A Thick Film Platinum Resistance Thermometer

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A novel temperature detector, known as Matthey Thermafilm, has been developed. It consists essentially of a platinum film firmly bonded to a ceramic substrate. The film is protected from the possible corrosive effects of gaseous environments by an overglaze of impervious, electrically insulating glass, forming a device that is mechanically and thermally robust. Since the sensing unit generally does not require further protection by encapsulation in a metal or ceramic sheath, it responds very rapidly to thermal changes. The construction of the detector renders it eminently suitable for monitoring transient thermal changes in most environments.

The unique stability and conformity to thermal cycling of pure platinum wires have long been recognised and over a century ago were used in the construction of the first resistance thermometer (1). In 1887 the late Professor H. L. Callendar presented the findings of his research on the variation of the electrical resistance of platinum as a means of measuring temperature to the Royal Society (2). Callendar pioneered the use of platinum resistance thermometers for accurate temperature measurement by his continued research and constant encouragement for the production of high quality platinum wire. His enunciation of the principles remains fundamentally unchanged as we know them in platinum resistance thermometry today.

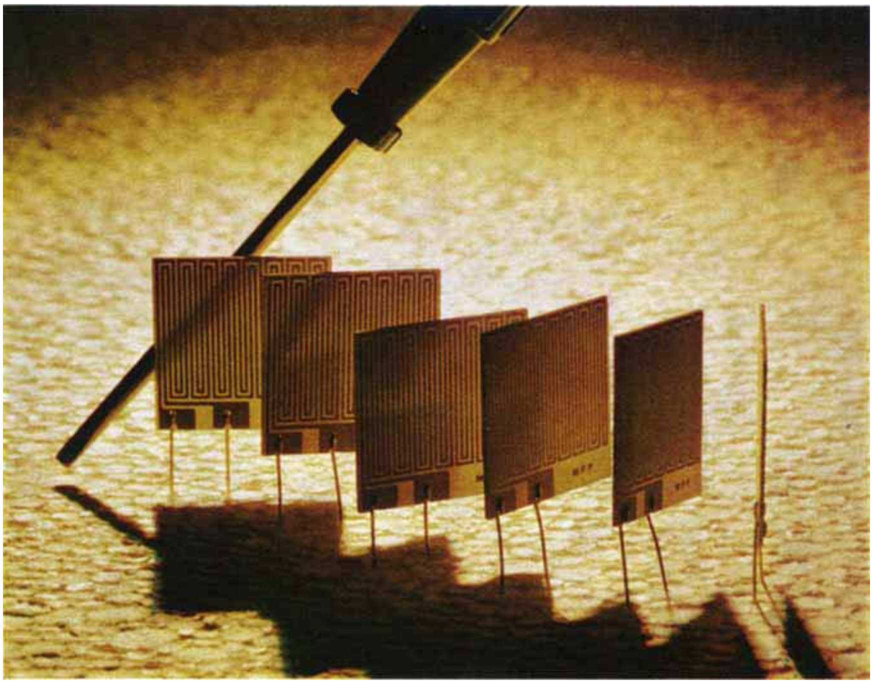
Basic Principles

Industrial platinum resistance thermometer elements, manufactured to BS 1904:1964, require that the temperature coefficient of resistance, the α value of the pure platinum wire should be 3.910×10^{-3}. This value is determined from the relationship between the resistance of the element at the steam point (R_{100}) and its resistance at the ice point (R_0), where:

$$\alpha = \frac{(R_{100} - R_0)}{R_0 \times 100}$$

Various workers in universities, standards institutions and industry maintain that only from platinum wire of such quality can thermometers of high precision and reliability be successfully produced. Apart from its chemical purity, attention must be paid to the method of supporting the platinum wire element and the degree of post-manufacturing treatment required to stabilise it for use as a precision unit. A measure of the success of these methods has been reflected throughout the last decade by the increased demands made upon the platinum refining and wire-drawing industries. Perhaps the ultimate in purity and hence α of platinum (3.927×10^{-3}) has been attained; a satisfactory state for the academic worker but unlikely to excite the industrial user. Through his eyes such an achievement carries only one meaning—greater unit cost.

