

Appendix F: Platinum Heating Strip

Resistance and handling

(Abstract from DEGUSSA Specifications in German language)

How to handle Pt heating strips

Advantages of the Pt heating strips

Platinum is one of the most resistant metals. Due to its high chemical resistance, its high melting point (1768 °C) and its low vapour pressure it is better suited for heating strips than any other material. No other material can compete with its resistance to acids, especially its perfect resistance to hydrofluoric acid - even in a mixture with sulphuric acid and/or nitric acid.

Finally it is of great value that platinum can be machined reliably so that forming and shaping hardly faces any restrictions. A special benefit is that it can be homogeneously welded without troubles, thus completely avoiding soldering points which generally have reduced chemical and thermal resistance.

Quality of the Pt heating strips

Naturally, the described properties of the Pt heating strips can only be perfectly achieved with a platinum that is faultless in every respect. The purity of the primary material, the homogeneity as well as appropriate processing of the material are preconditions for the production of reliable heating strips.

Pure platinum is very soft and solidification occurs during the manufacturing and shaping processes. However, its original softness is regained during annealing at 700 to 1000 °C.

Despite the numerous benefits of the material, the extremely resistant platinum can be very reactive in particular cases. It can be strongly attacked or even be completely destroyed by a few samples.

General remarks on detrimental substances

The detrimental substances for Pt heating strips are listed more or less completely in most of the handbooks of inorganic and especially analytical chemistry.

The mainly mentioned substances are chlorine, chlorine of hydrochloric acid - nitric acid mixtures (nitrohydrochloric acid), hydrochloric acid with other oxidants such as chromic acid, manganates or ferric salts as well as certain molten salts from which platinum is separated chemically; furthermore the low-melting metals such as lead, tin, zinc, silver, aluminium, mercury, alkali metals, antimony, bismuth - already present or formed secondarily by reduction of compounds - elementary phosphorus, arsenic, boron and silicon which form an alloy with platinum, reducing considerably its melting point.

The extent to which these different substances are detrimental is greatly varying. In some cases a few hundredth of a milligram can make a Pt heating strip completely unusable, whereas other detrimental substances can be in touch with the heating strip for a long time without considerably limiting its usability. Just on this matter you can hardly find any detailed information, although the use of Pt heating strips often offers big advantages when operating with some substances which are in general detrimental.

In the following we give a survey of the most important substances having a detrimental effect on platinum and consider the extent of the influence on platinum. With our experiences we hope to contribute to the knowledge of platinum used for heating strips, thus not only sparing the users of the heating strips a lot of troubles but also providing the heating strips with a longer life and possibly extending their fields of application.

Substances with destroying effect

Apart from the chemically dissolving action of atomic chlorine in liquids - e. g. in hydrochloric acid-nitric acid mixtures - and of some molten salts, each definite destruction of Pt heating strips is caused by the fact that platinum forms alloys with other metals or non-metals. In most cases the melting point of these alloys, which is exceeded at the usual working temperatures, is much lower than that of platinum. Then local melting causes holes or cracks in the heating strips.

Forming of alloys with metals

The low-melting point metals such as lead, tin, antimony or bismuth reduce the melting point of platinum even in little concentrations thus causing holes in the heating strips. There is no need to put the metals as such on the heating strips. It occurs only very rarely that these metals are heated with Pt heating strips, but occasionally one ignores that a part of their compounds - mainly their oxides - can very easily be reduced to metal, e. g. by filtering charcoal. Sometimes it occurs that traces of fusible metal - mainly minute soft solder particles - reach the Pt heating strips, adhere to them and cause holes when heated next time.

The explanations about the fusible metals (including mercury) and their compounds in principle apply to the higher melting-point metals, too, in the case of the heating approaching their melting point. Therefore contact between these and a Pt heating strip should be avoided. Even if the forming of an alloy with a higher melting-point metal such as iron does not decrease the melting point so much that the heating strip is immediately destroyed, the forming of these alloys reduces considerably the heating strip's general corrosion resistance and the material embrittles. As a result secondary influences can cause the complete destruction. A platinum-iron alloy is formed e. g. if a Pt heating strip is heated up to temperatures higher than 1200 °C in the presence of iron oxide.

