

Pollution of aluminum ingot during the melting-freezing transitions

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1. INTRODUCTION

These last years, several papers were devoted to the effect of impurities on the temperature of the phase transition. Generally, the authors take into account the impurities present at the origin in the sample of metal. On the contrary, the pollution brought during the usage of the cell is very often neglected.

To improve the uncertainty of the aluminum fixed point, a study was launched by LNE-INM in the frame of the EUROMET Project 732 “Toward more accurate temperature fixed points” (Coordinating laboratory: LNE-INM/CNAM, 17 partner countries).

To investigate the influence of impurities and filling protocol a new aluminum thermometric cell was constructed at LNE-INM using:

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

The experimental study of this cell led us to better understanding the behaviour of the impurities.

2. THE ALUMINUM CELL

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 analysed by GDMS in a laboratory of CEA (Commissariat à l’Energie Atomique).

The sum of the concentrations of impurities above the detection limit is equal to 357 ppb (Table 1). The sum of the concentrations below the detection limit is 88 ppb. So, the maximum impurity content is 445 ppb. However:

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

The 6N5-grade sample was purchased in the form of three cylinders (Figure 1) :

- ✓ One cylinder $\phi= 32.5$ mm $h= 9$ mm
- ✓ Two cylinders $\phi= 32.5$ mm $h= 104$ mm with a clear well $\phi= 16.4$ mm

Figure 1 : Aluminum cylinders**Table 1. Impurity concentrations in aluminum sample before filling and melting-freezing realisations**

Element	Concentration 10^{-9} g/g (ppb)
Au	3
B	2.5
Br	3
Ca	12
Co	0.5
Cr	35
Cu	60
Fe	10
Ga	6
Ge	1
In	4
K	15
Mg	12
Mn	25
Mo	7
Na	10
Ni	7
P	0.8
Pb	2
S	10
Sc	0.5
Si	65
Sn	5
Ti	45
V	7
Zn	5

The aluminum sample was introduced into a graphite crucible. This crucible was placed in a silica envelope. All the elements of the cell were cleaned with a validated procedure; at the end, the impurity concentrations in graphite do not exceed 1.6 ppm (main impurities: B, P, S, Fe) (Table 2). The melting and freezing transitions were studied using a sealed sodium heat pipe insert in a traditional furnace. A type-S thermocouple associated with an electronic cold junction is connected to the control unit in order to ensure the temperature stability of the working volume.

3. FREEZING PLATEAU

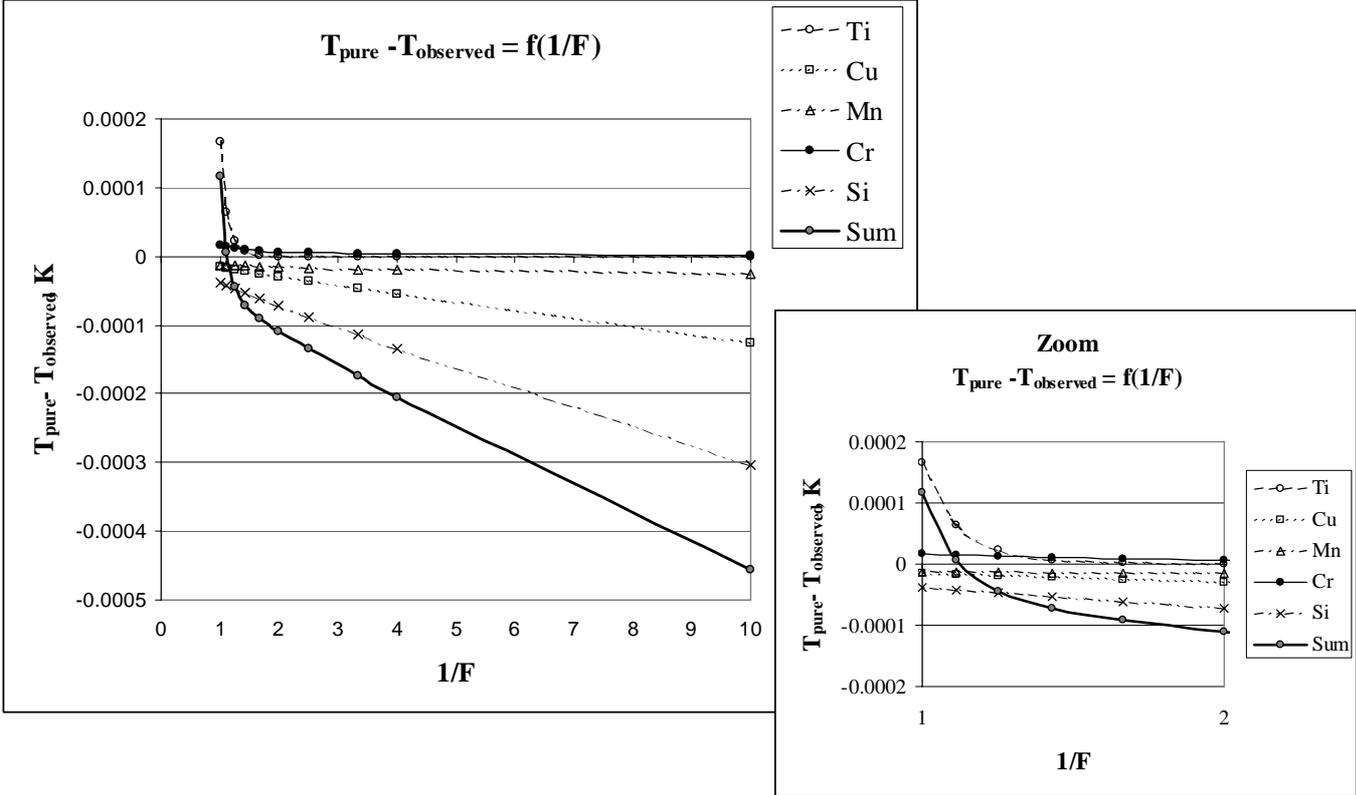
We were disappointed by the results obtained with the new cell. Taking into account the impurities discovered in substantial concentration (Cr, Cu, Mn, Si, Ti) the expected freezing range should have been about 1 mK (Figure 2). The experimental freezing range, from 80 % to 20 % of metal in liquid phase, achieved with the new cell is approaching 3 mK; it is larger than the one obtained with the cell filled with aluminum sample 6N (1.3 mK). It was also observed a significant dependence of the gradient in the thermometer well according to the percentage of metal in liquid phase. For the sake of explaining this behaviour, we decided to open the graphite crucible in order to inspect the aluminum ingot.

