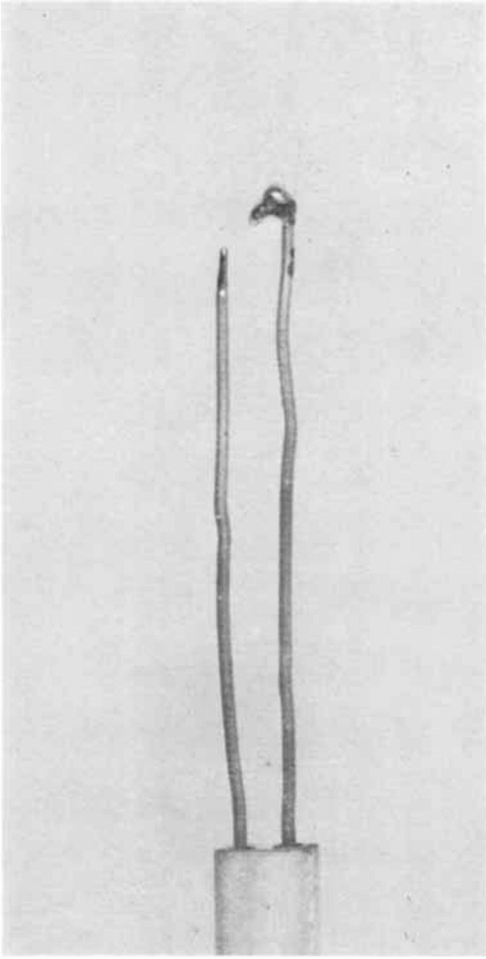

Fig. 2 Fusion at the hot junction of a platinum : 13 per cent rhodium-platinum thermocouple sheathed with alumina and inserted vertically upwards into a furnace containing an atmosphere of dissociated ammonia at 1450°C. ×25

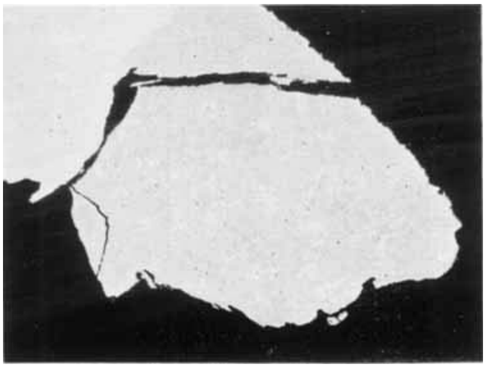

Fig. 3 The microstructure of the fused zone on the failed thermocouple illustrated in Fig. 3. ×200

equivalent to about 3 deg C after 1000 hours at temperature. The thermocouple had ½ mm diam. limbs, was insulated with twin bore "Purox" alumina tubes and protected externally with a loosely fitting "Purox" alumina thermocouple sheath.

The bottom curve on this illustration relates to a similar thermocouple, insulated in exactly the same way, which was run in a flowing atmosphere of dissociated ammonia rather than in air. The thermocouple sheath has obviously provided some degree of protection as mechanical failure of the couple wires has not occurred although a fall in output equivalent to ~100 deg C, has taken place after 500 hours at temperature. Subsequent analysis of this thermocouple showed that it had taken up substantial quantities of aluminium, and some silicon which was originally present as silica in the nominally pure alumina.

This type of deterioration can be intensified by changing the orientation of the thermocouple. In one instance rapid thermocouple failure was encountered when the same type of nominally impervious alumina thermocouple sheath was inserted vertically upwards into the hot zone of the furnace. Complete fusion and breakage of the hot junction occurred in dissociated ammonia after about 2 hours at 1450°C, a typical illustration being given in Fig. 2. The microstructure of one area of this failure is shown in Fig. 3. Large quantities of silicon and aluminium were found by microprobe analysis, and this type of geometrical arrangement seems very dangerous, as any hydrogen which penetrates the tube is, by virtue of its low density, trapped in concentrated form at the hot junction, thus causing very severe reactions between platinum and the refractory tube and insulators.

