HIGH TEMPERATURE PLATINUM RESISTANCE THERMOMETERS, THEIR HISTORY AND CURRENT DEVELOPMENTS

ABSTRACT

Many early High temperature Standard Resistance Thermometers (HTSPRT's) suffered from contamination without the manufacturers understanding the mechanisms affecting the HTSPRT.

Gradually the various effects were discovered and the results published.

Using this information it is possible to design HTSPRT's which eliminate the negative aspects of the original designs and to progress onto a design that works to milliKelvin stabilities up to 1100°C.

This paper describes the resulting thermometers and the performance of same, concluding that the original expectations of ITS-90 have now been achieved.

INTRODUCTION

In preparation for the ITS-90 many National Laboratories designed Platinum Resistance Thermometers that would work to the Gold Point of 1064°C. Thermometers failed to perform to the expected stabilities and so the ITS-90 reduced the upper temperature of contact thermometry to the Silver Point (961.78°C) [1].

The first producers included Rosemount, John Evans (NBS), the Chinese, the Japanese, Maurice Chattle (of NPL), Dr. Nubbermeyer (PTB) [2, 3, 4, 5, 6].

The ITS-90 objective was to change from thermocouples to HTSPRT's. This would reduce the uncertainties from Antomony (630°C) to Silver (962°C) from ±0.3°C to ±0.03°C.

As HTSPRT's became more popular researchers began to discover limitations to HTSPRT design and materials.

A number of scientists noted that metallic ions could pass through the quartz glass sheath surrounding the winding and contaminate the platinum in a matter of minutes at 1000°C.

Dr Marcarino of IMGC performed a carefully controlled series of tests to show the effect. He tried a number of different materials to prevent the ion migration eventually finding a fine grained silicon carbide as the best material to stop ion penetration [7, 8, 9, 10].

Dr J R Berry of NRCC had done a considerable amount of research into the semi conductive effects in quartz glass at high temperature and had found a solution by biasing the thermometer above 7V DC [11, 12, 13].

Dr. Marcarino showed that moisture could migrate through the quartz sheath at high temperature.

John Ancsin of NRCC reported that platinum can form a eutectic with silicon with a eutectic temperature of 830°C [14].

The combined effects noted above explained why thermometers had limitation at high temperatures.

BACKGROUND

As early as 1962 Nakaya et al [15] described a 0.1ohm R_O HTSPRT for the Copper Point (1084.62°C) (CCT 6th Session P57).

A.D. McLachlin [16] used 3 such thermometers to evaluate the Copper Point. Reported in 1972 he claimed uncertainties of ±0.005°C. The thermometers had alumina sheaths.

Alumina has a tempco of 9ppm/°C against quartz whose tempco is 0.5ppm/°C, and so quartz will withstand thermal shocks better than alumina.

Most researchers therefore chose quartz for the sheath material and persisted with it during the 1980's, 90's and into the 2000's. As researchers revealed the limitations of quartz as a sheath material and its ease of contamination at high temperature, solutions were sought [17, 18, 19].

The semi conductor industry used furnaces made of quartz and to prevent contamination, a producer, Thermal Syndicate Ltd had patented the idea of positively biasing the furnace. This was found to repel the offending metallic ions.

Biasing as Berry had noted also increased the impedance of the glass at high temperature.

Also after a few hundred hours at the Silver Point moisture condensed inside the sheath.

To summarise, some kind of mechanical and electrical barrier was required between the environment and the platinum winding of the HTSPRT and some means of drying the inside of the thermometer.

<u>Some methods that prevent moisture build up and contamination in HTSPRT's</u>

1. A silicon carbide pocket or platinum sheath over the quartz sheath acts as a barrier to metallic ions.
2. An air flux around the outside of the sheath oxides the ions and renders them harmless.
3. A positive voltage of 7V DC or more repels ions and increases the resistance of the quartz.
4. Ventilation of the HTSPRT enables moisture to be removed and oxygen to be introduced.

AN EXAMPLE OF A HTSPRT IN QUARTZ SHEATH TO THE SILVER POINT (961.78°C)

Taking note of the insight, and understanding available it is possible to produce a HTSPRT that will work up to the Silver Point in a quartz sheath with quartz mandrel.

