Direct Cell Comparison for Evaluation of Impurity Effect in Fixed-Point Realization

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Introduction

Direct cell comparison is one of the recommended methods for evaluating the influence of impurities on the realization of temperature fixed points [1]. It is known as the Estimates based on Representative Comparison (ERC). Compared to the other recommended methods, the ERC seems be the lowest in rating because the method depends strongly on a reference cell. It is required for a reference cell used in an ERC to have an accurate chemical analysis on its ingot. The Sum of Individual Estimates (SIE) or the Overall Maximum Estimates (OME) can be used to correct for the fixed point departure of the reference due to impurities based on the chemical analysis. In an ERC, the departure of fixed point realized in the cell under study (CUS) from that in the reference cell is measured and used to evaluate the impurity effect in the CUT. This scheme may illustrate how low-level in terms of uncertainty the ERC is, since it must cover uncertainties coming from both the chemical and thermal measurements. However, most earlier-cells that may still be acting as national standard in some NMIs were probably made from ingots that have no detailed chemical analysis, and as a consequence the fixed point correction based on the SIE or the OME methodology is not possible. Some of these earlier cells might have comparable with or even better performance than any ingots available nowadays. There is a need, therefore, to evaluate the impurity effect of such cells by means of a non destructive way, namely the direct cell comparison.

Considering the importance of the ERC, we challenge to study on protocol for conducting reliable direct cell comparison. A note on fixed point realization based on different methods, namely inner mantle and outer mantle will precede the direct cell comparison description.

Inner Mantle and Outer Mantle Realization

Study on indium point realization based on different realization techniques was conducted [2]. One is the inner mantle realization method, and the other is the outer mantle realization method. The inner mantle realization method is done by inserting glass rods for a time interval into a melting indium, the (indium furnace) temperature of which has been set constant below the indium freezing point, for initiating solidification. The outer mantle realization is done only by setting the indium furnace temperature in such manner that solidification is initiated. After this the furnace temperature is set constant until the freezing plateau is completed. It is predicted that inner mantle realization, as recommended by the Supplementary Information for the ITS-90 [3], will produce higher temperature than the outer mantle realization will.

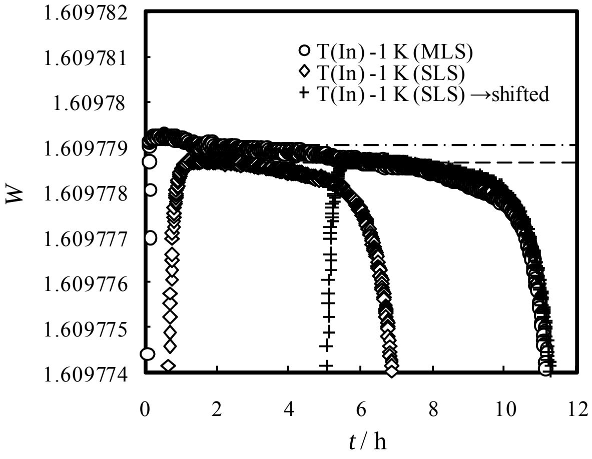

Fig. 1 Freezing curves from SLS and MSL

Figure 1 illustrates the freezing plateaus obtained from inner mantle and outer mantle realizations using the same indium cell with furnace temperature setting 1^{o}C below the predicted indium point. MLS in Fig. 1 refers to the inner mantle realization, while SLS to the outer mantle realization. The temperatures were plotted after recalescence from supercooling. The abscissa is time progressing, while the ordinate the ratio of SPRT resistance to its value at water triple point. In the MSL, temperature fluctuation happens during temperature recalescence, after which the temperature decreases slightly along with the progressing solid mantle. On the other hand, in the SLS method, supecooling takes more time but with relatively less temperature fluctuation. Since the fraction of solid formed by the SLS method is greater than that by the MSL method, the freezing time of the SLS would be shorter, and the peak temperature lower. If the end point of the curve obtained by the SLS is adjusted to that of the

MSL, as shown in Fig. 7 (+ plot), both curves would agree on each other. Difference in the peak temperature between the MSL and SLS methods was 0.1 mK, as represented by the gap between broken line and broken dot line.

