7
Results of Ni-C-Sn eutectic cells

7.1. Ni-C-Sn 828 ppm doped cell (Ni-C-Sn #9)

7.1.1. Experimental results

After the promising results obtained with the Ni-C doped with copper, with regards to changing the transition temperature but maintaining reliable melting plateau, it was important to select another dopant. It was important to check that the temperature of the HTFPs can be adjusted with a different dopant AND that reliability of plateau be maintained – i.e. that the influence of doping is more general and can be more widely applied to alter HTFP temperatures. As with Cu a dopant, whose properties are relatively similar to those of nickel, tin was chosen. Important considerations were relative matching of atomic radius (Ni = 149 pm and Sn =145 pm) and crystal structure (Ni = cfc and Sn = tetragonal). The second dopant selected that met these criteria was tin, which has a much lower melting temperature than the nickel. The first cell doped with tin at a concentration of 828 ppm, and the second at a concentration of 392 ppm of tin. The fact that Sn had a very different melting temperature (232 °C as opposed to 1329 °C for Ni-C) rendered it a very promising dopant. The final selection of Sn was made, after checking that its vapor pressure was still very low at the melting temperature of Ni-C eutectic.

The doped cell was constructed in the same way as the Ni-C-Cu cells as described in the previous chapter and so construction details are omitted here. The first Sn doped cell (Ni-C-Sn #9) contained a mass of 34,138 g of eutectic alloy and was doped at a molar concentration of 828 ppm of tin (0,0609 g). The dopant had a purity of 99,9999 % and was available in the form of small shot. The dopant was added at the last step of the filling of the cell.

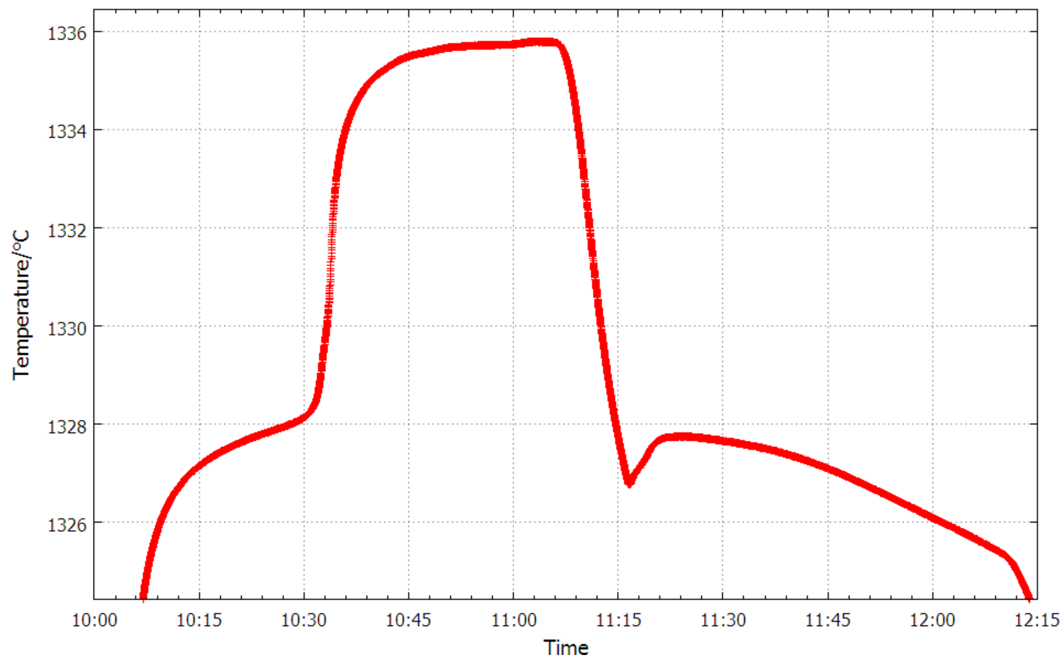

Figure 33: Realization of the Ni-C-Sn #9 eutectic cell

Figure 33 shows a typical realization curve of the Ni-C-Sn #9 cell. It is possible to see that the effect of the tin was to make the melting plateau slope and also to displace it downwards. When compared to the pure Ni-C eutectic, the melting temperature (of the point of inflection) was 0,8 °C lower in the doped cell.

