Report on the characterisation of the protection against contamination

Work package 1: Deliverable D1.5

EMRP ENG 06

Metrology for improved power plant efficiency

Power Plant Metrology

Introduction

Platinum resistance thermometers (PRT) are used over a wide range of temperatures in a wide array of applications. One aim of this work package was to investigate processes leading to instabilities and drift of platinum resistance thermometers.

The sources for this are manifold and one has to investigate the processes with the most significant impact. These processes can be distinguished into two groups; materials and operation procedures.

Impurities can be categorised into the first group of processes and were investigated as step 1.1.1 of Task 1.1 (for a detailed report see [1]). In short summary, even though high purity platinum is used for thin film sensors[a] several impurities were found in the investigated thin film sensors prior to any ageing. Ageing experiments at 700 °C were carried out in air and MgO powder. These experiments showed an increased drift of the Pt thin film sensors which were embedded in the MgO powder. X-ray fluorescence analysis (XRF) revealed Fe, Cr, Ni, Ag, Mg and Cu being present in the sensors. Sensors which were aged in the MgO powder had a significantly increased Mg content indicating a poisoning of the sensors by the ceramic powder. A direct relation though is not possible as the other impurities are known to cause drift of PRT's, but the location of them in the sensors, i.e. Pt conductor lanes or Al_2O_3 substrate, cannot be determined.

For this report we will focus on two other aspects concerning the influences on the stability of PRT's. The first one is about the effect the surrounding atmosphere can have on platinum, i.e. oxidation of platinum and reduction of its oxides. The second one is about the impact operating conditions can have on PRT's, where ageing experiments are carried out to investigate handling to improve stability of the thermometers.

Oxidation of platinum

This report will give a summary of the paper on the oxidation of platinum and the impact of its thermal stability on resistance thermometry which is submitted to the International Journal of Thermophysics (D1.11).

The oxidation of platinum and the reduction of PtO_2 are of great importance for the performance of a PRT. Because of its stabilising effect on the performance of a thermometer the international temperature scale ITS-90 is requesting a minimum partial pressure of oxygen to be present in a thermometer [2]. This means that standard platinum resistance thermometers (SPRT) are more stable when a small amount of oxygen is present. The exact mechanism for this is still under discussion, but a common explanation is the passivation of impurities by oxidation. The optimum oxygen content in a thermometer is a compromise between this stabilising effect and the effect of the oxidation of platinum.

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[a] Data from the manufacturer states purity of the Pt used for fabrication to be better than 99.995%.

The oxidation of platinum and how it affects the resistance of a wire has been extensively studied by Berry. He found that even a sub monolayer of platinum oxide is having a considerable effect, i.e. 0.1 mono layers (ML) of platinum oxide leads to a resistance change of approx. 4 ppm for a 75 µm thick wire [3]. 0.1 ML means that not the whole surface is covered with an oxide layer, but as a mean value only around 10 % of the area is covered by a one ML thick oxide layer. Furthermore Berry found that a simple two layer model is sufficient to model the effect of oxidation on the resistance changes of platinum wires, where the change is induced by the change of the mean diameter of the wire. It has been shown by solving experiments in acid that the oxide present on a Pt wire is PtO_2 [3] and it can grow as thick as 90 nm [4], but doesn't have to stop there. The experiments were stopped at this thickness, because it went for several months and no saturation has been found.

In more recent investigations Sakurai et. al investigated the oxidation in a SPRT [5,6]. They calculated the Gibbs free energy for PtO_2, PtO and Pt and proposed a complex reduction behaviour and the reduction process to involve another Pt oxide namely PtO; i.e. the reduction follows $PtO_2 \rightarrow PtO \rightarrow Pt$. Other oxides were not considered as the authors believed them to be not relevant for thermometers. Calculations by other groups based on density functional theory on the thermal stability of platinum oxides suggest Pt_3O_4 to be more stable than PtO and PtO_2 [7, 8].

A method to investigate the decomposition process of platinum oxides is simultaneous thermal analysis (STA). This consists of thermogravimetry (TG), i.e. the mass of the sample measured at different temperatures, and differential scanning calorimetry (DSC). We carried out STA experiments with a coupled mass spectrometer (MS), so that parallel to the STA measurements the decomposition products can be analysed. Commercially available PtO_2 powder has been analysed. The mass at the beginning of the experiment was 25 to 30 mg and measurements were carried out in different atmospheres, i.e. synthetic air and helium. Heating rates were 3 K/min and the maximum temperature was 1000 °C.

