Reproducible Metal-Carbon Eutectic Fixed-Points

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Abstract. The potential reproducibility of high-temperature metal-carbon fixed-points has been investigated. Crucibles and metals from NPL were used to construct fixed-points using NMIJ facilities. Agreement at 2700 K was better than the 80 mK uncertainty. Appropriate construction should permit this level of reproducibility between cells made at different National Measurement Institutes.

Introduction

High-temperature fixed-points would provide reference standards for radiance and temperature scales. The needs for radiance are primarily highest temperature to provide stable UV output; while temperature metrology would benefit from additional fixed-points from the freezing temperature of gold (1337 K) upward. Fixed-points based on metal-carbon (or metal-carbide carbon) eutectic alloys have been shown to give a range of repeatable transition temperatures from about 1426 K to above 3300 K.

A key requirement for reference use is demonstrated good reproducibility, i.e. agreement between sources constructed at different institutes. So far there has been limited success in achieving the suggested 100 mK at 2300 K [1] between clearly independent sources.

In 2004 a comparison was carried out at PTB of fixed-points constructed by BNM-INM, NMIJ and NPL [2]. While the results were approaching the required reproducibility there were clear differences between the sources from different institutes. In particular the cells of NMIJ had longer melts, better defined plateaus, and were more repeatable. They also consistently gave the highest radiance temperature for the melt temperature, as defined by the point of inflexion in the melt curve.

There are scenarios in which specific impurities raise the melt temperature or modify grain structure in a way that would explain the differences. However it is unlikely this would show a consistent trend. It is more likely that the NMIJ cells were better than those of NPL. This could be due to impurities or poor ingot formation. It was suspected that the NPL cells were being contaminated during construction.

To check for this NPL took crucibles and metals to NMIJ to construct fixed-points. This would show the level of agreement that should be possible given suitable filling facilities when using different design crucibles and materials from different suppliers. Differences to the results given in [2] would show effects due to the method of fixed-point manufacture.

Filling of Fixed-Points

NPL uses the same furnace (blackbody) to make and evaluate fixed-points and to perform radiation thermometer calibrations. It works horizontally which complicates cell construction and hinders visual monitoring of the ingot quality. Before making a fixed-point the furnace is heated to about 100 °C above the temperature of use as the empty crucible is baked for 15-30 minutes in argon. Other than this no purification steps are taken. Furnace tubes as supplied are purified (<5 ppm ash content) but are replaced as they wear out rather than between different fixed-point materials. The NPL crucibles are made at the NPL graphite workshop. To reduce risk of contamination where possible ceramic tools are used.

The NMIJ facilities include a furnace solely for filling fixed-points. The crucibles are post-purified after manufacture. Cells are filled vertically which simplifies the operation. The furnace itself is first baked, then used to bake the empty crucible and then used to make the fixed point. The furnace can be evacuated while baking to improve purification.

Filling of fixed-points is carried out separately from any other operations, and care is taken to avoid cross-contamination between different materials. Disposable items are used where possible and all items are cleaned with ethanol. Plastic wrap is used to avoid contact with any surface.

To make the cells metal and graphite powders are weighed out and mixed at approximately half eutectic composition. Material is added to the crucible in an argon filled glove-bag, and each filling melt is carried out under argon, after pumping and backfilling the furnace two times. Once the crucible is considered sufficiently full the crucible end cap is screwed into place and the fixed-point is complete.

For this study NPL supplied materials were used to make cells of; rhenium (99.999 % nominal purity) in an NPL Ringsdorff graphite crucible (R1), cobalt (99.998 %) in an NMIJ Toyo Tanso crucible (C1), cobalt in an NPL Poco crucible (C2), cobalt in an NPL Ringsdorff crucible (C3) and platinum (99.999 %) in an NMIJ Toyo Tanso crucible (P1).

These fixed-points were then compared to NMIJ cells previously prepared with the same facilities, and used in the comparison at PTB [2].

Realisation of Fixed-Points

Measurements were made in two furnaces. The larger Nagano M (VR10-A23) able to reach 2500 °C and smaller Nagano S (VR10-A20) limited to 2000 °C have very similar temperature distribution [2]. The radiance temperature of a melt was determined using an IKE LP3 radiation thermometer with a wavelength of about 650 nm.