Under strongly reducing conditions thermocouples used in contact with magnesia are relatively free from this type of deterioration. The third curve on Fig. 1 indicates some results obtained when a thermocouple was run in dissociated ammonia at 1450°C

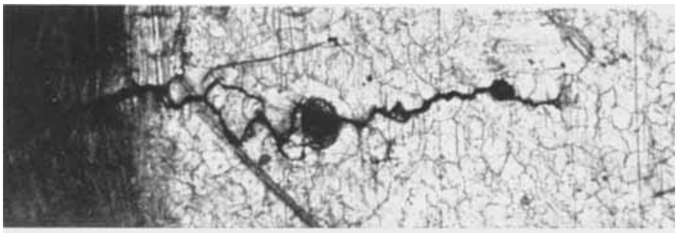

Fig. 4 Intercrystalline cracks associated with oxide inclusions embedded within the surface layers of a rhodium-platinum wire. ×20

Fig. 5 A microsection taken through a defect of the type illustrated in Fig. 4 showing the fused area resulting from reaction between a refractory particle and the rhodium-platinum alloy. ×50

for 450 hours while packed in a bed of fine magnesia powder. The extent of the deterioration which occurred was comparable with that encountered with the alumina insulated thermocouple run in air.

Failure Caused by Superficial Contamination

Premature failures caused by platinum-refractory reactions are occasionally encountered in atmospheres which appear at first glance to be highly oxidising. This behaviour can usually be traced to circumstances in which a fortuitous juxtaposition of platinum and refractory has resulted in a particularly unfavourable geometry.

Small particles of alumino-silicate forced into platinum or rhodium-platinum wires occasionally cause intercrystalline cracking of the type shown on Fig. 4, which occurred on heating in air to 1450°C. Fig. 5 provides another illustration of the way in which intercrystalline failure can proceed at a considerable distance away from the region where the original refractory particle had reacted with the platinum to form low melting point phases in which platinum silicide predominated.

The first attempts to reproduce such effects in the laboratory met with limited success. Mullite particles rolled into sheet normally showed little tendency to react. Some working operations, however, particularly wire drawing, sometimes gave rise to an inclusion which was almost completely encapsulated by platinum. This type of inclusion tended to react strongly with the platinum when heated in air. As shown in Fig. 6 networks of platinum-platinum silicide eutectic have penetrated round the grain boundaries for a considerable distance away from the inclusion.

It has recently been shown that this type of failure is usually associated with the presence of sulphur-bearing organic lubricants such as those used for rolling and wire drawing. Traces of these liquids are trapped in the cavity with the refractory particle and the partially sealed conditions obviously facilitate the reaction, based on the formation of volatile silicon sulphide which was first observed twenty-five years ago by Chaston et al. (1).

Reactions at Lower Temperatures

At temperatures below 1000°C reactions do occur between platinum and refractory oxides, although as many investigators have demonstrated (2, 3, 4), contamination of the thermocouple by impurities from the ceramic protection tubes is the most usual cause of instability in this temperature range. Walker et al. (4) have described in detail the way in which iron can be transferred from nominally pure alumina powder into platinum, and suggested mechanisms for this vapour phase transfer process.

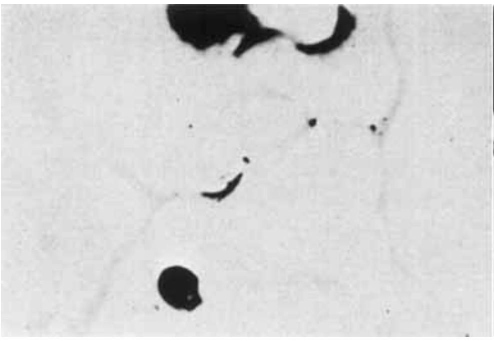

Fig. 6 Networks of the platinum-platinum silicide eutectic formed in the vicinity of a siliceous inclusion, encapsulated in rhodium-platinum, on heating in air. ×*1500*

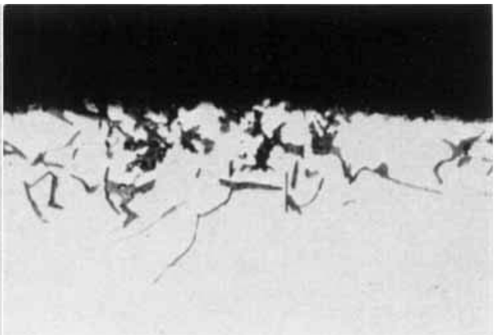

Fig. 7 Subsurface rhodium oxide in a 13 per cent rhodium-platinum thermocouple wire operated in air for approximately 5 years at about 400°C. ×*750*

The slow changes in thermoelectric output which occur in rhodium-platinum thermocouples heated for long periods in air at moderate temperatures have generally been attributed to contamination processes of this type. Recent investigations in these laboratories have shown, however, that such explanations are not always justifiable. In one instance for example a reduced output, equivalent to about 2 deg C, was detected after a 13 per cent rhodium-platinum thermocouple had been used at 625°C for 40,000 hours or 5 years in air in a steel creep testing furnace. Very thorough examination showed little change in the composition of the limbs up to 2 ft from the hot junction. Towards the colder end of the wires changes in alloy homogeneity were, however, detected and micro-examination disclosed the presence of areas which contained substantial quantities of solid rhodium oxide as shown in Fig. 7. The platinum alloy matrix contained only 11 per cent by weight of rhodium, and the presence of this depleted region in the strong temperature gradient between the hot and cold regions of the thermocouple accounted for the change in electrical performance.