Figure 1 shows the TG and DSC measurements which were carried out in synthetic air. The unit for the TG measurement is chosen to be a relative unit (%), so that the mass changes can be better compared to the measurements in helium atmosphere.
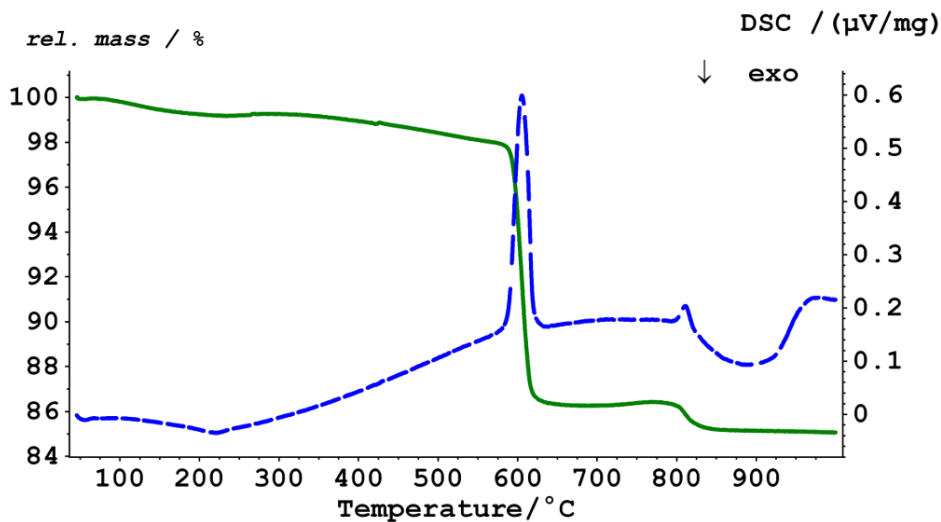
Fig. 1 Thermogravimetric (relative mass; green solid line) and differential scanning calorimetry signal (DSC, blue broken curve) of PtO_2 from 100 to 1000 °C in synthetic air.

Examining the TG signal reveals several processes. Below 460 °C there are small mass changes, indicating instabilities of the oxide. A small plateau is visible at around 230 °C, with a barely visible increase in mass just above this temperature[b]. A small and steady mass decrease follows which evolves to a big mass step at the decomposition temperature $T_D = 595$ °C. This temperature marks the decomposition of PtO_2. The mass loss is determined to be $\Delta m = 11.4$ %. For a decomposition of PtO_2 to PtO and PtO to Pt one would expect $\Delta m = 8\%$ for both processes. Our findings are in contrast to the decomposition sequence proposed by Sakurai et. al [6]. From TG no unambiguous determination is possible at this stage, as reasoning can be made for the decomposition of PtO_2 to Pt ($\Delta m = 16$ %) and Pt_3O_4 to Pt ($\Delta m = 11$ %) which includes a decomposition from PtO_2 to Pt_3O_4 below T_D. Heating above 600 °C leads to an increase in mass ($\Delta m = 0.2$ %) at 800 °C. At this point another decomposition is observed. Above 800 °C no further decomposition is seen by TG up to 1000 °C. The oxidation above 600 °C is consistent with X-ray diffraction data in the literature [9].

The decomposition processes are accompanied by signals shown by DSC in figure 1. The reduction processes at T_D and 800 °C are seen as endothermic peaks. Furthermore there is a small exothermic process at 230 °C. There is also a large exothermic reaction visible from 800 °C up to approximately 950 °C. This coincides with the reduction starting at 800 °C. Looking solely at the DSC signal one has to assume an oxidation happening in this temperature range, but as the TG is showing no change this exothermic signal has to be assigned to a reaction of the remaining oxide in the DSC pan with the environment. A closer look at the DSC peak at T_D reveals the PtO_2 to be β-PtO_2 as the peak is consisting of two peaks which indicates the β^1 and β^2 phases [10].

