



1

thank organisers for giving me the opportunity to

① Before starting and because I'm not sure I will have time at the end I would like to thank a few people that have contributed somehow to the present talk. I ~~should~~ <sup>want to</sup> thank Ursula Rattner for copying <sup>me</sup> an email discussion on this topic a few months. I'd like to thank Wei Xiong, Qing Chen, Alan Dinsdale, Suzanne Fries ~~and~~ Bo Sundman and Xizogang for unfamiliar talks on this topic over the years. I may have forgotten some. Please forgive me ~~if~~. I will first ~~talk~~ explain why we do need to define a value for the empty bec in the Calphad approach. Then I will show you the path follow to define a value. I will end up with a discussion.

② The story I want to tell you began with the first CEF description of the <sup>Al-Ni</sup> binary system published in 88 by Ausare, Sundman and Willemin. Let's focus on the AlNi compound whose homogeneity range is here shown in cyan. On the right its crystallographic structure is schematised. It is the B2 structure corresponding to the CoAl prototype. The site in cyan <sup>on the corner of the cell</sup> has a different occupancy than the site in white in the center of the cell.



9

It was then modelled with two sublattices corresponding to the crystallographic site allowing point defects corresponding to those found experimentally. The ideal compound is  $\text{AlNi}$ . ~~PREST~~ Ni can substitute Al site and the Ni site shows some vacant site. The vacancies are here schematized as  $V_a$ . Such defects are usually called triple defects as when one Ni is introduced on the Al site, 2 vacancies should be introduced on the Ni site in order to keep the composition constant. ~~PREST~~

This figure represents the site occupancies for this phase at ~~look~~ when composition changes. At the stoichiometry the 1st sublattice is fully occupied by Al while the second is filled by Ni. On the Al rich side Ni is ~~replaced~~ replaced by  $V_a$  until reaching pure Al corresponding to an empty occupancy of the Ni site. On the Ni rich side Ni replaces Al until reaching Ni pure element.

The description had been assessed taking some assumption for the Gibbs of energy of the hypothetical I mean pure Al in the simple cubic structure, pure Ni in the bcc structure and pure Ni in the simple cubic. The Gibbs energy of formation of the stoichiometric ~~is~~  $\text{AlNi}$  was



(3)

optimised as well as two interactions parameters

~~RES~~ The amount of atom by unit cell was in agreement with the value determined experimentally by Taylor and Doyle.

~~RES~~ When following this amount as a function of temperature. The dotted line correspond to the state without vacancies. It is not calculated. It is just to guide the eyes.

~~The bending of~~ The solid lines corresponding to the number of atom over the number of site calculated for three compositions close to 50/50. The symbols correspond to the experiment values for two of these composition.

The bending of the solid lines is related to the increase of the number of triple defects with temperature. The system has a degree of freedom.

Following a traditional Calphad modeling, phase diagram data and thermodynamic data had been used in order to obtain a description of all the phases stable in the system.

(3) A few years later ~~was~~ Lacoze and Sundman published the first CEF description of the A2 and B2 phases. On this figure taken from this paper, note that the phase diagram is plotted only up to 50% Si. The cyan field is the B2 stability



(4)

region. The region of stability of this phase is quite far from the 50/50 composition. The blue area correspond to the A2 region. This structure is similar to the B2 structure where all the sites have the same occupation. (PRESS) The B2 structure correspond to a state where each site accommodate Fe and Si but in different composition. ~~press~~ The A2 and B2 have 2nd order relationship. This is what is observed experimentally at least in a reduced composition - temperature area - as we have seen during one of the presentation yesterday. The model used in this paper consider the two elements in two equivalent sites. Some relationship between the thermodynamic parameter describing the phase allow the disorder to happen. (PRESS) On this figure the site fraction of the two ~~phases~~ sites are represented as a function of the composition of the phase. The dark blue part of the curves correspond to the A2 state, when the site fraction are identical on both sites. In the B2 field for the Fe rich region, one site, the 1st one, is mostly occupied by Fe and the other one by a mixture of Fe and Si. When going from the 50/50 composition towards



(5)

Fe, the amount of Si on that site passes from almost 1 to less than 20% when the phase disorders:

(4) A model able to describe the metallic B2 phases on a wide multicomponent range should be able to describe the triple defects exhibited by AlNi for instance but also the second order transition of this phase with the A2 phase like in the FeSi system. We end up with a model with 2 sublattices considering the mixing of all the metallic elements under consideration - hence B doesn't stand for boron - as well as vacancies. The model needs to have all that species in both sublattices. When doing so a pure configuration of the phase corresponds to the full occupation of both sites by vacancies. A Gibbs energy of formation for this parameter thus need to be given a value. This state corresponds to the empty bcc lattice and thus comes my need to define a value for this state.



