

## **4. Thermodynamic modeling of multicomponent phase equilibria**

At the early stages of this work, it was necessary to select an adequate material to be used as a dopant for the metal-carbon eutectic. The first metal-carbon alloy chosen for study was the cobalt-carbon eutectic, due to the easy availability of high purity powders, price and simple phase diagram. So, having defined the base metal-carbon alloy, it was necessary to select the material to be used as dopant, which should have, in principle, physical properties matching those of cobalt. Also, this material should form relatively simple phase diagrams with carbon and cobalt. In order to check these desirable characteristics, it was necessary to make use of a thermochemical simulation software; in this case the Thermo-Calc program was chosen.

With the aid of this software, it was possible to simulate the effect of the addition of the dopant at a particular concentration on the melting temperature of the cobalt carbon-alloy. This simulation could be run several times until the right concentration could be obtained to yield the desired temperature change.

Thermo-Calc makes use of thermochemical databases and thermodynamic relations and properties, combined with elaborate mathematical tools, based on the Calphad method, which stands for Calculation of Phase Diagrams. This method will be described in the following section.

### **4.1. The CALPHAD method**

#### **4.1.1. Introduction**

Phase diagrams are visual representations of the state of a material as a function of temperature, pressure and concentrations of the constituent components and are tools for alloy design, development, processing and helps their users to understand the physics of the alloying process.

The state of a two-component material at constant pressure can be presented in the well-known graphical form of binary phase diagrams, shown in figure 6. In the case of three-component materials, it is necessary to add an additional dimension for a complete representation. However, this kind of systems is usually presented by a series of sections or projections. For systems with more than 3 components, the graphical representation of the phase diagram is not very common, and it lacks reliability because of insufficient background experimental data. However, the calculation of phase diagrams does not depend on their graphical representation.

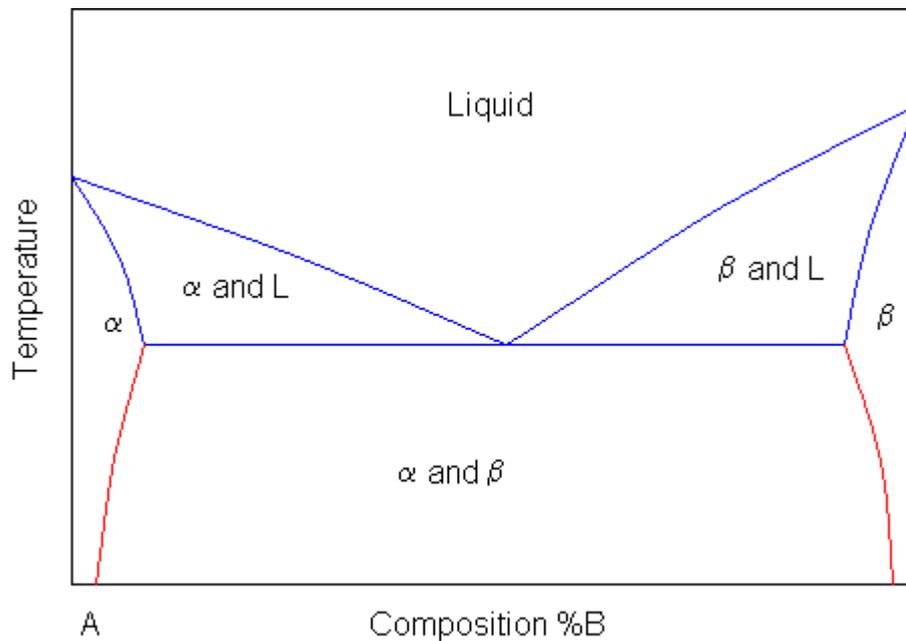


Figure 6: Example of a binary phase diagram

#### 4.1.2. History

More than a century ago, J. W. Gibbs [30] first established the correlation between thermodynamics and phase equilibria. During the early seventies, the pioneer work of Kaufman and Bernstein developed the first computer programs for the calculation of binary and ternary phase diagrams, establishing the foundation for the CALPHAD method (CALculation of PHase Diagrams) [31]. In 1973, the first international meeting of the so called CalPhaD group took place and since then this group has grown consistently. More recently, with many developments in modeling and computational technology, the computer

calculation of multicomponent phase equilibria has been considered a true possibility.