Its features are:-

1. It is aspirated – a valve in the handle allows the thermometer to breathe out at high temperatures, breath in as it cools and to be sealed before it is cooled below the dew point where moisture will condense. This ensures there is always enough oxygen around the platinum measuring coil and that any excess moisture can escape.

2. It is biased to +9V. This rejects the ions and increases the resistance of the quartz glass.

3. When pre-warming or annealing a flux of pre-warmed air surrounds the thermometer to oxidise any ions coming from the annealing/prewarming furnace.

RESULTS AT THE SILVER POINT

To evaluate this design 5 such thermometers were calibrated from the silver point to the water triple point.

Each thermometer was calibrated a minimum of 3 times at each fixed point in descending temperatures. W values were calculated and a table generated for each thermometer showing the maximum and minimum deviation from the mean.

The table shows the thermometers are extremely stable with no signs of contamination. Each calibration took around 3 weeks. Maximum deviation around 1mK.

Serial No.	**026AA**	**027**	**029**	**036**	**038**	**Mean**	**ø** $\sqrt{14}$
Ag							
Min	-1.73	-0.96	-0.84	-0.913	-0.09	**-0.9**	**-0.24**
Max	+0.94	+1.02	+1.09	+2.0	+0.09	**+1.0**	**+0.27**
Al							
Min	-0.31	-0.35	-1.0	-0.23	-0.22	**0.42**	**-0.11**
Max	+0.24	+0.26	+0.61	+0.41	+0.22	**0.35**	**+0.1**
Zn							
Min	-0.33	-0.15	-0.1	-0.25	-0.34	**0.23**	**-0.06**
Max	+0.22	+0.11	+0.16	+0.16	+0.31	**0.2**	**+0.05**
Sn							
Min	-0.09	-0.13	-0.07	-0.27	-0.13	**0.14**	**-0.04**
Max	+0.17	+0.07	+0.12	+0.17	+0.13	**0.13**	**+0.04**
Ga							
Min	-0.025	-0.15	-0.009	-0.134	-0.134	**-0.063**	**0.02**
Max	+0.025	+0.15	+0.009	+0.134	+0.134	**+0.063**	**0.02**
H_2O							
Min	-0.55	-0.43	-0.36	-0.24	-0.16	**-0.348**	**-0.09**
Max	+1.0	+0.30	+0.48	+0.35	+0.24	**+0.47**	**+0.13**

Reproducibility of 5 thermometers W values at;

Ag	±0.25mK
Al	±0.1mK
Zn	±0.06mK
Sn	±0.04mK
Ga	±0.02mK
WTP	±0.13mk

EXTENDING THE RANGE TO 1100°C

There are some real issues in taking quartz to 1100°C. Its softening temperature is 1050°C and its insulation resistance is dropping rapidly. John Ancsin suggests that the quartz support for the platinum winding forms a eutectic at 830°C.

Replacing the sheath with alumina and the support mandrel with synthetic sapphire seem obvious changes, whilst keeping the bias and aspiration features from the quartz thermometer research.

Alumina can be slightly porous and so the air inside the thermometer is at a few mb above ambient pressure ensuring any leakage is outwards, and that the winding is in a oxygen-rich atmosphere.

RESULTS AT THE COPPER POINT

The design was tested without any prior annealing. After about 400 hours cycling to the Copper Point the thermometer had become very stable [20, 21, 22, 23].

This is illustrated by the changes in R_{TPW}, W_{ga}, R_{Cu} and W_{Cu}.

THE GRAPHS

Four graphs are presented:

The First Plots R_{TPW}
Second Plot W_{ga}
Third Plot R_{Cu}
Fourth Plot W_{Cu}

They can be considered in 3 parts. The first part comprises the measurements made during the first 3 months of 2010[+]. The second parts are measurements made in April/May 2011. The third part comprises measurements made in October 2011.

[+]See "A New Thermometer for the Copper Point" Tempmeko 2010.