6

⑤ In 2001, myself, Anzawa and Sundman published a description of the ternary Al-Ce-Ni system following this scheme. So 4 species are considered ~~on~~ mixing on two sublattices. On this isothermal section the B2 field is in cyan. The A2 field is here in the Ce corner and follows the Al-Ce edge until the first 3 phase field here. In this case, there is a 1st order relationship between the two phases. A large area of this section correspond to two phase field A2+B2 where tie lines connect the ternary extension of the two phases.

⑥ In order to obtain this description, the Gibbs energy of these phases was expressed as the sum of two contributions. One is a function of the composition of the phase. The second one is a function of the site occupation. Mathematical relationships makes that this term cancels when the phase is disordered i.e. when the site fractions are identical on both sublattice.

During this work a value equal to zero was given to the Gibbs energy of the empty bcc. At that time that was just sounding obvious. The interaction parameters for the Ni with vacancies and Al with vacancies



(7)

were taken from mathematical equivalence to the previous B2 description.

For the interaction between Cu and V it was taken big equals to 10000.

⑥ The description was rather satisfactory and was used as ~~one~~ one of the basis of a multicomponent database aiming the description of systems of interest for Ni superalloys. As seen already yesterday, these alloys are mostly constituted by two phases the  $\gamma$  Al disordered phase and the  $\gamma'$  ordered L12 based on Ni<sub>3</sub>Al. The strength of the alloys is coming from the coherency between these two phases. The modeling of these 2 phases was thus my main concern. The B2 phase is actually also of technological interest as it is the basis of many thermal coatings as ~~examples~~ show yesterday.

On this figure I've plotted the vacancy fraction in the bcc structure versus temperature for different pure elements constituting that database. The symbols correspond to the melting temperature of the different element in the bcc state using the SGTE descriptions. The bcc elements are in blue.

The hcp in green. The fcc in red. The element hcp at low temperature, bcc at higher temperature are in black. These temperatures at ~~shown~~ <sup>plotted</sup> for an arbitrary  $10^{-5}$  Va content. **CALPHAD XLV**



The plots obtained results from the choices made for the interaction parameters between the elements and vacancies at the different steps I was adding a element. Today I can say that some choices were quite bad.

On this figure we notice that the curves all stop around  $10^{-2}$  Va fraction. This correspond to some instability of the phase. Then the order of the different curves ~~is~~ is not what it is expected from the most basic physical understanding. We expect the amount of vacancy to be somehow ordered as the melting temperature. Having the amount of vacancies in Ni higher than in Al sounds unrealistic. The position of the Hf curve seems to show too low vacancy content. For Ta and W, there is a single curve as the same interaction parameter was used <sup>the same for Re and Zr</sup> For Cu, the amount of vacancies at its melting temperature is so high that it increased this temperature by 8K.

(7) In order to rationalise this behavior, ~~the~~ ~~new~~ ~~interaction~~ I've ~~define~~ define new interaction parameters in a more systematic way using some DFT inputs.





(9)

Xiaogong Lu kindly provided me the total energy for the simple cubic and bcc structures for the elements under consideration. The mathematical equivalence of the ~~the model~~ ~~for the B2~~ one sublattice formalism for the A2 phase with the 2 sublattices formalism for the B2 when it is disordered allow to relate the interaction parameter for the bcc to the energy of formation of the simple cubic structure with respect to the bcc state. This relationship actually hides that no reference state for  $V_a$  is used or actually a value equals to zero. It was not possible getting any FP values for a configuration of nothing.

Thanks to this procedure, the curves are displayed in a more logical order. Still we have an instability around  $10^{-2}$   $V_a$  amount. Moreover, for some elements, the high amount of  $V_a$  induced an increase of the melting point higher than 0.1 K.

Let's try to understand where comes from the systematic instability. Before, I'd liked to mention that this was implying the same calculations where actually finding in their result an almost empty bcc phase.

**CALPHAD XLV**



(10)

⑧ The Gibbs energy formalism used to draw these curves is the one. It is just the classical substitutional most simple formalism applied to an element A mixing with vacancies (PRESS) this implies that the enthalpy of formation of the mixture from the pure element by site follows this equation. (PRESS)

If we consider this behaviour by atom then the expression is this one.

