

Applying the Effective Bond Energy Formalism (EBEF) to describe the sigma (σ) phase in the Co-Cr-Ni-Re system.

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Abstract

Proper descriptions of Topologically Closed-Packed (TCP) phases in thermodynamic databases are essential to adequately design new alloys. Thus, the recently introduced Effective Bond Energy Formalism (EBEF) is used in this work to describe the sigma (σ) phase in the Co-Cr-Ni-Re system. The EBEF is applied to a five-sublattice (5-SL) thermodynamic model consistent with its crystal structure and its implementation was supported by new data from Density Functional Theory (DFT). The Matrix Inversion Method is described and used to automate the generation of the EBEF parameters. Good descriptions of the ternary systems are obtained even without any ternary parameters for any of the phases. This is the first time that an EBEF description of a quaternary TCP phase is established using the SGTE descriptions for the pure elements.

Keywords: Effective Bond Energy Formalism; sigma phase; Calphad; Co-based superalloys; DFT calculation.

1. Introduction

Proper descriptions of Topologically Closed-Packed (TCP) phases in thermodynamic databases are important to evaluate their formation during processing since these phases are brittle and, in many cases, undesirable [1,2]. One of the most important TCP phases is the sigma (σ) phase, which occurs in many binary and ternary systems with quite different composition ranges and topologies [3–5]. The thermodynamic description of the σ phase thus plays an important and challenging role in obtaining self-consistent thermodynamic databases for steels, Ni-based superalloys, and Co-based superalloys.

Due to its importance and crystallographic complexity, several authors from different research groups have been using different thermodynamic models to describe the σ phase in different systems [6–23]. In general, simplified thermodynamic models are applied to describe this phase using both classical [6–10,12,14,15,17,19,22] and two-term [10,11,13,18,20,21,23] Compound Energy Formalism (CEF).

The possibility of using thermodynamic models that are more consistent with the real crystallography of the phase to obtain proper descriptions in multicomponent databases has been discussed [24,25]. However, thousands of Density Functional Theory (DFT) calculations that would be needed to obtain the formation energies of all the endmember compounds when using the CEF are an important concern. In endmember compounds each sublattice (SL) is occupied only by one kind of species resulting in n^s endmember compounds where n is the number of component and s is the number of sublattices. The advent of the Effective Bond Energy Formalism (EBEF) allows the use of thermodynamic models to describe the TCP phases closer to their crystallography as it does not require the formation energies of the ternary and higher-order endmembers [25].

Therefore, the EBEF has been considered to describe Laves_C14, Laves_C36, mu (μ), chi (χ) and σ phases in the multicomponent thermodynamic database being developed by the Center for Hierarchical Materials Design (CHiMaD) [26] to assist the design of new γ (FCC_A1)/ γ' (L1₂) Co-based superalloys. Here, this formalism and its ability to extrapolate is tested using a 5-sublattice (5-SL) model to describe the σ phase in the Co-Cr-Ni-Re system. One of the reasons for choosing this system is the fact that σ is the only stable intermetallic phase in the constituent binary and ternary systems. Thus, the extrapolation ability of the EBEF can be tested without the

competition with other intermetallic phases whose modelling could interfere. In this quaternary system, the σ phase is stable in only two binary systems, Co-Cr and Cr-Re, with quite different composition ranges. These systems also differ in the behaviour of Cr, as it preferentially occupies the sites with coordination number 12 (2a and 8i2) in the Cr-Re system, while it occupies the sites with higher coordination number in the Co-Cr system. The continuous solution of the σ phase observed in the Co-Cr-Re system is thus coupled with the change in Cr behaviour. The two ternary systems obtained by adding Ni to the binary systems where the σ phase is stable present different topologies for the extension of the σ phase into the ternary systems. When Ni is added to the Cr-Re system, the topology of the σ phase looks similar to that observed in the Mo-Ni-Re system studied in the EBEF introductory article [25]. It widens by extending towards the Cr-Ni and Re-Ni systems, while in the Co-Cr-Ni system the σ phase extends only towards the Cr-Ni side. It is interesting to study the ability of the EBEF to describe these different cases.

