Innovations in Thermal Metrology Improvements at the Copper Point

Isothermal Technology Ltd, UK (Isotech)

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Three Copper Cells, 3 New Thermometers

- One Silver, and Three Copper Cells were made and tested in a new and novel desktop apparatus designed specially to melt and freeze Silver and Copper Metal Clad Cells
- To measure the Cells a new design of thermometer was realised. Three such thermometers were used
- The thermometer design is described elsewhere

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Results Summary

- The Silver Cell had a melting range of 3 mK and 50% of the freeze was flat. Melt and freeze were coincident within 50 µK
- Copper Cell 1 was contaminated during the development phase of the project.
- It had a melt range of 18 mK and a freeze range of 6mK

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Results Summary

- Copper Cell 2 had a manufacturer's certificate claiming the purity was 6N9.
- The measured melt range was 9 mK, the 50% freeze was 4 mK

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Results Summary

- Copper Cell 3 was made from copper shot with a comprehensive independent impurity analysis totalling 85ppb. The main impurity was Iron at 63ppb, this will elevate the Cell's temperature by 0.1 mK
- The 80% melt range was 3 mK, the 50% freeze was flat.
- The 3 thermometers were stable within 0.1 mK per hour or better at the Copper Point after 100 hours of stabilisation

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Results Summary

- The first thermometer had a quartz mandrel and was unstable at RWTP.
- The second and third thermometer had mandrels of synthetic sapphire and these were stable at RWTP.
- The third Copper Cell associates to ITS-90 within ±1 mK. The Synthetic Sapphire HTSPRT's are able to follow the melt and freeze curves within a fraction of a mK

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Introduction

- Part One [1] of this sequence described the development of a novel combination of Cell, Apparatus and Immersion Compensation for the ITS-90 Fixed Points of Indium, Tin, Zinc and Aluminium
- It had always been the intention to extend the range to Silver and Copper

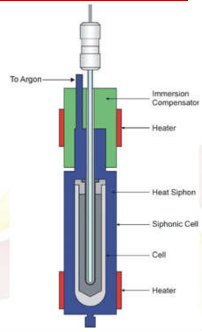
Description

- One objective in extending the range to Silver and Copper is to eliminate the use of quartz glass that traditionally surrounds these cells. The glass is not only fragile and not transportable except by hand, but the glass is porous to ions such as Nickel, Chromium and Iron for example. The glass also softens and deforms especially at the Copper point and easily devitrifies
- Solutions already exist in Radiation Pyrometry for the Copper and Silver points which do not rely on glass
- Pyrometry has to use open cells where the graphite surrounding the metal is exposed so that it can be viewed by optical pyrometers.
- This is achieved by flushing the cell assembly with 6N0 pure Argon. The cell assembly is supported at these temperatures inside a sodium isothermal liner. A typical copper point furnace is illustrated in Supplementary Information for ITS-90[2]
- In pyrometry the cells are horizontal, whereas in Contact Thermometry the cells are mounted vertically

Construction of the Siphonic Cell

- The cell was housed in a heat syphon in the shape of a dewar, with extended inner tube as shown in Figure 1. A removable lid with re-entrant tube and Argon supply tube was fitted above the cell.
- A heated metal collar was used to compensate for the stem conduction of the test thermometer.
- 6N0 grade Argon was used to blanket the cell with a flow of 0.2l/m.
- Argon is heavier than air and so quickly displaces the air in the cell.
- To measure the temperature at the Silver and Copper point a new thermometer was designed and used.
- The new thermometer differs from existing models in a number of novel ways.
- Described elsewhere, it has an alumina rather than a quartz sheath to provide rigidity at these high temperatures.
- Readings were made using a microK 100 with an external Tinsley 1 ohm resistor held at 20°C.

