

Effects of Quartz Glass Insulation on Platinum Gold Thermocouples

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Au/Pt thermocouples are considered as an alternative to High Temperature Platinum Resistance Thermometers and are one of the prime candidates to replace them as the interpolating instrument of the International Temperature Scale of 1990 (ITS-90) in the temperature range between about 660 °C and 962 °C. This work presents the results of investigation of two Au/Pt thermocouples that used exclusively quartz glass (SiO₂) as insulation material. Measurements in fixed points of Zn, Al, and Ag were realized on these thermocouples as well with interchanged inner insulation made of high purity aluminium oxide (Al₂O₃). The conducted experiments tested the performance of Au/Pt thermocouples with the use of different insulation materials. The measured electromotive forces were found to be sensitive to the replacement of the quartz glass by aluminium oxide as an insulation material of the Au/Pt thermocouples. This change of insulation has resulted in a temperature increase up to about 0.5 K measured at the freezing point of silver. The decreasing insulation resistance of quartz glass at higher temperatures is believed to be the source of thermoelectric instability.

Keywords: Au/Pt thermocouple, quartz glass insulation, insulation resistance.

1. INTRODUCTION

According to the International Temperature Scale of 1990 (ITS-90), High Temperature Standard Platinum Resistance Thermometers (HTSPRT) are used as interpolation instruments in the temperature range between the freezing points of aluminium (660.323 °C) and silver (961.78 °C) [1]. Their sensitivity to contamination, lack of stability, non-uniqueness effects and poor repeatability are well-known problems [2]-[6]. Au/Pt thermocouples are considered to be an alternative to the HTSPRTs in this temperature range. As further improvements in manufacturing processes of Au/Pt thermocouples have been made, an increase of their thermoelectric stability and homogeneity has been achieved. This has resulted in excellent measuring properties which allow reproducible measurements of high accuracies which are better by about one order of magnitude compared with Pt/Rh alloyed thermocouples [7]. The task group for the mise en pratique for the definition of the Kelvin of the Consultative Committee for Thermometry (MeP-K, CCT) has recommended further research on Au/Pt thermocouples as a potential candidate for a new interpolation instrument within the ITS-90 for the temperature range between the aluminium and silver fixed points [8].

In order to see the typical sensitivity and temperature range of Au/Pt thermocouple an emf-temperature dependency is provided in Table 1.

Table 1. Typical emf output of an Au/Pt thermocouple [9].

emf [μV]	t ₉₀ [°C]
0	0
777.56	100
1844.64	200
3141.26	300
4632.85	400
6300.29	500
8134.22	600
10131.09	700
12289.49	800
13428.71	900
16124.11	962

The two Au/Pt thermocouples that were subject to the investigation used quartz glass as the outer and inner insulation. The quartz glass tubes have a higher purity of 99.995 % compared to typical purities of 99.7 % of aluminium oxide and have a smoother surface of the inner holes of the insulation tubes compared to aluminium oxide tubes, allowing an easier movement of the thermoelements. In this way the creation of stress relieving coil in hot junction, which is normally used to compensate the effect of the different expansion coefficients of gold and platinum, is no longer required. Instead, the unhindered movement of the

thermoelements inside the smooth quartz glass tubes avoids the formation of mechanical stress in the thermoelements.