These calculations are generally computationally very intensive, but the recent advances in the area of algorithms and computer speed, can deal with them with no difficulties. It is worth noting that, despite the predicted phase diagrams can represent reliably the gross features, they still lack enough accuracy for many applications.

#### **4.1.3. Scope of phase diagram calculations**

The CALPHAD method [31] is based on the fact that a phase diagram is a representation of the thermodynamic properties of a system. So, if the thermodynamic properties are known, it can be possible to calculate the multicomponent phase diagrams, based on the combination of the thermodynamic descriptions of lower order systems (e.g., the Gibbs energy of each phase) to extrapolate higher order systems.

The experimental determination of phase diagrams is a time consuming and costly task. When the number of components increases this becomes critical. As far as the experimental results are available, this information can then be used to improve the original thermodynamic functions.

Another possibility of use of the numerical phase diagram information is to supply them to more sophisticated modeling, which can consider that the phase equilibria can be applied locally (local equilibrium) to describe the interfaces between phases. In these cases only the concentrations at this interface are assumed to obey the requirements of thermodynamic equilibrium. The fact that the phase diagram is only a portion of the information that can be obtained from these calculations, justify the use of the expression “computational thermodynamics” rather than "calculation of phase diagrams".

#### **4.1.4. Thermodynamic descriptions and models**

The Gibbs energy ( $G$ ) is the most useful thermodynamic function of state and it is used when the temperature, the pressure and the composition of a system are controlled. The system is considered in equilibrium when its content of Gibbs energy reaches the minimum value [32].

Typically, the Gibbs function is calculated from the equation 11:

$$G(T) = H(T) - S(T) \cdot T \quad (11)$$

Where  $H(T)$  and  $S(T)$  are calculated, respectively, from

$$H = H(T_0) + \int_{T_0}^T C_p \cdot dT \quad (12)$$

and

$$S = S(T_0) + \int_{T_0}^T C_p \cdot \frac{dT}{T} \quad (13)$$

It is worth noticing that  $C_p$  is also a function of absolute temperature  $T$ , generally experimentally obtained and modeled by:

$$C_p(T) = x + y \cdot T + \frac{z}{T} + w \cdot T^2 \quad (14)$$

Where  $x$ ,  $y$ ,  $z$  and  $w$  are numerical coefficients.

In order to calculate the phase equilibria in a multicomponent system, it is necessary to minimize the total Gibbs energy,  $G$ , of all the phases that take part in this equilibrium

$$G = \sum_{i=1}^p n_i G_i^\phi = \min \quad (15)$$

where  $n_i$  is the number of moles,  $G_i$  is the Gibbs energy of phase  $i$  and  $p$  is the number of phases.

A thermodynamic description of a system requires assignment of thermodynamic functions for each phase. The CALPHAD method employs a variety of models to describe the temperature, pressure and concentration dependencies of the free energy functions of the various phases. The contributions to the Gibbs energy of a phase can be written:

$$G^\phi = G_T^\phi(T, x) + G_p^\phi(p, T, x) + G_m^\phi(T_C, \beta_0, T, x) \quad (16)$$

where  $G_T(T, x)$  is the contribution to the Gibbs energy from the temperature,  $T$ , and the composition,  $x$ ,  $G_p(p, T, x)$  is the contribution due to the pressure,  $p$ , and  $G_m(T_0, \beta_0, T, x)$  is the magnetic contribution arising from the Curie<sup>3</sup> temperature,  $T_C$ , and the average magnetic moment per atom,  $\beta_0$ .

<sup>3</sup> Curie temperature is the temperature at which a material changes its magnetic behavior.

The temperature dependence of the concentration terms of  $G_T$  is usually expressed as a power series of  $T$ , calculated from equations 11 to 14:

$$G = a + b \cdot T + c \cdot T \cdot \ln(T) + \sum d_n \cdot T^n \quad (17)$$

where  $a$ ,  $b$ ,  $c$  and  $d_n$  are coefficients and  $n$  are integers. This function is valid for temperatures above the Debye<sup>4</sup> temperature.

