

Reliability of Platinum-Based Thermocouples

INFLUENCES OF CONTAMINANTS AND OPERATING ATMOSPHERE

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A series of articles in this Journal by Wilkinson on platinum-based thermocouples and their use (1–4) addressed most of the potential problems and performance-limiting factors. The author referred to the possibility of deterioration of thermocouple performance through contamination. This article expands on this, demonstrating that the prevailing atmosphere in which the thermocouple is operating can have a profound effect on its life and accuracy.

In his article on minimising thermocouple drift (2), Wilkinson referred to the possible effects of contaminants, and recommended cleaning each limb of the thermocouple thoroughly prior to use. This is excellent advice, and will help to reduce the potential for subsequent performance deterioration. However, despite the best efforts to keep the system clean, it is still possible for performance-affecting contaminants to be introduced into the thermocouple.

Refractory Insulators

In practice, thermocouples are fitted with refractory insulation between the two limbs (5). Either the limbs are threaded through insulators, or they are surrounded by compacted refractory (as in a metal sheathed unit). In either, alumina has been the most frequently used refractory. The premise here is that platinum and its alloys can be heated in contact with the more refractory oxides, including alumina, without deleterious effect. Indeed platinum thermocouples have shown great stability in contact with alumina at temperatures up to 1600°C for 1000 hours, in a variety of atmospheres, including high grade argon with an oxygen content of only 50 ppm.

This long-established view of the stability of platinum in contact with refractory oxides must however be tempered by the knowledge that this apparent inertness is not invincible. The mechanisms by which some contaminants can be introduced into the platinum thermocouple, subsequently to affect its performance, can be complex. They involve the active participation of the refrac-

tory insulation material. At high temperatures, particularly above about 1300°C, the potential for such processes to occur, under specific conditions, can increase. Serious platinum limb contamination and even catastrophic failure of the unit can result.

Platinum–Refractory Reactions

So what are these specific conditions? The nature of any potential reactions between the platinum and the refractory must first be understood. Alumina is generally considered a very stable oxide – after all, as bauxite, it is one of the most prevalent natural sources of aluminium. It dissociates as follows:



In air, as the temperature is increased the equilibrium shifts from right to left, i.e. the stability of alumina increases. This remains true even when oxygen levels are reduced, for instance, by the use of a vacuum or argon/nitrogen/hydrogen/cracked ammonia atmospheres. However, if platinum is introduced into the system, with an alumina-sheathed platinum *versus* rhodium-platinum thermocouple, the renowned stability of alumina can be undermined. The phase diagram for the platinum-aluminium system (6) confirms that at the platinum-rich end, intermetallic compounds are formed – generally readily; the process is exothermic and typical of those where intermetallic compounds are formed. The resultant product, probably Pt₃Al in the first instance, is very stable.

Thus at high temperatures, if the partial pressure of oxygen in the working atmosphere is

reduced, and is maintained so, the potential increases significantly for two reactions to occur to the detriment of thermocouple performance:



(Oxygen is removed by the ambient atmosphere.)



(A stable intermetallic compound is formed and heat is evolved.)

Darling *et al.* studied these reactions in some detail in the early 1970s, (7–10) with respect to a number of refractory materials such as alumina, thoria, boron nitride, hafnia, zirconia and magnesia. (Boron nitride and hafnia are not referred to in References (7–10) but were included in the original investigation.) Thorium, boron, hafnium and zirconium will, similarly to aluminium, form intermetallic compounds with platinum given appropriate conditions. Darling *et al.* demonstrated that intermetallic reactions are possible with these refractories, in fact extremely probable, at temperatures above about 1300°C, once the oxygen potential of the ambient atmosphere is maintained at a reduced level. Such levels were shown to be achievable by evacuation using a conventional roughing/diffusion vacuum pump system down to 10^{-3} Pa pressure or by the use of hydrogen-containing atmospheres where oxygen removal was ‘continuous’, as found in many high-temperature melting or heat treatment furnaces. If silica, or a silicon-containing compound, is present, for instance a silicate-containing alumina, the reaction potential is further increased through the very strong affinity between platinum and silicon (10). The resultant Pt/Si compound has a very low melting point – less than 1000°C; therefore once the compound has formed in the limb of the thermocouple, catastrophic failure through incipient fusion will occur once this temperature has been exceeded.

Preconditions for Adverse Reactions

The timescale for such reactions depends strongly on the efficiency of oxygen removal. In a continuously maintained vacuum, the reaction will progress quite slowly, and it is unlikely that any sig-

nificant detrimental effects will occur before at least 100 hours usage at temperatures in excess of 1300°C. In extreme instances, where strong reducing conditions prevail, ensuring very low oxygen levels, such reactions will occur quickly, within a few hours. Even then, compositional changes in the platinum limb would only adversely affect thermocouple accuracy if they occurred in that part of the unit located in the thermal gradient. Any contamination occurring in that part of the thermocouple held in the stable hottest zone of the furnace would not affect accuracy. Catastrophic failure through incipient melting of the intermetallic products could occur where the furnace running temperature exceeds the melting point of the compound. Such failures have been observed in a platinum thermocouple limb after reaction with alumina at 1450°C (10).

There is one exception to vulnerability to reduction and intermetallic reactions among the commonly available refractories, namely magnesium oxide (magnesia). Given the absence of ‘the usual suspects’ such as silicon, it is extremely difficult to promote significant dissociation of magnesia and the formation of platinum-magnesium compounds, even in the most aggressive oxygen removal environments at temperatures up to 1700°C. The affinity between platinum and magnesium is very low, and there is therefore no thermodynamic driver for them to react to form stable compounds.

It is important to remember that these reactions can only continue in environments where the oxygen is continuously removed; once the partial pressure of oxygen increases, the reaction will slow down and eventually cease as the equilibrium partial pressure is attained. Therefore one would not expect deleterious breakdown of a dispersed oxide phase such as zirconia in, for instance, a dispersion-strengthened platinum product, since dissociated oxygen cannot normally be continuously removed. However, it has also been shown that silica can be reduced simply by the presence of oil, *via*, for example, an oil-soaked refractory particle being rolled or drawn onto the surface of the platinum (10). At high temperatures a very local reducing environment is created by the oxidation

of the oil, promoting the dissociation of the silica, and the exothermic reaction of the silicon with the platinum to form a platinum silicide.

Specification and Maintenance of Thermocouples

The selection of the appropriate refractory insulation material is clearly very important. For instance, a range of 'grades' of alumina insulator are available, some containing quite high levels of silicates, while others consist of virtually pure alumina. At low operating temperatures, say below 1000°C, the potential for contamination between thermocouple and insulator will be small, and alumina insulators of lower specification can be used. At higher temperatures, particularly above about 1300°C, the presence of silicates and other impurities can increase the potential for contamination and subsequent catastrophic failure of the unit, depending on operating conditions.

It is possible that thermocouples fail or lose accuracy in service, particularly during long-term, high-temperature usage, more often than is realised through the reactions described here. Paraphrasing Wilkinson's point, 'cleanliness is next to godliness' if optimal performance is to be obtained from the thermocouple. However, the user must also be fully aware of the conditions under which the thermocouple is to be used, to

ensure that these reactions do not occur to the detriment of its performance. Clearly, where the prevailing environment might either very locally or generally tend towards low oxygen/reducing conditions, and if a conventional unit is to be employed, then the user must consider carefully the thermocouple/refractory combination, the quality of the refractory and the prevailing operating atmosphere. In such instances, the use of a metal sheathed thermocouple, although these have their own drift problems (2), would at least prevent thermocouple/refractory reactions from occurring.

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