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# Thermodynamic Modeling by the CALPHAD Method and its Applications to Innovative Materials

Among the different steps leading to a multi-scale lifetime prediction for aero-engine components and other industrial components, one seems to be apart from the other mechanical engineering concerns: thermodynamic and microstructural modeling. Here is given an introduction to the CALPHAD method [19, 27], explaining how it actually models the thermodynamic properties of multicomponent systems. Then, a number of applications are described, while emphasizing the relevance of using the CALPHAD method for the purpose of developing integrated engineering methods. Finally, the importance of building thermodynamic databases creates a high need for the development of *ab initio* calculations, as well as high-throughput experiments and, generally speaking, combinatorial materials science.

## Introduction

There have recently been many incentives or ideas for new methods to accelerate the development and maturation of innovative materials: the DARPA-AIM program [45], the Materials Genome Initiative [36], the Integrated Computational Mechanical Engineering (ICME) approach [1] and European programs [16]. Numerical modeling is a key tool within this context and in particular multi-scale modeling, in order to achieve virtual optimizations of new materials and their associated processes as fast as possible. The final purpose of the ICME approach is to be able to model the entire chain, from the elaboration of a material to the in-service behavior of the industrial component, covering the full range of process / structure / property / performance relationships.

However, the first step in this chain – or the first floor of the building – is to model microstructures. This step is crucial, since microstructures have very strong impacts on the local mechanical properties, for example through precipitation hardening. This requires, at least, a relevant thermodynamic model for the various phases in relationship with the alloy composition. Therefore, this thermodynamic model represents the foundations of our building. By the term “relevant”, we mean both the efficiency (or precision) and the tractability of this thermodynamic model, since both are highly necessary in multi-scale modeling. The CALPHAD method has proven to be capable of both efficiency and simplicity: it is in fact the only known method to calculate the thermodynamics of multicomponent alloys in a simple way. This is why both academic and industrial uses of the CALPHAD (CALculation of PHase Diagrams) method are strongly developing nowadays. Many microstructural models have, or become modified to have, CALPHAD-based thermodynamic inputs [2,9,20]; so do commercial software applications like MICRESS [38] or TC-PRISMA [42].

This article will give a theoretical introduction to the CALPHAD method, showing how the various data from experiments or numerical simulations can be collected and translated into a simple and consistent thermodynamic description, called a thermodynamic database. Then, a brief overview of CALPHAD industrial applications will be given. Finally, the importance of supporting the development and optimization of thermodynamic databases will be stressed, with examples of original dedicated experiments.

## CALPHAD method basics

The simplest way to have a complete description of the thermodynamic behavior of a system at fixed temperature, pressure and chemical composition, is to know – i.e. to be able to calculate – its Gibbs energy  $G$  (also called free energy), as a function of these state variables. Once  $G$  is known, the thermodynamic equilibrium is calculated by minimizing  $G$ . Then, it is possible to have access to any phase diagram, any chemical potential (or activity), or any chemical composition of the stable phases. The main idea of the CALPHAD method is to evaluate the free energy of every phase by simple polynomials, called Redlich-Kistler polynomials. There are two main advantages of this solution: data storage is easy, since a polynomial is fully described by the list of its coefficients, and minimization is “not so hard” because a polynomial and its derivatives are easily calculated. These polynomial coefficients are the fitting parameters for the CALPHAD thermodynamic database optimization; hence, they are very often called “parameters” by the CALPHAD community.

How approximate descriptions of  $G$  give rise to polynomial expressions with physical relevance is now explained. The first step is to investigate the Gibbs energy of a pure element. The Gibbs-Helmholtz equation gives:

$$G(T_0) = H_{298} + \int_{298}^{T_0} C_p dT - T_0 \left( S_{298} + \int_{298}^{T_0} \frac{C_p}{T} dT \right) \quad (1)$$

where  $H_{298}$  and  $S_{298}$  are the standard enthalpy and the standard entropy of the pure element at atmospheric pressure and at a temperature of 298 K. Contrary to the entropy  $S$ , the enthalpy  $H$  (and hence  $G$ ) has no absolute value: by convention,  $H_{298}$  is chosen to be equal to zero.  $C_p$  is the heat capacity of the element at constant pressure. Equation (1) is highly important, because it is the source of our formulation for the expression of the Gibbs energy of a pure element, that is :

$$G^0(T) = a + bT + cT \ln T + \sum_2^n d_n T^n \quad (2)$$

where  $a$ ,  $b$ ,  $c$  and the  $d_n$  are user-defined coefficients, called parameters, that drive the temperature dependence of the Gibbs energy of the pure element in a particular phase. Equation (2) must be fitted for each stable phase of the investigated element, the parameters being associated to the temperature range where the phase is stable. Moreover, differentiating equation (1) gives a very interesting result, since we obtain the following expression for the heat capacity:

$$C_p(T) = -c - \sum (n-1) d_n T^{n-1} \quad (3)$$

Equation (3) means that, given the heat capacity, there are only two parameters ( $a$  and  $b$ ) missing from the Gibbs energy expression. The next step is to develop an expression for single-phased alloys. When no interaction takes place between atoms of a different nature, it is easy to add the  $x_i \ln(x_i)$  term corresponding to the configuration entropy in the case of ideal mixing. However, it is necessary to add an excess Gibbs energy, due to the interactions between the different atoms. Assuming the absence of ternary interactions, the molar Gibbs energy  $G_m$  is written as:

$$G_m = \sum_i x_i G_i^0 + RT \sum_i x_i \ln x_i + \sum_i \sum_{j>i} x_i x_j \Omega_{ij} \quad (4)$$

where  $x_i$  and  $G_i^0$  are, respectively, the mole fraction and the Gibbs energy of the  $i^{\text{th}}$  pure element,  $R$  is the ideal gas constant and  $\Omega_{ij}$  is the excess Gibbs energy associated with the interaction between the  $i^{\text{th}}$  and the  $j^{\text{th}}$  pure element. It must be noted that the excess Gibbs energy contribution in equation (4) is automatically canceled when  $x_i$  or  $x_j$  is zero. Eq. (4) is called the regular solution theory. Given that this excess energy  $\Omega_{ij}$  has no physical relevance, it may vary with temperature, as well as with  $x_i$  and  $x_j$ . In order to be able to break the symmetry between the  $i^{\text{th}}$  and  $j^{\text{th}}$  element,  $\Omega_{ij}$  is developed in powers of  $x_i - x_j$ . This development of  $\Omega_{ij}$  in the expression (4) of  $G_m$  is called the Redlich-Kistler (RK) polynomial. The various expressions of the Gibbs energy are not limited by RK polynomials, and far more complex analytical expressions can be written, including contributions due to pressure, magnetism, etc. [7].

In ternary and higher-order systems, ternary interactions  $L_{ijk}$  (ternary Gibbs excess energy) can be added, but there is no need to model quaternary interactions in common systems. This is a crucial remark: it implies that the thermodynamic model for a system of  $n$  elements can be approximately considered as an extrapolation of various ternary systems. These ternary systems can be modeled separately, the extrapolation being performed

through the use of Kohler's rule or Muggianu's rule [14], as shown in figure 1. Gathering these ternary systems, containing data for each of the above parameters, produces what is called a thermodynamic database. Gathering systems supposes that the same description is made for shared pure elements, shared binary systems and any shared subsystems. Namely, the CALPHAD community shares a public pure element database [7].