Here are plotted this two behaviors versus the composition. When considering only the ideal ~~and~~ contribution, the green curves are obtained. When adding to this ideal contribution an interaction parameter, the blue curves are obtained. They correspond the 3 different values for the interaction parameters. It is the case where we have been working up to now I mean the Gibbs energy for vacancies is zero. The red curves correspond to different values for this parameter.

The value zero for empty lattice allows the instability when considering the enthalpy of formation of the mixture by site. It correspond to a miscibility gap between A with very little vacancy and emptiness with little A.



(11)

If the ~~thermodynamic~~ software we are using were working properly they would actually run into a numerical underdetermination. The Gibbs energy minimum should be found for a given amount of matter, not for a given amount of lattice. This is a detail.

We now know that if we want to get rid of this instability and that's what we want, we need to use a value that is not zero for empty bcc.

⑨. Here is another plot of the vacancy fraction versus temperature for the same elements. You notice that ~~there~~ there is no more instability. This figure was obtained with the value 307 for the empty bcc. This value actually comes from an optimisation considering all the elements here with a fake experiment that is that the amount of  $V_a$  is  $10^{-5}$  at the melting temperature. Different expressions have been tested for this parameter. Having a value independent of temperature did not allow having a reasonable result for all the elements. Having a linear expression of  $T$  was leading to a weakly constrained expression.



18

This value has been used systematically in the database that became the nowadays commercial TCNI.

It was recommended in the book by Zuckor, Fries and Sundman or in a recent paper by Dinsdale and Kirk. It has already been used in some published assessments like the  $\text{Al-C}$  description published by Stein and coworkers.

(10) I'd like to show you the curves you are now familiar with in the case of a empty bec gibbs energy equals to 100 000. This is a value that have been used in some works. It is doing a similar work than the 30T value for the high melting elements but induce very low vacancy amount for the low melting temperature elements

(11) When using a 80T value that appeared in some works, the  $V_a$  amount becomes very low. Even optimising the interaction parameters doesn't bring a satisfactory description then.



(13)

(12) this is what is obtained when using an expression proposed by Peter Francke. In this case the vacancy amount is much higher - ~~the~~ the instability seems close for low melting elements.

(13) Finally I'd like to present what is obtained when using a value proposed in a paper resulting from a Ringberg meeting. ~~(PRES)~~ It is very close to the 30T case.

(14) I now come to the discussion. the 30T value is recommended for bcc when using the current SBT description of the pure elements.

just read.

I'd like to point the talk given by professor Neugebauer yesterday. You may remember the curve he has shown for  $V_a$  formation in Cu. The agreement with experiments makes me think that such calculations can be used as input in the generation of ~~the~~ more physical based descriptions for the pure elements.

**CALPHAD XLV**



(15)

~~the physical description that was used~~

If you have followed me the 30T value just result of the wishes I had to not disturb ~~the~~ the pure elements agreed by SGTE. But the effect of vacancies should actually impact the description of the elements.

By the way if we manage to set up descriptions taking this issue into account we will be able to provide ~~the kinetic simulation~~ ~~with a realistic amount of vacancy~~ kinetic simulation with a realistic amount of vacancy contributing to diffusion. More physical based kinetic tools could be developed.

Thank you for your kind attention.



15

Extra

(15) Not to be shown - relief of the preparation of the talk. Could maybe be used to answer a related question.

It is an example taken from a paper published by Tomas Gomez-Acebo & coworkers in 2004. It is related to the Al-Co-Cu ternary system based on the three binary systems at the bottom. You recognize the Al-Ni system with the large  $\beta 2$  stability range in the middle. Then the Cu-Al binary system with a large solubility of Al in the bcc Cu. Finally the Co-Cu system where Co also substitute Cu up to quite high level.

The <sup>ternary</sup> V-section on the left is from that 2004 paper using the first TERNI database containing only 7 elements. It is at 1300°C, just above the sigma stability in the Co-Cu system.



(16)

that database was not pretending to describe ~~high~~ Co based system. This section result from the extrapolation of the binary description. It is ~~striking~~ striking to notice the ability of the model used to describe this system. Some experimental results are compared to the calculation. It is interesting to notice that the different kind of ordering transition (2nd order close to the Co-Cu edge and 1st order for higher Al content) are similar to the experimental information.

This is very different on the right section that was calculated using the same binary description but without coupling the A2 and B2 descriptions. The B2 ternary extension is totally missing

This example shows how much coupling B2 and A2 can bring.