Siphonic Cell & Immersion Compensator



Results at Silver Point 961.78C

- The apparatus was built and a series of melts and freezes performed on the cell
- A typical Silver melt and freeze are shown in Figures 2 & 3.
- The three hour melt had an 80% slope of 3mK whilst the first 50% of the 3 hour freeze was flat
- Melt and freeze were coincident

Figure 2. Silver Cell Melt Curve

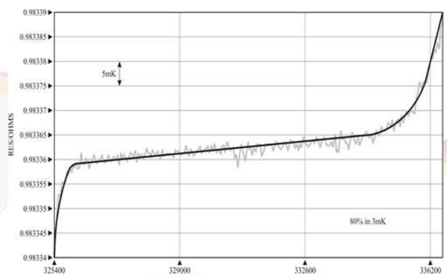
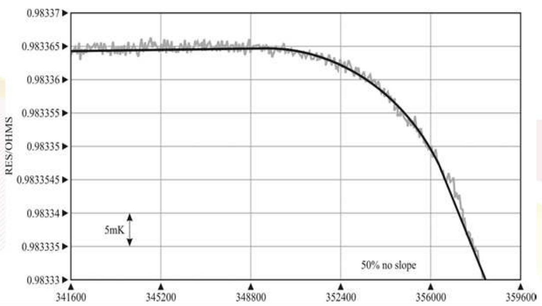


Figure 3. Silver Cell Freeze Curve



Discussion of Results

- The Silver cell was constructed in early June 2009
  - total time at temperature some 200 hours
  - during which it was cycled a number of times through its melt/freeze curves
  - remaining molten around 80 hours of the total test time
- During the whole test sequence the cell was within the metallic heat syphon with 0.2 l/m of 6N0 Argon flux around it
- A small amount of corrosion of the first sacrificial graphite washer was observed

Discussion of Results

- Regarding the performance of the cell its curves remained consistent with other quartz clad cells made with the same lot of silver
- Regarding the model 108462/s thermometer, it remained very stable during the tests including being removed from the cell and reinserted during the cold rod process.
- These results are encouraging, suggest little or no contamination over a 200 hour period of either the cell or its monitor thermometer

Introduction The Copper Point 1084.62C

To assess the quality of a copper cell. Firstly its purity is important.

Cells 1 & 2 in this report had a manufacturer's certificate indicating impurities of Iron of 0.1 ppm.

Cell 3 was made from shot having a much more comprehensive analysis from an independent laboratory. These impurities totalled 85ppb.

Next a series of melts and freezes were performed on the Cell, monitored by stable thermometers, the melts and freezes were plotted and then analysed.

The three Copper Cells described in this sequence of tests were housed in a metallic cladding and so the melts and freezes were analysed to see if the Copper was becoming contaminated - contamination shows as an increased melt and freeze slope.

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Introduction The Copper Point 1084.62C

During the testing of the Copper Cells, three thermometers, developed for this project were used. The first had a quartz mandrel supporting the winding. The second and third have a synthetic sapphire mandrel

Oxygen is reported as being a problem with Copper. 1ppm of oxygen can depress the Copper's temperature by 5mK

At the end of testing Cell 2, it was taken to 1100°C for 24 hours under vacuum

The change in its measured temperature was less than 1mK

Copper Cell No. 1

This development Cell was made in March 2009 and was tested using a Type R Thermocouple. The apparatus was developed and improved and the first of a new range of thermometers was developed. It had a quartz mandrel and an alumina sheath. In November a +9V charge was added to the thermometer. The rest of the measuring system was a microK 400 and internal Vishay 1 ohm resistor.

Results:-

April: ±15mK on melts R T/C.

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Table 1 & 2 Melts & Freezes of Copper Cell 1

Table 1					
Copper Cell 1			108462/001 Thermometer with a quartz mandrel		
October 14	20 Hr	M, 80%	5mK	1.061,555Ω	
October 15	12 Hr	F, 50%	8mK	1.061,545Ω	
October 16	2 Hr	M, 80%	15mK	1.061,527Ω	
October 17	6 Hr	F, 50%	0	1.061,521Ω	
October 18	10 Hr	M, 80%	20mK	1.061,525Ω	
Mean Melt = 17mK, Mean Freeze = 4mK, Drift 30mK					

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Table 1 & 2 Melts & Freezes of Copper Cell 1

Table 2

November 9	3 Hr	M, 80%	20mK	1.061,520Ω
November 10	22 Hr	F, 50%	10mK	1.061,525Ω +9V
November 11	9 Hr	M, 80%	16mK	1.061,540Ω +9V
November 12	21 Hr	F, 50%	5mK	1.061,525Ω +9V
November 13	3 Hr	M, 80%	20mK	1.061,535Ω +9V
November 14	21 Hr	F, 50%	10mK	1.061,525Ω +9V

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Summary of results for Copper Cell 1

Summary of Copper 1 results

Mean Melt = 19mK Mean Freeze = 8mK Drift = 5mK

Means of all measurements on Cu 1

80% Melt = 18mK 50% Freeze = 5mK

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Copper Cell 2

Of the same purity copper as Cell 1, Cell 2 was made early in December 2009.