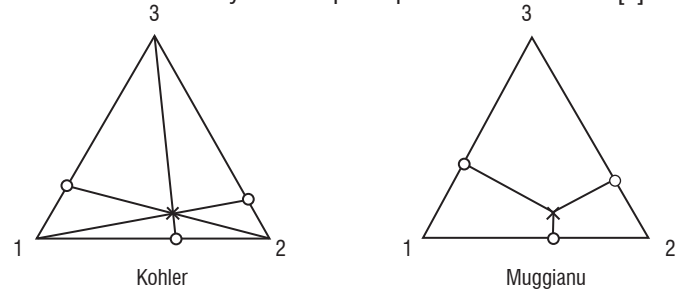


Figure 1 – Kohler's and Muggianu's rules illustrated in the example of a ternary system [14]

This is why the thermodynamic databases are said to be best described as a brick assembly, where the "unit" bricks are the pure elements, whose CALPHAD models allow binary models to be built, then ternary models and so on. This is also why there is research activity about very accurate calculations of the Gibbs energy and heat capacity of pure elements, to be compared with the CALPHAD unary database [10, 28].

The way in which the database can be built and optimized is far beyond the scope of this article. In brief, the relevance of the database parameters is tested by calculating the discrepancy between the thermodynamic data that the database produces and the corresponding experimental (or numerical) data. Optimization loops are performed and this is the know-how of the expert researchers in the field, to be able to optimize the numerous parameters of a database, with the aid of the special algorithms included in the thermodynamic software (Thermo-Calc PARROT [42], PanOptimizer [39], FactSage Optisage [35], etc.). It must be highlighted that there are many different models that can reproduce a particular binary phase diagram. The accuracy of the CALPHAD assessment will be revealed when the extrapolation into higher order systems is performed. This accuracy depends strongly on the accumulation of reliable experimental results concerning: phase diagram, calorimetric measurements and activity measurements.

Another set of data comes from what is called *ab initio* calculations, or first-principle calculations, which means that the calculation directly solves the Schrödinger equation and obtains the well-known wave functions of the quantum mechanics for the desired system. These calculations have become popular since the DFT method [23] became readily available *via* commercial software (VASP [46], Wien2k [47], ABINIT [34], etc.) and personal computers are able to solve simple systems in moderate CPU times. The accuracy of the results is often discussed, because various approximations lead to significant differences in the obtained results and, also, because unskilled researchers will very easily get irrelevant *ab initio* results.

In any case, these calculations are an appreciated help for temperature ranges that are difficult to reach, metastable or unstable phases, or for dangerous elements such as actinides. However, they have a strong limitation in regard to the number of atoms that they are able to simulate, so that – most of the time – only a unit cell of the crystalline structure is considered. For this reason, it is not possible to simulate disordered alloys, where the position of alloying atoms is not always in the same place within the unit cell, but rather random. The point is that there are specific CALPHAD models for the Gibbs energy of ordered phases that will be able to incorporate these *ab initio* calculations.

## Box 1 - Regular solution theory and topological features of the binary phase diagrams

In order to understand the topology of phase diagrams, Pelton and Thompson modeled in 1975 a basic binary phase diagram and added constant excess Gibbs energies  $\Omega$  in the solid and in the liquid phase [24]. This corresponds to the regular solution theory. The figure B1-1, taken from [27], has been created in the same way, starting from the red-framed reference A-B binary diagram. If  $\Omega$  is negative in the liquid or in the solid phase, this means that A and B “like” to be mixed together, so nothing complicated happens. Conversely, if  $\Omega$  is positive, it means that A and B “dislike” to be mixed together. Two-phased domains appear and become larger. For example, adding an excess mixing energy in the solid phase leads to an eutectic diagram. The liquid alloy may also demix, if  $\Omega$  is positive in the liquid. The upper-right corner of figure B1-1 shows that almost no single-phased domain remains when large amounts of excess energies are added in both the liquid and solid phases. In conclusion, the regular solution theory gives many different topological features for phase diagrams, even with the two-phase simplest binary diagram.

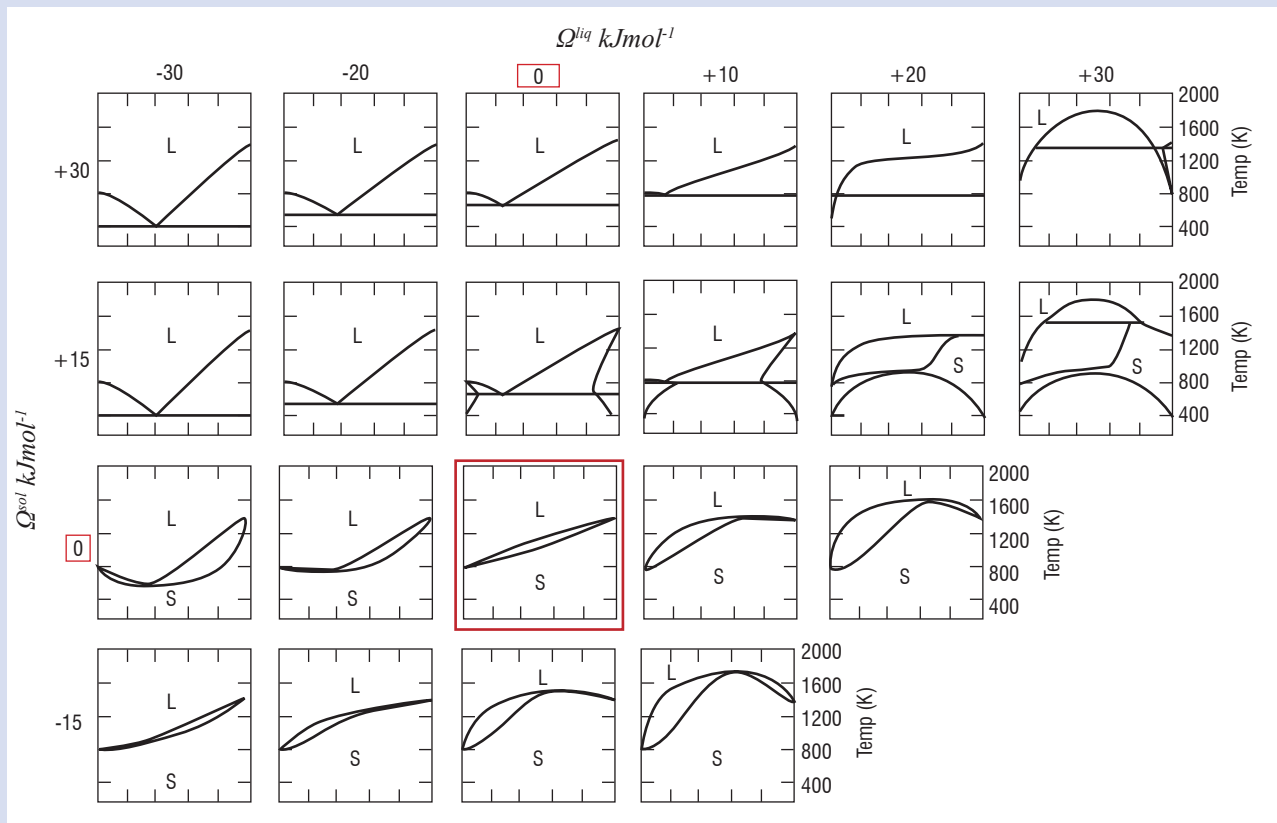


Figure B1-1 – Topological features of phase diagrams calculated using the regular solution theory [27]