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[b] As the uncertainty is large for the determination of the mass this increase is too small to be associated to a physical process with great confidence and is therefore mentioned just for completeness.
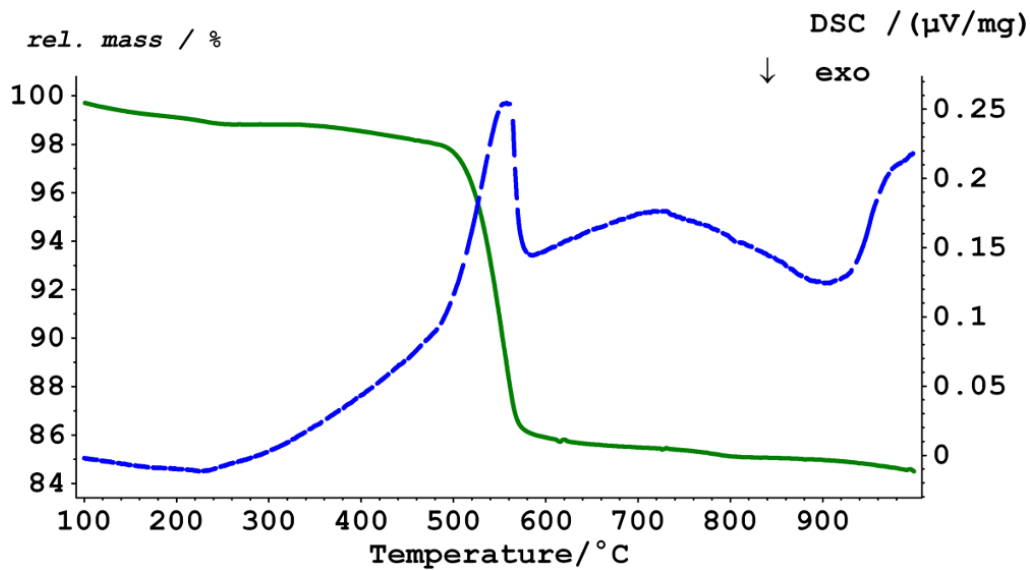
Fig. 2 Thermogravimetric (relative mass; green solid line) and differential scanning calorimetry signal (DSC, blue broken curve) of PtO_2 from 100 to 1000 °C in helium atmosphere.

Mass spectrometry shows that the exothermic reaction at 230 °C is an oxidation of CO as there is a peak in the signal for $m/Z = 44$, i.e. CO_2.

Figure 2 represents the TG and DSC measurements carried out in helium atmosphere. It is evident that the atmosphere is having a great impact on the stability of the PtO_2. The decomposition temperature T_D shifts from the value in of 595 °C in synthetic air down to 490 °C in helium. The mass loss is larger in helium (12.0 %) than in synthetic air (11.4 %) and there is no sign for further oxidation above 600 °C. As there is still a small kink visible in the TG signal at approx. 780 °C for the measurements in helium it is reasonable to assume a fraction of remaining platinum oxide being present above T_D in helium up to this temperature. This is corroborated by the DSC measurement where again a reaction of the powder with the environment is visible for high temperatures.

By DSC a strong endothermic reaction can be observed at T_D, but no endothermic peak at 780 °C, which can be attributed to the low signal which can be expected by the very small reduction depicted by TG. Again DSC indicates an exothermic reaction at 230 °C, which is supported by mass spectrometry to be the production of CO_2. Mass spectrometry further reveals NO to be produced differently for both atmospheres. In helium it consists of two clearly resolved peaks in the temperature range from 170 °C to 250 °C and 340 °C and 450 °C, while in synthetic air this two peaks are not clearly resolved and only the large signal from approx. 350 °C to 520 °C can be observed. This catalytic activity is accompanied with small losses of the mass, which indicates instabilities of the oxide powder towards catalytic activity.

The findings from STA help to understand the performance of thermometers at various temperature ranges and different environments. Especially the large shift of the decomposition Temperature T_D with the partial pressure of oxygen and the oxidation at high temperatures are of interest. Furthermore the effects of catalytic activity on the stability of

the platinum oxides, hence the resistance changes this implies for a thermometer, have to be further investigated for the low temperature use, i.e. below 450 °C.

The shift of T_D shows that a thorough knowledge of the thermometer is necessary to evaluate its performance. This is important as not all parameters of the thermometer are documented, e.g. the gas filling is not always known. There are several gas mixtures used in practical applications and the partial pressure of oxygen may vary. The supplemental information for the ITS-90 recommends the partial pressure of oxygen in a standard PRT (SPRT) to be 2 kPa [11], but this is not a strict rule and thermometers used in industrial applications may have different specifications. When thermometers are used for calibration by a comparison method or when the measured temperature is between the fixed points defined by the ITS-90 the gas filling of the thermometer can therefore have significant effect on the performance of the thermometer, especially when measurements are carried out in the temperature range from 450 °C to 800 °C.

The possible oxidation of Pt above 600 °C is not considered when the drift of a resistance thermometer is investigated at these temperatures and this can lead to an incorrect determination of the temperature. The oxidation will cause a considerable drift as Berry has shown that the resistance is sensitive to this [3, 4]. As STA shows (figure 1) this is a considerable fast process, cannot be avoided and is drastically different to the behaviour in a low oxygen environment (figure 2).