Figure 2 (unpublished) represents the relation between the peak temperature and its position in freezing plateau in terms of 1/*F*, where *F* is the liquid fraction. The broken line in Fig. 2 is the slope of the freezing curve, which is the locus of the plateau itself. Data shown in Fig. 2 imply that both the inner and the outer mantle realizations produce peak temperatures that are originally from the 'same plateau'. The difference among them is only be caused by the progressing mantle. It is a fact that making a relatively uniform 'thin' inner mantle having small solid fraction is easier than outer mantle because of a greater radial outer size. When the slope of a freezing curve is identified, temperature at any locus in the plateau can also be identified. This may imply the importance of identifying the locus of measurement point in a plateau, especially for calibration measurement.

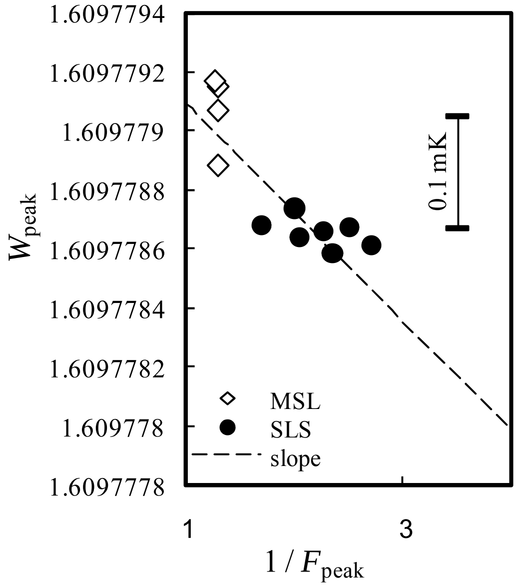

Fig. 2 Peak temperature in SLS and MSL

Direct Cell Comparison

The fact described above may give criteria for a 'fair' international comparison. The current protocol adopted for international comparison aims to compare maximum temperatures that are realized in fixed point cells of participants without caring the locus of that temperature in the related plateau. The protocol usually requires a common technique for initiating solidification. However, since the specification of the participating cells is not always same, the maximum temperatures reported by participants do not also always at the same locus. The difference in this locus is usually accounted for as uncertainty due to choice of location in freezing curve. A reference value taken in such situation does not give the real characteristics, for example the purity level, of all participating cells. It is simply a comparison of realization technique: even highly pure fixed point cell would not always produce high maximum temperature realized.

Our study on cell comparison in relation to the level of purity was started by the work on aluminium [4]. The work is summarized in Fig. 3. Horizontal axes in the figure are for the furnace setting, showing the rate of solidification, $\Delta T_{setting}$, and the locus at freezing curve, 1/*F*. Cell comparisons were done at $\Delta T_{setting}$ = 0.6 K and 1/*F* around 1.33. Lines connecting the value at 1/*F*=1 and 1/*F*=1.33 corresponds to freezing curve. Figure 3 shows that if the locus of cell comparison as well as the slope of freezing curve, at which the cell comparison is done, is known, difference in temperatures at 1/*F*=1 is identical within the uncertainty with the difference in purity level of the cell, identified by the SIE values.

A more detailed study was on tin [5], as represented in Fig. 4. Here, two cells that have significant difference in purity level were compared. The cell comparison, whose locus of measurement point is identified, is compared with the freezing curves obtained by the participating cells (coded Sn No. 4 and Sn No. 6), as well as with the theoretical freezing curves of the cells derived based on the impurity information of their ingots. Direct cell comparisons (○) are plotted at their respective loci by taking temperature in freezing curve of cell Sn No. 4 as the reference. As shown in Fig. 4, the direct cell comparisons are in satisfactory agreement with the measured freezing curves, while the measured freezing curves themselves are in good agreement with the related theoretical ones. Consequently, the direct cell comparisons reflect accurately the difference in the impurity (purity level) of the tin ingots.

