6
Results of Ni-C and Ni-C-Cu eutectic cells

After the preliminary studies with Co-C, because of robustness issues it was decided to base the rest of the doping studies on Ni-C. In this and the subsequent chapter measurements of Ni-C, the two doped cells (with Cu and in Chapter 7 with Sn) their differences from the pure Ni-C cell are reported. Comparison with thermochemical modeling was inconclusive in one case indicating that the modeling may need to be refined, or the background data for the modeling improved, to produce more reliable results.

6.1. Ni-C reference cell (Ni-C #6)

6.1.1. Experimental results

To perform the studies, a reference cell needed to be prepared and measured. The subsequent doped cells were constructed from the same lot of Ni to ensure that any residual impurities were the same to all HTFP cells studied avoiding confounding of results. The filling was made in two steps with a final mass of 34,960 g of Ni-C. The first results obtained with this cell were compared with the ones achieved by other national metrology institutes and also with the one already obtained in a much bigger cell that was designed at Inmetro for contact and non-contact thermometry measurements [49]. The results showed good agreement with those from others authors [50, 60] with this cell yielding the same temperature within 0,050 °C. This level of agreement with earlier results shows that the base Ni used was of high quality and increases our confidence in the results of the doped cells reported in the next sections.

The Ni-C HTFP was placed in the Carbolite TZF18 furnace, as described in section 5.8.2. An argon flow of 0,3 to 0,4 l/min was provided to prevent the oxidation of graphite parts. The furnace auxiliary heating zones were previously adjusted in a way that gradients lower than 0,2 °C were achieved along the eutectic cell.

The phase transition cycle was initiated as it was shown in figure 21. This same procedure was followed in every measurement, with all the cells.

An important experimental detail is that after the end of each of the melting transitions, the cell was kept molten for at least 40 minutes. This is to ensure the uniform diffusion of impurities which may have become segregated by the previous freeze.

A typical melting and freezing plot is shown in figure 27, correlating pyrometer signal [photocurrent] (A) to time (hh:mm:ss).