In order to model ordered phases, the CALPHAD formulation should discriminate between the various sublattices occupied by the system elements. These sublattice models had a tremendous influence on the development and success of the CALPHAD method, because it is able to model not only line compounds, but also, through the associated defects (substitutions, vacancies and interstitials), interstitial phases, complex intermetallic compounds and order/disorder transformations [27]. Assuming two sublattices S1 and S2 in a binary system A-B, there are now four reference states: A:A (pure A), A:B (A occupying S1 and B occupying S2), B:A (B occupying S1 and A occupying S2), B:B (pure B). These four reference free enthalpies, known as the end-members, are very important in CALPHAD modeling. The excess Gibbs energy also has a new formulation, taking into account the sublattices through different contributions [19,27].

The phases corresponding to the end-members are very often thermodynamically (or dynamically) unstable, except for the ordered compound investigated, that is, only one among the four phases. However, each end-member must be evaluated, even though only one is experimentally available. Here, it should be understood that the *ab initio* calculations are

mandatory to provide these values, which are necessary for the construction of a relevant thermodynamic database. Results are, in general, more accurate if the CALPHAD sublattices come closer to the real crystallographic sublattices.

However, given that modeling a phase with  $m$  sublattices in an  $n$ -element thermodynamic system does require the calculation of  $nm$  end-members, there is actually a high demand for *ab initio* calculations from the CALPHAD community. For example, the work of Yaqoob *et al.* [30] details a 5 sublattice model for the  $\sigma$  phase in the Ni-Mo-Re system. This phase has a complex crystallography, which is shown on the left in figure 2. However, this is highly relevant to model this phase, because it is known to deteriorate the behavior of Ni-based superalloys, which are widely used in the high pressure turbines of aeroengines. Due to the 5 sublattice combination, the authors of [30] had to perform calculations for  $3^5 = 243$  different structures, representing 90 different chemical compositions, but the results are very satisfactory. It should be emphasized that there is a recent trend towards accumulating the results of *ab initio* calculations in the form of databases, which are growing very quickly [37].

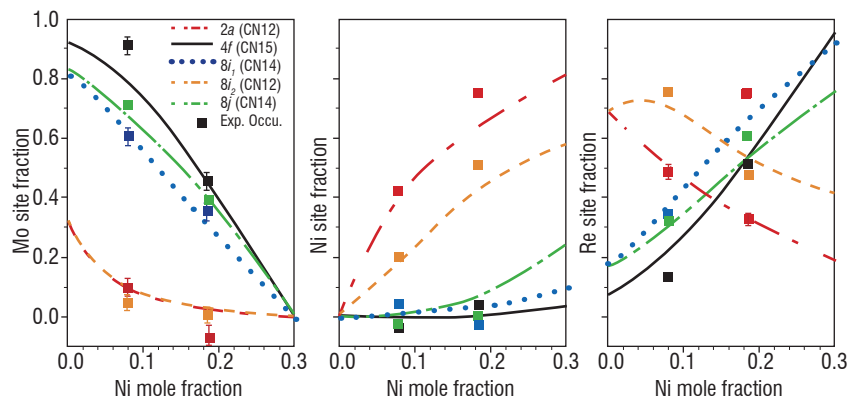
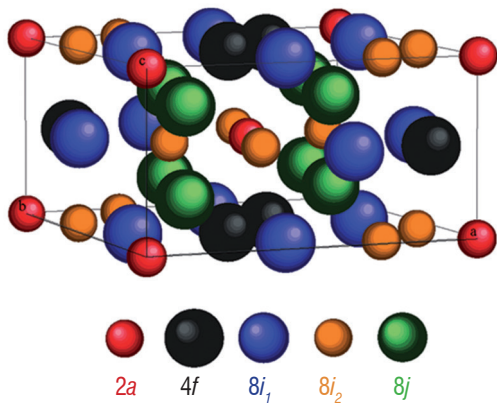


Figure 2– Crystal structure of the  $\sigma$  phase (left); comparison between experimental (squares) and calculated (lines) site occupancies of the Ni-Mo-Re  $\sigma$  phase at 1873 K along a line of the ternary diagram [30]

Once the thermodynamic model has been completed, equilibrium calculations may be performed by minimizing the Gibbs energy. The classical method for obtaining the minimum of the Gibbs energy is the use of Lagrange multipliers  $\mu_i$  and  $\lambda^\phi$  related to the  $N_{el} + N^\phi$  physical constraints (mass balance equation for each of the  $N_{el}$  elements, sum of the molar fractions equal to unity in each of the  $N^\phi$  phases), as described in [15]. The Lagrange function, noted as L, is written as:

$$L = \sum_{\phi=1}^{N^\phi} n^\phi G_m^\phi + \sum_{i=1}^{N_{el}} \mu_i \left( n_i - \sum_{\phi=1}^{N^\phi} n^\phi x_i^\phi \right) + \sum_{\phi=1}^{N^\phi} \lambda^\phi \left( 1 - \sum_{i=1}^{N_{el}} x_i^\phi \right) \quad (5)$$

where  $G_m^\phi$  is the molar Gibbs energy of the phase  $\phi$ ,  $n^\phi$  is the number of moles of the phase  $\phi$  and  $x_i^\phi$  is the mole fraction of the  $i^{th}$  element in the phase  $\phi$ . Then, a non-linear system of  $N_\phi (N_{el} + 1)$  Lagrange-type equations (6a) and (6b) must be solved, usually using a Newton-Raphson algorithm, in addition to the  $N_{el} + N_\phi$  initial constraints (6c) and (6d).

$$\frac{\partial L}{\partial n^\phi} = G_m^\phi - \sum_{i=1}^{N_{el}} \mu_i x_i^\phi = 0 \quad (6a)$$

$$\frac{\partial L}{\partial x_i^\phi} = n^\phi \left( \frac{\partial G_m^\phi}{\partial x_i^\phi} - \mu_i \right) - \lambda^\phi = 0 \quad (6b)$$

$$1 - \sum_{\phi=1}^{N_\phi} x_i^\phi = 0 \quad (6c)$$

$$n_i - \sum_{\phi=1}^{N_\phi} n^\phi x_i^\phi = 0 \quad (6d)$$

The final result gives the values of the initially unknown quantities: the amount  $n^\phi$  of the various phases, their composition given by the  $x_i^\phi$  and the Lagrange multipliers  $\lambda^\phi$  and  $\mu_i$ , these  $\mu_i$  being considered as the chemical potentials of the  $i^{th}$  element. All information regarding the thermodynamic equilibrium has been calculated.