Table 16: Results for the Ni-C-Sn 828 ppm eutectic cell

Date	Temperature (°C)
5/12/2012	1327,794
	1327,805
	1327,804
	1327,843
	1327,832
	1327,837
6/12/2012	1327,826
	1327,819
	1327,820
	1327,799
	1327,819
	1327,821
Mean	1327,818
s	0,004

7.1.2. Simulation results

A Thermo-Calc simulation was performed on Ni-C It was simulated the effect of with the addition of tin at a molar concentration of 828 ppm. The result of this simulation was compared to the results obtained experimentally and can be seen in table 17. For this dopant, the Thermo-Calc results match more closely those obtained experimentally, at least compared to the copper simulation. The experimental results show that the addition of tin decreased the melting temperature in 0,90 °C, while the simulation gave a result 1,34 °C lower than the base Ni-C eutectic. For this element it seems that simulation gives more reliable results than for copper.

Table 17: Simulated and Measured Temperatures for Ni-C-Sn 828 ppm

Eutectic	Melting Temperature °C	
	Measured	Simulated
Ni-C	1328,72	1326,36
Ni-C-Sn (828 ppm)	1327,82	1325,02
Difference	-0,90	-1,34

7.2. Ni-C-Sn 392 ppm doped cell (Ni-C-Sn #10)

7.2.1. Experimental results

A fourth doped cell was prepared with less Sn than the cell described in 7.1. The Ni-C-Sn #10 cell had a mass of 35,088 g of Ni-C alloy and it was doped at a molar concentration of 392 ppm (0,0294 g). The dopant was added at the last filling step. In figure 34 it is possible to see a complete realization curve for the Ni-C-Sn #10 cell. The addition of tin at approximately half of the previous molar concentration changed the melting and freezing temperatures in a proportional way. That is the melting curve was not as sloped nor was the depression in temperature so great.