The fine gauge of platinum wire used to wind the small helical elements found in



The performance, reproducibility and low cost of the Thermafilm platinum resistance thermometers make them technically and economically attractive. They are available on flat alumina substrates but a tubular form is currently being developed

conventional platinum resistance thermometers calls for great skill on the part of operators during manufacture and subsequent calibration. The processing does not lend itself readily to automation, and therefore remains a labour intensive method of production with its attendant costs increased by the current inflationary spiral. The novel construction of the Matthey Thermafilm temperature detector lends itself to automation, and therefore offers to the consumer the advantage of a lower cost thermometer capable of temperature measurement with the precision usually associated only with conventional wire wound thermometers.

Unlike thermocouples, which generate voltages by the thermoelectric effect, a resistance thermometer requires to be driven by a current source in order to develop voltages across the changing resistance of the sensing element. To measure temperatures within the range −50 to 600°C, the standard value of R_0 is 100Ω and the fundamental interval is 38.5Ω for thermometers conforming to BS 1904:1964 and to DIN 43760. The sensitivity of a thermometer is therefore an order of magnitude greater per degree Celsius than that of a thermocouple. Conversely, a semiconductor device, a thermistor, is extremely sensitive over short temperature ranges of about 50°C, but since its resistance decreases in an exponential manner with increasing temperature its sensitivity decays rapidly. Therefore it cannot compare with the technical superiority of a platinum resistance thermometer.

Research Background to Platinum Film Thermometry

Conventional platinum resistance thermometers require mechanical protection by electrically insulating sheaths owing to the frailty of their helical resistance elements. To comply with the various standard specifications, the quality of the platinum wire used in their manufacture must be controlled to within closely defined limits of chemical purity and dimensional changes. Furthermore their electrical performance must not be impaired during normal service by the ingress of impurity elements or by physical strains arising from thermal mismatch between the component parts of the sensor unit. These restrictions further increase the cost loadings already imposed by the high intrinsic value of the resistance windings.

To overcome these cost disadvantages and to maintain performance and robustness, deposition by vacuum and sputtering techniques of thin films of platinum on ceramic substrates was investigated. Such methods are well known in the microelectronics industry for the deposition of circuit components. However, in common with the findings reported by other workers in this field, the α values of such films were found to fall considerably short of the value reported for pure bulk platinum metal (3.927×10^{-3}), and seldom exceeded about one third of it. The occurrence of anastomosis—or branching—in gold films, varying in thickness from 50 to 10,000Å, is well known to workers in this field and it is not uncommon for large discrete areas to remain isolated until they have exceeded 1000Å in thickness (3). The mechanism of electrical conduction becomes complex under these circumstances, and the structure of these films is instrumental in preventing the α value from approaching that of the bulk metal (4).

Investigation was turned to the evaluation of composite film devices similar in structure to those found in hybrid microelectronics technology. A thermosensitive unit was devised consisting essentially of an electrically continuous line pattern of a composite platinum and glass film, terminated by larger areas known as "lands". The patterns were deposited on to flat, electronic grade alumina substrates by screen printing and firing; a technique well known in thick film technology. Subsequent firings were applied to stabilise the electrical parameters of the composite unit. Platinum wire terminations were attached to the lands and the overall printed area protected from the environment by an insulating overglaze. Various sizes of units were prepared and subjected to long-term testing at elevated termperatures, as well as to short term cyclic and resistance ratio tests.

It was shown in the early work that the form and chemical purity of the platinum powder, as might be expected from analogy with thermo-grade platinum wire, was of prime importance for the establishment of relatively high α values, i.e. to within 94 per cent of that for bulk pure platinum. Further development of the chemically satisfactory grade of platinum powder to the required physical form, together with the exertion of rigorous control over the sequential steps of screen printing, drying and firing, resulted in the achievement of α values within the limits required to satisfy BS 1904:1964 and DIN 43760.

Method of Calibration

Various methods of calibrating the resistance meanders to the required ice point resistance (R_0) included air abrasive and laser trimming, both of which are subtractive methods, reducing the width of a part of the total track to raise the resistance within the set limits, and a third additive method, in which a spot of platinum is used to short circuit adjacent tracks at the calibrated balance point. The latter has the advantage that it does not mechanically damage the fired film and can be carried out cheaply.