## Industrial applications

### Outside ONERA

The domains of application of the CALPHAD method are so numerous that it is impossible to list them here. The list of thermodynamic

databases proposed by the TCS-AB company for the Thermo-Calc software gives an idea of the number of material classes that have been assessed with the CALPHAD method [42]. It includes metallic materials (steels, Ni-based superalloys, titanium alloys and aluminum alloys), ceramics, cemented carbides, intermetallics, nuclear fuels, cermets, solders, etc. Some striking examples will be given here, showing what can be expected in the future for alloy design and optimization.

The Ford company has developed the ability to perform so-called “virtual castings” [1]. Using the Procast [40] and Abaqus [33] software applications, the sole inputs for the calculation are: the complex die geometry, the alloy composition and the required properties. The castability, phase transformations and resulting mechanical properties (tensile strengths, as well as low-cycle fatigue properties) are simulated together in the same 3D virtual object. The Ford company claimed that this new approach reduced time from 15-20% for the design of new engine blocks and hence saved millions of dollars. This required state-of-the-art calculations and experiments. As an example, they investigated how to calibrate heat-transfer coefficients for the solidification simulation. Moreover, solid-state diffusion was coupled to the dendrite structure evolution, with the entire calculation being actually coupled with the CALPHAD software Pandat [39]. The influence of each length scale in their multi-scale simulation is summed up in figure 3. The acceleration effort for the ultrahigh-strength steel design, such as Ferrium S53 and M54,

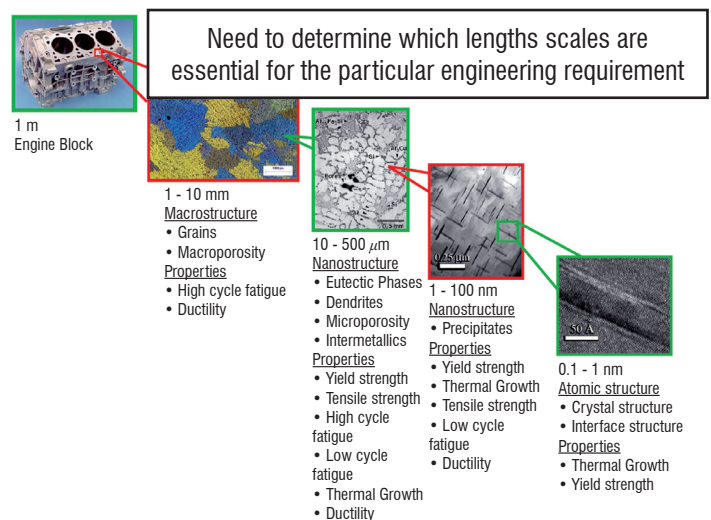


Figure 3 – Relevant length scales behind the multi-scale modeling from atoms to engine that was developed by Ford company to simulate so-called “virtual castings” [1]

is a very good illustration of the success of Accelerated Insertion of Materials [45] (see figure 4). The microstructural modeling was performed by the Precipicalc software, which uses the Thermo-Calc and DICTRA software as engines for the calculation of equilibrium and diffusion [42]. The most surprising fact may lie in the ability to predict the manufacture variation. Big simulation datasets have allowed designers to evaluate the 1% minimum ultimate tensile strength and to compare it to the material requirement. This proved the necessity of additional process optimization before starting the material evaluation at a larger production scale, saving approximately one year in time and a half million dollars. Finally, the evaluation of the 1% minimum ultimate tensile strengths (over 10 heat values and 600 observations) showed only a 7 MPa difference between the calculation results and the experiments, revealing how relevant this approach has been.

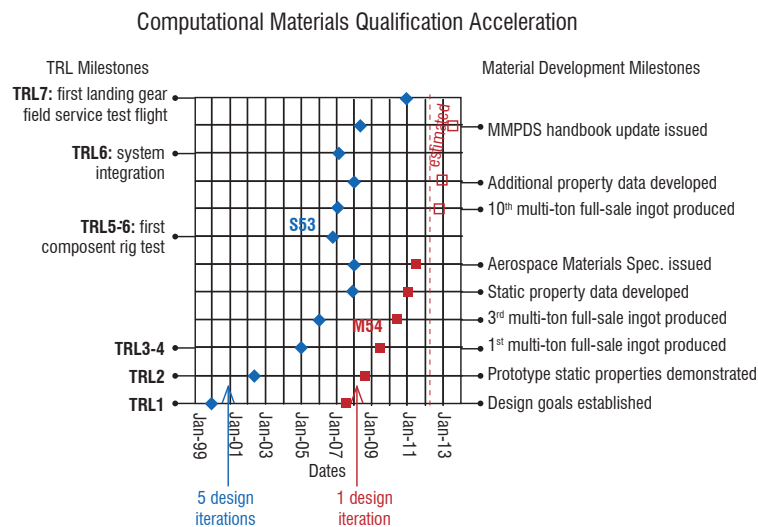


Figure 4 – Accelerated insertion of materials. Example from American steel-making industry given by G.B. Olson [22]

The European contribution to advanced material design is of course very significant, namely by the very high level of knowledge in terms of quantum mechanics modeling, microstructural or process modeling, although the full integration of the various length scales remains a challenge. The CALPHAD method is widely used in Europe: the SGTE group in Grenoble France, founded by E. Bonnier, laid the foundations for this method since the 1970s, with a crucial role played by H. Ansara [11]. There has been a strong presence of CALPHAD developers and users in Europe: the Thermo-Calc Software in Sweden, the Thermotech company in England, the MatCalc project in Austria, the MICRESS team in Germany coupling phase-field methods with CALPHAD and the Zircobase project (development of a thermodynamic database for Zr-based alloys) in France thanks to the CEA. Only two examples are detailed below, illustrating the microstructural modeling of Ni-based superalloys: the first concerns oxidation behavior and the second concerns microsegregation and its influence on  $\gamma'$  precipitation.

An English research team succeeded in predicting the formation of an alumina layer during the oxidation of Ni-based superalloys at high temperature [2]. Not only does the model calculate the evolution of the oxide thicknesses at the surface, but also the  $\gamma'$  fraction as a function of the distance to the outer surface. The authors use a combined model: the parabolic growth of the oxides is coupled with a DICTRA multi-element diffusion calculation, focusing mainly on the Al content evolution (see figure 5). The input parameters are few and mainly used to describe the parabolic-type behavior of the superalloy oxide growth.

