The Care of Platinum Thermocouples

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Platinum thermocouples are sensitive instruments. Exceptional care and control are given to their preparation in order to ensure reliability in service, but their accuracy and working life can be adversely affected if a few simple precautions are neglected.

The platinum thermocouple is probably the most accurate and convenient method now available for the measurement of high temperature in industrial processes. Provided that the correct conditions of use are properly understood, the platinum thermocouple with auxiliary equipment is a robust and reliable industrial instrument.

Because of its small size and low thermal capacity, the couple can be introduced directly to the point at which measurement is to be made, and will respond immediately to temperature changes. The protective sheath can be small and inexpensive, and by the use of compensating leads it is easy to take the indicating point well away from the measuring point, which is often hot and dirty.

Because of their nobility, platinum and its alloys will withstand much more adverse conditions than will base metal thermocouples, but they none the less have their limitations. The melting point of platinum is 1769°C and that of its highest melting rhodium alloy useful for thermocouple purposes is about 1890°C. This is therefore the absolute limit of temperature that a platinum alloy couple will measure, and then only for a short time. In immersion pyrometry for measuring the temperature of molten steel, platinum alloy couples—in conjunction with a quick-response indicator—can be used momentarily at temperatures approaching these high values. For many other purposes thermocouples must be kept at temperature for long periods of time, and caution must then be observed if the couple is to have a reasonable life. Grain growth, which occurs particularly in pure platinum when couples are kept at temperatures around 1500 to 1600°C, need not be deleterious provided that the wire is not under any appreciable stress and that it is kept free from contamination, but these conditions are not particularly easy to obtain.

Effect of Prolonged Heating

The harmful effect of prolonged heating at high temperature is the migration of the alloying constituent from one wire to the other. The platinum element of the platinum: rhodium-platinum couple tends to pick up rhodium and as it does so the e.m.f. at any given temperature becomes progressively less. If the platinum wire is protected by a refractory insulator the pick-up of rhodium is minimised.

It is difficult to give a definite figure for the expected useful life of a thermocouple as so much depends upon particular conditions. Instances have been recorded of platinum: rhodium-platinum couples being in use continuously for three years at about 1300°C with a loss in e.m.f. equivalent to only a few degrees. Obviously the higher the temperature of operation the greater the migration of rhodium and consequently the more rapid the change in calibration.

Increase in e.m.f. at 1200°C against Pure Platinum by addition of 0.01 per cent Rhodium	
	Microvolts
Platinum	150
1 per cent rhodium ..	20
5 ,, ,, ..	11
10 ,, ,, ..	6
13 ,, ,, ..	4

It can be seen in the table that a small pick-up of rhodium does not have such a great effect on a rhodium-platinum alloy as it does on pure platinum. For this reason a 1 per cent rhodium-platinum: 13 per cent rhodium-platinum thermocouple can be used where it is important that changes in calibration shall be kept to a minimum over long periods. In practice, however, it is usually found that the thermocouple has deteriorated by contamination from other sources before the calibration has changed significantly.

Contamination by Metallic Vapours

Metallic vapours of lead, zinc and bismuth are among the commoner contaminants which readily alloy with platinum to form brittle intercrystalline constituents and so to cause premature failure of thermocouples. The presence of these impurities is often quite unsuspected, but they can arise from solders, galvanised iron, brass, or molten glass that may be present in the furnace, and couples need to be protected against them. The couple wires must be insulated from each other and the use of a double-bore refractory tube is to be recommended so that both wires are confined. This assembly should be placed in a closed refractory sheath capable of withstanding the required temperature, as well as temperature changes and the furnace atmosphere. Silica may be used continuously at temperatures up to about 1000°C but for higher temperatures fireclay, graphite, silicon carbide mixtures or aluminous porcelain may be used. Fused alumina refractories are excellent for use in a hydrogen or other reducing atmosphere, in which platinum will be contaminated by any material containing silica, but they are not resistant to thermal shock and they must be heated and cooled very slowly to prevent cracking. Sometimes for added protection it is advisable to place the refractory sheath inside a metal sheath.

