

A Survey on the Uncertainty in the Realization of ITS-90 Metal Fixed Points Due to Impurities

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Abstract

A survey on the current methods in estimating uncertainties related to the impurity content in the ITS-90 fixed-points has been conducted. The survey covers the thermodynamics of the metal at its fixed-point temperature, the methods of realizing it, the current impurity analysis, and the related uncertainty estimation. Recent study on the $1/F$ analysis for estimating the impurity effect is also reported.

1. Introduction

Temperatures where selected pure metals are in thermodynamic equilibrium while freezing are adopted in the International Temperature Scale of 1990 (ITS-90) as defining fixed points¹⁾. In the high-temperature region of the platinum resistance thermometer range, the defining fixed-points are the freezing points of aluminium (Al, 660.323 °C) and silver (Ag, 961.78 °C), defined as the temperatures where these metals freeze under atmospheric pressure (101.325 kPa). Temperature standards in this temperature range are usually disseminated through a high-temperature standard platinum resistance thermometer (HTSPRT) calibrated against fixed-point cells that are capable of realizing the freezing points of aluminium and silver. The freezing point is realized in the fixed-point cell through the freezing process of a high-purity metal initiated by supercooling. This supercooling is a prelude to nucleation in the saturated liquid metal. The freezing process, during which measurements by means of the HTSPRT are conducted, will appear in the measured signal as a plateau until the liquid metal is completely frozen. Although the ITS-90 assigns the fixed-point temperatures, the temperature scale realized through such a process undoubtedly includes uncertainties due to the imperfectness of the measurement system, consisting of the HTSPRT, the fixed-point cells, the resistance bridge (including standard resistor for resistance measurement) and the pressure gauge. Moreover, at high temperatures the HTSPRT faces serious unresolved problems of leak-

age currents in conjunction with the decrease of the resistance of the insulating quartz tube, and of contamination by the fixed-point metal. It has been reported that the reliability of the fixed-point cells is determined largely by the purity of the metal^{2),3)}; its effect exceeds that of the other uncertainty sources described above.

The uncertainty estimation related to the impurity content of the fixed-point metal is one of the important issues discussed in a Working Group of the Consultative Committee on Thermometry (CCT)⁴⁾, where thermometrists from eight leading national metrology institutes are represented. The uncertainty of typical impurity analyses, the determination of impurities whose effects to the freezing-point depression must be considered or those that can safely be ignored, and the effect of gaseous impurities were reviewed. The overall conclusion was that none of the existing estimation methods can satisfactorily be promoted as the best one.

Concerning the topic of the effect of impurities present in fixed-point metals, this study aims at summarizing the existing methods of analysis, as an effort to define a procedure for estimating the associated uncertainties which should be adequate for a calibration service.

2. Freezing-point Depression

Impurity in any substance will generally decrease the freezing point of the substance. The depression of the freezing point due to impurities is theoretically expressed by eq. (1). x in eq. (1) denotes the total impurity mole fraction, L is the molar enthalpy of fusion, T and R are the temperature and the molar gas constant, respectively. T_{observed} stands for the liquidus temperature of the impure

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substance where an infinitesimal amount of solid has frozen, while T_{pure} stands for that of the pure substance. Equation (1) is often called Raoult's law.

$$T_{\text{observed}} - T_{\text{pure}} = -\frac{xRT^2}{L} = -Ax \quad (1)$$

$A=L/(RT^2)$ is the the so-called first cryoscopic constant. Equation (1) is derived by assuming that all impurities are insoluble in the solid phase, i. e., when the alloy freezes the impurities are rejected into in the liquid phase, and the temperature change during freezing is inversely proportional to the liquid fraction of the metal, F , as given in eq. (2).

$$T_{\text{observed}} - T_{\text{pure}} = -\frac{x}{A} \left(\frac{1}{F}\right) \quad (2)$$

F equals 1 at the liquidus point where the metal starts freezing, and 0 at the solidus point where the metal is completely frozen. The freezing process expressed by eq. (2) will appear as a straight line in $\Delta T - (1/F)$ diagram. Equation (2) is obviously only a simplification of a more complicated real freezing mechanism, where impurities are soluble in the solid phase, and assumes the ideal solution law being valid.

When solid solutions of a metal and its impurities are formed (solid solution - liquid solution system), in most cases, the diffusion in the solid can be neglected⁵⁾. Based on this assumption, three possible freezing processes may occur, as follows⁶⁾.

The *first* possible freezing is when the freezing process is slow enough that a complete equilibrium mixing in the liquid can be assumed. In this case, the freezing process is expressed as eq. (3)⁷⁾.

$$T_{\text{observed}} - T_{\text{pure}} = \sum_i x_i \left(\frac{\partial T}{\partial x_i}\right) \left(\frac{1}{F}\right)^{1-k_{0,i}} \quad (3)$$

$k_{0,i}$ in eq. (3) describes the equilibrium distribution coefficient of impurity component i , which is defined as $k_{0,i} = \frac{c_{s,i}}{c_{l,i}}$, the ratio of the mole fraction concentration of impurity in the solid phase, $c_{s,i}$, against that in the liquid phase, $c_{l,i}$. $\left(\frac{\partial T}{\partial x_i}\right)$ is the slope of the liquidus line in the phase diagram for the binary system consisting of metal + impurity component i . At low concentrations for many systems, the slope of the liquidus line can be expressed by eq. (4)⁸⁾. Substitution of eq. (4) into eq. (3) results in eq. (5).

$$\left(\frac{\partial T}{\partial x_i}\right) = -\frac{(1-k_{0,i})}{A} \quad (4)$$

$$T_{\text{observed}} - T_{\text{pure}} = -\sum_i \frac{x_i}{A} (1-k_{0,i}) \left(\frac{1}{F}\right)^{1-k_{0,i}} \quad (5)$$

Equation (2) can be obtained from eq. (5) by substituting $k_{0,i}=0$. As will be discussed later, equations (1) to (5) are often applied in thermometry as a means to estimate the freezing point depression due to the impurities present in the defining fixed points of the ITS-90.