Various methods of attaching the terminal wires were investigated. These were capacitor discharge, series resistance, electron beam and ultrasonic methods of welding, and thermocompression bonding. None of these methods was entirely successful. Mechanically superior bonds were made by passing nail-headed wires through holes drilled in the lands and sintering the wire heads to the lands by a subsequent heating process. All the methods of attachment were made more secure by the subsequent overglazing stage.

Every Thermafilm detector unit is calibrated to value. The operator is manually determining and marking the balance point between a test piece and the standard unit, located in juxtaposition to a heat-sink of aluminium acting as a thermal stabiliser, with the aid of probes on a micromanipulator connected to a comparator bridge. A small spot of platinum ink is then placed accurately on the mark at the balance point to short circuit adjacent tracks. Subsequent firing fuses the platinum link to the printed film and gives the required adjustment to the correct resistance value

Plots of the change in steam-point resistance with time for units stored at various temperatures up to 600°C, and an Arrhenius plot of change in resistance with absolute temperature after 1000 hours thermal exposure were made in order to deduce whether the device was likely to remain useful in the long term. The first plot did not reveal the presence of any abnormal degradation reactions since the plot followed the form:

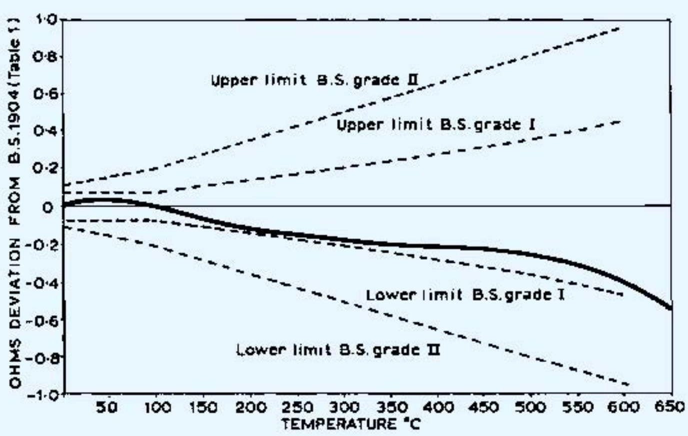
$$y^2 = e^{a/T}.t$$

where: y is related to resistance drift, $\Delta R/R$.
t is time in hours
T is absolute temperature
a is a constant.

This was confirmed by an estimate of the mean activation energy of the degradation reaction calculated from the slope of the Arrhenius plot. This was found to be of the order of 16kJ/mole, which suggests that composite films are fairly resistant to oxidative changes. These estimates were sufficiently encouraging to allow further commercial development to proceed.

Development of Thermafilm Temperature Detectors

Since considerable experience in the research, development and use of thick film materials for precision electronic components was available in Matthey Printed Products Limited, further development of the novel form of platinum resistance thermometer was carried out there. The concept was commercially attractive, since each step in the manufacturing process could be rendered



A typical linearity curve for a Thermafilm detector, showing its good conformity with the requirements of British Standard 1904:1964

less labour intensive as occasion demanded and the process maintained within the cost effectiveness governed by market trends.

The objectives for the first generation of temperature detectors were to:

(1) retain the simplicity of construction;

(2) build on the basic robustness, and offer better vibration and shock resistance, than shown hitherto by conventional thermometers;

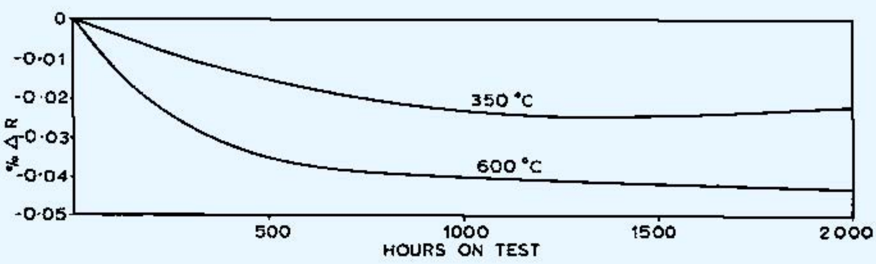
(3) ensure that the thermal response was superior to that of other forms of detector;

(4) achieve the performance required by BS 1904:1964 and DIN 43760 over the temperature range −50 to 600°C;

(5) keep costs low.