The Au/Pt thermocouples marked Au/Pt 12-01 and Au/Pt 13-03 were made of pure platinum wire (99.997 %) supplied by Alfa Aesar. The diameter of the wire was 0.5 mm and its length was 2 m. The gold wire for Au/Pt 12-01 had a nominal purity of 99.999 % and was supplied by M&K GmbH. The gold wire for Au/Pt 13-03 had an unknown purity and was supplied by Berliner Metallhütten und Halbwerkzeuge (BMHW). Both gold thermoelements had a diameter of 0.5 mm with a length of 2 m. Before the annealing process, the thermoelements were cleaned by using ethyl alcohol and distilled water. The platinum wires were electrically annealed at about 1300 °C for seven hours. The gold wires were inserted section by section into an auxiliary insulation tube made of aluminium oxide (99.7 %, Al₂O₃) and annealed in a horizontal furnace at 1000 °C for seven hours. After inserting the thermoelements into the four-tube insulation assembly made of quartz glass, the measuring junction was created by welding the gold and platinum thermoelements together. A cross section of the thermocouple quartz glass insulation tubes can be seen in Fig. 1. Each of the tubes used in the inner insulation assembly was 650 mm long with an inner diameter of 1.5 mm and had a wall thickness of 0.25 mm. The dimensions of the outer one-end-closed protection tubes were 7 mm (outer diameter) x 5 mm (inner diameter) and 650 mm in length. After assembling, the two Au/Pt thermocouples were annealed at 1000 °C in a horizontal furnace for six hours to remove any physical strains (e.g., cold-work) introduced during mounting.

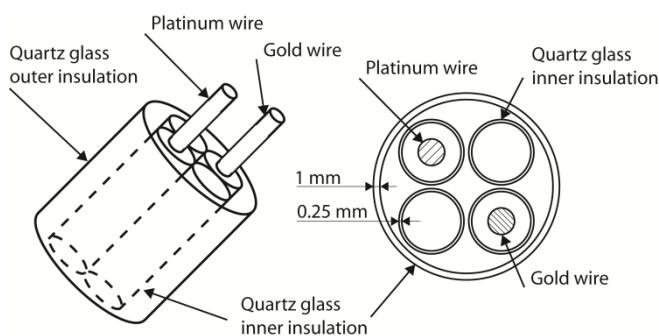


Fig. 1. Cross section of the Au/Pt thermocouple with four-tube inner insulation tube and outer insulation made of quartz glass.

2. MEASUREMENTS

The measurements presented were arranged in a way to investigate the effects of using different inner insulation materials (SiO₂ and Al₂O₃) on the electromotive force (emf) of both Au/Pt thermocouples. These measurements were performed using a calibrated voltmeter and the determined uncertainty ($k=1$) of the emf determination was 0.017 μ V for measurements at 419.527 °C, 0.026 μ V for measurements at 660.32 °C, and 0.044 μ V for measurements carried out at 961.78 °C. The thermocouple homogeneity, as one of the most important uncertainty contributions affecting their accuracy, was measured, before starting measurements in a

fixed point. The homogeneity measurements were performed in a salt bath at a stable temperature of 300 °C and over a length of 16 cm of the thermocouples. The thermocouples were fully immersed into a protective tube, which was directly in contact with the liquid salt solution, and slowly raised by 1 cm steps. The values were recorded after a stabilisation time of 3 min at each measuring point. Additional homogeneity scanning procedure was performed at the freezing point of silver. The homogeneity was measured by withdrawing the fully emerged thermocouple from the fixed-point cell. The thermoelectric homogeneity was measured over a length of 12 cm with steps of 2 cm.

The investigation was focused on the effects caused by the use of different insulation inner materials that separate the Au and Pt thermocouple wires. This investigation was performed by repeated measurements at the fixed points of Zn (419.527 °C), Al (660.323 °C), and Ag (961.78 °C) using Au/Pt thermocouples constructed with quartz glass inner insulation tubes and repeated measurements after the insulation replacement for aluminium oxide inner insulation tubes. The results of both of these measurement cycles were compared in order to determine the presence of a leakage effect possibly caused by the inner insulation.