When partial mixing occurs in the liquid phase, as the *second* possible freezing process, the segregation of impurities depends strongly on the freezing conditions and is governed by an effective distribution coefficient, k_{eff} ; k_{eff} has a value between k_0 and approaching 1, if the rate of freezing is high. The *third* possible freezing process is when there is no mixing in the liquid phase. In this case, the diffusion is inadequate for mixing the impurities throughout the liquid. When the freezing advances, the impurity concentration in liquid layer adjacent to the liquid/solid interface increases ($k_{0,i}<0$) or decreases ($k_{0,i}>0$) because the impurities are rejected or gathered by the freezing solid. Quantitative analysis on estimating the uncertainty due to impurity is generally conducted under the assumption of the first freezing process, described by eq. (3), since reliable data of k_0 for binary alloys are often available. Even in the case of the second freezing process where $k_0 \leq k_{\text{eff}} \leq 1$ or the third freezing process where k value may vary, adoption of k_0 into eq. (5) is sufficient to cover the uncertainty estimation based on the actual k value.

3. Impurity Analysis

To apply eqs. (1) to (5), reliable measurements of impurity levels, from which the compositions x 's in the equations are determined, and of the liquid fraction F are essential. In the following paragraphs the main methods of impurity analysis will be described.

The conventional method to check the purity of metals (solids) is by using the differential scanning calorimetry (DSC). In a DSC a reference is used as a comparator: the difference in the heat flow to the sample and the reference at the same temperature, from which the enthalpy of fusion of the sample may be derived, is recorded as a function of the temperature. The enthalpy value is then used to calculate the impurity concentration based on eq. (1). This method is clearly the application of the freezing point depression analysis given by Raoult's law, from which only the total effect of the impurity within the metal can be obtained, assuming no solubility in the solid phase.

The recent trends in impurity analysis of solid are the

inductively coupled plasma mass spectrometry (ICP-MS) and glow discharge mass spectrometry (GDMS). The ICP-MS is intrinsically a solution based technique where the metal sample is put into a solution using various combinations of acids or bases and subsequent heating. The sample solution is then diluted to bring the concentrations of the elements of interest into the mass spectrometer. The ICP-MS has the disadvantages of possible contamination, the need for dilution and consumption of time. Using this method one can obtain the amount of impurity determined to better than 10 % at ppm ($\mu\text{g/g}$) level⁹. GDMS involves the atomization of a solid sample by sputtering in a low-pressure (1 Torr) DC plasma. The sputtered atoms are then ionized in the plasma and extracted into the mass analyzer for separation and detection. Bogaerts and Gijbels made a review on the fundamental aspects and applications of glow discharge spectrometry¹⁰. Compared to the ICP-MS, GDMS requires no pretreatment, such as utilizing solutions, so that metal samples do not suffer from contamination and even metals that are difficult to dissolve can be analyzed, and more than seventy components can be analyzed simultaneously in sophisticated sensitivity (ppb order)¹¹. It should be noted, however, that the uncertainty of analysis is large, and is generally said to be 50 % to 200 %¹¹.

The above paragraphs may give an illustration of how sensitive the currently available impurity-analysis technologies are. Having our high-purity fixed-point metal precisely analyzed is one thing; however, purchasing the fixed-point metal itself is another. When one purchases a high-purity fixed-point metal, one gets a list of impurities present in the metal. These impurities are limited to those that are detectable by the conventional analysis methods practiced by the producers. Impurity analysis using such an advanced technology as the GDMS described in the previous paragraphs requires additional expenses that will increase the price of the fixed-point metal. In fact, not all fixed-point metal producers have their own GDMS or equivalent advanced analysis-apparatus, so that a more precise impurity-analysis must be sub-ordered to other institutes or companies who own such facilities. The end user who wants to know precisely the impurity contents of its metal may send part of the metal directly to the analyzing institutes or companies after purchasing the metal. This part of the metal in most cases would be left over after having filled the crucible. It should be decontaminated by a melt-freeze process before being sent to the analyzing institute, through which the impurities with low boiling point are exhausted from the sample.

Following this procedure, however, will elongate the path between the purchasing and the impurity analysis processes along which contamination of the metal may occur.

In view of the above, it is important to find an appropriate method to evaluate the uncertainty of the fixed-point realization due to the effect of impurities. The following sections introduce the uncertainty evaluation method currently used in thermometry. Prior to this, however, the paper will firstly describe the practical temperature measurements, from which the effect of impurities may be derived.

4. Measurements of Melting and Freezing Plateaus

There are two major methods for melting curve measurements known as the stationary method and the adiabatic method. The stationary method is the conventional one, where a fixed-point cell is located within a furnace whose temperature is set above and below the melting point of the metal for melting and freezing, respectively. On the way to melting, the metal ingot will absorb heat to raise its temperature until one part of it melts, from which point the temperature will effectively be unchanged: a liquid-solid equilibrium has been achieved. This equilibrium arrest in temperature is called a plateau in the melting (freezing) curve. When most of the metal ingot has melted, the temperature will start to rise to the set value. This is illustrated in Fig. 1 (a)¹². The abscissa in Fig. 1(a) is the time and the ordinate the temperature.