The ingot was extracted easily, since no sticking to the crucible has occurred. The 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 [1]. We supposed that these “craters” were related to the presence of gases dissolved in aluminum. So, in order to withdraw the potential gases, this cell was heated to a temperature of 670 °C under vacuum during 3 hours.

Table 2 : Impurity concentration in graphite

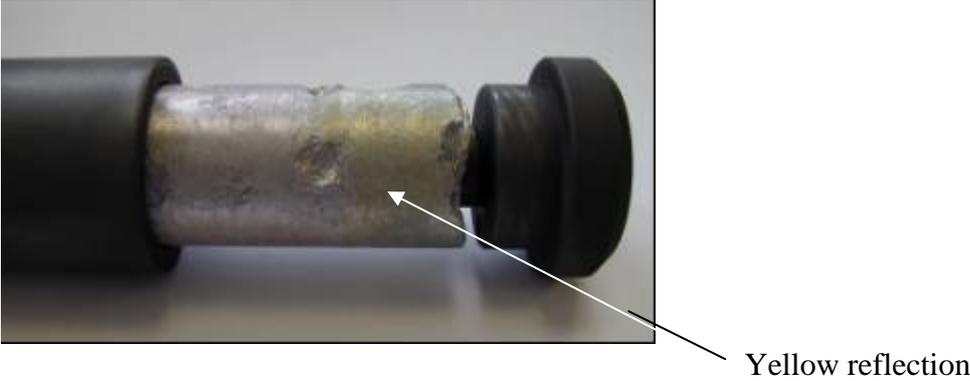
Element	Concentration 10^{-9} g/g (ppb)	
	Before cleaning	After cleaning
Li	45	15
B	380	210
Na	210	90
Mg	1350	15
Al	1400	140
Si	2400	70
P	1700	370
S	250	350
Cr	310	10
Fe	1700	250
Ni	350	90
Co	10	1
Cu	45	5
Zn	70	10
W	65	5
Pb	75	20

Figure 2 : Effect of impurities discovered in substantial concentration. F=fraction of liquid



After having applied this procedure three melting-freezing transitions were recorded. The last solidification was carried out by simply reducing the temperature of the heater without any other action to form a solid mantle around the well. Consequently, the solidification is initiated from the outer parts of the ingot. In all cases, the observed freezing range was greater than the predicted one. At the end, we again decided to open the thermometric cell. We remarked that the "craters" had disappeared. The aluminum displayed a bright surface but we observed the presence of yellow reflections on the outside of the ingot (Figure 3).

Figure 3 : Aluminium ingot with yellow reflection



4. CHEMICAL ANALYSIS

The ingot was analysed in the same laboratory of CEA. To detect the nature of the impurities several analyses were completed.

The first analysis is related to an area with yellow reflection. To define the distribution of the impurities, an analysis in the thickness of metal was achieved. The results are given Table 3. These analyses reveal an important pollution of the surface of the ingot (Na: 35 ppm, Mg: 21.5 ppm, S: 12 ppm, Fe: 4.2 ppm, W: 3 ppm). A fast decrease of pollution in the thickness of metal was observed. Nevertheless, with a 100 μm depth, 3 ppm of Na remains (Figure 4).

