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Influence of Impurities and Filling Protocol on the Aluminum Fixed Point

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Abstract To improve the uncertainty of the aluminum fixed point, a study was launched by LNE-INM/CNAM in the framework of the EUROMET Project 732 "Toward more accurate temperature fixed points" (Coordinating laboratory: LNE-INM/CNAM, 17 partner countries). A new open cell was filled with aluminum of 99.99995% purity. A French laboratory carried out elemental analysis of the sample using glow discharge-mass spectrometry (GD-MS). The values of the equilibrium distribution coefficient k and of the derivative $\delta T_l/\delta c_l^i$ of the temperature of the liquidus line with respect to the concentration of impurity i will be obtained through collaboration with a French physical and chemical laboratory. In the past, some aluminum cells were opened after several melts and freezes. The aluminum ingot was sticking to the graphite crucible, indicating that physicochemical reactions had likely occurred between Al and C. To avoid this reaction, an effort was made to draw benefit from the Al_2O_3 film that appears immediately on the surface of the aluminum ingot when it is exposed to oxygen. The open aluminum cell was tested in different furnaces and with different thermal insulator arrangements inside the fixed-point assembly. The observed drifts of the plateaux were always larger than the expected values. The cell was opened to inspect the aluminum ingot. The ingot was extracted easily, since no sticking to the crucible had occurred. The aluminum showed a very bright surface, but the presence of many "craters" throughout the thickness of the ingot was surprising. In some cases, the thermometer well was even apparent.

Keywords Aluminum · Equilibrium distribution coefficient · Fixed point · Impurity · Liquidus

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1 Introduction

In the International Temperature Scale (ITS-90), the long-stem platinum resistance thermometer (PRT) is used to realize the scale from the argon triple point (83.8058 K) to the silver freezing point (1234.93 K). The defining fixed points used in this range correspond to the triple, freezing, or melting points of ideally pure substances. Within the last 10 years, the results of temperature comparisons show unexplained discrepancies in the calibration results, and sometimes a relatively large spread of the uncertainty components. To clarify these points, the EUROMET thermometry community decided to work together on a long-term project, EUROMET Project 732: "Toward more accurate temperature fixed points." The aims of this project are:

- to improve European temperature standards and to reduce the uncertainty of the primary fixed points by exploiting the technological progress of the last decade in many fields such as: chemical analysis, metallurgy, monitoring of thermal exchange,…
- to show the consistency of the European realizations, and
- to increase confidence in the uncertainty budget.

This project is coordinated by LNE-INM/CNAM (France). To be realistic, the objective of this project has been limited to the range covered by long-stem standard platinum resistance thermometers (SPRTs), i.e., from the argon triple point to the silver freezing point. The associate partner laboratories are NPL (UK), UME (TR), METAS (CH), CEM (SP), MIRS Fe-LMK (SI), SMU (SK), IPQ (PT), OMH (HU), PTB (DE), LNE-INM/CNAM (FR), LNE-CMSI (FR), CMI (CZE), SMD (BE), NMi-VSL (NL), INRiM (IT), DZM (HR), and VNIIM (RU). The technical objective is to construct a new generation of temperature standards from substances of the highest available purity that have been characterized chemically by the best available means. The project also includes the development of temperature generators allowing control of the heat exchanges that can affect the practical realization of the fixed points. The aim is to reduce the uncertainty of the primary fixed points by a factor of two to three by the end of this project.

Within the framework of this project, a new generation of an aluminum fixed-point cell was developed at LNE-INM/CNAM. Before realizing the cell, all the pending difficulties were considered: effects of impurities, chemical analysis of the substance, cell material, protocol to clean the container, filling process, control of the thermal process, and the effect of pressure.

This paper is limited to an estimation of the influence of impurities and the effect of the filling process on the realization of the aluminum fixed point.

2 Pending Difficulties

2.1 Impurity Effect

The most delicate problem corresponds to impurities miscible not only in the liquid phase but also in the solid phase. The temperature of the phase transition is primarily determined by the sensitivity coefficient and the concentration of impurities. The shape

of the freezing and melting curves is related to the distribution coefficient:

$$k = c_s/c_l,$$

where c_s is the impurity concentration in the solid phase and c_l is the impurity concentration in the liquid phase. If we consider a situation of equilibrium in the concentrations in the two phases, the temperature of the phase transition is given by

$$T_{\text{pure}} - T_{\text{obs}} = -\sum_i c^i_{l,F=1}\left(\frac{\delta T_l}{\delta c^i_l}\right)/F^{1-k^i} \tag{1}$$

where c^i_l is the molar fraction of the impurity; $\left(\frac{\delta T_l}{\delta c^i_l}\right)$ is the derivative of the liquidus temperature with regard to the concentration of impurity i, and F is the fraction of metal in the liquid phase.