For multicomponent systems, it is interesting to separate three contributions from the concentration dependence to the Gibbs energy of a phase,  $G^\phi$ :

$$G^\phi = G^0 + G^{ideal} + G^{xs} \quad (18)$$

The first term,  $G^0$ , corresponds to the Gibbs energy of a mechanical mixture of the constituents of the phase, the second term,  $G^{ideal}$ , corresponds to the entropy of mixing for an ideal solution and the third term,  $G^{xs}$ , and is the so-called excess Gibbs energy term. Since the term "regular solution" was used for the first time to describe interactions of different elements in a random solution, a series of models have been proposed for phases which deviate from this condition, i.e. show a strong compositional variation in their thermodynamic properties, to describe the excess Gibbs energy,  $G^{xs}$ . According to Kattner [33], the most commonly used models (listed in the order of increasing complexity) are those for stoichiometric phases, regular solution type models for disordered phases, and sublattice models for ordered phases having a range of solubility or exhibiting an order/disorder transformation.

The Gibbs energy of a binary stoichiometric phase is given by:

$$G^\phi = x_A^0 \cdot G_A^0 + x_B^0 \cdot G_B^0 + \Delta G^f \quad (19)$$

where  $x_A^0$  and  $x_B^0$  are mole fractions of element  $A$  and  $B$  and are given by the stoichiometry of the compound,  $G_A^0$  and  $G_B^0$  are the respective reference states of element  $A$  and  $B$ , and  $G^f$  is the Gibbs energy of formation. The first two terms correspond to  $G^0$  and the third term to  $G^{xs}$  in Equation (18).  $G^{ideal}$  of Equation (18) is zero for a stoichiometric phase since there is no random mixing.

Binary solution phases, such as liquid and disordered solid solutions, are described as random mixtures of the elements by a regular solution type model:

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<sup>4</sup> Debye temperature is the highest temperature that can be achieved due to a single normal vibration.

$$G^\phi = x_A G_A^0 + x_B G_B^0 + RT \cdot \{x_A \ln x_A + x_B \ln x_B\} + x_A \cdot x_B \sum_{i=0}^n G_i \cdot (x_A - x_B)^i \quad (20)$$

where  $x_A$  and  $x_B$  are the mole fractions and  $G_A^0$  and  $G_B^0$  the reference states of elements  $A$  and  $B$ , respectively. The first two terms correspond to  $G^0$  and the third term, from random mixing, to  $G^{ideal}$  in Equation (18). The  $G_i$  of the fourth term are coefficients of the excess Gibbs energy term,  $G^{xs}$ , in Equation (18).

From the condition that the Gibbs energy at thermodynamic equilibrium reveals a minimum for given temperature, pressure and composition, Gibbs [30] derived the equilibrium conditions that the chemical potential,  $\mu_n$ , of each component,  $n$ , is the same in all phases:

$$\left| \begin{array}{l} \mu_1' \\ \mu_2' \\ \dots \\ \mu_n' \end{array} \right| \left| \begin{array}{l} \mu_1'' \\ \mu_2'' \\ \dots \\ \mu_n'' \end{array} \right| = \dots \left| \begin{array}{l} \mu_1^\phi \\ \mu_2^\phi \\ \dots \\ \mu_n^\phi \end{array} \right| \quad (21)$$

The chemical potentials are related to the Gibbs energy by the equation:

$$G = \sum_{i=1}^n \mu_i \cdot x_i \quad (22)$$

Equation (22) results in  $n$  non-linear equations which can be used in numerical calculations and solved using a Newton-Raphson technique.

In the solution of the above equations, it should be considered also the Gibbs phase rule, equation (23), which is an expression that calculates the degree of indetermination of the system of equations associated to the thermodynamic equilibrium of a closed system. With this expression it is possible to define how many independent intensive properties are needed to completely define the system and calculate the Gibbs energy.

$$F = C - P + 2 \quad (23)$$

Where  $F$  stands for the number of degrees of freedom,  $C$  is the number of components and  $P$  is the number of phases present.

#### 4.1.5. Continuous improvements

Thermodynamic databases of multicomponent system require consistency of the model descriptions and the parameters used. The CALPHAD group, with the

constant improvement of computational technology, aims to develop descriptions of systems, which can be used for the construction of more realistic models, obtaining more accurate descriptions of complex systems.