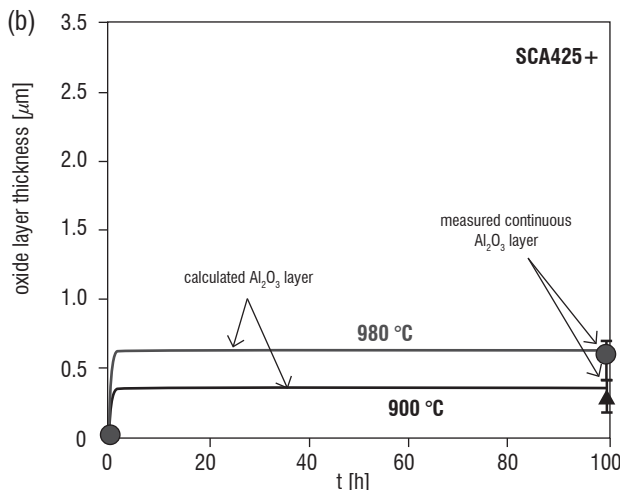
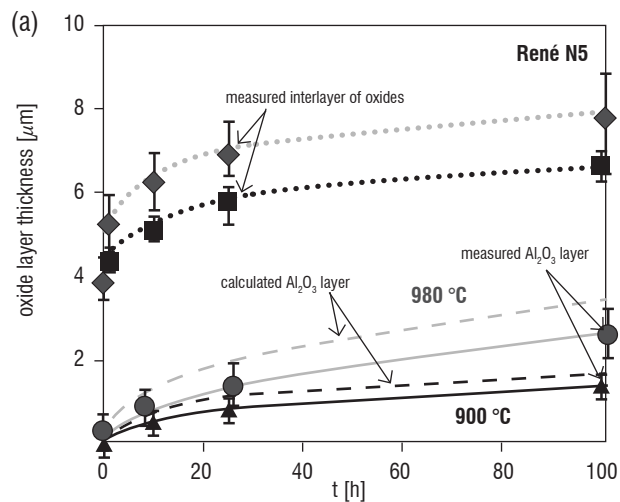
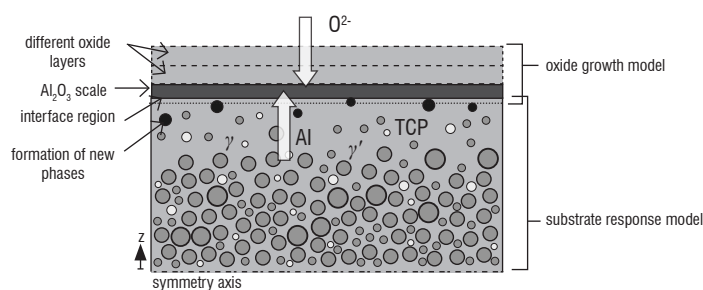


Figure 5 – Coupling an oxide growth model to a multi-element diffusion calculation: scheme of the physical process (top) and simulation results concerning two different alloys (a and b) [2]

An example of French research that strives to achieve the integration of multi-scale process modeling is the PhD work of Luc Rougier [26]. Its aim was to model successively the solidification, homogenization heat treatment and quench of cast Ni-based superalloys. In fact, the main goal was to model the  $\gamma'$  precipitation occurring during the quench. However, the precipitate mean size (for one, two, or more different populations) depends on the quench rate and on the local chemical composition. The latter can only be calculated by modeling the micro-segregation processes of the solidification step and the following solid-state diffusion during the homogenization heat treatment. Satisfying results were obtained, showing in particular the great influence of cross diffusion on the final microstructure, in the case of a Ni-Al-Cr ternary alloy. This means that the diffusion of an element in the Ni-based  $\gamma$  matrix should be known, not only in relationship with its own mole fraction gradient (classical diffusion), but also with the mole fraction gradients of all of the other elements (cross diffusion), leading to a need for the knowledge of the entire diffusion matrix with sufficient precision.

There has been a lot of work within ONERA concerning powder metallurgy Ni-based superalloys for high-pressure turbine disks. An example of the ICME approach has been applied to the N18 superalloy used in the Snecma M88 engine. The size distribution of its  $\gamma'$  precipitates was first modeled in the late 1980s using a binary alloy model [21]. The precipitation model has been recently revised at ONERA, upgraded in a pseudo-binary alloy model and finally used in a multi-scale mechanical model for the calculation of the fatigue life under low cycle fatigue conditions [3]. These calculations were able to successfully predict the lifetime of the disk and also to guess its dangerous locations due to cycling deteriorations of the material.

The new calibration of the precipitation model for the N19 superalloy has been accelerated through the use of the Thermo-Calc software, its TCNI5 thermodynamic database [43] and its MOBNI2 mobility database [44]. We give a brief reminder here of the approach, the main assumptions and the input parameters associated with the model. This is a particle size distribution model, based on classical nucleation and Lifshitz-Slyozov-Wagner (LSW) coarsening theory [17], where precipitates are distributed in size classes. It calculates the size distribution of intragranular  $\gamma'$  precipitates over time, depending on the material thermal history (which is supposed to be given as an input of the model). The distribution obtained is bimodal most of the time, or even n-modal ( $n > 2$ ). This results in the knowledge of relevant parameters for the microstructure at the end of the heat treatment: mean sizes and volume fractions of each mode of the distribution (i.e., secondary and tertiary  $\gamma'$  precipitates for  $n = 2$ ). Primary precipitates do not interact directly with the calculated intragranular precipitation, but their existence strongly modifies the matrix chemical composition inside the grains, which is taken into account in the model.

Given that this kind of calculation is performed at each Gauss point of a mesh, it is necessary to simplify the problem. It is therefore assumed that the precipitates are isolated spheres (no interaction between precipitates), that the influence of elasticity is neglected and that the precipitate/matrix interfaces are at local equilibrium. A pseudo-binary approach is used to calculate the equilibrium mole fractions: the Al, Ti and Nb  $\gamma'$ -forming element mole fractions are summed, in order to deduce a “solute” mole fraction, like in the PhD work of J. Mao [20]. A single “effective” energy-activated diffusion coefficient is used to match the precipitation kinetics. The driving force is taken from [29] and consists in a simple analytical expression of the matrix supersaturation and is not specific to the material.

The list of the material-dependent input parameters is: initial solute mole fraction, interfacial energy, pseudo-binary phase diagram, effective diffusion coefficient and its activation energy, volume fraction of primary  $\gamma'$  precipitates. The molar volume of the  $\gamma'$  phase is also needed, but its slight variation has only slight impact on the kinetics, since the elasticity influence is not taken into account. The interfacial energy is assumed to be constant, whatever the temperature or the size of the precipitates. This simple model has few material-dependent input parameters, but it was successfully used to describe N18 precipitation kinetics. However, experimentally determining the N18 pseudo-binary phase diagram and in addition evaluating the effective diffusion coefficients by investigating the isothermal long-time microstructural dynamics at several temperatures was time consuming. It was thus decided to test, for the calibration of N19 precipitation kinetics, a Calphad-based calibration with even fewer experiment-based input parameters.

at. %	Ni	Cr	Co	Mo	Ti	Al	W	Nb	Zr	Hf	B	C	$\gamma'$ solvus	$\gamma'$ frac.
N18	bal.	12.3	14.8	3.8	5.1	9.1	/	/	.018	.16	.083	.075	1195°C	55-60%
N19	bal.	14.6	12.0	2.9	4.6	5.5	1.0	1.0	.038	.1	.08	.1	1145°C	40-45%

Table 1 – Chemical compositions (at. %),  $\gamma'$  solvus temperature and typical  $\gamma'$  fraction at room temperature of N18 and N19 alloys [25]