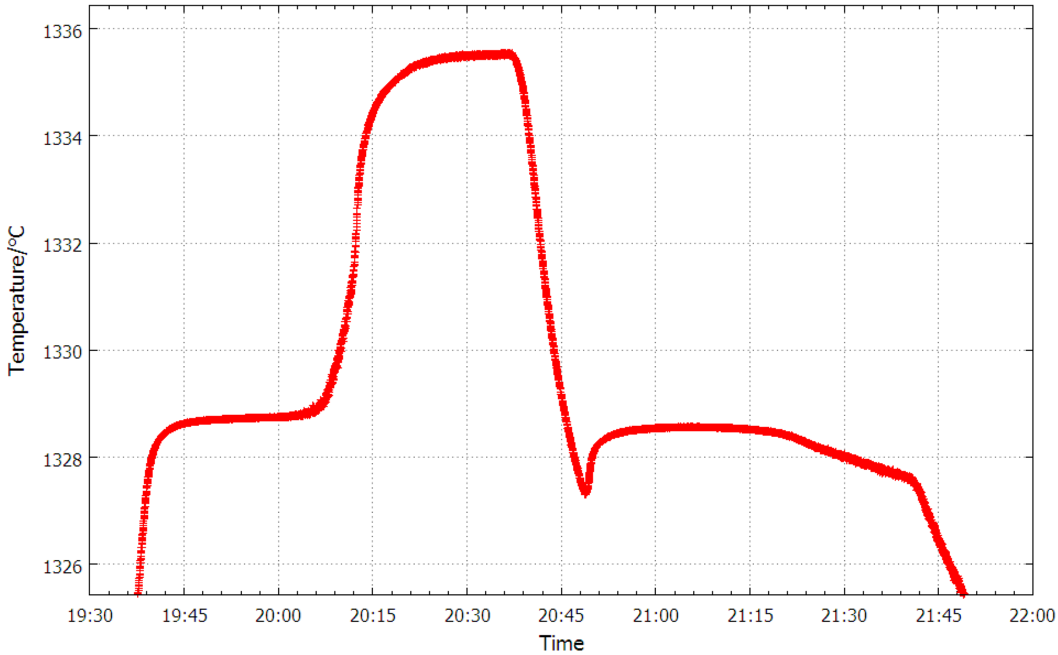

Figure 27: Realization of the Ni-C #6 eutectic cell

The cell (Ni-C #6) was realised twelve times, with a mean value for the point of inflection melting temperature of 1328,718 °C, with a standard deviation of the mean of 0,008 °C. This value compares positively to the ones obtained by other authors [17, 50, 60]. The melting plateau lasted for almost twenty minutes. According to Lowe and Yamada [25], a sharp rise in the end of the melting plateau is an indication of the quality of the realization of the melting of the cell, both due to low thermal gradients in the furnace and also an indication that there is low occurrence of voids coupled with good filling of the cell. Essentially a sharp rise out of the melting plateau indicates a good (i.e. uniform) furnace has been used and a good ingot has been formed during the casting process. Although not important for the objective of this thesis it is worth noting that the freezing temperature is 0,2 °C lower than the melting point with the supercool being about 1,25 °C lower than the maximum temperature during the freezing plateau, these results are similar to those reported by Park *et al*. [50].

In table 10 it is shown the results of all the measurements. These were all taken with the same step size of melt (8 °C) and freeze size (8 °C)

Table 10: Ni-C #6 realisations

Date	Temperature (°C)
04/10/2012	1328,660
	1328,679
	1328,697
	1328,710
	1328,721
	1328,739
22/11/2012	1328,713
	1328,724
	1328,733
	1328,738
	1328,745
	1328,751
Mean	1328,718
s	0,008

The realisations took place on two different dates, showed small temperature drifts, well within the uncertainty of the measurement itself, which was typically 0,22 °C. Each of the two measurements cycles lasted for approximately twenty eight hours, during which time the Ni-C cell was always in excess of 1300 °C. From a reference standard point of view it is important to note that during the measurements this cell experienced more than 50 hours at temperatures higher than 1300 °C, with no clear evidence of significant drifts, considering the measurement uncertainty.

With stability established for the melting plateau for this cell, this undoped Ni-C cell was then used as the reference temperature for the evaluation of the effect of the doping in the melting temperature of Ni-C doped cells.

6.1.2. Simulation results

As it was shown in 4.2.2, the simulation of the Ni-C eutectic indicated a melting temperature of 1326,36 °C, which is lower than the measurement obtained, 1328,72 °C. This temperature difference between the calculation and the experiment reported in table 11 is probably due to the accuracy of the model and background data used in the Thermo-Calc simulations. Nevertheless, the objective here is not to validate the software or databases, which is already considered a useful tool by the metallurgical community but rather attempt to determine relative changes due to doping.

Table 11: Ni-C melting temperature

Eutectic	Melting Temperature °C		
	Measured	Simulated	Difference °C
Ni-C	1328,72	1326,36	2,36

6.2. Ni-C-Cu 4168 ppm doped cell (Ni-C-Cu #7)

6.2.1. Experimental results

This cell (Ni-C-Cu #7) was realised twelve times, with a mean value for the melting temperature of 1328,463 °C, with a standard deviation of the mean of 0,020 °C. To ensure consistency in the results the same melt and freeze steps as were used for the pure Ni-C cell were used here.

Compared to the Ni-C reference cell, the addition of 4168 ppm (~0,158 g) of copper modified the melting (and freezing) temperatures by -0,255 °C. It is also possible to notice a longer melting plateau and a shorter freezing plateau. The temperature difference between these two points remained the same as the undoped cell i.e. a 0,255 °C lower value for the freezing temperature. The undercooling was -1,32 °C lower than the maximum temperature during the freezing, consistent with the value obtained with the undoped cell. There is no sign of change in the slope of the melting curve; the whole freezing curve was shifted lower by 0,255 °C, which can be seen in figure 28.