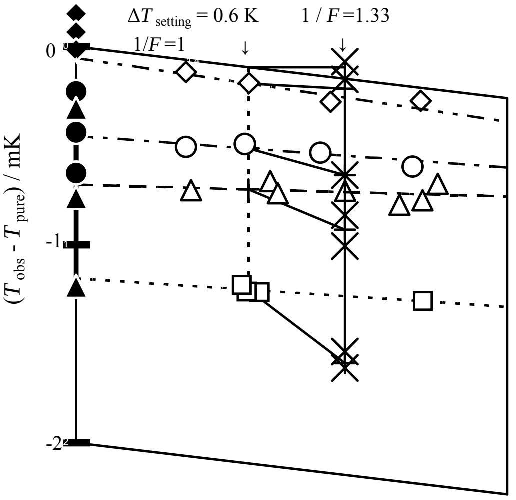

Fig. 3 Three-dimensional representation of relations among SIE, freezing curve and cell comparison: NRLM Al 97-1 (□); Al No. 4 (△ and ▲); Al No. 5 (○ and ●); Al No. 6 (◇and◆), and cell comparison (×)

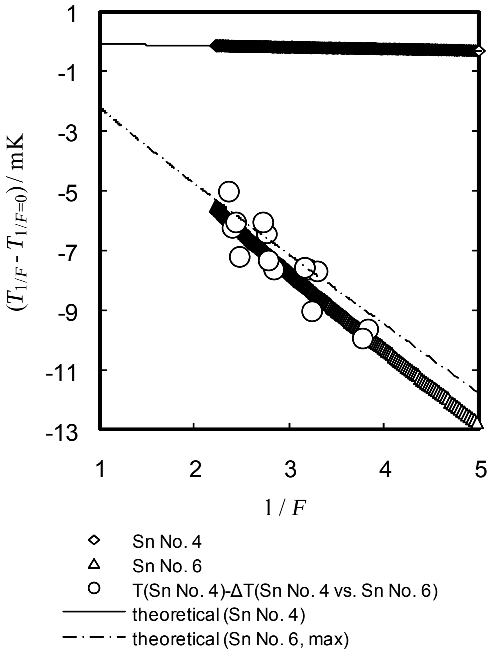

Fig. 4 Freezing curve and direct cell comparison for tin

Discussion

Some facts can be drawn from cell comparison. *First fact* is that cell-to-cell temperature difference changes along with the progressing solidification (increasing 1/*F*), where the rate of change is proportional to the difference in the freezing-curve slope. The greater the difference in the slope, the faster the change is. As a consequence, a cell comparison should define the locus (1/*F* coordinate) at which the measurement is done. Although, due to supercooling, it is not possible to directly measure the cell-to-cell difference at 1/*F*=1, trend of the measured data may lead to the smallest cell difference at 1/*F*=1, where the freezing point is defined. It is worthy, therefore, not to take data only in the vicinity of peak temperature, but in wider range.

Second fact is that cell comparison without knowing the freezing-curve slope of cells under comparison is incomplete, especially in case when one wants to use cell comparison as a measure of impurity effect (ERC). The slope helps correlating the locus of the measured temperatures and gives information about the cell's purity level as well.

Besides the above facts, our further study (to be published soon) shows, as *third fact*, that the cell comparison depends strongly on the combination of measuring SPRT and bridge. Thermal effect on SPRTs during its exchange between cells may be the factor for such this dependency. However, any SPRT–bridge combinations seem approach to same point at 1/*F*=1. This fact gives more emphasis on the necessity of making measurement at wider range, as described above as the *First fact*.

References

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