Of further interest is the coincidence of the decomposition temperature T_D = 595 °C of PtO_2 in synthetic air and the temperature at which the performance of Pt thin film sensors starts to get delicate, i.e. around 600 °C.

The thermal analysis of the stability of PtO_2 reveals several aspects about the thermal stability of PtO_2 which were not considered in high temperature thermometry, but are necessary for the understanding of the performance of thermometers. For a correct evaluation of the processes influencing the stability of platinum resistance thermometers oxidation of Pt and reduction the platinum oxides has to be considered up to at least 800 °C, but 1000 °C would be better for a complete understanding as there are signs for high temperature reactions between 800 °C and 960 °C. Contrary to the current understanding of the influences of the platinum oxide on thermometers, which inspired procedures for preparation of thermometers, there is no easy way to get rid of the oxide layers on the Pt sensing element and there is no general rule of thumb applicable which will cover all types of thermometers and make them be in the same oxidation state, e.g. "heat to 650 °C and then there is no platinum oxide present". Each thermometer has to be known as there are wide arrays of specifications used and so different decomposition temperatures T_D are to be expected.

But general recommendations for the thermometers can still be derived from our STA results. In a thermometer high oxygen content leads to more stability of the oxide layers and hence the resistance for the temperatures below 600 °C and the reduction is not complete.

For a reproducible oxidation state the thermometer should be heated slightly above the decomposition temperature (approx. 20 K).

STA emphasizes the importance of oxidation, but the performance of a thermometer is not solely determined by it. The supplementary information to the ITS-90 states the importance of oxygen in a thermometer not because of the platinum oxide layer, but as a way to avoid the effect of impurities on the resistance of the Pt wire in a SPRT [11]. There are several other processes to be considered, e.g. impurities [1] and they can really be passivated by oxygen, and also how the thermometers are operated and treated prior to their use.

Operation of Pt resistance thermometers

Most of the time thermometers for industrial applications are made of thin film sensors. This has several reasons. Thin film sensors are considerably cheaper than wire wound ones, which is the design for the high accuracy SPRT's. Another common reason for the use of thin film sensors is their robustness to mechanical shocks, as they are specified to withstand at least accelerations of 40 g[c].

The typical design of a thin film sensor consists of a ceramic substrate, typically this is alumina, on which a thin film of platinum is deposited via a sputtering technique. The film is then structured and trimmed to the desired resistance. On top of the platinum layer a protective coating is applied which is made of glass, TiO_2 or another oxide compound. This sensor is then used in a thermometer, where it is embedded in a ceramic and a sheath, which is a metal for the typical applications, e.g. in a power plant.

When such a thermometer is not stable this can originate from several sources. The effect of impurities was shown in [1], but there are other influences which have to be considered. In the first part of this report the stability of platinum oxides has been shown, where data from literature indicates the impact for resistance thermometry [3,4,5,6]. This has to be further investigated as there is a way to manipulate the stability of metal oxides by an applied external voltage of a few V [12,13]. Furthermore the sputtering technique yields a grainy film. A grainy film has a different resistance than a bulk single crystal. Usually this can be approximated[d] in absence of scattering on the surface, i.e. thickness of the film is in the range of 500 nm to 1 µm, to be of the form:

$$\frac{\rho}{\rho_{\text{bulk}}} = 1 + \left(\frac{\lambda}{d}\right) \tag{1}$$

λ being the mean free path of the electrons and d the mean grain size [14]. The resistivity of a grainy film will therefore always be bigger than that of a bulk film. This in itself is no problem as the films are trimmed to the desired resistance, e.g. 100 Ω for a Pt100. The stability of a thin film sensor though can be influenced by changes in the grain size as this

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[c] As an example without any recommendation or claim to be the best solution: Heraeus states for a PRT 40 g vibration resistance and 100 g shock resistance. Product data sheet (online)
[d] For a more thorough quantum mechanical treatment see [15].

now changes the resistance. It is even possible that the temperature coefficient can change sign due to boundary effects, i.e. scattering of electrons on grain boundaries [15].

There are some effects altering the grain size and therefore impacting the performance of thin film sensors for the use in a thermometer. The two most prominent are thermo-migration and electromigration. The former means change and diffusion of grain boundaries, impurities and defects due to the thermal energy and the latter is based on the effects of a current, i.e. momentum transfer of conduction electrons to defects and impurities in the metal film. Both are related and mix together with the mechanical stress and strain effects [16].