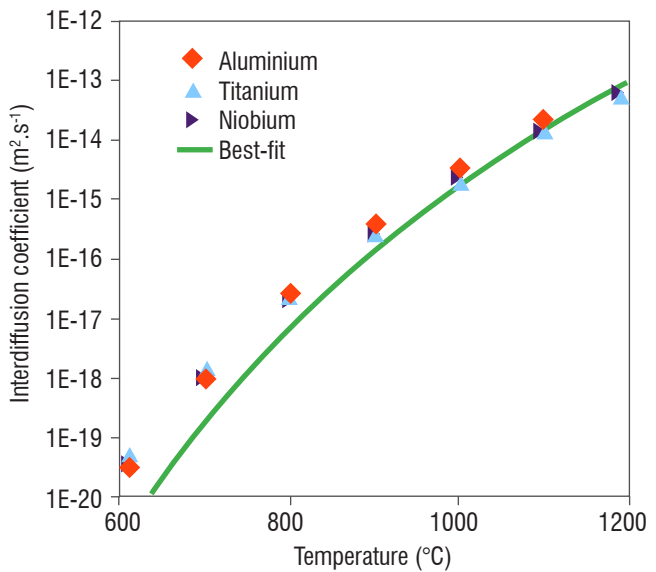
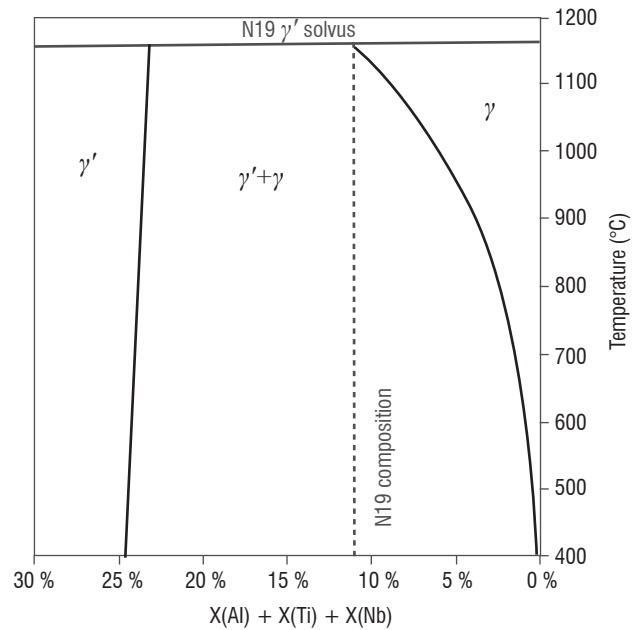


Figure 6 – Pseudo-binary phase diagram of the N19 alloy obtained by the Thermo-Calc software (top); Interdiffusion coefficients of Al (red squares), Ti (blue triangles) and Nb (purple triangles) in the N19  $\gamma$  phase for various temperatures, obtained with the DICTRA software and compared with the effective diffusion coefficient (green line), which better fitted the experimental results (bottom)

Figure 6 shows the phase diagram obtained and the diagonal interdiffusion coefficients for the elements Al, Ti and Nb in the  $\gamma$  phase at its temperature-dependent equilibrium composition [25]. It must be noted that no coupling between the Thermo-Calc (or DICTRA) and Z-set is performed, but rather only a priori calculations for the input parameters.

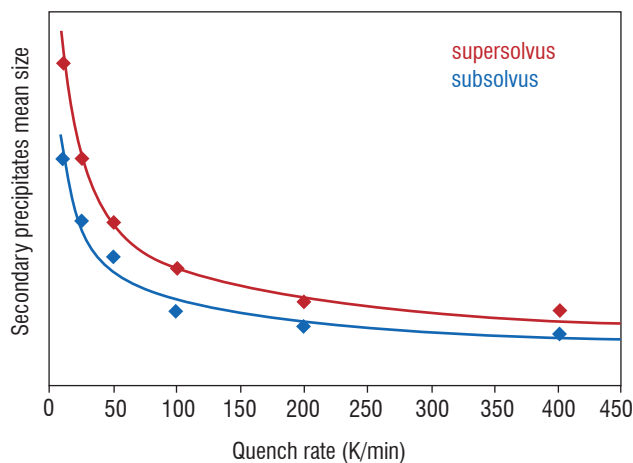
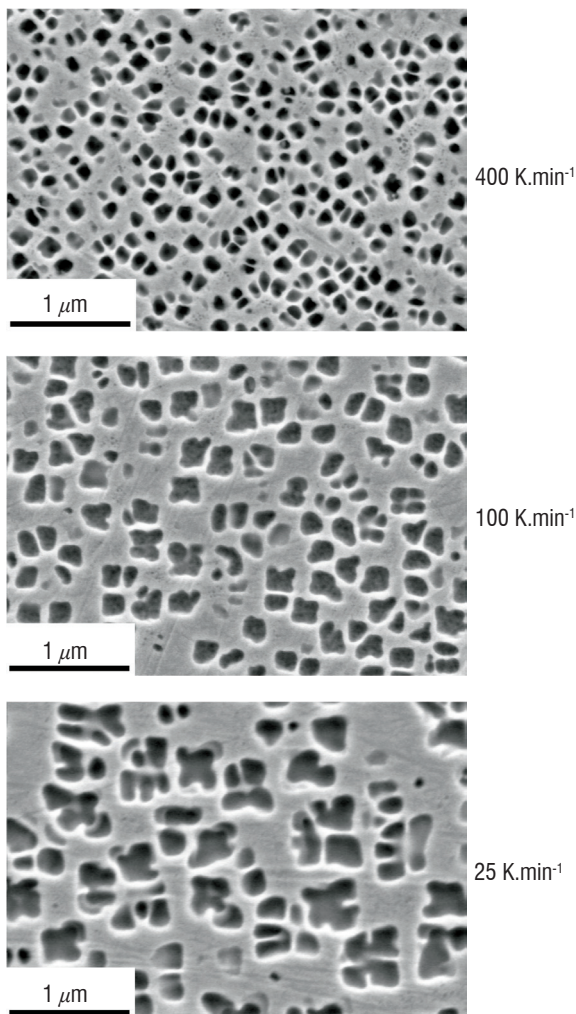


Figure 7 – Influence of the quench rate on the precipitate mean size: experimental microstructures (top) and comparison between numerical simulations and experimental measurements (bottom) [25]

The phase diagram obtained allows the calculation of polynomial fits of the equilibrium molar fraction evolution in  $\gamma'$ -forming elements of the  $\gamma$  phase and of the  $\gamma'$  phase, from room temperature up to the calculated  $\gamma'$  solvus temperature (1153°C). There is no need to optimize these calculated fractions. Concerning diffusion coefficients, it can be noted that the three elements investigated have similar diffusion coefficients, which greatly simplifies the problem. However, we had to optimize the effective diffusion coefficient by comparison with our experimental results. The calculated interdiffusion coefficients give a good initial estimate, especially at high temperatures, but the activation energy must be taken slightly higher to fit the experimental

values of the precipitate mean sizes. The last input parameter that strongly influences the precipitation kinetics is the energy of the  $\gamma - \gamma'$  interface. It was determined by fitting the experimental results, while keeping it within a relevant range (1 to 100 mJ.m<sup>-2</sup>).

The validation of this approach was carried out by comparison with experimental mean sizes of secondary precipitates and corresponding surface fractions. Micrograph examples are shown in figure 7 (bottom), where the microstructures are very different due to the variation in the applied cooling rates. A very satisfying agreement was found between the calculations and the experimental results, as shown in figure 7 (right), for both the subsolvus and supersolvus heat treatments. When considering air cooling or oil quenching, the effects of the precipitation latent heat will not be counteracted, which has been discussed in [25].