GRAPH 1 R_{TPW}

R_{TPW} remains the same throughout the complete investigation with the exception of the strange dip in R_{TPW} (accompanied by an exceptionally high W_{ga}. Measurements repeated but after annealing the thermometer reverted to its original values). Oxygen in Cu is known to depress the transition temperature (5mK per 1ppm). During testing the Cu Cell was exposed to 1100°C for 100 hours under vacuum to remove any oxygen. This made no difference to the copper cell's temperature (less then 1mK). R_{TPW} was stable to two mK.

GRAPH 2 W_{GA}

Excepting the strange result, W_{ga} increases 2 to 3mK and then stabilises to better than 0.5mK.

Combined with graph 1 these results show an exceptionally stable thermometer with no signs of contamination after 800 hours of temperatures from 1084 to 1100°C – contamination would show as an increase in R_{TPW} and a drop in W_{ga}.

GRAPH 3 R_{CU}

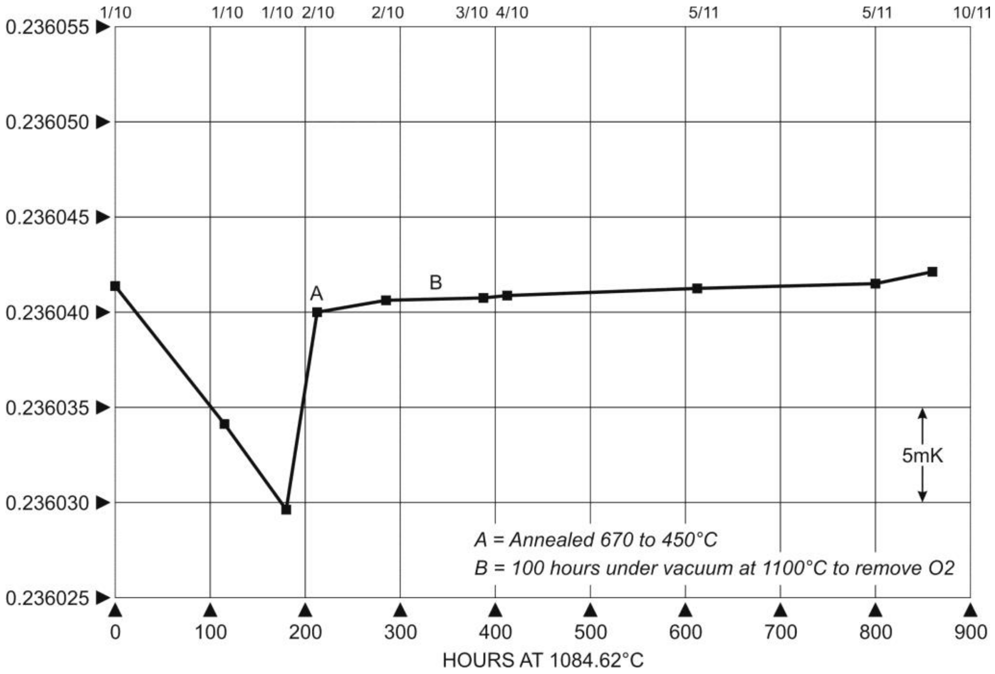
Unlike RTPW and W_{ga} R_{Cu} drops some 80mK during its first 100 hours at 1085°C, then drifts downwards slowly by a further 20mK for the 300 hours of the 2010 testing.

Examining the results showed the shifts occurred during the time the thermometer was removed for cold rodding, and so the 2011 melts and freezes were done by adjusting the furnace temperature rather than cold shocking the thermometer. During the 400 hours testing in 2011 the R_{Cu} remained stable within 3mK.