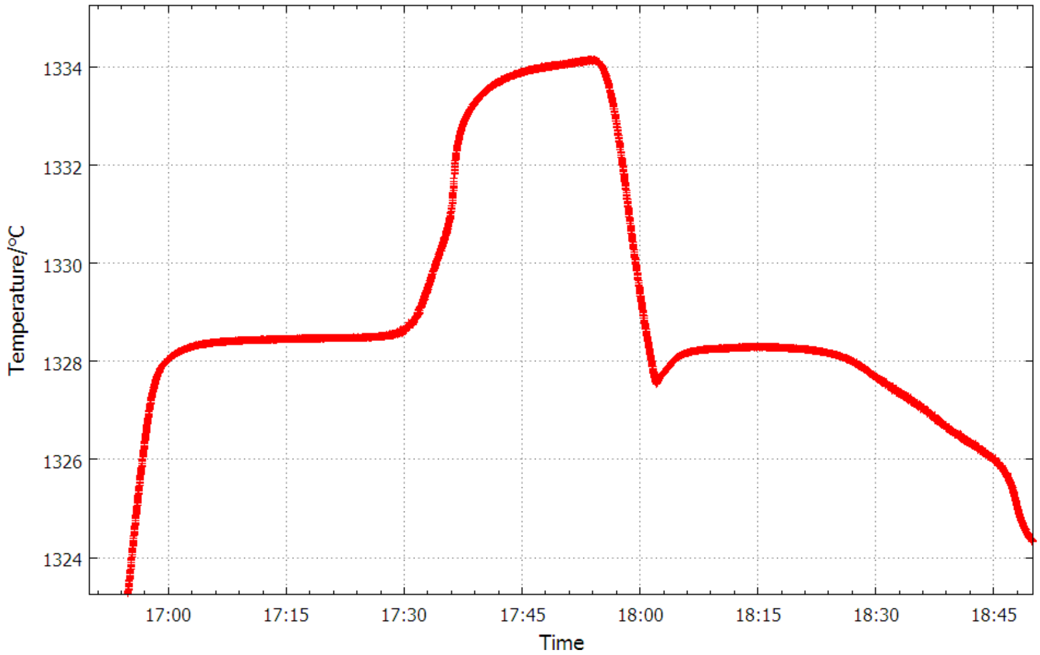

Figure 28: Realization of the Ni-C-Cu #7 eutectic cell

In table 12 it is possible to see the all the results of the measurements performed in two dates two and half months apart. Between these two times the cell was sent to NPL, UK for measurements – reported later.

One important point is that it is possible to notice that, in the first set of measurements, a small temperature drift (i.e. increase) with time. This behavior was not detected in the second set. This can be explained by the warming up of the interference filter of radiation thermometer LP3 during the measurements. This problem was avoided in the second set of measurements by the use of a radiation shield in front of the LP3 pyrometer and will be detailed in next section, 6.3 (in particular Figure 30).

Table 12: Ni-C-Cu #7 realisations

Date	Temperature (°C)
1/10/2012	1328,360
	1328,387
	1328,409
	1328,428
	1328,443
17/01/2013	1328,511
	1328,522
	1328,520
	1328,527
	1328,524
Mean	1328,463
s	0,020

The second set of measurements took place after the cell was sent to NPL (UK) by a courier service to be measured, in a blind comparison exercise between Inmetro and NPL. This was performed to undertake a proof of concept of the idea of using doped HTFPs to perform a blind key comparison. The results of this comparison will be shown in chapter 8. Because of that, this cell accumulated more than 75 hours in excess of 1300 °C, showing a good performance in the long term temperature stability. Unfortunately the blackbody cavity of cell Ni-C-Cu #7 was cracked at 10 mm from the opening probably during the NPL measurements in the large gradient Thermogauge furnace. However, useful measurements were still possible because the blackbody was still coaxially aligned with the axis of the crucible.