We will focus now on the electromigration, as this involves mass transport, i.e. impurities, voids and host metal (Pt) atoms. Electromigration is influenced by the electrical current in the metal film and thus instabilities due to it can be controlled by adjusting the operating conditions of the metal film, i.e. thin film sensor. The mass transport can lead to multiple changes of the film. There can be a diffusion of impurities and voids, which leads to changes in the grain size and the grain boundary properties. Furthermore this can lead to changes of the bonded contacts. The impact of electromigration is described by Black's law [17], which leads to an equation to calculate the mean failure time t_f of a thin metallic film as

$$t_f = \frac{A}{J^n} \exp\left(\frac{E_a}{k_B T}\right) \tag{2}$$

A is the geometric dependent constant, J is the current density and T is the temperature. The number n and the activation energy for failure E_a are values which must be obtained by experiment. The number n typically has the value of 2, but it is not constrained to it and can have different values. Equation 2 shows the interplay between current density and temperature. Increasing one of those quantities leads to a shorter failure time. Because of this a test of the impact of electromigration on the stability of thin metal films has to incorporate both quantities. There are also variations of Black's law, featuring different temperature dependence, while still having the same current density dependence [18]. Furthermore the Blech product has to be considered [16].

The Blech product combines mechanical stress and electromigration, as both represent different contributions to the gradient in the chemical potential, which is the fundamental driving force for the flux of voids, impurities and so the changes in grain boundaries. This yields a critical product $(JL)_c$ of the current density J and the length of the conductor L. The Blech product is [16]

$$(JL)_c = \frac{\Omega(\sigma_{th} - \sigma_0)}{|Z^*|e\rho} \tag{3}$$

where Ω is the atomic volume, σ_0 is the stress at the beginning of the conductor line and σ_{th} is the maximum mechanical stress it can withstand. e is the charge of the electron, Z^* is called the effective charge and ρ being the resistivity. Below this critical product there will be no visible effect of electromigration as it is compensated by mechanical stress.

The combination of Black's law and the Blech effects leads to several conclusions affecting the evaluation and comparison of thermometers. From (3) it is evident, that it is not sufficient to consider only the current density when the importance of the impact of electromigration is evaluated. The length of the investigated conductor is also relevant. This is important as the design of thin film sensors varies and so different lengths of the conductor lines are present on these sensors, implying different sensitivity to the current density. The current density itself will also be different as the diameter of the conductor line can vary between designs and manufacturers. However when the width of the conductor line is of the same magnitude as the grain size the diffusion paths change and stability can be increased, even though the current density is increased [16].

Equation 2 shows that a film which is stable at a fixed current needs not to be stable at the same current when the temperature is raised. In fact a raise in temperature decreases the failure time by a large amount [16]. So designs of thin film sensors which exhibit stability when tested at the ice point need not have the same stability when they are operated at high temperatures, however those instabilities exhibited at high temperatures will persist and be observable to some degree when the sensor is being cooled again.

The stability of resistance thermometers was tested by ageing experiments with industrial thermometers made with Pt100 thin film sensors which were provided by the manufacturer Wetzer Endress+Hauser. The test procedure involves the measurement at the ice point (0 °C) and measurements in a Fluke block calibrator type 9173 at 200 °C, 400 °C and 600 °C. After the initial characterisation several sets of thermometers were aged at 600 °C for one week. 5 thermometers were aged without any current applied during ageing (Fig. 3), 5 with 1 mA (Fig. 4), 5 with 3.16 mA (Fig. 5) and 5 thermometers with 10 mA current (Fig. 6).

The thermometers which didn't have any applied current during ageing (Fig. 3) do drift by only a small amount (max. 0.14 Ω after 3 weeks at 200 °C, 0.10 Ω after three weeks at the ice point). However there is no trend observable which indicates any stabilisation and the thermometers seem to drift as ageing goes on. The thermometers which were aged with an applied current of 1 mA (Fig. 4) drift by a larger amount (max. 0.5 Ω at 400 °C after two weeks and 0.43 Ω at the ice point after two weeks), but they exhibit a backwards trend, i.e. values for the resistance at the ice point decrease after the initial increase, but at elevated temperatures there is still some increase in resistance detectable. On the other hand the thermometers which were aged with 3.16 mA applied current don't stabilise and drift as ageing continues (Fig. 5). The thermometers which were aged with 10 mA applied current show the biggest increase of all thermometers, as one thermometer of that series drifts by