In freezing, heat must be taken away from the liquid metal in order to create nucleation initiating the freezing process via supercooling. Nucleation is realized by insert-

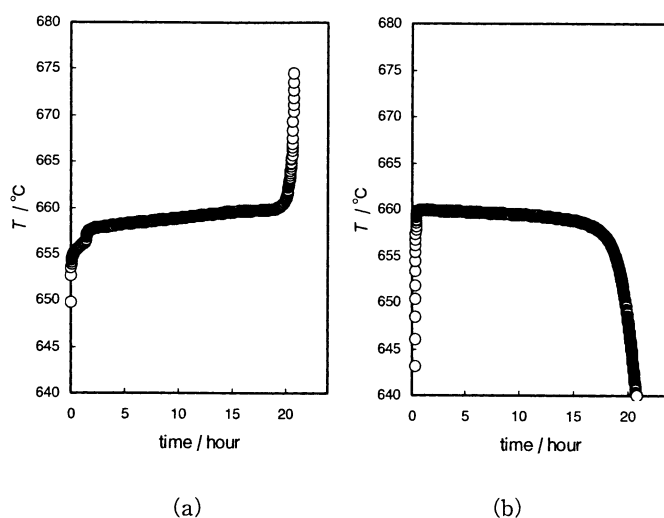


Fig. 1 The melting (a) and freezing (b) plateau of aluminium¹²

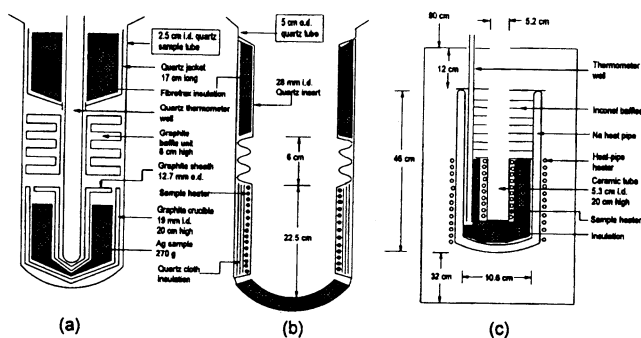


Fig. 2 Calorimeter: (a) and (b) are sample housing, (c) furnace¹⁴⁾

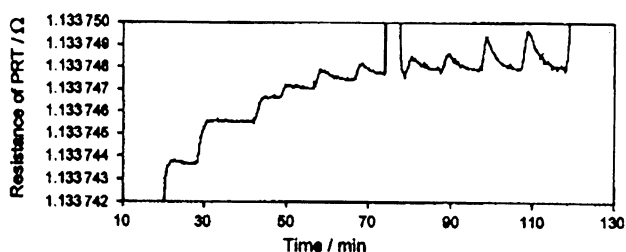


Fig. 3 Melting curve obtained using a calorimeter¹⁴⁾

ing a cold material (a rod, an amount of gas, etc.) into the thermometer well of the cell containing the liquid metal or by taking the cell shortly to room temperature. When an accurate temperature-control system is used, the nucleation can be achieved by simply setting the heater temperature some degrees below the melting point. After supercooling and nucleation, the liquid metal will recalesce and the temperature increases to the freezing point before it drops to the set-point temperature of the furnace. Such a freezing process is depicted in Fig. 1(b)¹²⁾ whose abscissa and ordinate are defined as in Fig. 1(a). The plateaus in both Figs. 1(a) and 1(b) appear as an inclined line rather than a horizontal one up to the vicinity of the liquidus point. The slope of the “plateau” reveals the presence of impurities in the metal ingot. In general, the higher the impurity content the larger the slope.

The other method to realize metal melting is the adiabatic method, also called the calorimetric method since here a calorimeter is used. Calorimeter design for metal fixed-points can be found in the report by Bonnier and Renaot¹³⁾, and Ancsin¹⁴⁾; the latter one is given in Fig. 2. In this method, heat is added at certain time intervals to the adiabatic chamber to generate partial melting. This procedure is then repeated until a complete melting is

achieved. An example of melting obtained by this method is illustrated in Fig. 3¹⁴⁾. Transient thermal conditions form a number of ‘small hills’ in the melting curve before the return to equilibrium.

In practice, time dimension in the melting curve is converted into the liquid fraction by comparing the partial melting time with the overall melting time. The relation between the melting metal temperature and its liquid fraction is often used to estimate the freezing point depression of the metal. The parameters influencing the uncertainty estimation, are the stability of the thermometer (SPRT) used in the measurements and the precision of the time-to-melting-fraction conversion.

SPRTs are known to suffer from the problem of oxidation of the Pt sensing element at temperatures within the range 300–450°C¹⁵⁾. However, at higher temperatures the oxide dissociates to be no longer an influencing factor to the temperature measurements. SPRTs are also facing the problem of the deterioration of the electrical insulation at high temperatures, especially above the silver point^{16–20)}. The most serious problem of using an SPRT at high temperatures, especially at the silver point, is the contamination of the SPRT by silver from the silver crucible^{21–25)}. Once the SPRT is contaminated it will lose its stability with no possibility of recovery.

In freezing, the curve depends strongly on the solidification conditions. Usually, especially for higher contents of impurities, the slope of a freezing curve will depend on the set-point temperature of the furnace, which also determines the rate of solidification. This phenomenon, often used to evaluate the uncertainty due to the variation in the surrounding temperature, may imply that every freezing has its particular impurity profile within the metal.