Impurities in the material cause the phase-transition temperature to depart from that of the pure material. If the target uncertainty of realization assigned to the aluminum fixed point is 0.5 mK [1], the required purity of the aluminum contained in the thermometric cell has to be better than 99.99993% [1]. Samples of aluminum of sufficient purity are not routinely produced and always contain a certain amount of impurities, even after various stages of intensive refining.

The estimate of the change in the freezing temperature due to impurities requires that the effect of each impurity be quantified. Through an exchange of information with researchers in other fields (chemical analysis, metallurgy, etc.), LNE-INM/CNAM is able to access the current state of thermodynamic knowledge to evaluate the liquid-to-solid transition temperature in the presence of various impurities.

2.2 Perturbing Thermal Exchanges

Heat exchanges by conduction or radiation can occur between the sensing element of the thermometer and the surroundings (furnace, ambient temperature) that may be at temperatures different from that of the phase transition. These exchanges can occur through the connecting wires or the sheath of the thermometer.

These disturbances may affect the phase transition itself. They can lead to non-uniform displacement of the solid–liquid interface inside the cell (due, for example, to a temperature gradient affecting the working volume of the furnace). If the interface moves more quickly in certain places, it can lead locally to the disappearance of the solid–liquid interface and the development of a "thermal short circuit" between the sensing element of the thermometer and the furnace.

To solve these difficulties, it is necessary to work under quasi-adiabatic conditions. At high temperatures, it is necessary to control the radiative heat exchanges that become increasingly important with increasing temperature.

3 Experimental Apparatus

3.1 New Fixed-Point Cell

Except for triple-point-of-water cells, the LNE-INM/CNAM fixed-point cells are made in-house or constructed under license by the French company Chauvin-Arnoux Pyrocontrole. Our standard cells at the aluminum fixed point (Al 100, Al 113, Al 123, and Al 130) were fabricated using commercially available 6N aluminum samples with incomplete chemical analyses. The aluminum samples were provided by Johnson Matthey (Al 100, Al 113, and Al 123) and Pechiney (Al 130). The new fixed-point cell (Al 159) was constructed in this study using:

- ✓ Purest aluminum sample with chemical analysis
- ✓ New method of filling
- ✓ New cell design

3.1.1 Purest Aluminum Sample

We supplied a sample of aluminum coming from the company "Arnaud Electronics." This company sells aluminum (99.99995%) purified by the French company Pechiney with a chemical analysis carried out by "SHIVA Technologies Europe." A sample of aluminum of the same batch was analyzed by GDMS in a laboratory of the Commissariat à l'énergie atomique (CEA). Table 1 summarizes the impurity concentrations detected.

The sum of the concentrations of impurities above the detection limit is equal to 357 ppb. The sum of the concentrations below the detection limit is 88 ppb. So, the maximum impurity content is 445 ppb. Nevertheless:

- ✓ chemical analyses for oxygen, hydrogen, nitrogen, and carbon are not available.
- ✓ the uncertainty of the concentration value lies between 5% and 100%, depending on the element

3.1.2 Quantitative Effect of Impurities

Estimating the change in the freezing temperature at the liquidus point using Eq. 1 requires the values of $\left(\delta T_{\mathrm{l}}/\delta c_l^i\right)$ and k^i. LNE-INM/CNAM collaborated with the laboratory of Mineral Chemistry–Physics of the University of Paris-South (EA 401) to obtain the values presented in Table 1. These values are calculated using the "CALPHAD" method (calculation of phase diagram) in association with the "Thermocalc" computer program and the database "SGTE" (Scientific Group Thermodata Europe). In Table 2, experimental $\left(\delta T_{\mathrm{l}}/\delta c_l^i\right)$ values of some binary systems reported by Ancsin [2] are compared with those in Table 1. Except for Al–Ni, there is very good agreement between the theoretical and experimental values.

The estimate of the uncertainty in the realization of the aluminum fixed point was obtained using the "sum of individual estimates (SIE)" for those impurities for which the concentration and the liquidus slope are known and the "overall maximum estimate (OME)" for the remainder [3–6]. ($\Delta T_{\mathrm{SIE}} = 0.15\,\mathrm{mK}$; $\Delta T_{\mathrm{OME}} = 0.15\,\mathrm{mK}$, with

Table 1 Impurities in aluminum sample 6N5. Values of $\left(\delta T_{\mathrm{l}}/\delta c_l^i\right)$ and k^i