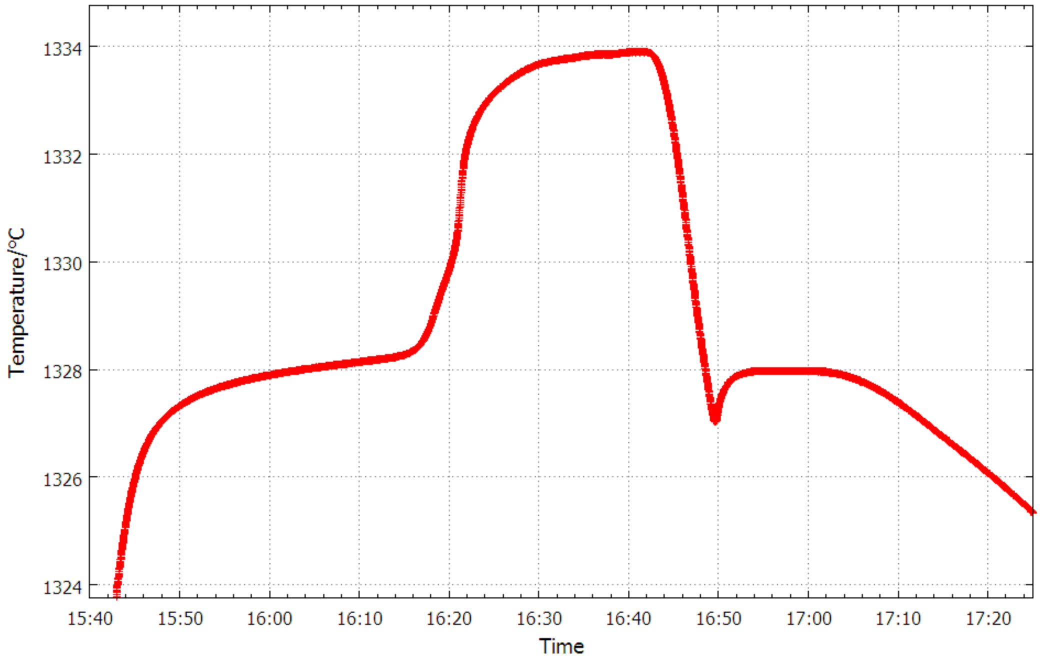

Figure 34: Realization of the Ni-C-Sn #10 eutectic cell

Table 18 shows all the temperature measurement results for this cell. A set of 12 results was achieved for this cell, showing a very small dispersion, with a standard deviation of the mean of the order of 4 mK. In order to fully characterize this cell in the long term, extra measurements need to be made in the future, to see if this initial excellent stability can be confirmed.

Table 18: Results of the realization of Ni-C-Sn #10

Date	Temperature (°C)
16/04/2013	1328,049
	1328,087
	1328,086
	1328,084
	1328,093
	1328,088
24/04/2013	1328,064
	1328,081
	1328,083
	1328,089
	1328,090
	1328,090
Mean	1328,082
s	0,0037

7.2.2. Simulation results

Another Thermo-Calc simulation was performed on Ni-C, in this case with the addition of tin at a molar concentration of 392 ppm. The result of this simulation was compared to the results obtained experimentally this can be seen in table 19. As for the other tin simulation the Thermo-Calc results match more closely those obtained experimentally, at least compared to the copper simulation. The experimental results show that the addition of 392 ppm of tin decreased the melting temperature in 0,64 °C, while the simulation gave a result 0,65 °C lower than the base Ni-C eutectic.

Table 19: Simulated and Measured Temperatures for Ni-C-Sn 392 ppm

Eutectic	Melting Temperature °C	
	Measured	Simulated
Ni-C	1328,72	1326,36
Ni-C-Sn (392 ppm)	1328,08	1325,71
Difference	-0,64	-0,65

In summary, for the case of using tin as a dopant, the temperature differences between the Ni-C and Ni-C-Sn eutectics obtained by the simulation are broadly in line with those obtained experimentally, though it must be recognized that, for the higher concentration of tin cell, the measured depression is about 60 % of the calculated value.

7.3. Summary of Ni-C-Sn measurements

On figure 35 is a comparison of the base Ni-C eutectic cell with the two doped Ni-C-Sn eutectic cells. It is possible to see that the addition of tin significantly affected the slope of the melting and freezing curves; the higher the concentration of tin, higher was the slope of the melting curve. Also the addition of tin shifted the melt and freeze features to lower temperatures. The supercool was also affected by the doping and also the freezing temperatures. It should be noted that 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 – so the features seen here are a result of the doping not the furnace.