A short heat treatment in air at 1200°C dissociated this oxide, returned the rhodium to solid solution in the platinum and restored the thermocouple output. This type of internal oxidation has not, so far as can be ascertained, previously been reported. Very long periods of time are needed for its development but, since all noble metal thermocouple wires must at some point between hot and cold junctions pass through the temperature range 400–600°C, a tendency towards the internal formation of solid particles of rhodium oxide must always exist. The rate at which this internal oxidation proceeds is now being assessed.

Thermocouples in the Vacuum Furnace

Under industrial conditions thermocouple deterioration can usually be ascribed to the operation of various processes and this is particularly true in vacuum metallurgical melting and heat treatment furnaces. The contamination which occurs is usually characteristic of the impurities in the refractory rather than of the refractory itself. Superimposed on such effects are the changes in composition caused by the selective volatilisation of rhodium under vacuum conditions, and by the absorption of vapours from the material being heated within the furnace.

Premature thermocouple failure was occasionally encountered in a vertical vacuum sintering furnace generally operated at a pressure of about 2×10^{-5} Torr. This furnace had molybdenum heaters, and during one series of production runs made at 1500°C adhesion between the components being sintered was prevented by dusting with

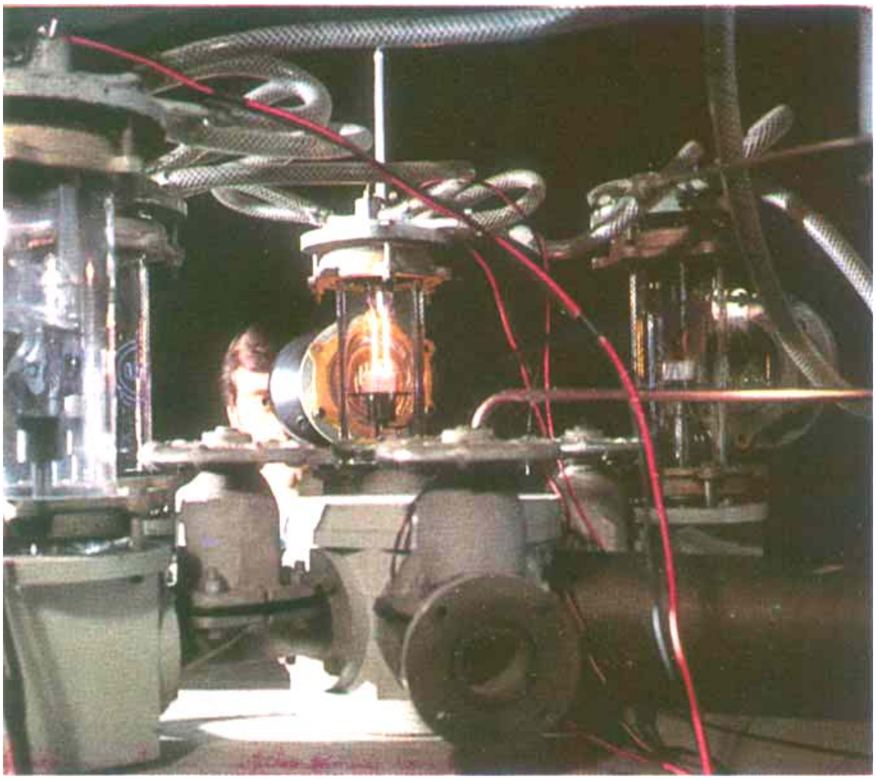

Fig. 8 Within the confines of this glass envelope platinum filaments are heated in contact with refractory oxides under any desired atmospheric conditions. The wire under test and the refractory in contact with it are the only parts of the system maintained at high temperature, and the complicating effects of spurious contamination are thus avoided. Differences between the simplicity of this experimental arrangement and the complex environments in which thermocouples normally operate in industry are discussed in this article.

alumina powder. The thermocouple calibration changed rapidly under such conditions, and useful working lives were limited to about 70 hours. Both limbs of the thermocouple tended to absorb substantial quantities of both silicon and aluminium. Although the precise source of this siliceous contamination was not detected, it and the aluminium have obviously reached the thermocouple via the vapour phase. The thermocouple was in fact at a slightly lower temperature than the furnace heaters and their supports, and this situation obviously encourages contamination by volatile species. It is in this important respect that practical conditions differ greatly from the test cell geometry described in the previous articles, where thermocouples were intentionally run at much higher temperatures than their environment so as to discourage spurious contamination.