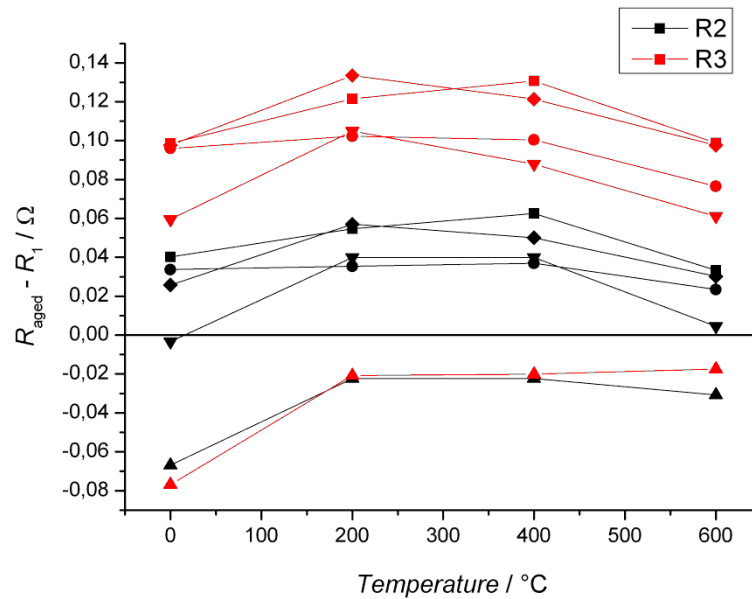more than 3 Ω at the ice point after one week of ageing (Fig. 6), i.e. a drift of approx. 7.8 °C at

Fig. 3 Resistance change of thermometers in comparison to thermometers which were aged for one week. R2 is the resistance after two weeks ageing, R3 is the data for thermometers which were aged for 3 weeks. There was no current applied to the sensor during the ageing process.

the ice point. However, when aged further, this thermometer recovers after two weeks to 101.7 Ω (4.4 °C) for the ice point value and 0.7 Ω (1.8 °C) after three weeks. As this thermometer recovers two other thermometers start to fail and drift more than 2 Ω at the ice point. It remains to be seen if those thermometers also recover when the ageing is continued.
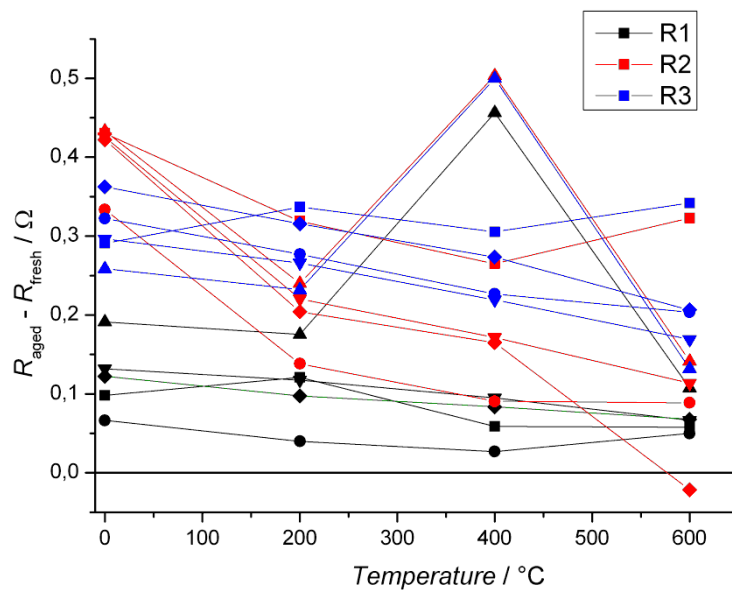