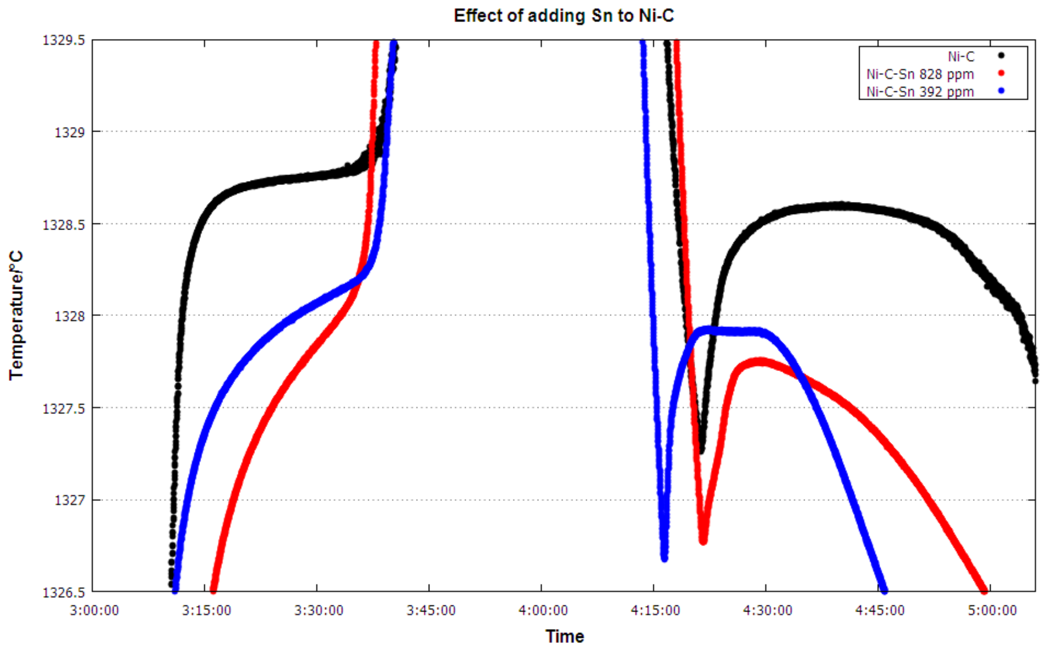

Figure 35: Comparison of realization curves of Ni-C and Ni-C-Sn eutectic cells

In figure 36 the effect of the addition of tin on the melting temperature of the Ni-C eutectic alloy can be seen and in this case the effect can be considered linear.

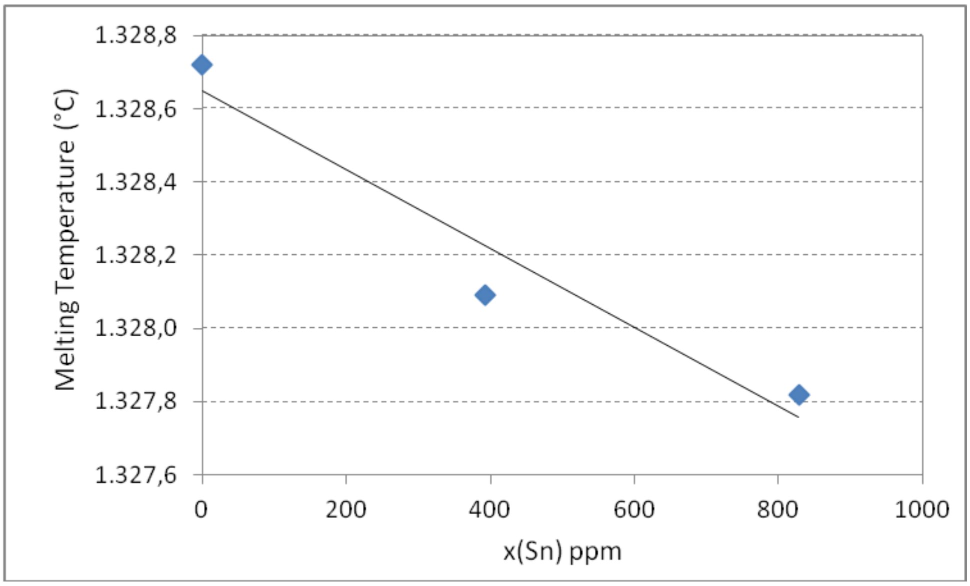

Figure 36: Effect of addition of tin in the Ni-C eutectic alloy

7.4. Summary of the chapter

Two Ni-C cells have been doped with differing concentrations of Sn and their melting curves measured and compared to an undoped system. Despite the dramatic increase in the slope of the melting curve with level of dopant the point of inflection remains very stable. This confirms that their use as temperature references for blind key comparisons would in principle be possible. In addition the thermochemical modeling of Sn with Ni-C gave reasonable agreement with the measurements. This latter result holds promise for developing HTFPs with tailored temperatures using such modeling – provided the thermochemical data underlying the simulation is reliable (this may not have been the case for the Cu dopant).