6.2.2. Simulation results

A Thermo-Calc simulation was performed on Ni-C with the addition of copper at a molar concentration of 4168 ppm. The result of this simulation was compared to the results obtained experimentally and can be seen in table 6.4. It can be concluded that, for this dopant, the Thermo-Calc results do not match with those obtained experimentally. The experimental results show that the addition of copper decreased the melting temperature in 0,26 °C, while the simulation gave a result 0,94 °C higher than the base Ni-C eutectic. This is probably due to the fact that the slopes of the distribution coefficient of Cu in Ni-C are not sufficiently well known at low solute concentrations.

Table 13: Simulated and Measured Temperatures for Ni-C-Cu 4168 ppm

Eutectic	Melting Temperature °C	
	Measured	Simulated
Ni-C	1328,72	1326,36
Ni-C-Cu (4168 ppm)	1328,46	1327,30
Difference	-0,26	0,94

6.3. Ni-C-Cu 7686 ppm doped cell (Ni-C-Cu #8)

6.3.1. Experimental results

Table 14 presents all the measurements performed with the Ni-C-Cu 7686 ppm eutectic cell. Again, as above, the melt and freeze step sizes were the same as for the pure Ni-C cell. The addition of 7686 ppm of copper in molar concentration changed even more the melting and freezing temperatures of the Nickel-carbon eutectic cell. Now these temperatures are 0,32 °C lower than the undoped cell. It can be concluded that the effect of the addition of copper is not linear with the melting temperature, because the amount of copper added almost doubled (+84,4%) in the cell and the temperature change was only -0,06 °C (-25%) compared to the previous cell Ni-C-Cu #7. In figure 29, a reduction in the duration of the freezing plateau can be observed but with no detected change in the duration of the melting plateau compared to the undoped cell. The temperature difference between the melting and freezing points remained the same as that for the reference undoped cell Ni-C #6 and the Ni-C-Cu #7 cell. The undercooling in this cell was of -0,65 °C from the maximum temperature during the freezing, quite different to the other two cells. The slope of the melting plateau remained similar to that of the undoped cell but for the freezing curve a greater roundness in the shape of the plateau is observable and also in the recovery from the supercool.