Embrittlement Due to Oil or Grease

The couple, the insulators and the inside of the sheath assembly must always be kept clean and free from oil or grease. Most refractories contain some silica, and it has been proved that in a reducing carbonaceous atmosphere the presence of sulphur (frequently present in oil) causes a complex reaction resulting in some reduction of the silica to silicon, which then alloys with the platinum to form a brittle grain boundary constituent. For this reason, thin leather gloves are frequently worn when handling thermocouples to prevent contamination by oil or grease. It cannot be emphasised too strongly that to obtain good service from platinum thermocouples, cleanliness and adequate protection from contamination must be taken seriously.

Tensile Stresses

A platinum thermocouple should also be as free from stress as possible. The table shows the hardness and tensile strength of platinum and rhodium-platinum alloys used for thermocouple purposes. The breaking load of a pure platinum wire 0.020 inch

Hardness and Tensile Strength of Platinum Alloys at Room Temperature

Rhodium per cent	Hardness VPN	Tensile strength tons per sq. in.
0	40	10
5	66	16
10	85	21
13	91	23
20	106	27
30	124	30

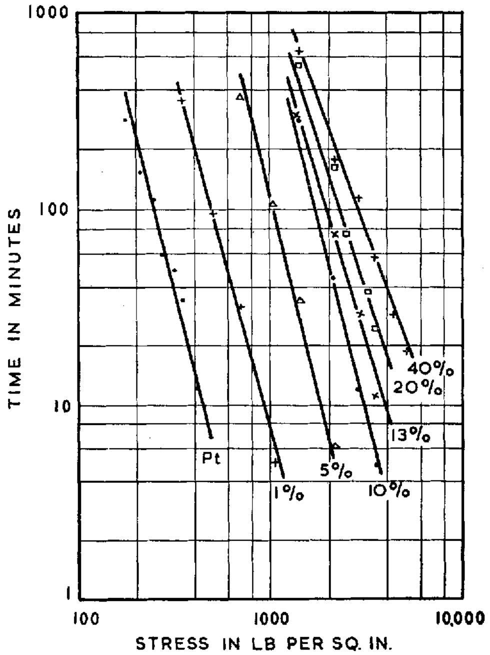

Fig. 1 Stress-to-rupture tests on rhodium-platinum alloys at 1400°C

diameter (the normal thermocouple size) is therefore about 7 lb. at room temperature; at 1400°C the breaking load is only 12 oz. This represents a load instantly applied; under prolonged loading, particularly at high temperatures, the wire will withstand only a fraction of this load. This type of failure is known as " creep ", and it has been shown as the result of creep tests that the safe loading for platinum is about 4.9 tons per square inch.

Creep Tests on Thermocouple Alloys

In order to compare the resistance to creep at high temperature of the platinum alloys normally used for thermocouples, annealed wires, 0.020 inch in diameter, were suspended under various loads in a furnace at a constant temperature of 1400°C. The investigation was limited to short-time creep tests and no attempt was made to determine the limiting creep stress at any temperature, but the results are sufficient to indicate the comparative creep resistance of these alloys.

Fig. 1 is a graph plotted on a log-log scale showing the results of these stress-to-rupture tests at 1400°C. The practical results are perhaps better illustrated in Fig. 2, which shows the load required to fracture the wire in 250 minutes. It will be observed that 10 per cent rhodium-platinum alloy will withstand about eight times the loading of pure platinum at 1400°C, but that above 20 per cent of rhodium there is little gain in creep resistance.

Heating under load at 1400°C produced very large grain growth in the pure platinum, the wire practically consisting of a chain of large crystals of the diameter of the wire. Under prolonged stress at low loads grain boundary sliding occurs as shown in Fig. 3, and ultimately leads to a brittle type of fracture, which is occasionally found in a couple after long service at a high temperature. Grain growth is far less evident in the 5 per cent rhodium-platinum alloy creep sample illustrated in Fig. 4, but cracks have developed at many of the grain boundaries.