3. FIXED-POINT MEASUREMENTS

The fixed-point measurements were performed in three open fixed-point cells of zinc, aluminium, and silver. These measurements were carried out in different vertical three-zone furnaces or furnaces equipped with a sodium heat pipe (each fixed point was placed in its own furnace which was optimized for each individual cell). The procedures used were identical to those of a normal fixed-point calibration providing a high level of precision and reproducibility with low uncertainty. The initial measurements were performed in all the fixed-point cells using the Au/Pt thermocouples equipped with the quartz glass insulation tubes. Subsequently, the inner quartz glass insulation tubes of both thermocouples Au/Pt 12-01 and Au/Pt 13-03 were replaced with pure aluminium oxide tubes (Al₂O₃, 99.7 %), annealed to remove any possible cold-work and then re-measured at all fixed points.

3. RESULTS

The homogeneity measurements of the two thermocouples Au/Pt 12-01 and Au/Pt 13-03 which were performed in the salt bath at 300 °C exhibited only negligible differences between the initial scans and the scans performed after experiments. These emf differences of the scans along the measured length of the thermocouples were smaller than 0.1 μ V and 0.5 μ V for Au/Pt 13-03 and Au/Pt 12-01, respectively. This indicates that the thermocouples within the region on which the homogeneity scan was performed, were not exposed to any chemical contamination, mechanical strain or any other influence that could affect their Seebeck coefficient.

The maximum emf deviations found as results of the homogeneity scanning at the freezing point of silver over the length of 12 cm were 1.8 μ V for Au/Pt 13-03 and 2.6 μ V for

Au/Pt 12-01. The repeated measurements before and after the position testing have shown only small differences from the initial values in the order of $0.5 \mu\text{V}$ for Au/Pt 12-01 and $0.6 \mu\text{V}$ for Au/Pt13-03.

The comparison of fixed-point measurements done by the thermocouples Au/Pt 12-01, Au/Pt 13-03 with quartz glass (SiO_2) and aluminium oxide (Al_2O_3) insulation have shown clear differences in the measured emf. Based on the measured data the generated emf with the use of aluminium oxide insulation was higher through the whole measured temperature range from 419°C to 962°C . The measured values have furthermore shown an increasing difference of emf with temperature with the peak at the fixed point of silver. The maximum measured at Ag point (961.78°C) differences of emf were $6.8 \mu\text{V}$ (0.273°C) for Au/Pt 12-01 and $11.5 \mu\text{V}$ (0.462°C) for Au/Pt 13-03. The detailed results are presented in Table 2.

Table 2. Emfs measured at fixed points when using the Au/Pt thermocouples 12-01 and 13-03 with quartz glass and aluminium oxide insulation tubes.

Thermometer	Au/Pt 12-01			
	emf [μV]		Δ emf [μV]	Δ t [$^\circ\text{C}$]
Fixed point	(Quartz)	(Al_2O_3)		
Ag	16084.9	16091.7	6.8	0.273
Al	9299.3	9300.6	1.3	0.065
Zn	4933.2	4934.0	0.8	0.050
Thermometer	Au/Pt 13-03			
	emf [μV]		Δ emf [μV]	Δ t [$^\circ\text{C}$]
Fixed point	(Quartz)	(Al_2O_3)		
Ag	16101.6	16113.1	11.5	0.462
Al	9312.6	9315.0	2.4	0.119
Zn	4942.6	4943.0	0.4	0.025

4. DISCUSSION

Comparison measurements in fixed-point cells with the thermocouples Au/Pt 12-01 and Au/Pt 13-03 with the quartz glass insulation tubes and replaced aluminium oxide insulation tubes have shown an evident effect on the measured emf. The observed lower emfs, when a quartz glass insulation tube was used, is believed to be caused by a leakage effect. Leakage effects were observed and investigated by Berry and Zang [10]-[15] in HTSPRTs using quartz glass and silica glass insulation. Their findings have shown that this effect occurs in a temperature range from 600°C to 1100°C . Decreasing insulation resistance with increasing temperature is also described in these publications as a possible cause of the disturbance.

To be able to confirm the mechanisms previously described, a relationship between the decreasing resistances with increasing temperature for each individual material needed to be determined. The specific resistivity of quartz glass and aluminium oxide in comparison is shown in Fig.2.