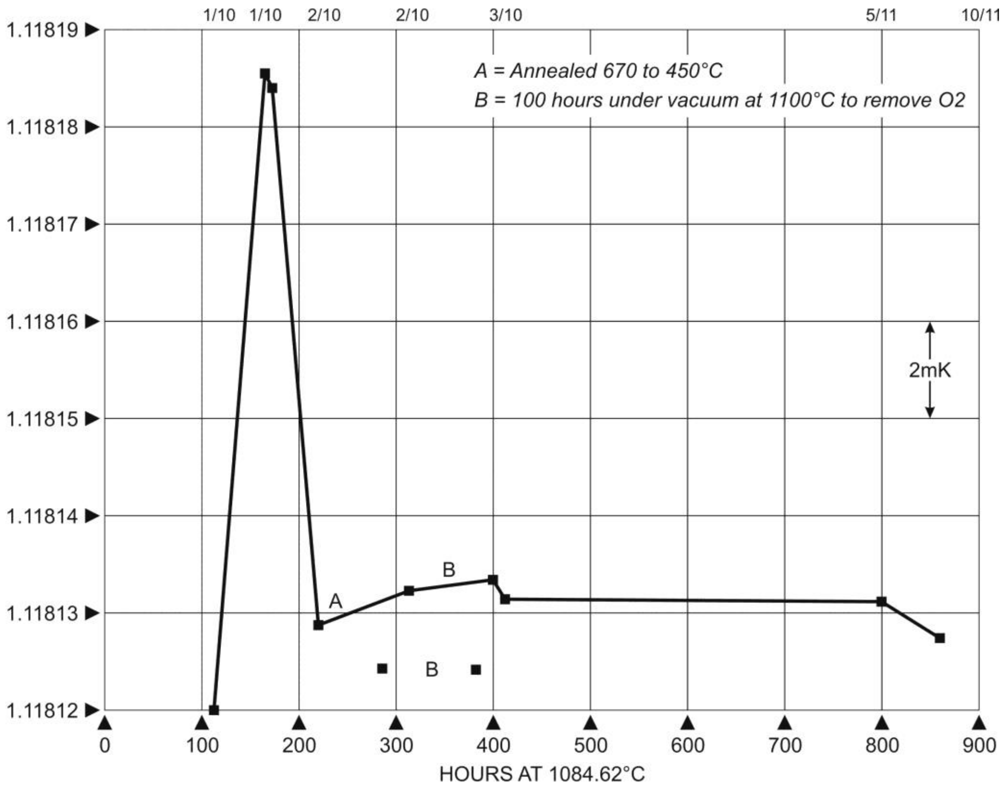
GRAPH 4 W_{CU}

As could be predicted W_{Cu} came down in sympathy with R_{Cu} and stabilised with R_{Cu} during the 2011 testing.