In addition to free carbon and filtering charcoal, all organic compounds, e. g. inorganic salts of organic acids, can be used as reducing agent for metal oxides - just like in all the cases that will be mentioned later. Reducing flame gases from heating sources act similarly. Please note that hydrogen is occluded at a temperature of approx. 400 °C and diffuses at higher temperatures into the

heating strip. Contrary to wrong indications in literature, hydrogen as such cannot be considered as a detrimental substance. Nevertheless, its action on reducible compounds in the annealing material has to be taken into account.

Forming of alloys with non-metals

Like metals, non-metals also form low-melting alloys with platinum, a fact to which there has not been paid sufficient attention yet. In particular silicon, phosphorus and arsenic have to be mentioned on whose effect as detrimental substances there are indications in recent publications and to which special care must be taken because of their topochemically specific attack. Whereas the formation of a platinum-tin alloy expands on the whole surface, the formation of a phosphorus-arsenic alloy occurs along the grain boundaries where alloying progresses fast and causes very quickly cracks.

Silicon, considerably reducing the platinum melting point, forms the silicide Pt₃Si which in turn forms an eutectic melting with platinum at 830 °C.

The forming of alloys in the presence of free silicon, resulting eventually from the reduction of primarily present silicon dioxide by carbon or hydrogen (in small quantities), causes the perforation of the heating strip due to the low-melting eutectic Pt-Pt₃Si.

Phosphorus reacts similarly. Already in fractions of a milligram, it forms with platinum the platinum phosphide Pt₂₀P₇, which yields with platinum a particularly low-melting (588 °C) eutectic Pt-Pt₂₀P₇. The melting temperature of the platinum contaminated by phosphorus is immediately locally reduced to app. 600 °C (eutectic melting), thus making cracks and holes inevitable.

Arsenic and platinum also form a low-melting eutectic (at 597 °C) which has been known for a long time and even made possible the first method for the production of machinable platinum (Achard, 1779); through arsenide, Berzelius won rhodium metal in 1836. Similar to phosphorus, platinum arsenides can be created by annealing arsenic compounds, e. g. Mg₂As₂O₇, if reducing substances (flame gases or filtering charcoal) are present.

Detrimental substances

Whereas the detrimental effect of the above mentioned substances is generally underestimated, the damages of the Pt heating strips caused by the following substances are very often less important than assumed.

In nitrohydrochloric acid, platinum is dissolved very slowly in the cold and even at temperatures of a water bath it takes many hours until the heating strip is dissolved.

Caustic alkali, carbonates, sulphides, cyanides and thiocyanates attack platinum at higher temperatures, but very often the use of Pt heating strips provides so many advantages that a certain loss of substance must be accepted.

In case of glasses and ceramic materials it has to be examined, whether metallic constituents (e. g. lead, antimony, arsenic, iron etc.) do occur by secondary reduction processes of heavy metal oxides. In oxidising atmosphere up to 1400 °C, platinum will not be attacked by magnesium silicates (asbestos). In atmosphere with little reduction, however, melting to a slag of unknown composition will occur already at red heat.

If carbon or reducing flame gases (from luminous gas flames or from the inner cone of a gas flame) act upon Pt heating strips, their surface is getting roughened. This surface roughening can only be partly undone by strong annealing of the heating strip in oxidising atmosphere, so that the original smoothness of the surface cannot be regained completely. The detrimental effect of carbon and the reducing flame gases on platinum is only insignificant and can be neglected as long as there are not any reducible compounds of the mentioned toxins for platinum such as metal oxides. Otherwise platinum forms alloys with the elements set free by reduction. Pt heating strips are likely to be damaged by sulphur and sulphurous gases only from 1550 °C upwards.

Heating

Unnecessarily long heating of Pt heating strips up to high temperatures has to be avoided, since this would cause coarsening of their crystalline structure, brittleness and even cracking.

Cleaning and Maintenance

After the use of Pt heating strips, a careful maintenance and cleaning is necessary. After boiling out using suitable solvents, it is to be recommended to occasionally clean the heating strips with fine sea sand, which essentially improves their look and their life span. Scrubbing with the round grains of sand does not only remove surface alloys, but also smoothens the surface thus making it more resistant to corrosions.

Careful cleaning can also be obtained by melting out the heating strips with potassium hydrogensulphate or potassium metabisulphate. Avoid to burn impurities out of the platinum by annealing. This method is only successful in particular cases, but it is recommended to remove impurities in a mechanical or chemical way before annealing a Pt heating strip.

Life span of the Pt heating strips

Although a premature destruction of the Pt heating strips can be avoided by taking into account the instructions mentioned above, it is not possible to guarantee unlimited durability.