It should be noted that the calculated phase diagram is not only able to reproduce the experimentally observed phase diagram, but it is also able to provide the thermodynamic functions for extrapolation into higher order systems.

#### **4.1.6. Computer software and databases**

A variety of software packages are available for the calculation of phase diagrams, such as JMatPro [34], FactSage [35], Pandat [36], MTDATA [37], Thermo-Calc [38] and DICTRA [38]. These software packages more recently are being developed with user friendly computer interfaces, which make phase diagram information more easily accessible for the non-expert user.

For these applications, the user needs only to supply a bulk composition and temperature limits for the calculation and the programs generate the remaining conditions that are needed for the calculation.

Depending on the application, there are many thermodynamic databases available, the data is supplied in a wide selection of databases for various purposes and for many different materials and applications, such as for compounds, general alloys, steels and Fe-Alloys, Ni and Ni-alloys, light metal alloys, solder alloys, nuclear materials, minerals and aqueous solutions. The databases are produced by experts by evaluation of experimental data.

#### **4.2. Systems modeled**

One of the important things that can be determined for metal-carbon eutectic systems by simulation is the carbon concentration of the eutectic composition. The simulation can also be used to get an understanding of the effect on the melting temperature of adding dopants to the base metal-carbon alloy. The main objective in performing such simulations was to estimate the amount of substance required to make a pre-determined change in the transition temperature of the base metal-carbon eutectic. In this work the eutectic systems modeled were the cobalt-carbon and nickel-carbon, pure and doped by selected elements.

For Thermo-Calc to simulate the metal-carbon or metal-carbon-dopant eutectic systems in this thesis, it was necessary to supply some input quantities to the software. They were the pressure, the molar fractions of the base metal (Co or Ni) or molar fraction of carbon for metal-carbon eutectic systems. When a dopant was added to the base alloy, another quantity should be supplied, which was the molar fraction of the dopant. One of the initial interfaces of Thermo-Calc is shown in figure 7. In order to find the melting temperature of the eutectic alloy, it was monitored its solid fraction. When solid phase was still present, the process was simulated again with a slightly higher temperature. This procedure was repeated until an accuracy of 0,01 °C was achieved in the melting temperature.