Fig. 4 Resistance change of thermometers aged with 1 mA applied current. R 1 is the data after one week of ageing, R2 after two weeks and R3 is the data after three weeks.
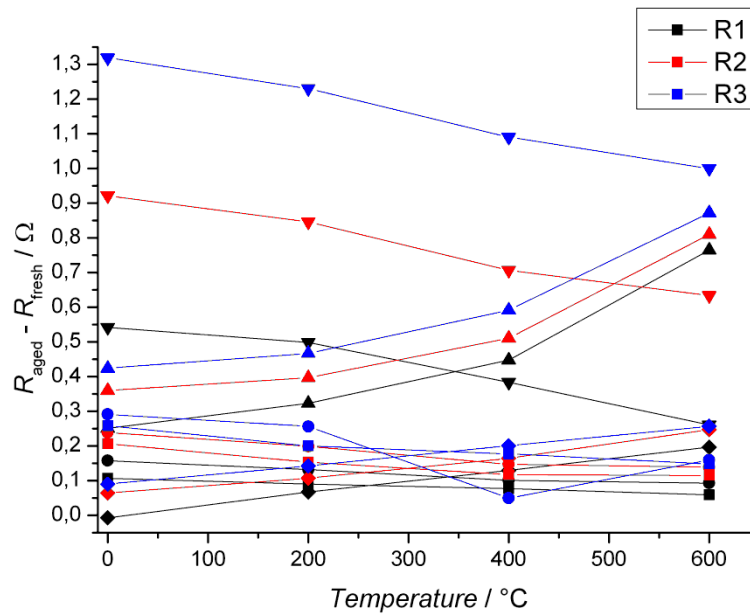
Fig. 5 Resistance change of thermometers aged with 3.16 mA applied current. R 1 is the data after one week, R2 after two weeks and R3 is the data after three weeks.
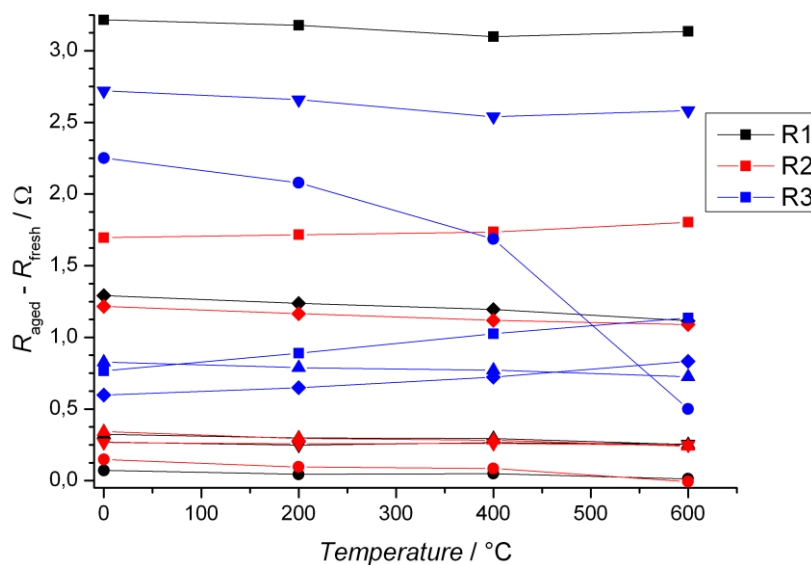

Fig. 6 Resistance change of thermometers aged with 10 mA applied current. R 1 is the data after one week, R2 after two weeks and R3 the resistance after three weeks of ageing.

The drift of the first thermometer to drift which was aged with an applied current of 10 mA resembles the behaviour of thermometers aged for longer periods of time at lower currents, e.g. the data ČMI reported for the calibration of Pt100-Thermometers used for tests of stability against vibration (Fig. 7). Furthermore the initial drift after one week fits to data collected in another project were resistance thermometers were tested which were operated in a power plant and compared to thermometers which were aged at the PTB. In this project the first thermometer started to drift by a large amount after approximately two years in the power plant.
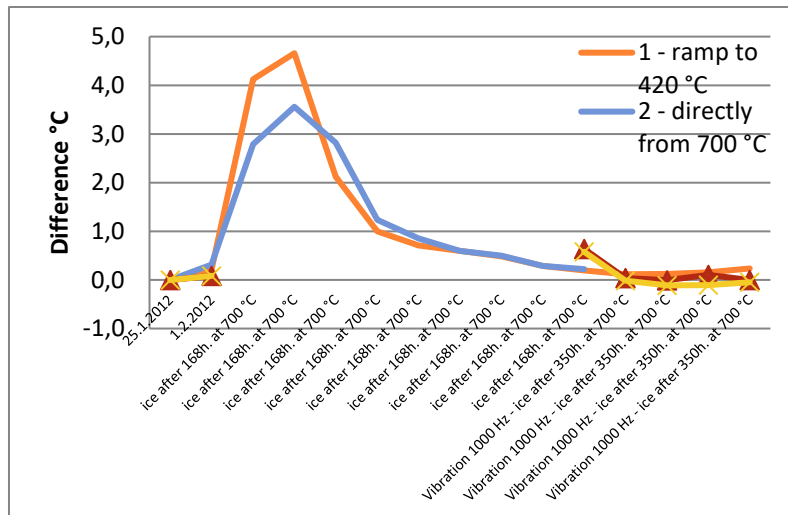
Fig. 7 Data from Thermometers tested at ČMI from the presentation at the final workshop [19].