5. Purity Management

The impurity of a fixed-point metal may have its minimum value at the time the metal is purchased. One should verify that the contamination by low boiling-point gases is eliminated by preheating the metal and pumping to higher vacuum than the pressure of the contaminating gases in the vicinity of the fixed-point temperature. When firstly filling the fixed-point cell, contamination from the environment becomes possible, so that it is important to evaluate the purity of the metal in the filled state. The following section will give a more detailed description on the evaluation methods of the purity of the metal.

Once the metal is filled into the fixed-point cell, it becomes virtually impossible to detect any change in its purity by impurity analysis. As an alternative, measure-

ment of the plateau using a highly stable SPRT can be made for a number of freezing rates to indirectly confirm that the purity of the metal used is well maintained⁹⁾. The measurements made soon after the completion of the fixed-point cell may be used as an initial or reference value in evaluating those obtained at a later time. The change in the slope with the progression of time from the initial one can then be correlated with the change in the purity of the fixed-point metal. Here, only the difference in the slope of the plateau which is greater than the stability of the SPRT can actually be detected.

Besides the above described method, the purity of the metal can also be confirmed to some extent by making direct comparative measurements among two or more fixed-point cells. The cell containing metal of the highest purity may be selected as a reference cell, while others are setting the status of the test cells. The direct comparison can be effectuated by realizing simultaneous plateaus for the test and reference cells in separate but nearly identical furnaces and making measurements at equal time intervals on their plateaus using a single SPRT. The results obtained would ideally be the differences in the slope of the plateaus of the fixed-point cells. Even if the difference observed would exceed the true difference of the slope of the plateaus which may due to a minute shift in resistance of the SPRT, it can be used to confirm whether or not the claimed purity of the metal is reliable. An example of such a comparison for Indium is reported by Strouse²⁶⁾ for the purpose of determining the realization temperature differences among newly fabricated cells, as given in Fig. 4.

Three series of direct cell-comparisons are depicted in Fig. 4, each of which is based upon three measurements, where the ordinate is the temperature difference derived from the difference in W (ratio of resistance at Indium

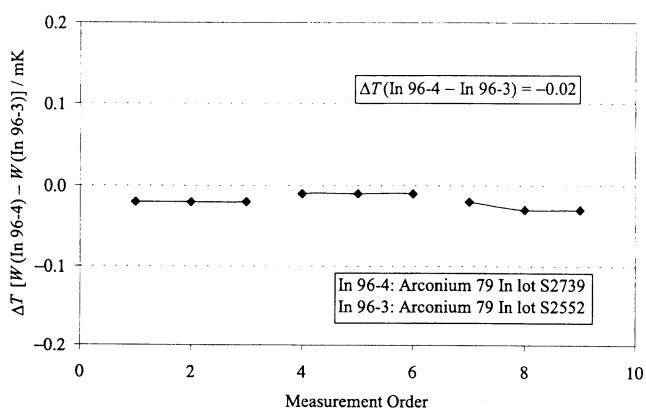


Fig. 4 Direct comparison of Indium-point cells²⁶⁾

point with respect to that at the triple point of water) between the reference cell and the test cell. From three series of measurements the cell denominated as In 96-4 shows a measured value lower than In 96-3. The temperature difference was determined to be 0.02 mK as listed in Table 1. Also listed are the impurity concentrations of the cells estimated from their freezing curves, given in the brackets in Table 1. The freezing curves of cells In 96-4 and In 96-3 measured prior to the direct measurements are

Table 1 Direct Comparison of Fixed-Point Cells

Cell	Mole fraction sum of impurities, $\sum x_i$ (FP depression)	Impurity concentration estimated from freezing curve	Temperature difference estimated from $\sum x_i$	Relative temperature difference from direct comparison
In 96-4	1.7×10^{-7} (-0.08 mK)	0.5×10^{-7} (-0.023 mK)	-0.01 mK	-0.02 mK
In 96-3	1.5×10^{-7} (-0.07 mK)	0.4×10^{-7} (-0.018 mK)		