Element	Concentration 10^{-9} g/g (ppb)	$\left(\delta T_{\mathrm{l}}/\delta c_l^i\right)$ (K/mass fraction)	k^i
Au	3		
B	2.5	4600	3.54
Br	3	466	2.32
Ca	12	−263	0.10
Co	0.5	−350	0.02
Cr	35	−500	0.32
Cu	60	−114	0.68
Fe	10	−1290	0.0022
Ga	6	−263	0.08
Ge	1	−406	0.10
In	4	−590	11.6
K	15	3710	22.66
Mg	12	2674	0.41
Mn	25	−163	
Mo	7		
N	unknown		
Na	10		
Ni	7		
P	0.8		
Pb	2		
S	10		
Sc	0.5		
Si	65		
Sn	5		
Ti	45		
V	7		
Zn	5		

a cryoscopic constant of $0.00149\,\mathrm{K}^{-1}$). Depending on the element, the uncertainty of the impurity concentration can be substantial. To be conservative, the correction is not applied. Consequently, the estimate of the uncertainty associated with the impurity effect is calculated from a linear sum, $U(T_{\mathrm{l}}) = \Delta T_{\mathrm{SIE}} + \Delta T_{\mathrm{OME}} = 0.30\,\mathrm{mK}$. Nevertheless, we must treat this result with caution. This calculation was carried out using the values of k^i provided by our collaboration with the laboratory of Paris South and not the values of k_{eff} (diffusion coefficient of impurity, velocity of the liquid–solid interface). The chemical analyses do not include elements such as oxygen and nitrogen. The presence of the latter can have an important impact due to the large value of its sensitivity coefficient, as presented in Table 1.

Table 2 Experimental and theoretical values of $\left(\delta T_l/\delta c_l^i\right)$

Binaries	$\left(\delta T_l/\delta c_l^i\right)$ (K/mass fraction)	
	Theoretical values	Experimental values
Al–Cu	−263	−290
Al–Fe	−350	−350
Al–Ni	−263	−430
Al–Si	−590	−660
Al–Ti	3710	3300
Al–Zn	−163	−160

Fig. 1 Old aluminum ingot

If the OME method is applied for all elements, the estimate of the uncertainty is equal to 0.59 mK, approximately twice the value obtained with the SIE + OME method.

3.1.3 Filling Procedure

The 6N5-grade sample was purchased in the form of three cylinders:

✓ One cylinder $\phi = 32.5\,\text{mm}$, $h = 9\,\text{mm}$
✓ Two cylinders $\phi = 32.5\,\text{mm}$, $h = 104\,\text{mm}$ with a clear well $\phi = 16.4\,\text{mm}$

The sample purity was determined after the Al was made in the form of the cylinders.

Previously, we tried to open old Al cells that had been used for a long time. Each time, it was necessary to break the crucible to extract the ingot of aluminum. We noticed sticking of the aluminum ingot to the graphite crucible, indicating that physical or chemical reactions were likely to have occurred between Al and C. The surface of the aluminum ingot was granular and not bright (Fig. 1).

To avoid this reaction, we tried to draw benefit from the Al_2O_3 film that appears immediately on the surface of the aluminum ingot when it is exposed to oxygen. It

is assumed that Al_2O_3 does not mix with the liquid and solid aluminum phases, so we used a glove box under an air atmosphere when filling the high-purity (5N-grade) crucible directly with the three cylinders. The graphite parts were not cleaned by the factory after machining, so they were cleaned in an ultrasonic bath filled with alcohol and then rinsed with distilled water. The parts were then baked under vacuum at 800°C for at least 20 h.

4 Measurements

The measurements were performed using a Guildline 9975 bridge to measure the resistance of a Chino thermometer. The melting and freezing transitions were studied using two different furnaces:

- ✓ A closed sodium heat-pipe insert in a traditional furnace. An S-type thermocouple with an electronic cold junction as a reference is connected to the control unit in order to ensure the temperature stability of the working volume.
- ✓ A cesium pressure-controlled heat pipe

The quasi-adiabatic method was not applied at this stage. It will be implemented in the future in collaboration with the LNE-CMSI by adapting the technological solutions studied at the indium fixed point. Solidification was carried out by forming a solid mantle around the thermometer well. Nucleation was induced by successively inserting two silica glass rods at room temperature into the thermometer well for 1 min.

We were disappointed by the results obtained with the new cell. During the freezing plateau, the temperature variation from 80% to 20% liquid fraction with cell Al 159 (3 mK) was larger than that with cell Al 123 (1.1 mK). Cell Al 123 was filled in 1997 with a sample of aluminum from Johnson Matthey (6N purity). The variation of the resistance of the thermometer versus $1/F$ is presented in Fig. 2.