These encouraging results open the path to extending our integrated approach for the calculation of a turbine disk lifetime to the N19 alloy and to many other Ni-based superalloys.

## Enriching the databases

### Outside ONERA

The impressive success of the CALPHAD method for various applications poses the question of how the scientific community can efficiently construct all of the thermodynamic data needed by industries in all fields. This is a difficult problem to address. The high demand for numerous and reliable ab initio calculations might not be met, due to the need for huge computational resources and the corresponding skilled materials scientists. The rapid progress in terms of supercomputing performances may greatly help. However, it is more difficult to imagine how phase diagrams could be experimentally assessed at a high speed and with high precision. There are 61 commercially available metals, resulting in around 1,800 binary systems that are not completely known (even some with much scientific or technological interest present still unclear areas), and 90% of the 36,000 ternary systems are said not to have been explored in any way [16].

The necessity of creating thermodynamic experimental data at a higher speed can be solved in two different ways: accumulating numerous experiments, at a very high rate, with the help of automated routines or performing experiments that yield, at once, a great amount of data. A combinatorial materials science project, called ACCMET (ACCelerated METallurgy), has been recently funded by the European Commission through a FP7 research program [16]. The main idea is to cast small samples of metallic alloys by mixing pure elements, producing a sample in only 30s, offering the opportunity to screen large compositional landscapes. Automated characterizations may follow, including micro-hardness, RX diffraction and resistivity measurements as a function of temperature. This is enough to reveal intermetallic phases and to evaluate the ability of these new phases to maintain their strength at high temperatures.

A famous high-throughput experimental method was reported in 1970 by Hanak, who prepared composition-spread films of metal alloys by sputtering mixed-material targets [12]. Since 1970, this method has unfortunately not been extensively used, but, more recently, Cui et al [6] have used co-deposition techniques to discover new shape-memory alloys and to rapidly assess the compositional domain of these (see figure 8). A serious concern is that these as-cast microstructures and as-coated microstructures may be very far from equilibrium and no accurate thermodynamic data can be deduced before a relevant thermal treatment.

Diffusion couple experiments were performed at ONERA in order to determine composition-dependent interdiffusion coefficients in the intermetallic compound  $\beta$ -(Ni,Pt)Al by numerical inverse analysis [4]. The intermetallic compound  $\beta$ -(Ni,Pt)Al is used as a high temperature protective coating for superalloys and a bondcoat for thermal barrier coatings. In this context, it is especially relevant to estimate the diffusion kinetics of the Al element, which has a high influence on the lifetime of coated Ni-based superalloy turbines in an oxidizing environment. It was possible to derive relevant interdiffusion coefficients from these experiments and to prove the consistency of the method [4].

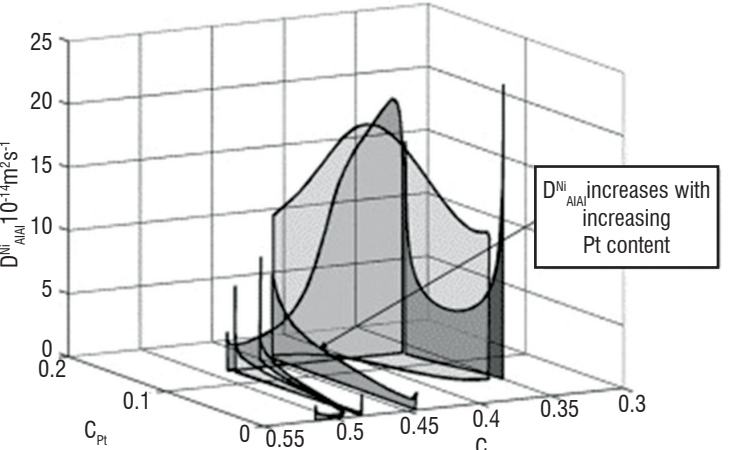


Figure 10 – Influence of the composition of the  $\beta$ -(Ni,Pt)Al phase on the interdiffusion coefficient of Al with respect to the gradient of the Al mole fraction [4]

More recently, inspired by the work of J.C. Zhao and based on our experience in diffusion couples, diffusion multiple experiments have been performed at ONERA. Our main idea was to perform quick and simple experiments, needing only common laboratory devices and quick chemical characterization. Contrary to Zhao's team, the hot isostatic press (HIP) was not used, but rather only a laboratory furnace with sufficient volume and a flat base, where two pure metals can be bonded according to the scheme in figure 11. The solid-solid bonding can be repeated on the obtained couple with a third metal. In most cases, it is helpful to use a melting process to build the triple, for example by cutting a hole in the first couple and using it as a crucible [8]. It is important to inspect the binary diagrams in order to predict how the liquid pure element will react with both other elements.

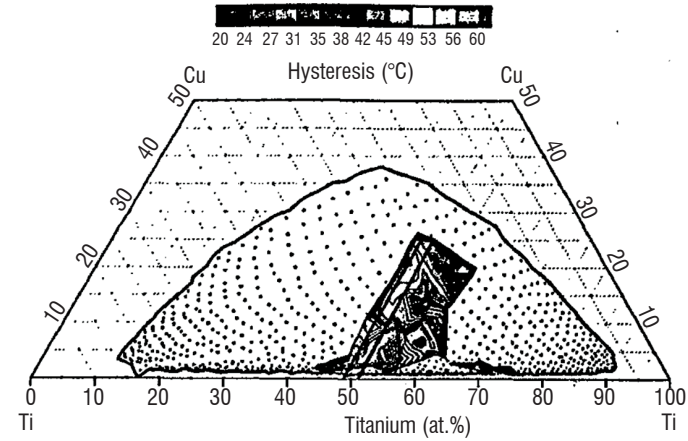


Figure 8 – Shape-memory hysteresis measured for many different compositions of the Ni-Ti-Cu ternary system with the help of high-throughput experiments [6]. The figure shows at a glance the interesting composition ranges to obtain the desired shape-memory effect

Another example of an interesting technique is the diffusion triples [8,13,31]. Diffusion couples are commonly used to determine interdiffusion kinetics between two materials. This technique could be extrapolated to three pure elements that are welded or bonded together. Long-term heat treatment leads this ternary system to thermodynamic equilibrium. As the three elements diffuse throughout the entire sample, most of the ternary phase diagram is explored and Electron Probe MicroAnalysis (EPMA) profiles are able to measure the compositions of the stable phases and the tie-lines that are associated with the interfaces between the phases. Zhao et al [31,32] provided many insights in regard to this experimental technique. The special interest is that the technique can explore, in one single experiment, a ternary diagram at a chosen temperature. The Zhao team has evaluated many ternary systems for the company General Electric during the 2000s.

However, some phases that have slow kinetics never appear during these diffusion experiments and – once again – there is a strong concern about the out-of-equilibrium nature of the microstructure. A well accepted assumption is that the mole fractions of the various elements at the interface between two phases correspond to the stable tie-lines of the phase diagram, but this is only an approximation. It is also not possible to determine the crystalline structures of the observed phases, only their chemical composition.