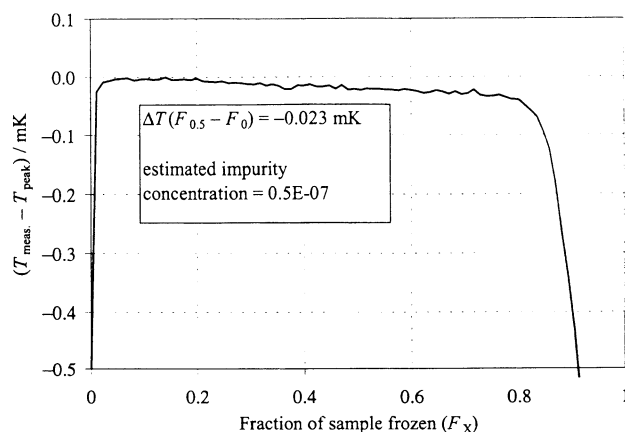


Fig. 5 The freezing curve of cell In 96-4 cited in Fig. 4²⁶⁾

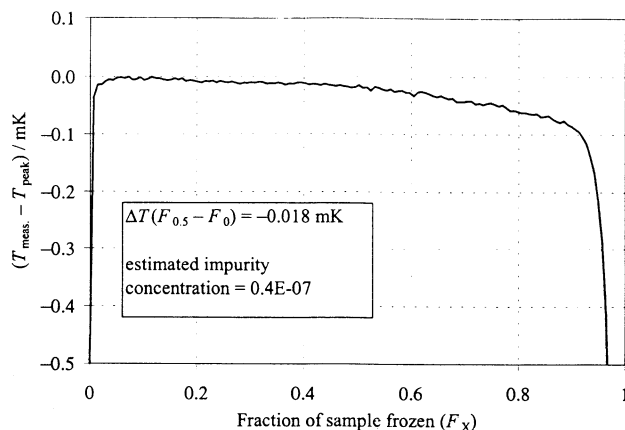


Fig. 6 The freezing curve of cell In 96-3 cited in Fig. 4²⁶⁾

given in Figs. 5 and 6, respectively. The abscissa of Figs. 5 and 6 shows the temperature deviation from the peak temperature T_{peak} , while the ordinate is the fraction of metal frozen F_x . The point in time corresponding to F_0 is chosen to be the instant of the recalescence and that corresponding to F_1 the time when the realized temperature reaches 10 mK below T_{peak} . A linear regression is performed from $F_{0.2}$ to $F_{0.7}$ to determine the slope and the intercept of the freezing curve. The temperature difference from the fit for $\Delta T(F_0 - F_{0.5})$ is used in conjunction with the first cryoscopic constant to estimate the mole fraction impurity concentration in the fixed-point cell, as listed in Table 1.

As shown in Table 1, the result of direct comparison is consistent with the temperature difference estimated from the mole fraction sum of impurities x_i : the temperature realized by cell In 96-4 is lower than that by In 96-3. The same conclusion can be drawn concerning the temperature difference estimated from the freezing curves of the cells, which results in a minus temperature difference value.

It should be noted that in a direct comparison using an SPRT, the SPRT will experience a thermal shock caused by withdrawal from one cell and insertion into the other that may affect its stability. This is also known as the quenching effect as reported elsewhere²⁷⁻³⁰. In the case of In point (156.5985 °C), such a quenching effect is relatively small and does not affect the stability of the SPRT. However, for temperatures around the Al point (661.323 °C), it would be equivalent to 1.5 mK²⁹ and exceeds 10 mK³⁰ around the silver point if the change in resistance at the water triple point before and after its exposure to Al point is used as a measure.

The above mentioned experiment implies that when a highly stable SPRT (HTPRT) is used both in the freezing curve measurement and the direct cell comparison, the cell difference would reflect the difference in the slope of the freezing curves. Periodical measurements using the above procedure may then be sufficient for checking whether or not the purity of the metal within the cell is well maintained.

To some level of accuracy, the above direct comparison can also be used to confirm the claimed purity of a set of fixed-point cells by comparing the differences in the freezing point depression predicted theoretically and that obtained from direct cell comparison.

6. Uncertainty Analysis

The above sections have treated the current development in impurity analysis and methods currently adopted

in thermometry related to the evaluation of the purity (impurity) of metals. However, how they can practically be utilized to estimate the uncertainty due to the effect of impurities in thermometry is a difficult question to answer. The main problem is the modeling of the metal melting and freezing to accurately correct for the freezing point depression and to estimate the related uncertainty. The following are methods of estimating uncertainty due to impurity as recommended in the CCT documents^{6),31-33}.

Method 1: Sum of Individual Estimates (SIE)

In this method, a detailed estimation requires the determination of the concentrations of all impurities using appropriate analysis techniques and the knowledge of the concentration dependence of the fixed-point temperature for the different impurities. The estimate is the sum of the individual shifts of the fixed-point temperature due to the impurities present in the fixed-point metal. This method is an application of equation (5), where impurities are distributed in solid and are completely mixed in liquid. The individual shifts can be calculated from the slope of the liquidus and the solidus lines in the phase diagram. The uncertainty of the estimate then results from the uncertainty of the impurity analysis and of the value for the concentration dependencies. The uncertainty of the impurity analysis depends on the accuracy of the analysis method used, such as ICP-MS, GDMS, etc. The uncertainty of the concentration dependencies depends on the reliability of the calculated liquidus and solidus in the phase diagram. To what accuracy the liquidus is determined can be learned graphically from Fig. 7, which shows

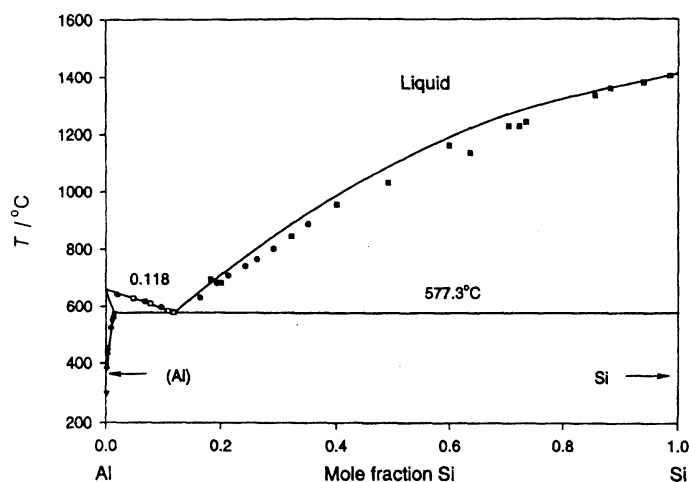


Fig. 7 Phase diagram of Al-Si alloy³⁴⁾

the phase diagram of Al-Si alloy as an example³⁴.

As shown in Fig. 7 and for the general case of metal alloys, phase diagrams are based on measurements at high order concentrations. Equilibrium curve to fit the measured data is then derived on the basis of thermodynamic considerations. In the case of impurity contents in a fixed-point metal, the impurities exist at the ppm order or even less, at which the measured data is unavailable. The use of method 1 therefore assumes that there is no peculiarity in the behavior of the liquidus line, so that interpolation can be used to derive its slope with sufficient accuracy.