2. The sigma (σ) phase

The σ phase is one of the most important TCP phases due to its stability in at least 43 binary and many ternary phase diagrams with different composition ranges and topologies [5]. The importance of controlling the formation of the σ phase during the processing of steels [27,28] and Ni-based superalloys [29,30] is well established in the literature. For Co-based superalloys, the scenario is similar, since the phase is reported to be stable in the following important Co-containing binary and ternary systems: Co-Cr [20], Co-V [21], Co-Al-Ta [31], Co-Re-Ta [32], etc.

The mentioned features of the σ phase are partly explained by its complex crystal structure with the unit cell consisting of 30 atoms located in five different crystallographic positions as shown in Table 1. Over the last few decades, Calphad studies have proposed different ways to properly describe this phase and the use of DFT-calculated formation energies as input data is currently considered very important [11,13,15,18,24,25]. Nevertheless, there is no consensus on the best compromise between an adequate description and the use of a convenient thermodynamic model. The use of 5 sublattices (SL) model (one for each Wyckoff position) was considered difficult to implement using classical Compound Energy Formalism (CEF) [33] since the number of endmembers energies required for multicomponent databases is almost prohibitive [24]. Just as an example, to fully describe a 5-SL σ phase in a database composed of 10 elements, one hundred

thousand (10^5) formation energies are needed. For this reason, simplified thermodynamic models are still being used to describe the σ phase.

Thus, the $B_8A_4(A,B)_{18}$ [7], $B_{10}A_4(A,B)_{16}$ [6,9,34] and $(A,B)_{10}A_4(A,B)_{16}$ [10,12] simplified thermodynamic models have been extensively used to describe the σ phase in different metallic systems. In these thermodynamic models, A atoms are generally larger and mostly exhibit a body-centered cubic (BCC) structure in elemental form, while B atoms are generally smaller and mostly exhibit a face-centered cubic (FCC) structure. It is important to note that some elements such as Re and Cr may occupy both A or B sites depending on the system [35–37][5]. Following the recommendation of the Ringberg workshop [38], the two-term CEF was increasingly more often implemented. This formalism makes it easier to consider the presence of all the elements in the sublattices, since defining a Gibbs energy value for all members is no longer mandatory. The two-term CEF was successfully implemented in describing the Co-Cr-Re system with a simplified 3-SL model [39]. In 2008, Joubert [5] suggested a simple 2-SL $(A,B)_{20}(A,B)_{10}$ model to describe the σ phase based on a detailed site occupancy study. Later, Palumbo et al. [13] showed that this simplification led to a poor approximation for the Cr-Re system. Furthermore, the importance of the use of thermodynamic models that are more consistent with the real crystallography of the phase was later stated by several authors [15,18,24,25].

Although the 5-SL model has already been successfully applied to describe a few binary and ternary systems [11,13,15,18], the use of this thermodynamic model for describing the σ phase in multicomponent databases was considered too difficult to use until the advent of the EBEF [25]. This novel formalism uses similar equations as the two-term CEF [38] and allows a full description of a phase using only formation energies of the binary endmember compounds. The EBEF description of the σ phase in the Co-Cr-Ni-Re system is presented and discussed here.

3. Thermodynamic models

Available thermodynamic descriptions of the binary and ternary subsystems were used as a starting point of this work. Their respective thermodynamic models and parameters are used here to describe all the disordered solution phases, i.e., FCC_A1, BCC_A2, HCP_A3 and Liquid. For the binary systems the used references are: [13,20,40–42] and for the ternaries the parameters established by Wang et al. [23] for the Co-Cr-Ni system were initially considered. For the Cr-Ni-

Re and Co-Cr-Re systems, there are very few experimental data available in the literature. The description of the Cr-Ni-Re system published by Huang and Chang [36,37] is not compatible with the current Re lattice stability and descriptions reported for the Co-Cr-Re system [39,43] are incomplete. Thus, a few ternary thermodynamic parameters were added to the description of the disordered solution phases to make the calculated isothermal sections consistent with the experimental results available in the literature. Regarding the intermediate compounds, σ is the only intermediate phase reported as stable in the binary and ternary subsystems of the Co-Cr-Ni-Re system. An EBEF description supported by DFT calculations was implemented to thermodynamically assess the σ phase.