NPL and NMIJ Re cells were measured in the M furnace alternating daily. Co and Pt cells were measured side-by-side in the M and S furnace, then exchanged. The following uncertainty contributions were considered; the stability of the LP3 during one days measurements and over the course of the comparison, the repeatability of the interval measurements, the repeatability of the fixed-point measurements.

The size-of-source correction was assumed to be the same for both fixed-points. No account was taken of differences due to the different lengths of the cells. Any difference in emissivity was assumed to be negligible.

Results

Figure 1 shows typical melt curves for the two Re cells. The difference between the NMIJ and NPL cells was found to be 25 mK with uncertainty 80 mK (*k*=2).

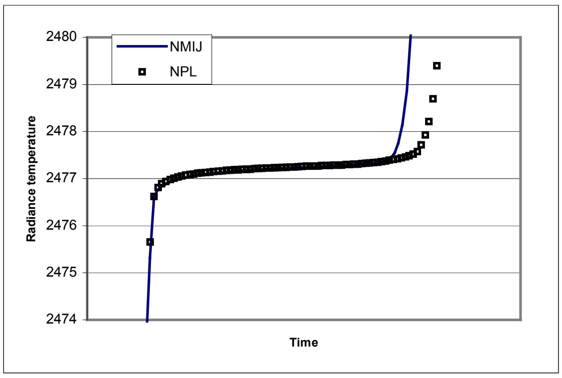

Fig 1. Typical melt curves for NMIJ and NPL Re fixed-points.

Three of the four cobalt cells agreed within ±15 mK of each other. The cell made from Poco graphite (C2) was found to be significantly lower than the others, over 100mK. There was no indication in the plateau shape or duration to suggest any impurities.

The melt temperature of the NPL Pt cell was 330 mK lower than the NMIJ cell. The NPL melt duration was only about half that of the NMIJ cell although in an identical crucible.

Discussion

The results show that with suitable filling equipment fixed-points can be made with the reproducibility between sources needed to establish M-C fixed-points as reference standards. The fixed-points made at NMIJ are generally much improved over previous NPL cells, better in some cases than the NMIJ standards. If rhenium cells continue to have this level of agreement using readily available material and crucibles of different design and graphite then at least one high-temperature fixed-point will have been established. Even rhenium-carbon on its own could significantly improve temperature scale realisation, and is high enough in temperature to satisfy the need for a stable UV reference source of radiance.

The cobalt measurements emphasize the need for comparison to verify the performance of high temperature fixed-points; there is nothing in the performance of C2 that indicates a problem. It is possible the crucible was contaminated either as the graphite supplied or during manufacture. The platinum result was especially disappointing. It was noted during filling that the ingot had an unusual, mottled appearance not seen before. Subsequent analysis suggested the platinum was not the claimed 99.999 % purity

Of the routes of contamination listed above (poor metal purity, contaminated graphite for crucibles and cross-contamination during filling) there is evidence that NPL has suffered from all three of them. The metal purity issue is not simple. Purity analysis rarely provides the definite answers needed. Graphite on the other hand is readily purified to ash contents of a few ppm. Any machining work to make crucibles should be followed by purification to this level. Cross-contamination is an area where measures can be taken. All items that come in contact with the cell should be considered as potential contaminants. Simple baking of furnace components that have been used to make fixed-points is not enough. Graphite furnace components should be properly purified between uses, or separate parts kept for different materials (or both).

The use of a vertical furnace makes it much easier to check the ingot quality during filling. It also simplifies handling and cell filling, which makes it less likely that contamination will happen.

Conclusions

There has been a lot of published work on M-C fixed-points, but little convincing evidence of reproducibility. This is at least partly due to the difficulties of measurement at the high temperatures involved. This work suggests that adequate filling arrangements should permit agreement between sources that satisfy the 100 mK at 2300 K requirement of CCT/CCPR. Knowing that sources agree would in turn help in the improvements to furnaces and instrumentation needed to get the full benefit from high temperature reference sources.

References

[1] CCT/96 Recommendation T2, see also T. J. Quinn, "News from the BIPM", Metrologia, Vol.34, pp.187-194, 1997

[2] Anhalt K., Hartmann J., Lowe D., Sadli M., Yamada Y., "A comparison of Co-C, Pd-C, Pt-C, Ru-C and Re-C eutectic fixed-points independently manufactured by 3 different institutes", to be presented at Newrad 2005