Fairly satisfactory protection against such vapour attack can usually be obtained if the impermeable alumina thermocouple sheaths are prolonged without join into the cold part of the furnace. Thus in a horizontal vacuum resistance furnace the thermocouple was supported within twin-bore alumina insulators and protected entirely by an impervious alumina sheath which continued into the colder part of the furnace where temperatures were below 200°C.

After about 150 hours of operation at 1475°C in vacuum conditions of about 5×10^{-5} Torr the output of such thermocouples decreased by the equivalent of about 3 deg C at the gold point. This deterioration was traced

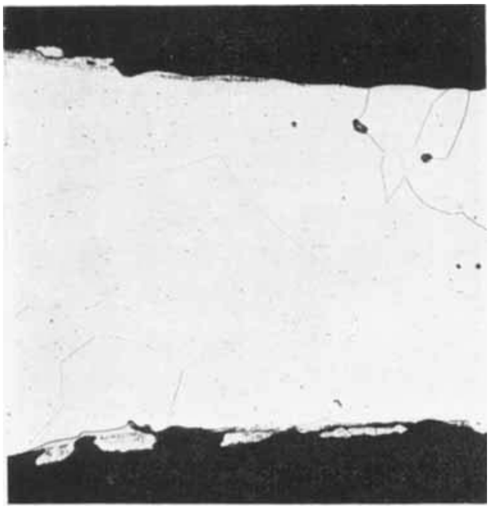

Fig. 9 Traces of the Pt_3Al intermetallic compound formed locally on the surface of a platinum thermocouple wire operated in a vacuum furnace for 100 hours at 1400°C. ×150

to the gradual loss of rhodium from the alloy limb which in some regions nearer the hot junction was reduced to 11·4 per cent by weight. No rhodium was detected in the pure platinum limb, and it must be remembered that the volatility of rhodium in vacuum is many times higher than that of platinum.

Reactions between platinum wires and their alumina insulators are detectable in ordinary vacuum furnace operations, although the areas of contamination are fairly local. Fig. 9 illustrates such a reacted area which developed where the thermocouple wire passed the junction between two alumina insulators. This region, although rich in aluminium, is not deep enough to weaken the wire seriously, and because of its short length is not able in normal temperature gradients to have a serious effect on the thermal EMF generated by the thermocouple.

Complete and rapid failure of thermocouples in vacuum furnaces is therefore rarely caused by direct reaction between platinum and refractories. Dangerous contamination generally emanates from the more volatile constituents of the materials being heated within the furnace and can usually be avoided by effective sheathing. Although rhodium does evaporate preferentially and reactions do occur between platinum and alumina refractories the changes thus caused are gradual, continuous, and tolerable under ordinary production conditions.

Conclusions

Under practical conditions of operation thermocouple behaviour cannot always be predicted because of the conflicting factors responsible for the changes in electrical output which occur. Although the best performances are generally obtained in air, satisfactory lives are attainable in vacuum and even under fairly strong reducing conditions. Rhodium-platinum thermocouples are most stable, however, when magnesia is used as a refractory, and when the surrounding inert atmosphere inhibits volatilisation of platinum or rhodium in either metallic or oxide form.

The 10 per cent and 13 per cent rhodium-platinum thermocouples perform very well in such conditions and further improvement is attainable by using the 6 per cent rhodium-platinum versus 30 per cent rhodium-platinum combination. Minor losses of rhodium metal vapour from the positive limb of this thermocouple have little effect on the thermal EMF. Any slight tendency for the negative limb to absorb rhodium can be controlled by surrounding the assembly with a 5 per cent rhodium-platinum "reservoir" of suitable capacity.

In practice it is not always feasible to provide the ideal climatic conditions necessary to ensure extreme stability in refractory sheathed thermocouples. Suitably controlled "micro climates" can, however, be retained within metal sheathed thermocouples, which will feature in a forthcoming article.

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