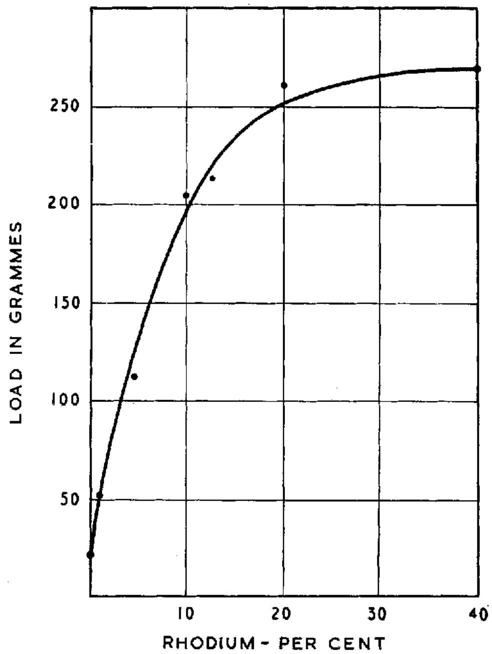

Fig. 2 Load-to-rupture in 250 minutes for rhodium-platinum alloy wires

The 5 per cent rhodium-platinum: 20 per cent rhodium-platinum thermocouple, which can be used continuously at temperatures up to 1700°C, has greatly improved creep resistance by comparison with the platinum: 13 per cent rhodium-platinum couple, the 5 per cent alloy wire having about five times the strength of platinum at 1400°C. In conditions of extreme loading the 20 per cent rhodium-platinum: 40 per cent rhodium-platinum couple has an even greater advantage, but against this must be set the much smaller e.m.f. of the 20/40 couple and also its increased cost.

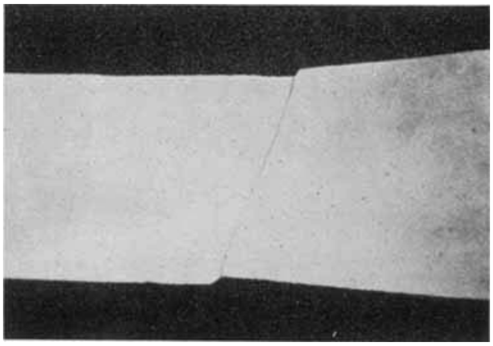

Fig. 3 Section of pure platinum wire after stressing at 1400°C, showing sliding at grain boundary ×120

Examination of Service Failures

In practice, however, it is seldom necessary to impose upon the thermocouple anything like these loads. A thermocouple placed horizontally rests on the sheath, but, if a thermocouple has to be placed vertically, care must be taken to ensure that the weight of the insulators does not apply a tensile stress to the wire. This can be overcome by allowing the hot junction to rest on the sealed end of the sheath. It is undesirable to remove a thermocouple from a hot sheath, particularly if there is any undue friction, as this will impose a considerable stress on the wire. Thermocouples that have failed in service are generally found, by spectrographic examination, to have been contaminated, resulting in embrittlement of the wire. Occasionally, even where there is no obvious contamination, there are clear signs of stress failure. Fig. 5 is a photomicrograph of 13 per cent rhodium-platinum, said to have failed after two months service at about 1100 C.

Spectrographic examination showed no contamination but there is considerable grain growth and sliding at the grain boundaries leading to rupture, which is typical of slow tensile deformation at high temperature and indicates that the wire has been subject to appreciable stress in service.

The practical significance of the points that have been made is clearly the great importance of handling themorcouple wires as little as possible in assembly and of ensuring that they are completely free from any kind of foreign matter when put into service.

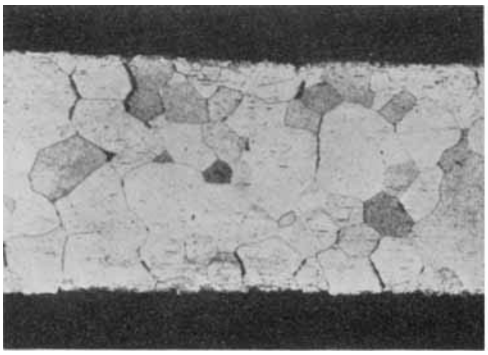

Fig. 4 Section of 5 per cent rhodium-platinum alloy wire after prolonged stressing at 1400°C ×120

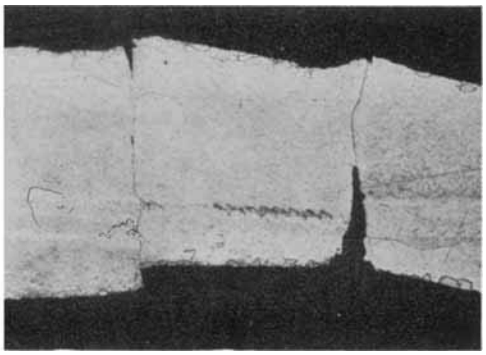

Fig. 5 Section of 13 per cent rhodium-platinum alloy wire after failure in service ×120