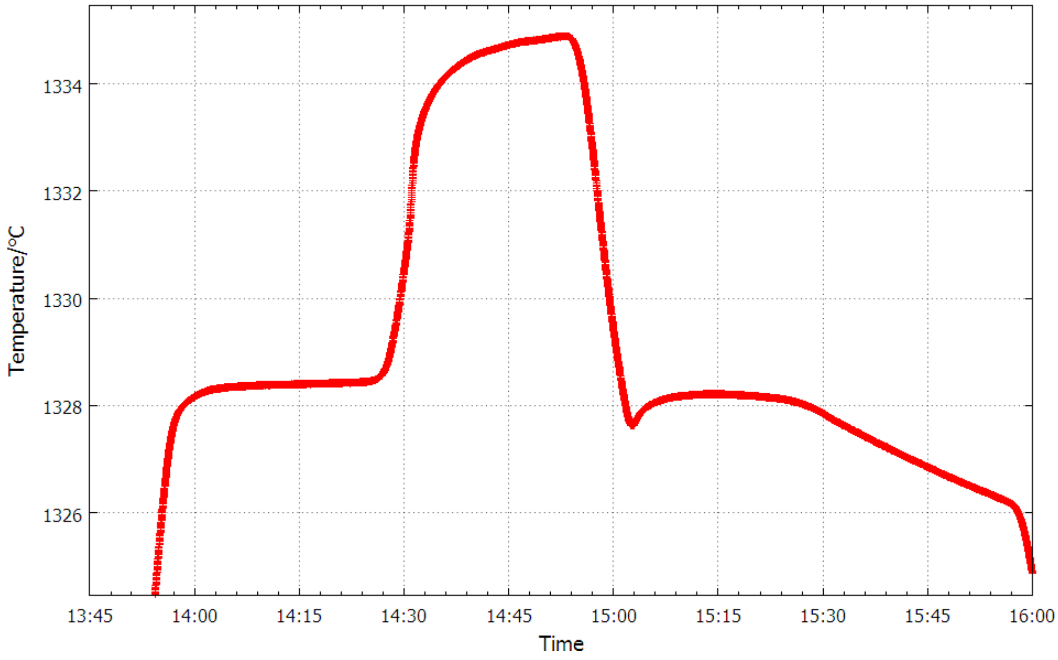

Figure 29: Realization of the Ni-C-Cu #8 eutectic cell

Table 14: Ni-C-Cu #8 realisations

Date	Temperature (°C)
8/11/2012	1328,347
	1328,401
	1328,403
	1328,404
	1328,404
	1328,414
21/01/2013	1328,393
	1328,409
	1328,415
	1328,414
	1328,417
	1328,420
Mean	1328,403
s	0,006

It can be seen in these two sets of data that a smaller standard deviation was achieved, in comparison with the previous results for the Ni-C #6 and Ni-C-Cu #7 cells. Each of the two sets of measurements lasted for more than 24 hours, with continuous measurements made using the linear pyrometer LP3. During the measurements, it was detected that the front plate of the pyrometer was heating up, because it was exposed to the thermal radiation from the furnace. The pyrometer includes a temperature control for the radiation detector, which is kept at 29,41 °C but not for the interference filters. The heating of the pyrometer's front plate, in turn heated the interference filters changing their spectral transmittance slightly. This is a well-known effect to radiometrists [11], and can, if not corrected for, have a significant influence on the final temperature determination.

To avoid this undesirable effect, before the beginning of these measurements a radiation shield was installed to protect the front plate of the pyrometer from the incident thermal radiation from the furnace. This radiation shield consisted of cardboard covered with aluminum foil, which could reflect the thermal radiation from the furnace. This shield was installed around the objective lens of the LP3 and was effective in keeping the pyrometer's front plate at ambient temperature. The effectiveness of doing this can be gauged by the fact that the drift in the results of the temperature measurements of the cell were much lower than those reported for the Ni-C #7 cell. In figure 30 a picture of the LP3 pyrometer equipped with the thermal radiation shield is shown.

