The Contamination of Platinum Metal Thermocouples

CAUSES OF FAILURE IN HYDROGEN ATMOSPHERES

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The attractive features of platinum metal thermocouples include their resistance to corrosion by the common acids and alkalis and their freedom from oxidation at all operating temperatures. On the other hand, unlike some base metal thermocouples upon which a protective oxide skin is formed, platinum is readily contaminated by contact at high temperatures with such elements as lead, zinc, phosphorus, arsenic and silicon, and adequate protection must be given where such contaminants might be encountered.

In an oxidising or neutral atmosphere, the use of an impervious refractory sheath that will withstand the operating temperature is generally adequate protection even against metal vapours, while in extremely contaminating atmospheres it is possible to employ an additional metal sheath. Where twin-bore insulators are used and a sheath is not employed in order to obtain the maximum response to temperature changes, there is always the liability of contaminating the wires at the bare junction and where the ends of the insulators meet.

From time to time platinum : rhodium-platinum thermocouples heated in hydrogen become embrittled and break. There is no reaction between the platinum metals and hydrogen, and therefore any failures associated with changes in structure must be due to contamination. It is well known that platinum heated in hydrogen in contact with a siliceous refractory becomes embrittled owing to the reduction of silica in these conditions, the subsequent diffusion of silicon into the platinum forming platinum silicide which segregates at the grain boundaries.

It is essential, therefore, that thermocouples employed for high temperature measurement in a hydrogen atmosphere be insulated and sheathed with refractories free from silica. For this purpose alumina is commonly used, but it has occasionally been found that when

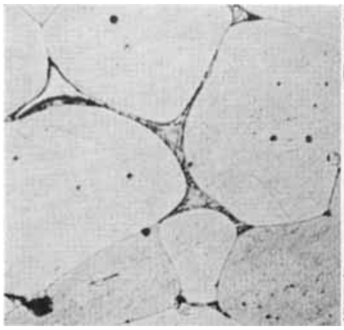

Fig. 1 Platinum wire showing grain boundary embrittlement after 15 hours in hydrogen in an alumina tube ×144

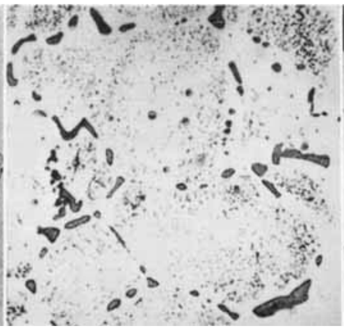

Fig. 2 A 40 per cent iridium-rhodium wire embrittled after 96 hours at 1400°C in hydrogen in an alumina tube ×320

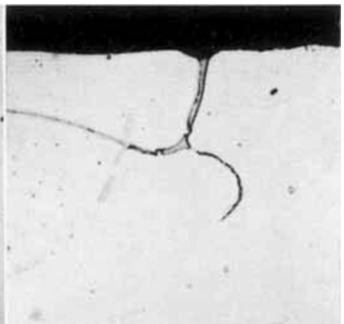

Fig. 3 A 13 per cent rhodium-platinum wire after 1 hour at 1400°C in hydrogen with alumina insulators ×320

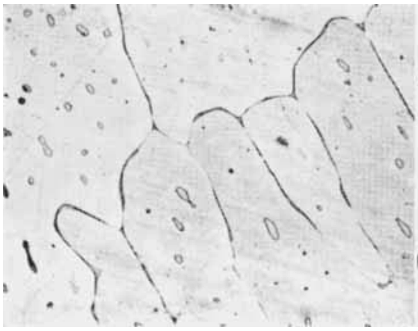

Fig. 4 The cast structure of a 0.3 per cent silicon-platinum alloy ×320

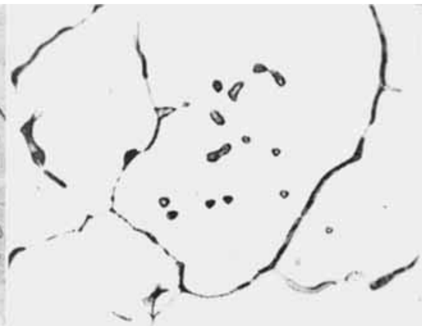

Fig. 5 The cast structure of a 0.6 per cent silicon-rhodium alloy ×320

using alumina insulators the thermocouple has failed by embrittlement. Some experiments carried out in this laboratory have shown that the small amount of silica present in commercially pure alumina refractories, of the order of 0.2 per cent of SiO_2, is quite sufficient to lead to the formation of embrittling silicides.

A platinum wire was heated to 1400°C for 15 hours in an alumina tube in an atmosphere of cracker gas. On removal, the wire would not withstand bending but broke into small pieces. Fig. 1 shows the microstructure of this wire after heat treatment, with intergranular platinum silicide clearly visible.

A Feussner thermocouple (iridium : 40 per cent iridium-rhodium) insulated with alumina tubes was placed in an alumina tube furnace, in cracker gas, and heated at 1400°C. The thermocouple was removed for inspection after 24 hours but after a total of 96 hours at temperature the wires broke on removal. The 40 per cent iridium-rhodium wire was very brittle, and the microstructure, showing grain boundary rhodium-silicide, is seen in Fig. 2. In the iridium wire there was no second phase present, but the wire had become embrittled through recrystallisation and grain growth, which occurs when the wire is heated in any atmosphere. If there was any pick-up of silicon it was within the limits of solid solubility.

The 13 per cent rhodium-platinum wire of a platinum : rhodium-platinum thermocouple that had been used to check the temperature in this furnace periodically, but had been in the furnace for an estimated total time of not more than an hour, was also embrittled. As frequently happens, the embrittled areas occurred in the wire at the junctions between the alumina insulators where the hydrogen flow had greatest access. The grain-boundary silicide can be seen in Fig. 3.

As a check on these microstructures, a sample of platinum was melted in an argon-arc furnace with 0.3 per cent of silicon. The microstructure of this alloy in the cast condition is shown in Fig. 4. It is stated in the literature that the solubility of silicon in rhodium is less than 0.5 per cent, so a sample of rhodium was argon-arc melted with 0.6 per cent of silicon. The cast structure of this alloy is shown in Fig. 5. These photomicrographs illustrate the effect on the structure of platinum and rhodium of small additions of silicon and give some idea of the small amount of silicon pick-up that will embrittle platinum alloys.

These experiments show that where hydrogen is present in contact with commercially pure alumina and platinum or rhodium alloys, embrittlement can occur through the diffusion of silicon and the formation of grain boundary silicides from the reduction of silica present in small amounts in the alumina. Experience has shown, however, that an alumina sheath impervious to hydrogen, or one containing no silica, will protect a platinum : rhodium-platinum thermocouple in a hydrogen atmosphere at around 1400°C for a year or more.