3.1. Disordered solution phases

The disordered solution phases FCC_A1, BCC_A2, HCP_A3 and Liquid are described using the substitutional solution model. The thermodynamic models adopted for these phases are: (Co,Cr,Ni,Re) for Liquid, (Co,Cr,Ni,Re)₁(Va)₁ for FCC_A1, (Co,Cr,Ni,Re)₁(Va)₃ for BCC_A2 and (Co,Cr,Ni,Re)₁(Va)₁ for HCP_A3, with Va symbol representing vacancy. The Gibbs energy functions for these phases are:

$$G_m^\varphi - \sum_i x_i^\varphi H_i^{SER} = \sum_i x_i^\varphi \Delta^\circ G_i^\varphi + RT \sum_i x_i^\varphi \ln x_i^\varphi + {}^{xs} \Delta G_m^\varphi + {}^{mag} \Delta G_m^\varphi \quad (1)$$

where G_m^φ is the molar Gibbs energy of the φ phase; x_i^φ is the molar fraction of the element i in the φ phase; $\Delta^\circ G_i^\varphi$ is the molar Gibbs energy of the paramagnetic or non-magnetic pure elements with the structure of φ referred to the standard element reference (SER) enthalpy at 298.15 K, H_i^{SER} ; R is the universal gas constant (8.3145 J/(mol·K)), T is the absolute temperature in K; ${}^{xs} \Delta G_m^\varphi$ is the excess Gibbs energy expressed by Redlich-Kister-Muggianu polynomials [44,45]:

$${}^{xs} \Delta G_m^\varphi = \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j \sum_v {}^v L_{i,j}^\varphi(T) (x_i - x_j)^v + \sum_{i=1}^{n-2} \sum_{j=i+1}^{n-1} \sum_{k=j+1}^n x_i x_j x_k (u_i L_i^\varphi(T)) + u_j L_j^\varphi(T) + u_k L_k^\varphi(T) \quad (2)$$

with

$$u_i = x_i + \frac{1 - x_i - x_j - x_k}{3}$$

where the temperature dependence of the interaction parameters $L_i^\varphi(T)$ is expressed as:

$$L_i^\varphi(T) = a + bT \quad (3)$$

where a and b are coefficients to be assessed to fit the experimental information. The binary parameters for the stable phases have been taken from the references [13,20,40–42]. The parameters for the metastable phases were roughly assessed assuming that they should be similar to the stable phases. Ternary interaction parameters were finally introduced in order to better fit the ternary isothermal sections with the available experimental information.

The magnetic contribution, $^{mag}\Delta G_m^\varphi$, of the elements is described by the Hillert-Jarl formula [46]:

$$^{mag}\Delta G_m^\varphi = RT \ln(\beta^\varphi + 1) g(\tau) \quad \text{with } \tau = \frac{T}{T_c} \quad (4)$$

where R is the universal gas constant (8.3145 J/(mol·K)), β^φ is the average magnetic moment, T is the absolute temperature, T_c is the Curie temperature and $g(\tau)$ is given by:

$$g(\tau) = 1 - \left[\frac{79\tau^{-1}}{140\rho} + \frac{474}{497} \left(\frac{1}{\rho} - 1 \right) \left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \right] / D \quad \tau \leq 1$$

$$g(\tau) = - \left(\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right) / D \quad \tau > 1$$

$$D = \frac{518}{1125} + \frac{11692}{15975} \left(\frac{1}{\rho} - 1 \right) \quad (5)$$

where ρ can be understood as the fraction of magnetic enthalpy absorbed above the Curie temperature and is $\rho = 0.4$ for BCC or $\rho = 0.28$ for non-BCC crystal structures. The composition dependence of β and T_c is expressed by:

$$\beta^\varphi(x) = \sum_i x_i^\varphi \beta_i^\varphi + {}^{xs}\beta^\varphi \quad (6)$$

$$T_c^\varphi(x) = \sum_i x_i^\varphi T_{c_i}^\varphi + {}^{xs}T_c^\varphi \quad (7)$$

where ${}^{xs}\beta^\varphi$ and ${}^{xs}T_c^\varphi$ are the excess terms expressed by the Redlich-Kister-Muggianu polynomials [44,45].