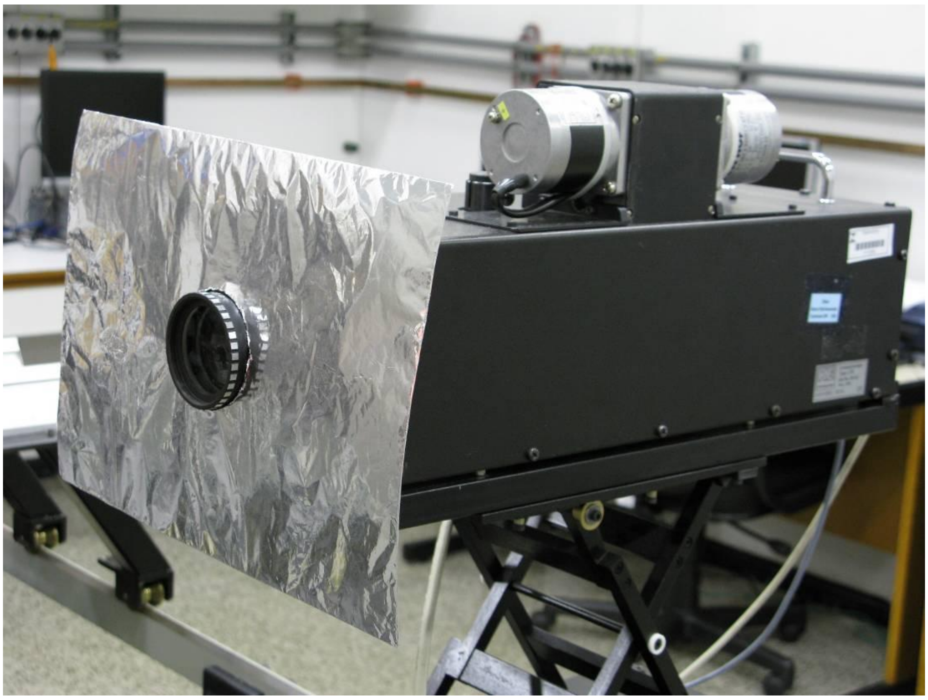

Figure 30: LP3 pyrometer equipped with thermal radiation shield.

6.3.2. Simulation results

The effect of the addition of copper at a molar concentration of 7686 ppm (~0,300 g) was simulated using Thermo-Calc. The result of this simulation was compared to the one obtained experimentally and can be seen in table 15. It can be concluded again that, for this level of dopant, the Thermo-Calc simulations poorly match with those obtained experimentally. The level of agreement is even worse than for Ni-C #7. The experimental results show that the addition of copper decreased the melting temperature by 0,32 °C, while the simulation gave the result that the temperature should have increased by 1,74 °C than the base Ni-C eutectic. It is clear that for these levels of dopant Thermo-Calc is not able to supply reliable results for temperature change for the alloy Ni-C-Cu.

Table 15: Simulated and Measured Temperatures for Ni-C-Cu 7686 ppm

Eutectic	Melting Temperature °C	
	Measured	Simulated
Ni-C	1328,72	1326,36
Ni-C-Cu (7686 ppm)	1328,40	1328,10
Difference	-0,32	1,74

6.4. Summary of Ni-C-Cu measurements

It can be seen in figure 31 a comparison of the base Ni-C eutectic cell with the two doped Ni-C-Cu eutectic cells. It is possible to see that the addition of copper did not change the slope of the melting and freezing curves; the effect was to shift downwards the realization curves. The undercooling apparently was not so affected by the doping, but different freezing temperatures were achieved. All the cells experienced basically the same heating and cooling cycles, that is, no change was made in the program in the temperature controller of the furnace as detailed above.