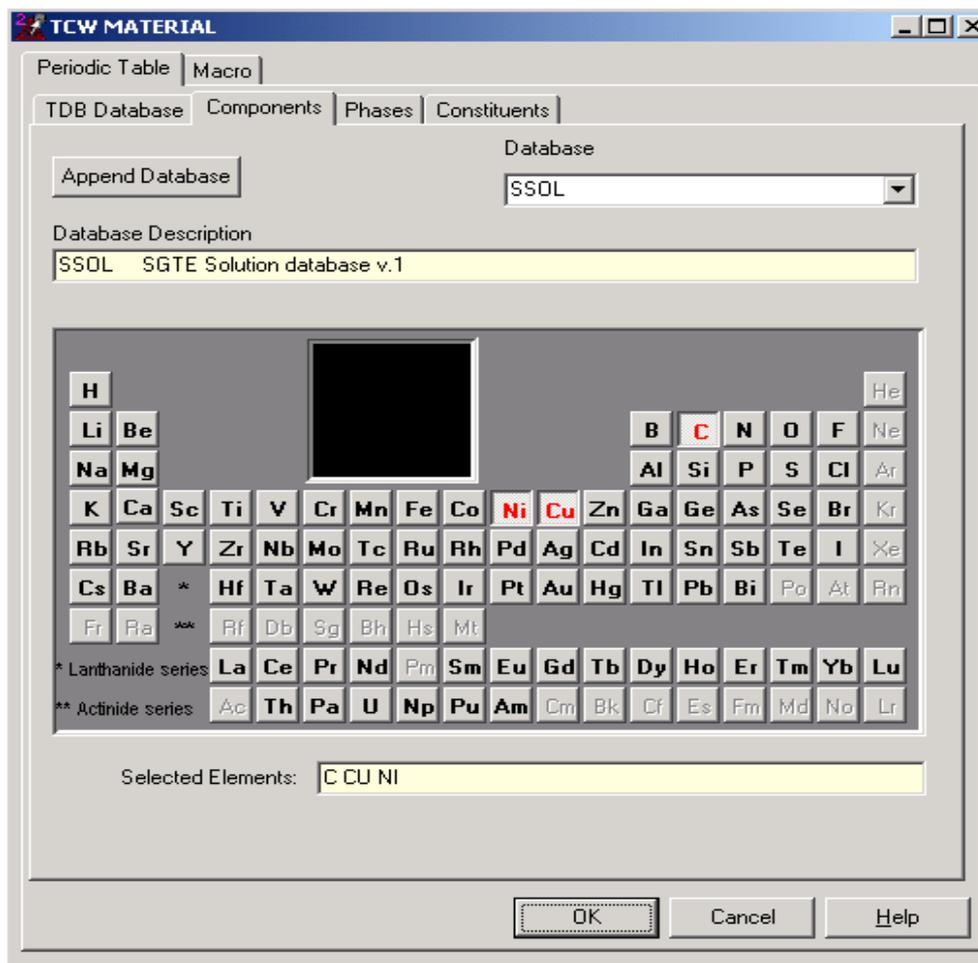


Figure 7: A Thermo-Calc screen to select the elements

#### 4.2.1. Cobalt-Carbon

The first eutectic system simulated was the cobalt-carbon. In figure 8 it is possible to see the phase diagram of this system, as simulated by Thermo-Calc.

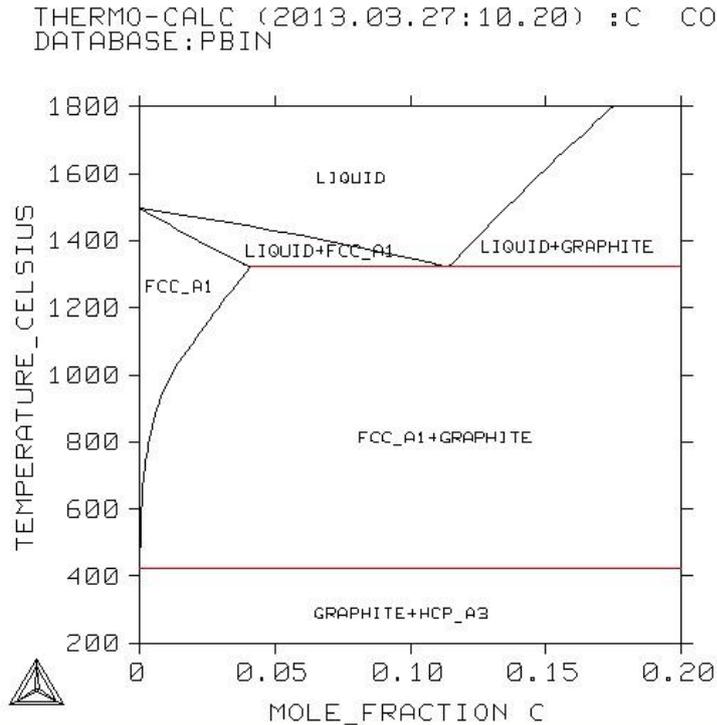


Figure 8: Phase diagram of the Co-C system

For this system, the melting temperature at the eutectic composition ( $x(C) = 0,114$ ) was calculated to be 1320,88 °C. In fact, the real measured transition temperature for this eutectic is 1324 °C. Copper was chosen to be a suitable dopant, considering its melting temperature, atomic radius and availability at high purity. The modeling indicated that the concentration of copper in the alloy Co-C to promote a temperature change of the order of 0,1 °C to 0,2 °C was around 800 ppm. The resulting melting temperature obtained by Thermo-Calc for the Co-C doped with 800 ppm of Cu was 1321,00 °C, which is 0,12 °C higher than the pure Co-C eutectic. Table 5 shows a summary of the results found for Co-C/Co-C-Cu system.

Table 5: Summary of temperatures calculated for Co-C/Co-C-Cu

	Co-C	Co-C-Cu (800 ppm)	Temperature Change (°C)
Melting temperature (°C)	1320,88	1321,00	+0,12

#### 4.2.2. Nickel-Carbon

The second system modeled was the nickel-carbon eutectic. The change to the Ni-C point was pragmatic and was driven by the fact that during the initial experimental phase of the project, some problems occurred with the cobalt-carbon alloy, which caused successive (and numerous) breakages of the blackbody cavities. It was thought that Ni-C would be less subject to breakage, hence the change. The second reason for choosing Ni-C as an alternative to Co-C is that its transition temperature is very close to that of Co-C. Co and Ni are very close to each other in the periodic table and its physical properties are also very similar to those of cobalt.