3.2. The EBEF description of the σ phase

The recently introduced EBEF [25] has been used here to describe the σ phase. The EBEF uses similar equations as the two-term CEF [38]:

$$G^\sigma - n^\sigma \sum_i x_i^\sigma H_i^{SER} = n^\sigma \Delta G^\sigma(x_i^\sigma) + \Delta G^\sigma(y_i^s) \quad (8)$$

where $\Delta G^\sigma(x_i^\sigma)$ is the composition-dependent term (“*disordered part*” of the σ phase) and n^σ is the sum of Wyckoff multiplicities of the different positions in the ordered phase. The Gibbs energy of this term is similar to that used for disordered solutions (BCC_A2, FCC_A1 etc.), but the ideal mixing term is ignored as it is considered in the configuration-dependent term ($\Delta^\circ G_i^\sigma$):

$$\Delta G^\sigma(x_i^\sigma) = \sum_i x_i^\sigma \Delta^\circ G_i^\sigma + \sum_i \sum_{j>i} x_i^\sigma x_j^\sigma L_{i,j}^\sigma + \sum_i \sum_{j>i} \sum_{k>j} x_i^\sigma x_j^\sigma x_k^\sigma L_{i,j,k}^\sigma + {}^{mag}\Delta G^\sigma \quad (9)$$

Where $\Delta^\circ G_i^\sigma$ is the molar Gibbs energy of element i in the structure of σ in the paramagnetic or non-magnetic state and $L_{i,j}^\sigma$ and $L_{i,j,k}^\sigma$ are the binary and ternary interaction parameters described by Redlich-Kister-Muggianu polynomials [44,45]. ${}^{mag}\Delta G^\sigma$ describes the contribution of magnetism.

$\Delta G^\sigma(y_i^s)$, the second term on the right side of equation (8), is described by the equations of the classical CEF [47]. However, the introduction of the composition-dependent term makes the Gibbs energy of the endmember compounds to be relative to the pure elements (Co, Cr, Ni, Re) in the structure of σ instead of their SER state; taking the *Co:Co:Cr:Ni:Re* endmember as an example the equations for the paramagnetic/non-magnetic endmembers are:

$$\begin{aligned} \Delta G_{Co:Co:Cr:Ni:Re}^\sigma &= G_{Co:Co:Cr:Ni:Re}^\sigma - a_1^{\sigma^\circ} G_{Co}^\sigma - a_2^{\sigma^\circ} G_{Co}^\sigma - a_3^{\sigma^\circ} G_{Cr}^\sigma - a_4^{\sigma^\circ} G_{Ni}^\sigma - a_5^{\sigma^\circ} G_{Re}^\sigma \end{aligned} \quad (10)$$

and

$$\Delta G^\sigma(y_i) = \sum_b y_{i_b}^1 y_{j_b}^2 y_{k_b}^3 y_{l_b}^4 y_{m_b}^5 \Delta G_{i_b:j_b:k_b:l_b:m_b}^\sigma + RT \sum_s a_s \sum_i y_i^s \ln y_i^s \quad (11)$$

where $\Delta G_{i_b:j_b:k_b:l_b:m_b}^\sigma$ is the formation energy of the endmember $i_b:j_b:k_b:l_b:m_b$ relative to the pure elements in the structure of σ , a_s^σ is the Wyckoff multiplicity of sublattice s and b is the number of endmember compounds, y_i^s is the site fraction of element i in the sublattice s . It should be noted that for the pure element endmembers $\Delta G_{Co:Co:Co:Co:Co}^\sigma = \Delta G_{Cr:Cr:Cr:Cr:Cr}^\sigma = \Delta G_{Ni:Ni:Ni:Ni:Ni}^\sigma = \Delta G_{Re:Re:Re:Re:Re}^\sigma = 0$. The second term on the right side of the equation is the ideal term, i.e., the summation of the configurational entropy of mixing on each of the sublattices.

In the EBEF the formation energies of the endmember compounds are decomposed into Effective Bond Energies (EBE) pairs. Thus, equation (10) is rewritten as:

$$\begin{aligned} \Delta G_{Co:Co:Cr:Ni:Re}^\sigma &= G_{Co*:Cr:**}^\sigma + G_{Co**Ni:*}^\sigma + G_{Co***Re}^\sigma + G_{*:Co:Cr:**}^\sigma + G_{*:Co*:Ni:*}^\sigma \\ &+ G_{*:Co**Re}^\sigma + G_{***Cr:Ni:*}^\sigma + G_{***Cr**Re}^\sigma + G_{***Ni:Re}^\sigma \end{aligned} \quad (12)$$