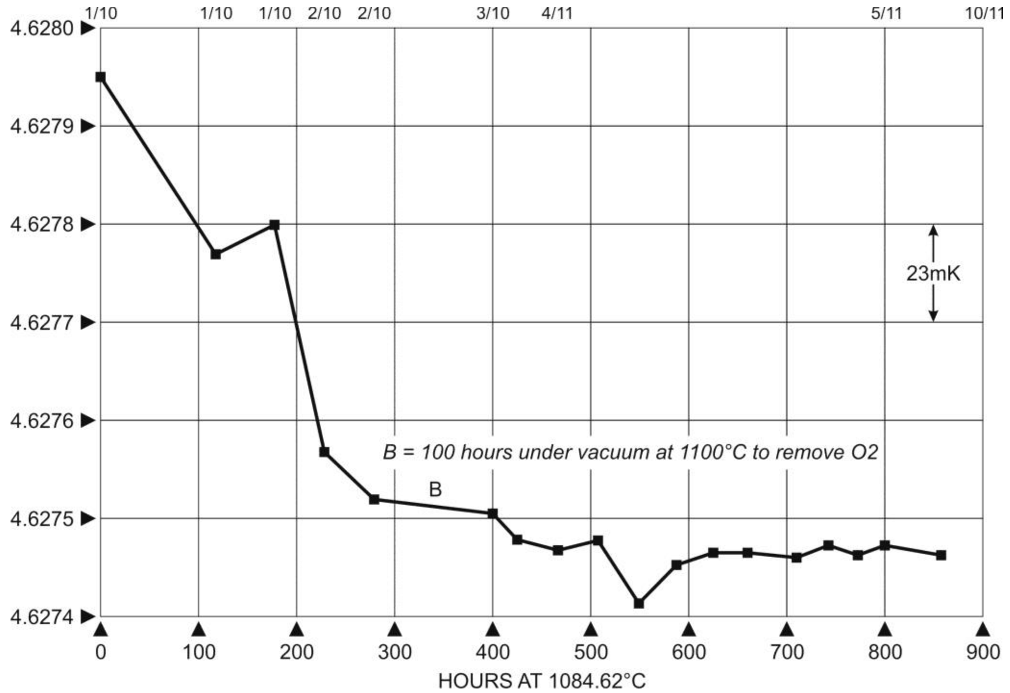
Changes in R_{TPW} 108462/S/002



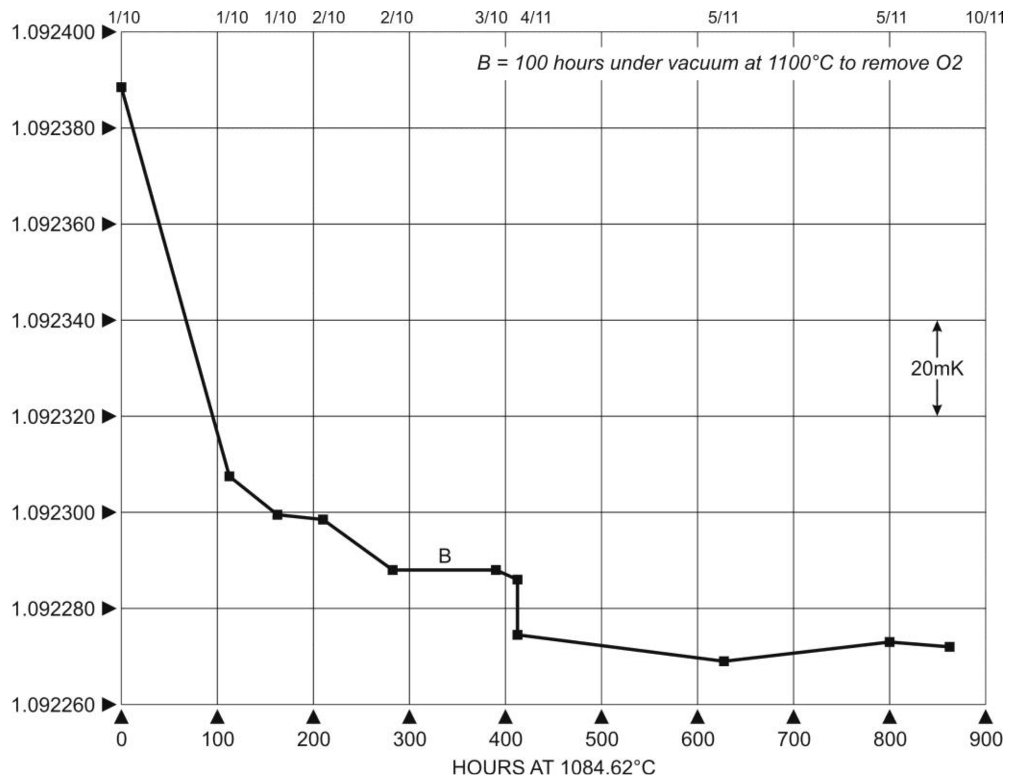
Changes in W_{ga} 108462/S/002



W_{Cu} 108462/S/002



R_{Cu} ohms 108462/S/002



DISCUSSION

Since the 1960's SPRT's have been available for use up to the Copper Point with very small uncertainties.

The decision made by researchers to pursue thermometers in quartz rather than alumina sheaths was, with hindsight probably a mistake because the porous nature of quartz was not understood.

Once the problems were discovered improvements could be made to the design of the quartz sheathed HTSPRT's so that they can function without contamination or drift up to the silver point.

The properties of quartz – its softness and low resistance, make alumina and synthetic sapphire more appropriate solutions above the silver point; however precautions are still required to protect the winding from contamination.

Once these are in place and after 4 to 500 hours of stabilisation, thermometers can be produced that remain stable within 2 to 3mK at temperatures up to 1100°C.

CONCLUSION

Since the 1960's Scientists have gained more and more insights into the design and properties of HTSPRT's. Using these findings designs incorporating them have provided thermometers which function reliably and without contamination to 1100°C fulfilling the expectations of the ITS-90.

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