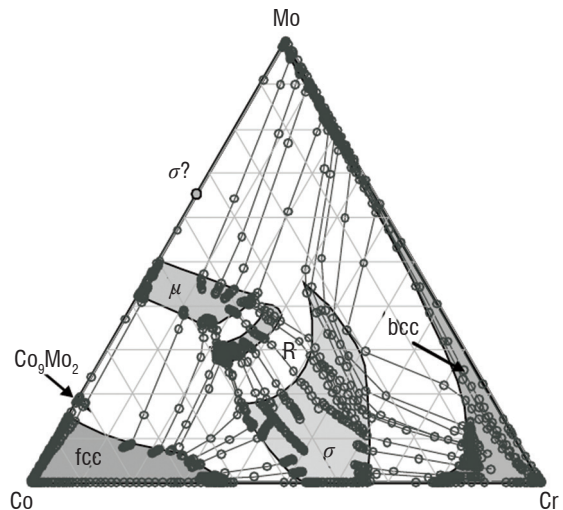
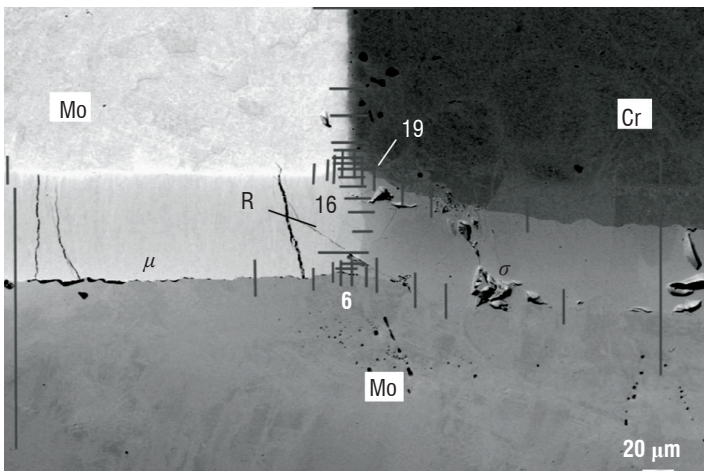


Figure 9 – EPMA profiles after the diffusion of a Cr-Co-Mo triple for 40 days at 1100°C (left) and the corresponding phase diagram data (right) [32]



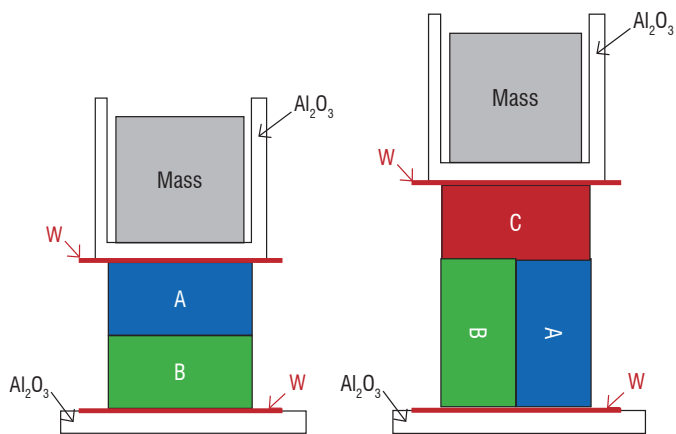


Figure 11 – Simple solid-solid bonding method that can be used with conventional laboratory furnaces

In fact, eutectic reactions often occur, preventing the system from maintaining the presence of the pure elements, which limits the width of the compositional exploration of the ternary system. For example, in the case of the Nb-Ti-Si system, considering that  $\text{Si (Liq)} \rightarrow 0.94 \text{ Si (diamond)} + 0.06 \text{ NbSi}_2$  (hexagonal), it is interesting to use pure Nb as a crucible for Si. Conversely, testing a pure Ti (or even a Ti/Nb couple) crucible led to the  $\text{L} \rightarrow \text{Ti} + \text{Ti}_5\text{Si}_3$  eutectic reaction, with no pure Si left in the sample. Some wetting problems could also occur. If the liquid metal wets the crucible completely, it escapes through the hole and, again, a very small quantity of the third metal is left.

The longest step in the experiment is due to the long-term diffusion heat treatment that is needed to explore the diagram, ranging from a duration of one day (high temperatures) to several months (intermediate or low temperatures). There are several ways to shorten the duration: downsizing the samples to thin layers, performing a diffusion treatment on an initial couple before bonding the third element, or performing a dual anneal diffusion multiple approach [5].

The last step is the chemical characterization of the obtained microstructure, which should reveal the ternary diagram properties. It usually consists in performing EPMA profiles around the triple point and perpendicularly to planar interfaces, so that the positions of the various ternary diagram tie-lines are evaluated [32]. We are now developing a new method at ONERA that is less reliable but very quick and does not need any EPMA. The EDS mapping technique is used around the triple point with a refined mesh, so that the EDS spectra are automatically acquired, typically overnight. The advantage is that all of the data can be post-processed, keeping the scanning electron microscope available for other experiments during the daytime. An automated quantification procedure has been specially developed by the company SAMx [41] in order to obtain a quantitative chemical composition at each pixel of the map, with the option of grouping several spectra into one larger pixel if the EDS spectrum quality must be improved. This is the recent technological progress in terms of X-ray detection (SDD detectors) that makes this current approach possible.

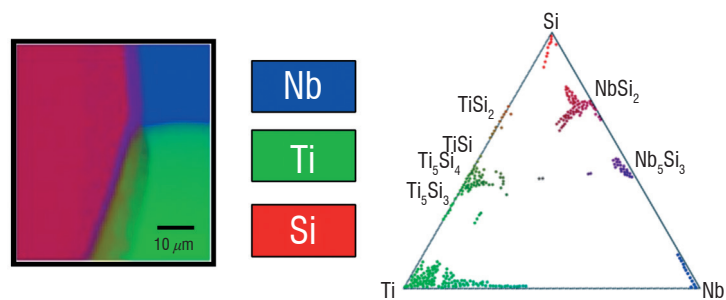


Figure 12 – Quantitative chemical imaging of a Nb-Ti-Si diffusion triple at 1200°C for 5 days (left); example of results given by an automated “image processing” of EDS maps for two different triples

The evaluation of ternary phase diagrams can be easily derived. It is even possible to obtain an automated “image processing” of the EDS map that gives a quick evaluation, if not a reliable assessment of the phase diagram. In any case, due to the EDS limitations compared to the EPMA, the method cannot be considered as precise enough to perform a proper assessment. Note that this approach is only beginning and is still under development. We believe that it offers a chance to obtain quick answers about the structure of a ternary phase diagram, i.e., about the zones of the diagram where ternary phases do appear or not, for intermediate temperatures: not too high (without liquid phase) and not too low (too long diffusion times). This can be of a great help when exploring some of the 32,000 unknown ternary diagrams.

## Conclusions and outlook

The CALPHAD method was presented and its high relevance for the microstructural modeling of multi-component systems was highlighted. The great number of fields in materials science where the CALPHAD method is already used strengthens the present and future impacts of CALPHAD in the processes for accelerated design and optimization of new materials and components. Nevertheless, the need for enriching thermodynamic databases must be met, which demands a very high number of experiments and ab initio calculations. In this perspective, high-throughput experiments, such as diffusion multiples, are a very relevant topic to be explored by the scientific community ■

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