In figure 9 it is possible to see the phase diagram for the nickel-carbon system as simulated by Thermo-Calc.

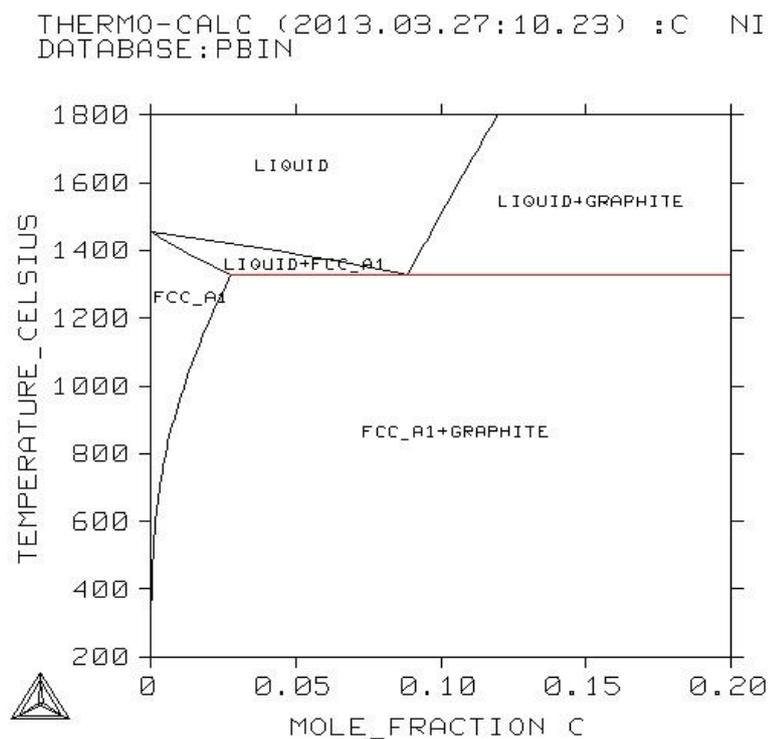


Figure 9: Phase diagram of the Ni-C system

For this system, the melting temperature at the eutectic composition ( $x(C) = 0,0886$ ) was calculated to be 1326,36 °C. Copper was again chosen to be a dopant. The start value for the concentration of copper in the alloy Ni-C to promote a temperature change of the order of 1,0 °C was found to be 4000 ppm. The resulting melting temperature obtained by Thermo-Calc for the Ni-C doped with 4000 ppm of Cu was 1327,26 °C, which is 0,9 °C higher than the pure Ni-C

eutectic. Table 6 shows a summary of the results obtained by Thermo-Calc for Ni-C/Ni-C-Cu system.

Table 6: Summary of temperatures calculated for Ni-C/Ni-C-Cu

	Ni-C	Ni-C-Cu (4000 ppm)	Temperature Change (°C)
Melting temperature (°C)	1326,36	1327,26	+0,90

Also a second possible dopant was simulated. One that would, in principle at least, cause a reduction in the transition temperature. This time tin was selected as a dopant, considering its similar atomic radius and crystal structure, but also its very different melting temperature, when compared to copper. Thermo-Calc was used to simulate the effect of the addition of 800 ppm of tin (Sn) in the Ni-C eutectic matrix. The model predicted that the effect of this addition was to decrease the melting temperature by 1,3 °C. In table 7 it is possible to see a summary of the results obtained by Thermo-Calc for the Ni-C/Ni-C-Sn system.

Table 7: Summary of temperatures calculated for Ni-C/Ni-C-Sn

	Ni-C	Ni-C-Sn (800 ppm)	Temperature Change (°C)
Melting temperature (°C)	1326,36	1325,06	-1,30

### 4.3. Summary of the chapter

On the basis of this modeling, four fixed points were constructed which were to have dopants, copper and tin, in two different molar concentrations, in a way to evaluate the effect of the dopant in a wider concentration. The results of the realization temperatures of these eutectic cells, and also their comparison with simulation results, will be presented in chapters 6 and 7.