When electromigration is assumed to have some impact on the stability of resistance thermometers this behaviour can be explained by the increase of the current. Equation 2 shows that the current density J^n is inversely proportional to the time of failure. Taking the typical value for the exponent n to be 2 and no change in the geometry of the film, this would lead to a time of failure which will be reduced by a factor of 100 when comparing data of thermometers aged with 10 mA current to those operated with 1 mA. This means that the ageing of two years can be carried out in one week when a higher current is applied. The exponent though needs not to be 2, but can have values ranging from 1 to 7. To evaluate the value for the exponent the data on the thermometers with 3.16 mA current have to be analysed. Up to three weeks of ageing there is only an increase in resistance observed (Fig. 5) which is consistent with the rest of the data. If the exponent is indeed 2 those thermometers should have their biggest drift around an ageing time of 10 weeks, i.e. 1 mA takes 100 weeks, 10 mA takes 1 week and 3.16 mA = √10 mA should be 10 weeks for $n = 2$. The tests will continue to investigate this behaviour.

If electromigration has an impact on the stability of the thin film sensors this presumes that the product of the current density J and the length of the conductor line L of the thin film sensor has to be bigger than the Blech Product $(JL)_c$ (Eq. 3). The resistivity ρ is part of the Blech product, which means that a metal like Pt will have large values for $(JL)_c$. So it is open if there will be an effect caused by electromigration be observable in thin platinum films or it will have a different statistical time of failure than described by Black's law (Eq. 2).

It remains intriguing to assume an impact of electromigration as this will also explain the stabilising effect of ageing while a current is stressing the sensor. As can be seen in equation 2 the mean time for failure of a thin film is not only determined by the current density and geometry, but also on an activated process with the activation energy E_a. Current stressing is significantly altering the film [16,17,18] and this can lead to the low activation energy related effects to be activated by the temperature and current, so effectively eliminating them after an initial period of stressing. If this low activation energy defects and impurities are gone there will be only processes remaining which need energies higher than the typical operating condition (current, vibration and temperature) provide. When they cannot be activated, the remaining effects leading to instabilities are inactive and the film is not changing anymore, i.e. the thermometer is not going to drift. The experiments

shown in this report are continued to evaluate the exponent *n* and to check if the time of failure for the thin film sensors can be described by Black's law.

The behaviour of the thermometers when stressed with 10 mA is promising to either be a way to stabilise the sensors or accelerate ageing to check the design or production processes of thermometers. To validate the validity of this predictions further ageing experiments need to be undertaken and the tests will go on.

Summary

The stability of Platinum resistance thermometers can be affected in several ways. In this report we have presented the results on the thermal stability of platinum oxides, i.e. STA measurements on β-PtO_2, and our characterisation and ageing experiments of industrial resistance thermometers.

The STA experiments show that the stability of PtO_2 is strongly affected by the partial pressure of oxygen, as the main decomposition shifts from 595 °C in synthetic air to 490 °C for helium. Furthermore the oxygen rich atmosphere leads to another oxidation process above 600 °C, which ends at 800 °C, where another decomposition process starts. This reduction is strongly suppressed in helium atmosphere. These results show that the oxidation of the platinum sensing element can be strongly influenced by the environment. This has to be considered when the platinum resistance thermometers are going to be used above 450 °C, especially when interpolating temperature measurements between fixed points like Al and Zn. Furthermore this oxidation mechanic has to be considered when PRT's are going to be used in comparison method measurements as two different gas fillings of thermometers can lead to different behaviour at elevated temperatures.

The ageing experiments on industrial type PRT show that the current is stressing the film, which leads to instabilities and drift. It is still unclear if this process is caused by electromigration. The failure time of one thermometer which was aged at 10 mA current is a hint for it as this fits to data gathered on thermometers which were used in a power plant or aged at CMI, but it is no unambiguous evidence. The recovery of this thermometer can be explained on electromigration effects, because all low activation energy effects are eliminated by this current stressing. It remains to be seen though if the thin film sensor element fulfils the criteria stated by Black's law. However this law is not theoretically derived, but empirically found and there is no reason to believe that it is a strict condition to be matched for electromigration to be relevant. A small current of 1 mA during ageing leads to a stabilisation of the thermometer after an initial drift, while an intermediate current of 3.16 mA leads to no stabilisation or recovery of the thermometer. For a stable operation of a platinum resistance thermometer it seems therefore advisable to either stress it during ageing with a low current or with a high current. When the processes during this stressing are better understood the latter is interesting, because the initial drift is recovered and all damaging and recovery effects seem to be accelerated compared to the low current stressing.

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