Method 2: Overall Maximum Estimates (OME)

If concentrations of all impurities or their individual influence on the fixed-point temperature are not known, a reliable estimate may be obtained by assuming that all impurities are insoluble in the solid phase of the fixed-point substance. Then the estimate results from the overall impurity content and the first cryoscopic constant. This method is merely an application of Raoult's law as given by eq. (2). When $k_0 < 2$ for each of impurities present in the standard metal, it follows from eq. (4) that $\frac{\partial T}{\partial x}$ lies in the range from $-1/A$ to $1/A$. It is possible then to estimate the maximum influence of impurities by using the overall impurity content and the first cryoscopic constant. An accurate maximum estimation is obtained if the overall impurity content is estimated reliably. Method 2 usually yields larger values than Method 1.

Method 3: Estimate based on Representative Comparison (ERC)

If the overall impurity content cannot be estimated reliably, a rough estimate can be deduced indirectly from the comparison of different fixed-point cells. It has to be ensured, however, that the compared cells have different material sources or purity. This method requires high quality measurements through utilization of a highly stable SPRT. As described previously, at lower temperatures, direct comparison finds no significant problem related to the stability of the SPRT. At higher temperatures such as the aluminium and the silver fixed-points, however, this becomes a very serious problem.

Combination of Method 1 and Method 2

This is combination of method 1 applied for the dominant impurities and method 2 for the rest of the impurities. The isotopic composition of the metal has to be analyzed if it may significantly influence the fixed-point temperature.

To evaluate the uncertainty due to the impurity contents within the metal, the freezing point depression derived from one of the above estimation methods is generally considered as a maximum error or a limit of tolerance in calibration service, and is treated as type B according to the Guide for the Expression of Uncertainty in Measurements (GUM)³⁵. It should be noted, however, that none of the estimation methods is recommended to be used for correcting the fixed-point temperature.

7. 1/F Analysis

7.1 General Descriptions

If the time dimension in the abscissa of the freezing or melting curves such as in Fig. 1 is changed into the inverse of the melted fraction (thus $1/F$), then Fig. 8³⁶ is obtained. The curve in Fig. 8, in a limited range below $1/F=4$, shows a slope that can be fitted by a straight line.

Another expression for melting or freezing curves is given in Fig. 9, in which the temperature is given in terms of the difference from that at $1/F=1$, the point where the freezing point is determined,¹³. Since both measurements given in Figs. 8 and 9 are performed using calorimeters, the data points are discrete.

To fit the data in Figs. 8 and 9 in a limited range, for

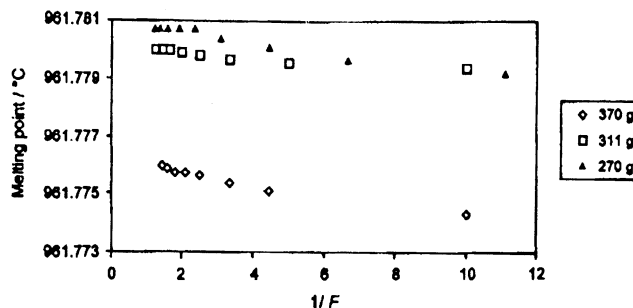


Fig. 8 Melting curves in terms of $1/F$ ³⁶

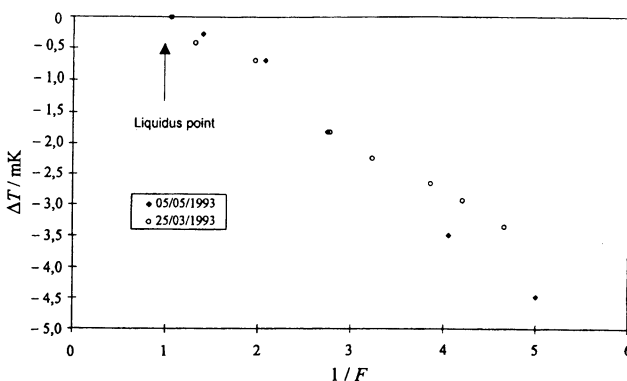


Fig. 9 Slope of $\Delta T-1/F$ curve¹³

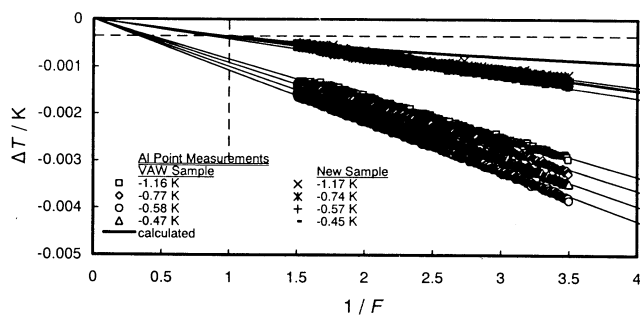


Fig. 10 $\Delta T-1/F$ curve¹²⁾

example those below $1/F=4$, a straight line can be drawn. The intersection of this line with the vertical axis (showing resistance or temperature) is often used as the hypothetical freezing point of the pure material. Such a situation is illustrated more clearly in Fig. 10¹²⁾. In Fig. 10, $1/F$ curves of two samples, denoted as VAW sample and New Sample, respectively, are depicted. Each sample has four curves corresponding to different set-point temperatures of the furnace. Data between $1/F=1.5$ and $1/F=3.5$ were used to draw a straight line to fit each curve from which the value at $1/F=0$ is derived. The difference from this value is then plotted for each data point to give the $\Delta T-1/F$ curve of Fig. 10. The purer the sample, the smaller the gradient of $1/F$ will be. This fact is then taken into account to estimate the freezing-point depression due to impurity: ΔT at $1/F=1$ can be considered to be the freezing point depression. Thus, the New Sample in Fig. 10 can be considered to have higher purity than the VAW sample. Such a freezing-point depression analysis is called $1/F$ analysis. To perform an accurate $1/F$ analysis, the plateau should be stable for as long as possible so that an equilibrium freezing is achieved. This can be done by setting the surrounding temperature as close as possible to the freezing point by a precise temperature control system. McLaren and Murdock^{37),38)} have, for example, carried out 18 hour silver freezes.