Table 3. Impurity concentrations in aluminum sample in an area with yellow reflections

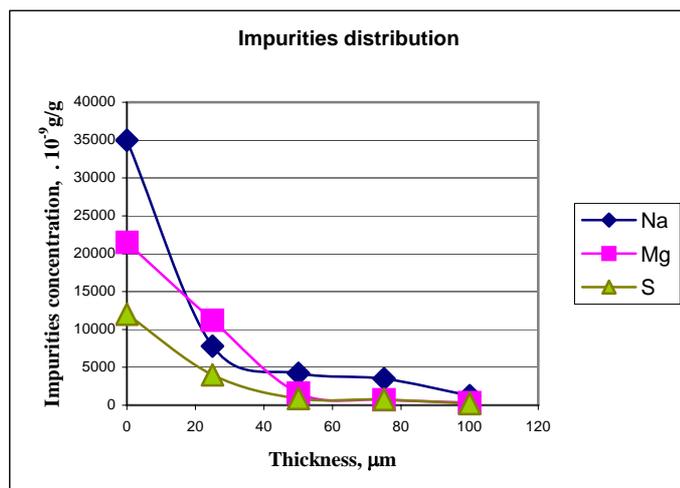
Element	Concentration 10^{-9} g/g (ppb)				
	0 à 25 μm	25 à 50 μm	50 à 75 μm	75 à 100 μm	100 à 125 μm
Li	12	18	22	6	3.5
B	1900	1400	420	350	280
Na	35000	7800	4200	3500	1250
Mg	21500	11200	1600	700	350
Si	250	120	45	5	5
P	215	130	40	8	2
S	12000	4000	900	750	225
Ti	115	65	55	20	7
V	75	2	2,5	<1	<1
Cr	620	340	240	185	65
Mn	1100	560	260	150	35
Fe	4200	2100	850	250	280
Ni	860	195	105	20	6
Co	10	4	2	<1	<1
Cu	45	12	2	<1	<1
As	95	55	2	4	<1
W	3000	600	100	3	<2
Pb	25	12	17	<2	<2

In total, the cell was implemented approximately 600 hours at a temperature close or equal to the temperature of the phase transition. Between the 8th and the 9th freezing-melting runs, the cell was exposed to a primary vacuum during 3 hours at a temperature of 670 °C.

It appears that the sodium diffuses through the successive Inconel, silica, and graphite walls. The origin of Fe is probably the envelope (Inconel) of the heat pipe. W comes from the heating resistor. Mg is used in the thermal insulators. The source of S is presently undetermined.

A second analysis involves an area without yellow reflection (approximately 10 cm down). This analysis concerns the surface of the ingot. The results are presented in Table 4.

The investigation of Table 1, 3 and 4 reveals that concentrations of Mg, S, Mn, and W in the aluminum ingot, except for the yellow areas, are close to their concentration in the initial sample.

Figure 4 : Impurity distributions related to an area with yellow reflection

The concentrations of Na and Fe significantly increased in all of the ingot but without reaching the values recorded in the yellow zones.

We can assume that the silica envelope of the cell presents in some areas a porosity that allows the contaminant vapors penetration (areas with yellow reflection). Nevertheless, during the pumping period (between the 8th and the 9th freezing-melting runs) a good quality vacuum has been obtained.

As it is shown in Table 3, there is no diffusion of impurities in the thickness of the ingot, or the diffusion is excessively slow and cannot allow a uniform distribution of the impurities. In addition last solidification was initiated from the outer parts of the ingot. It is generally assumed that impurities are pushed back in the liquid phase. It is not corroborated in this study, the strongest concentration of impurities is measured on the surface of the aluminum which froze first.

Table 4. Impurity concentrations in aluminum sample in an area without yellow reflections

Element	Concentration 10^{-9}g/g (ppb)
Li	3
B	<0.5
Na	450
Mg	5
Si	50
P	10
S	15
Ca	<5
K	<30
Ti	60
V	2
Cr	10
Mn	30
Fe	110
Ni	3
Cu	12
Zr	4.4
Mo	2
W	<1

5. CONCLUSION

These results show that, in reality, there is no diffusion of the impurities within the ingot. That is probably related to the fact that the speed of diffusion of the impurities is infinitely slow even in the liquid phase. Consequently, the mathematical models based on a uniform distribution of the impurities are not really suitable.

One of the important outputs of this ongoing study is that the conditions of usage of the cells should be given an important attention since large contaminations can be brought by the furnace, the crucible and other materials such as insulations ..etc.

BIBLIOGRAPHY

[1] E.Renaot, M.H. Valin, M. Elgourdou, Influence of impurities and filling protocol on the aluminum fixed point, *International Journal of Thermophysics*, ISSN:0195-928X (Print) 1572-9567 (Online)