First measurements were made with the same measuring system as Cell 1.

At the end of December 2009 a new thermometer with synthetic Sapphire coil support became available. The microK 400 was replaced by a microK 100 and a Temperature Controlled 1Ω Tinsley AC/DC resistor.

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Copper Cell 2

Results: - microK 400, Int. Vishay 1Ω, 108462/001 +9V

Table 3 Melts & Freeze of Copper Cell 2				
December 10	3 ½ Hr	M, 80%	10mK	1.061,562Ω
December 11	4 Hr	F, 50%	5mK	1.061,560Ω
December 12	17 Hr	M, 80%	10mK	1.061,560Ω
December 13	3 Hr	F, 50%	5mK	1.061,560Ω
Mean Melt = 10mK Mean Freeze = 5mK Drift = 2mK				

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Copper Cell 2

Tables 4 Melts and Freezes of Copper Cell 2.					
Instrument Upgrade:- microK 100 ext Tinsley 1Ω new sapphire Thermometer 108462/S/002					
December	30	3 Hr	M, 80%	5mK	1.092,387Ω
January	1	9 Hr	F, 50%	5mK	1.092,362Ω
January	2	4 Hr	M, 80%	15mK	1.092,350Ω
January	3	8 Hr	F, 50%	0	1.092,308Ω
Mean Melt = 10mK Mean Freeze = 3mK Drift = 80mK					

Copper Cell 2

Table 5

January	8	1 Hr	M, 80%	7mK	1.092,310Ω
January	8	4 Hr	F, 50%	3mK	1.092,302Ω
January	9	2 Hr	M, 80%	8mK	1.092,300Ω
January	10	3 Hr	F, 50%	4mK	1.092,299Ω
Mean Melt = 8mK Mean Freeze = 4mK Drift = 11mK					

Copper Cell 2

Tables 6 & 7 Melts & Freezes Copper Cell 2					
January	30	3 Hr	M, 80%	8mK	1.092,298Ω
January	31	6 Hr	F, 50%	4mK	1.092,294Ω
February	2	8 Hr	M, 80%	10mK	1.092,293Ω
February	3	8 Hr	F, 50%	5mK	1.092,287Ω
February	6	4 Hr*	M,80%	8mK	1.092,287Ω
February	7	4 Hr*	F, 50%	Failed	1.092,283Ω

* After 24 hours at 1100°C under vacuum

Summary of Copper Cell 2

Summary of Copper 2

Mean Melt = 9mK Mean Freeze = 5mK Drift = 10mK

Mean of all measurements on Cu2

80% Melt = 9mK 50% Freeze = 4mK

Copper Cell 3

This cell constructed in February 2010 was made from 7N pure Copper

The first measurement was made with the first Synthetic Sapphire thermometer whilst the last sequence was performed with a second Synthetic Sapphire thermometer

Copper Cell 3

Tables 8 & 9 Melts & Freeze Copper Cell 3					
Thermometer 108462/S/002					
February	23	1 Hr	F, 50%	0mK	1.092,287Ω
February	24	5 Hr	M, 80%	3mK	1.092,285 Ω
February	25	4 Hr	F, 50%	0mK	1.092,280 Ω
New thermometer 108462/S/001					
February	27	2 Hr	F, 50%	0mK	1.099,557Ω
February	28	2½ Hr	M, 80%	3mK	1.099,553 Ω
Mean Melt = 3mK Mean Freeze = 0mK					