Although the $1/F$ analysis seems effective for estimating the freezing-point depression due to impurity contents, there are at least two critical points of concern on its application. First is that the $1/F$ analysis is principally the application of Raoult's law given in eq. (1) in a limited range, which assumes that all impurities are rejected into the liquid phase during the freezing process, while in reality they are also taken into the solid phase to form a solid solution. If, for convenience, we assume that in the liquid phase the impurity forms a complete equilibrium

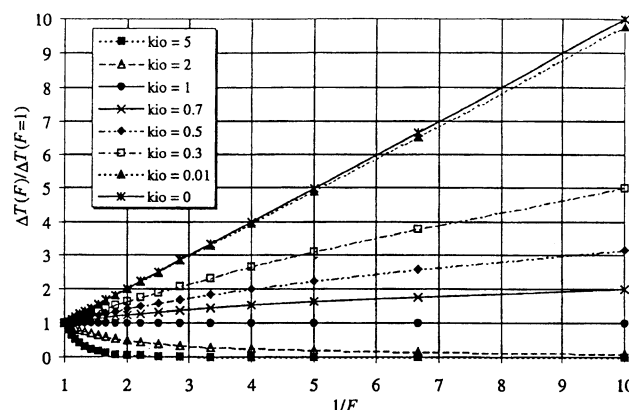


Fig. 11 $\Delta T(F)/\Delta T(F=1)$ vs $1/F$ for the case of complete mixing in the liquid⁶⁾

mixing with the pure material, then the deviation by using Raoult's law from the real mixing can be expressed by Fig. 11⁶⁾.

Figure 11 depicts a part of the melting curves ranging from the melting point to the point where the liquid fraction F is 0.1 ($1/F=10$). Here the ordinate is the ratio of the temperature deviation from the freezing point of pure metal ($T_{\text{pure}}-T_{\text{observed}}$) at any F value to that at $F=1$. k_{10} in Fig. 11 corresponds to the distribution coefficients: $k_{10}=0$ shows Raoult's law which appears as a diagonal line in the figure. $0 < k_{10} < 1$ corresponds to alloys whose freezing points are lower than the pure metal (freezing point depression), while $k_{10} > 1$ corresponds to alloys whose freezing points are higher. Figure 11 shows that any value of k_{10} produces smaller ratio than that of Raoult's law and that selecting any two or more data points on the curves of k_{10} other than zero produces underestimation of the freezing-point depression or elevation. Selecting data near $F=1$ for regression may reduce the inaccuracy of estimating the freezing-point depression. However, since the freezing process is in practice conducted through a supercooling, the data near $F=1$, being near the supercooling, has less reliability. On this point of concern, Fellmuth³³⁾ also has reviewed the underestimation of applying non-justified Raoult's law.

The second critical note is reported by Ancsin^{36),39),40)} on the impurity contents that elevate the freezing point of pure silver and aluminium. Ancsin showed that when such impurities are dissolved in pure metals, the melting curves will have positive slopes similar to metals that have impurities with depression effect. The evidence for this statement is given in Figs. 12 and 13.