A significant dependence of the gradient in the thermometer well on the percentage of metal in the liquid phase was also observed (Fig. 3). In seeking to understand this behavior, we decided to open the graphite crucible to inspect the aluminum ingot. The ingot was extracted easily, since no sticking to the crucible had occurred. The

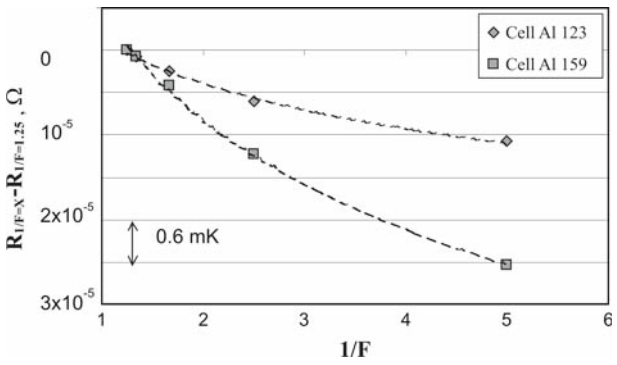

Fig. 2 Variation of the resistance of the thermometer versus $1/F$

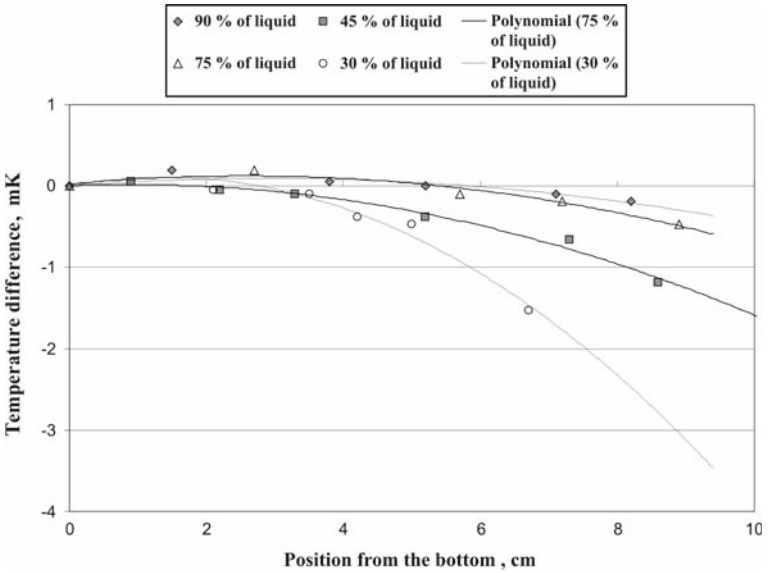

Fig. 3 Dependence of the temperature gradient in the thermometer well on the percentage of metal in the liquid phase

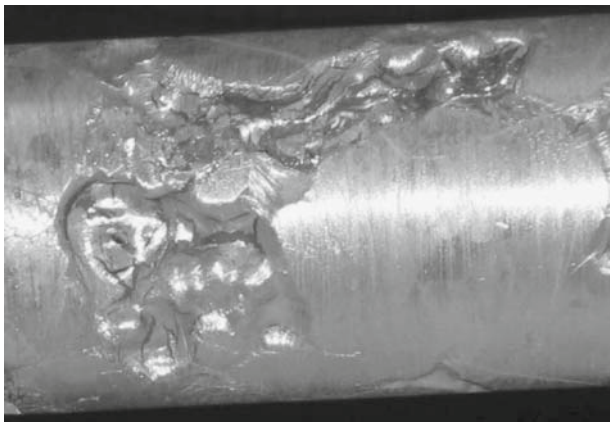

Fig. 4 Presence of "craters" throughout the thickness of the ingot. The thermometer well is even apparent

aluminum showed a very bright surface, but we were surprised by the presence of many "craters" throughout the thickness of the ingot. In some cases, the thermometer well was even apparent (Fig. 4). The origin of these "craters" has yet to be explained. Complementary experimental investigations are scheduled in the coming months in order to investigate this occurrence. With the hypothesis that the presence of a gas is responsible, we plan:

- ✓ to pump at least 2 h when the metal is in the liquid phase
- ✓ to study new freezing–melting plateaux
- ✓ to open the cell to inspect the ingot

In collaboration with the VNIIM, the possibility of metal contamination by the crucible material during cell operation was studied. Two samples of 6N5 aluminum were subjected to several freezing–melting plateaux in graphite and boron nitride crucibles. It appears that boron nitride is not a suitable material for the aluminum fixed point [7].

5 Conclusion

A new aluminum open cell was prepared by LNE-INM/CNAM using a 6N5-grade aluminum sample. A combined SIE/OME method was applied to estimate the uncertainty associated with the impurity effect. A new method for filling was used that avoids reactions between the aluminum ingot and the graphite crucible. We tried to benefit from the Al_2O_3 film that appears immediately on the surface of the aluminum ingot when it is exposed to oxygen. As the deviation of the temperature versus the percentage of metal in the liquid phase was larger than expected, the cell was opened and the ingot examined. The aluminum showed a very bright surface but we were surprised by the presence of many "craters" throughout the thickness of the ingot. The origin of these "craters" has yet to be explained. Forthcoming experimental investigations are planned in an effort to explain their presence.

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