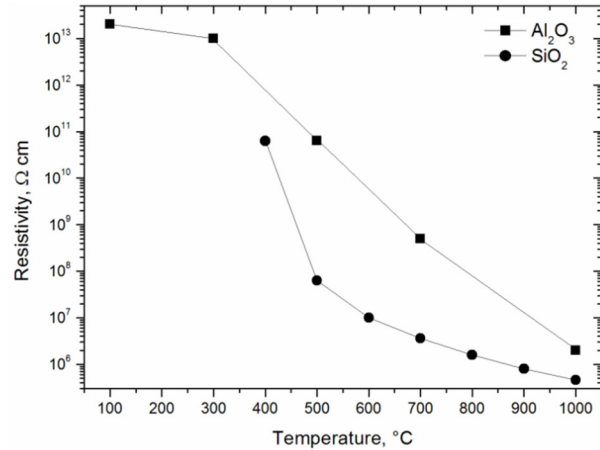


Fig.2. Resistivity of quartz glass (SiO_2) and aluminium oxide (Al_2O_3) at elevated temperatures [16].

As can be seen both of the materials have a different decreasing trend of resistivity with temperature elevation. When compared at the same temperatures it is clear that aluminium oxide (Al_2O_3) has a volume resistance which is several levels of magnitude higher than that of the quartz glass (SiO_2) material. This corresponds with our previous findings and the assumption that the insulation material resistance change influences the measurements with Au/Pt thermocouples.

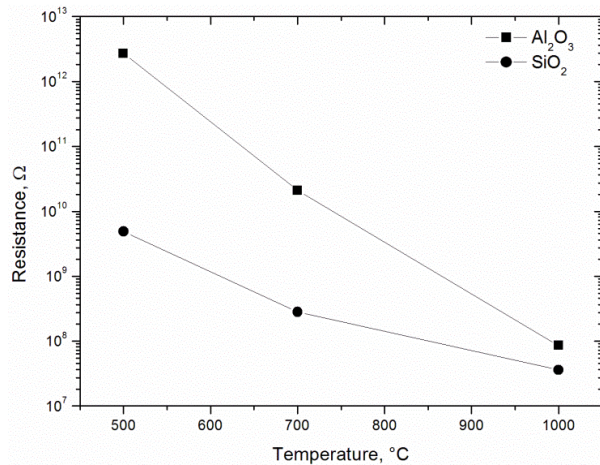


Fig.3. Resistance of a 1 cm long insulation tube segment the quartz glass (SiO_2) and aluminium oxide (Al_2O_3) in the temperature range from 500°C up to 1000°C .

As the wall thickness of the insulation material influences the resulting final resistance and the thickness differed with the use of quartz glass and aluminium oxide tubes, it was necessary to take into account this parameter as well.

The resulting resistance for a 1 cm segment of quartz glass and aluminium oxide for the temperature range from 500°C up to 1000°C can be found in Fig.3. This graph shows that even after taking into account the different wall thicknesses, the aluminium oxide insulation tube maintains its higher resistance at a value of $8.5 \times 10^7 \Omega$ at 1000°C in comparison

to quartz glass which only has a resistance of $3.6 \times 10^7 \Omega$ at the same temperature.

Based on these findings there is a strong indication that quartz glass suffers from a reduction of insulation resistance at higher temperatures, and an interaction between the thermoelements becomes possible.

5. CONCLUSION

The investigation of the Au/Pt thermocouples which were made by using solely quartz glass as an insulation material exhibited considerable deficiencies when used at temperatures higher than about 660 °C. This unsatisfying performance is suspected to be caused by the reduced insulation resistance of the single thin walled quartz glass tubes used. If it were possible to use quartz glass tubes with thicker walls resulting in higher insulation resistance, the benefit of the unhindered movement of the thermoelements in the smooth quartz glass holes might compensate the effects of the reduced insulation resistance found in this work.

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