All these objectives have been realised. The standard size of thermofilm detectors is 25.4×25.4 mm (1×1 in), based on well-established electronic grade alumina substrates for first generation evaluation. The pattern fills the entire area, so that thermal sensitivity is evenly distributed, and uses the additive calibration method (shorting link) to produce an R_0 of 100Ω in three grades of accuracy, all with a fundamental interval of 38.5Ω, measured between the ice and steam points. Grades I and II conform to the accuracies of BS 1904:1964 and DIN 43760, yielding 100Ω±0.075 per cent and 100Ω ±0.10 per cent respectively at the ice point. The widest tolerance offered is "Grade III", with R_0=100Ω±0.50 per cent.

Careful consideration was given to the attachment of wires to the technical lands. Excellent mechanical and electrical integrity is achieved by passing a gold wire through the pierced land, clenching it in intimate contact



Typical changes in resistance values of Thermafilm detectors during prolonged exposure to elevated temperature with the land, then reinforcing the joint with conductive cement before finally overglazing the entire resistance area. The whole detector is now effectively transformed into a monolithic structure, which vibration and mechanical shock fail to separate.

The overglaze performs a second and equally important function of electrically insulating the detector from unprotected sources of potential, e.g. exposed furnace windings. The insulation resistance is $> 10M\Omega$ at 240V at room temperature and $> 1M\Omega$ at 50V at 600°C.

The thermal response of the Thermafilm detector is superior to that of a conventional wire-wound platinum resistance detector when measured in accordance with BS 1904. Similarly self-heating is within the required specification and is typically $+0.02$°C/mW.

Finally, the Matthey Thermafilm temperature detector shows excellent linearity when compared with conventional resistance thermometers, and tests confirm the cyclic and long-term stability of earlier predictions after exposure to elevated temperatures.

Conclusion

The Matthey Thermafilm Resistance Thermometer is a novel temperature detector, developed from thick film technology to high standards of quality, eminently suitable as a low cost replacement for industrial platinum resistance thermometers and thermocouples. It is technically superior to a thermistor over a wider range of temperatures. It is ideally suited to automation for large quantity production and is currently being developed in tubular form.

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Platinum Alloys in Corrosive Environments

HIGH TEMPERATURE RESISTANCE TO MOLTEN GLASS AND AIR

The ability of platinum and its alloys to resist the corrosive effects of a wide variety of media that rapidly cause other metals to decay has been the basis of their use in many industries, and especially in the glass industry. However, the mechanism by which molten glass and air attempt to attack platinum alloys has not been completely worked out as yet. Certainly some platinum alloys resist attack better than others and so a report on Russian studies on three important platinum alloys is particularly interesting.

E. I. Rytvin and L. A. Medovoi (*Vliyanie Fiz.–Khim. Sredy Zharoproch. Metal. Mater.*, 1974, 87–94) investigated the corrosion of the alloys 10 per cent Rh–Pt, 10 per cent Rh–25 per cent Pd–Pt and 1.5 per cent Ru–10 per cent Rh–25 per cent Pd–Pt in air and in a molten glass of composition 54 per cent SiO_2, 14.5 per cent Al_2O_3, 10 per cent B_2O_3, 16 per cent CaO, 4 per cent MgO. The ductility and high temperature strength of the alloys were assessed by measuring the rate of sublimation and dissolution at 1400°C in the unstressed state and during creep induced by an initial stress of 0.5 kg/mm^2.

It was discovered that the corrosion which occurs is intergranular in nature. This is illustrated by a series of photomicrographs and the results are tabulated. It appears that the rate of intergranular corrosion mainly depends upon the alloying elements and that dissolution of the alloys in glass is slower when tensile stress is applied. Molten glass affects the high temperature strength and ductility of the platinum alloys so that, when the degree of intergranular corrosion is greater, then the reduction in the ductility of the platinum alloys also increases.

It can be concluded from examination of the results that 10 per cent rhodium-platinum is superior to either of the alloys containing palladium in its ability to withstand the corrosive conditions met with when in contact with molten glass, as well as when exposed to air at high temperature. F. J. S.