Figure 12 depicts the melting curves of Al-Fe alloy at

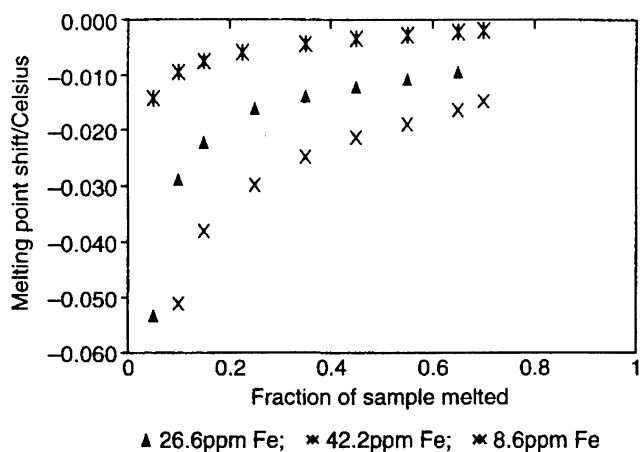


Fig. 12 Melting curve of Al-Fe alloy³⁹⁾

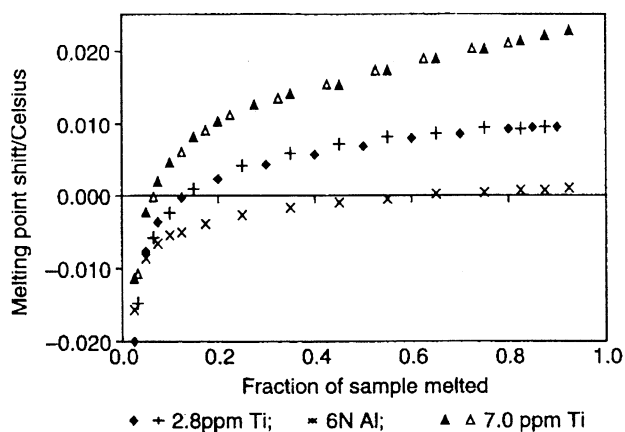


Fig. 13 Melting curve of Al-Ti alloy³⁹⁾

three Fe compositions. Fe depresses the freezing point of Al. The greater the Fe composition, the greater the freezing point depression, as shown by the absolute temperature value, and the slope of the curve. This phenomenon is usually observed in most impurity contents. If the curves in Fig. 12 are treated in the same way as Fig. 10, then negative temperature differences will be obtained, showing that the freezing point of a hypothetical pure sample (at $1/F=0$) has higher value than that containing impurities. It is expected, on the other hand, that when the sample contains impurities having elevating effect on the freezing point, a positive temperature difference would be obtained. However, as depicted in Fig. 13 for the case of Al-Ti alloy, the curves of such impurity also have the same shape as those in Fig. 12, i. e., the slopes of the plateaus are positive. If they are converted in the style of Fig. 10, not positive as expected but negative temperature difference will be obtained. This fact, which is a weak point, implies

that the $1/F$ analysis is not able to distinguish accurately whether the impurity contents are depressing or elevating the freezing point. Moreover, when impurities which elevates the freezing point exist in almost same composition as those that depress one, then the curve will appear as a nearly horizontal plateau as if it were of extremely high purity. Based on these two critical notes, the $1/F$ analysis is said to be an inappropriate method for estimating the uncertainty due to impurities³⁶⁾ and is simply a kind of verification method, for example, for evaluating whether or not a fixed-point cell has been contaminated during fabrication or during a long-time use (long-time stability check). A similar method based on the $1/F$ measurements has been reported by Strouse²⁶⁾.

7.2 Special Case

From the concern described in the above subsection, an aluminium-point cell was prepared from a single rod-shaped high-purity aluminium by a filling into the crucible in a single melt¹²⁾. Measurements done on the newly developed cell are already shown in Fig. 10. The nominal purity of the aluminium used in the "New Sample" (6N) was the same as that used in the cell denominated 'VAW Sample', except that the VAW Sample was filled into the crucible through multi-step melting from pellets. As expected, the ingot pre-forming and the reduction of the number of melting reduced effectively the contamination from the surroundings, which can be known from the smaller slope of the $1/F$ curve of the New Sample compared to that of the VAW Sample. Furthermore, since the single-rod high purity aluminium itself was accurately analyzed for its seventy seven elements⁹⁾, it was possible to estimate the freezing point depression using the sum of individual estimates described in previous sections. The authors found an excellent agreement in the freezing point depression between that obtained from $1/F$ analysis (i.e., the temperature deviation at $F=1$ in the $\Delta T-1/F$ curves), 0.37 mK (averaged from four measurements), and that from the sum of individual estimates, 0.45 mK, considering that the slope of liquidus line, $\frac{\partial T}{\partial x}$, in the phase diagram of the binaries might be overestimated due to the graphical estimation resulting in a greater value. Theoretical calculation assuming the metal to be a ternary alloy consisting of Al and the dominant impurities, Si (0.43 mass ppm) and Mg (0.29 mass ppm), was also done, whose result is shown by a bold solid line in Fig. 10. In spite of the difference in the shape of the freezing curves, the ternary alloy calculation for the freezing-point depression agrees satisfactorily well with the value estimated from the $1/F$ analysis at

$F=1$. It can be concluded from this result that within a restriction the $1/F$ analysis can be an effective method for estimating the impurity effect. It should be noted, however, that in this case as the restriction, the dominant impurities were those depressing the freezing point.

8. Conclusions and Future Challenges

The estimation of the freezing-point depression, which is used to estimate the uncertainty due to the impurity contents, depends strongly on the thermodynamic model that can considerably be affected by the combined condition of the fixed-point cell and the furnace during freezing, even if the whole impurity elements are analyzed very accurately.

Among the methods for estimating the freezing-point depression, Raoult's law is used to estimate the maximum impurity influence. When a reliable value for the overall impurity content is available, the maximum influence is obtained by substituting the overall impurity content and the first cryoscopic constant.

The sum of individual estimates is used when each impurity contents are available, and is the sum of individual shifts caused by each impurity element with the fixed-point metal as host, assuming that especially the dominant impurity elements have no peculiarity in their liquidus lines.

A direct comparison among fixed-point cells is used to estimate roughly the uncertainty due to impurity contents when reliable impurity analysis is unavailable. At low and moderate temperatures the direct comparison may be more applicable than at high temperatures where highly stable SPRT becomes difficult to obtain.

Although in many cases the $1/F$ analysis is used to estimate the effect of impurities, it should be considered as an experimental verification. The use of the $1/F$ analysis favors the detailed information of the dominant impurities: it would become accurate when the dominant impurity elements are those depressing the freezing point. The analysis is also dependent on the freezing conditions (rate of solidification). The recent work showed excellent agreement among the sum of individual estimates, estimation using the $1/F$ analysis (at $F=1$) and theoretical calculation assuming the fixed-point sample as a ternary alloy of the fixed-point metal with two dominant components.

It should be noted, however, that none of the estimation methods is recommended to be used for correcting the fixed-point temperature.

As future challenges, it is important to establish the

fabrication method of the highest reliable fixed-point cell and to develop a sophisticated fixed-point furnace which is capable of realizing accurately the melting and freezing curves, whose combined application can be used to conduct an accurate $1/F$ analysis. A further study on the freezing phenomenon may then find a breakthrough.

As a possible application of such an apparatus to other fields, it can be utilized as a tool for checking whether or not a fixed-point metal really has the purity (or impurity) as claimed by the manufacturer. One step further, the apparatus may also be used for consistency checks of the metal analysis obtained from such methods as GDMS, etc.

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