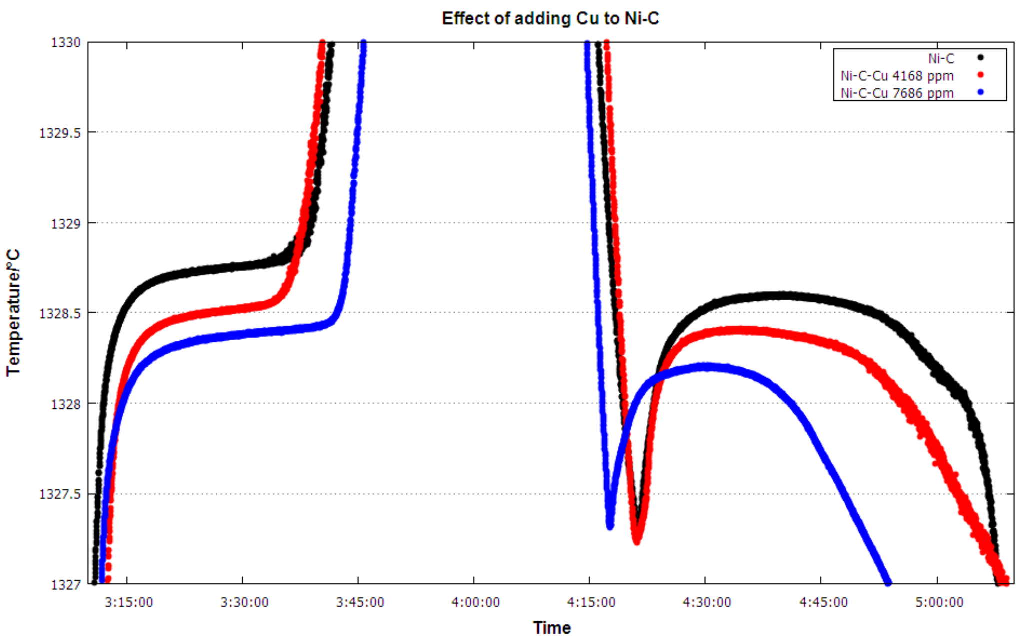

Figure 31: Comparison of realization curves of Ni-C and Ni-C-Cu eutectic cells

In figure 32 the effect of the addition of copper in the melting temperature of the Ni-C eutectic alloy is given. It can be seen that a straight line does not fit very well, however there is insufficient data to get a full understanding of the effect of doping on the temperature depression. For a better understanding of what the sensitivity coefficient of this relation would actually be, a larger number of points would be required, and this is outside the scope of this thesis. However this data could potentially be used to refine and improve the modeling performed by Thermo-Calc for the addition of Cu in the Ni-C eutectic.

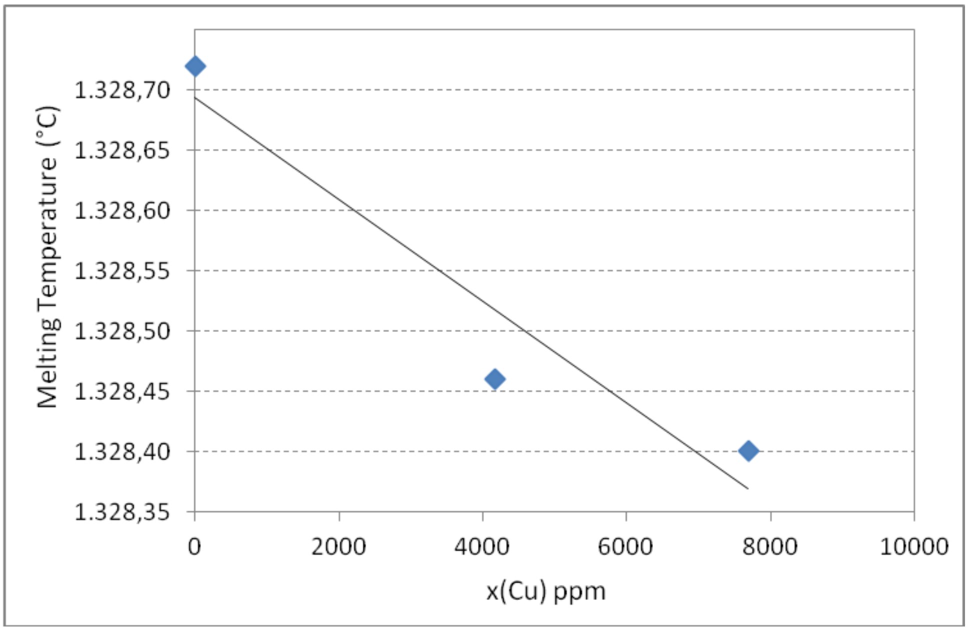

Figure 32: Effect of addition of copper in the Ni-C eutectic alloy

6.5. Summary of the chapter

The base Ni-C eutectic cell melting temperature measured was 1328,72 °C. The temperature of a doped cell with Cu at 4168 ppm (cell Ni-C-Cu #7) was 1328,46 °C. When the quantity of copper was increased to 7686 ppm (Ni-C-Cu #8), the temperature changed to 1328,40 °C. The stability of the artefacts to long duration testing over more than 50 hours above 1300 °C has been demonstrated, assuring their stability as potential comparison artefacts. However, in order to verify if this behavior was particular to copper, another dopant was studied. The results of the cells doped with tin are shown in chapter 7. Thermo-Calc did not reliably predict the changes in temperature with dopant level.