Figure 4 Copper Isotower Melt Plateau 24th February 2010

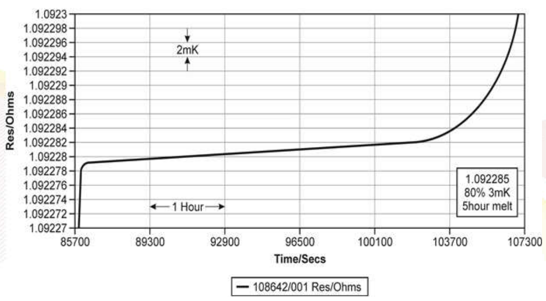


Figure 5 Copper Isotower Freeze Plateau 25th February 2010

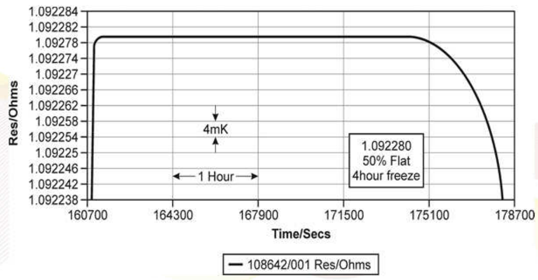


Table 10 Summary of results for Copper Cells 1, 2 & 3 plus the Silver Cell

Table 10 Means Of All Measurements		
Cu	**80% Melt**	**50% Freeze**
Cell 1	**18mK**	**6mK**
Cell 2	**9mK**	**4.2mK**
Cell 3	**3mK**	**0mK**

Silver Cell	**3mK**	**0mK**

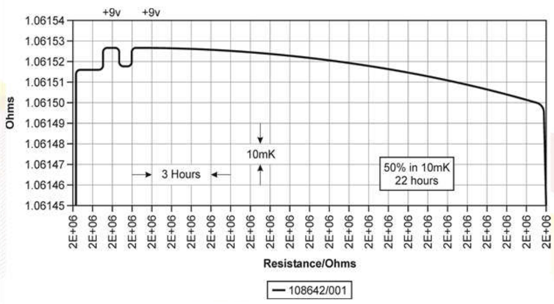
Figure 6 Copper 10th October 2009 showing effect of Electrical Bias

On the freeze dated 10th October 2009 a +9V dc bias was added to the thermometer with quartz mandrel, its resistance increased by the equivalent of 7mK

The battery was disconnected then permanently connected.

The Sapphire reduced the offset to 2mK

Figure 6 Copper 10th October 2009 showing effect of Electrical Bias



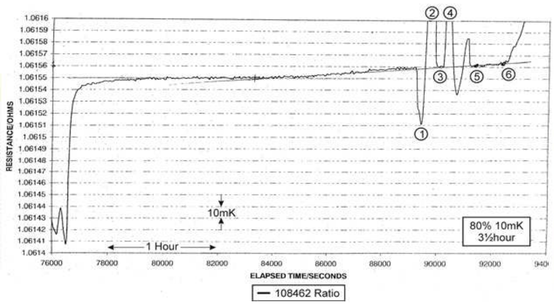
Immersion

On the melt dated 10th December 2009 the heated block above the cell is being optimized

The monitor is raised 100mm (1) and the temperature drops

The blocks temperature is raised (2) the monitor is re-inserted (3) and raised again 100mm (4) the heated block is adjusted until there is no gradient over the 100mm (5) the monitor is reinserted and the melt is completed(6)

Figure 7 Copper 10th December 2009 showing Immersion Compensation



Discussion

Three Copper Cells of increasing purity have been evaluated using 3 thermometers designed specifically for this project.

Thermometer drift after the initial 100 hours of use settled to less than 0.1mk per hour enabling accurate melts and freezes to be plotted and analysed.

No trace of oxygen was found in the Cells.

Cells 2 & 3 had similar temperatures with Cell 3 perhaps 2mK higher in temperature than Cell 2.

The purity (7N) and melt/freeze slopes (3mK & 0mK) suggest that Cell 3 is within 1mK of its ITS-90 temperature. (See graphs dated 24th February and 25th February 2010).

No reduction in purity of the Copper Cells was noted during testing.

Conclusion

A Copper Cell and Apparatus with association of 1mK to the ITS-90 value has been produced. Using a new design of thermometer the Cells performance can be measured to within 1mK per 10 hours or better

My laboratory has a reference standard that can be used to certify other Copper Cells of our manufacture

Future Work

To work within UKAS we are required to intercompare our cell with a National Standard. At present this will add 30mK to our uncertainties

We need to find a National Laboratory interested in reducing its uncertainties with purer Copper and better thermometers

References

[1] Improvemnets Relating to the Calibration of Thermometers, John P. Tavener, NCSLi 2009.

[2] Supplementary Information for the ITS-90, page 67, ISBN 92-822-2111-3