where G_{Co**Re}^σ represents the EBE pair between *Co* in the first sublattice and *Re* in the fifth sublattice and it is independent of the occupation of the second, third and fourth sublattices,

indicated by *. Using indices to represent the sublattices and elements forming the pairs, i.e., $G_{A::B::*::*}^\sigma = g[A^1B^3]$, the term $\Delta G^\sigma(y_i^s)$ can be written as:

$$\Delta G^\sigma(y_i^s) = \sum_i \sum_{j>i} \left(\sum_s y_i^s \sum_{t>s} y_j^t g[i^s j^t] + \sum_s y_j^s \sum_{t>s} y_i^t g[j^s i^t] \right) + RT \sum_s a_s \sum_i y_i^s \ln y_i^s \quad (13)$$

where the first term is the summation of all binary pair interactions, and the second term is the summation of the configurational entropy of mixing on each of the sublattices.

The energies of these EBE pairs can be obtained using DFT-calculated formation energies of the binary endmember compounds and are used to predict the formation energies of the binary and higher-order endmembers. Thus, only DFT-calculated formation energies of the binary endmembers are required to describe complex TCP phases in multicomponent systems, which leads to a significant reduction of the DFT calculations needed to fully describe these phases.

Considering the description of a 5-SL σ phase, the benefit of EBEF becomes immediately apparent: using the two-term CEF, 1024 and 100000 DFT-calculated formation energies are required to fully describe the σ phase in the Co-Cr-Ni-Re system and a 10-element system, respectively. On the other hand, in an EBEF-type description, only 184 (6 binary systems x 30 binary endmembers + 4 unary endmembers) and 1360 (45 binary systems x 30 binary endmembers + 10 unary endmembers) formation energies are needed. Moreover, if the EBEF-type description is implemented, the number of parameters is reduced to 120 (6 binary systems x 20 EBE pairs) and 900 (45 binary systems x 20 EBE pairs) EBE pairs, respectively.

In this context, the use of simplified thermodynamic models is no longer necessary and thermodynamic models that are more consistent with the real crystallography of the phase can be used, improving its description in multicomponent systems. Therefore, the 5-sublattices model is adopted in the present work to describe the σ phase reflecting its 5 Wyckoff positions as shown in Table 1. The EBEF-type description is already implemented in the OpenCalphad [48] and Thermo-

Calc¹ [49] software. The procedure adopted in this work to implement the EBEF to describe the σ phase is detailed in the next section.

4. Procedure

As mentioned in section 3, the available thermodynamic assessments of the binary and ternary sub-systems [13,20,23,40–42] were used as a starting point for the present work and the thermodynamic models and parameters of the disordered solution phases were maintained, while the EBEF was used to describe the σ phase.

4.1. DFT calculations

DFT calculations were performed to obtain the formation energies and magnetic moments of all binary endmember compounds derived from the thermodynamic model of the σ phase. As mentioned earlier, all Wyckoff sites were considered in the thermodynamic model. The DFT calculations settings used in the present work are identical to those used for hundreds of thousands of calculation results in the Open Quantum Materials Database (OQMD) [50]. The Projector Augmented Wave (PAW) method [51], which is implemented in the Vienna ab initio simulation package (VASP) [52,53], was used. The calculations were performed using Generalized Gradient Approximation (GGA) within Perdew-Burke-Ernzerhof (PBE) parametrization for exchange and correlation effects [54]. The structures were first allowed to relax, and then subsequent static calculations were performed with cutoff energy of 520 eV and k-point mesh based on 8000 k-points per reciprocal atom. Spin polarization was used for calculations involving Co, Cr and Ni. The results obtained for all endmembers of the σ phase in the six constituent binary systems are available in the supplementary material A.

The formation energies are calculated for each of the endmembers according to the following equation, using the *Co:Re:Co:Co:Re* endmember as an example.

¹ Certain equipment, instruments, software, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement of any product or service by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

$$\Delta E_{Co:Re:Co:Co:Re}^{\sigma} = E_{Co:Re:Co:Co:Re}^{\sigma} - \alpha_1^{\sigma} E_{Co}^{SER} - \alpha_2^{\sigma} E_{Re}^{SER} - \alpha_3^{\sigma} E_{Co}^{SER} - \alpha_4^{\sigma} E_{Co}^{SER} - \alpha_5^{\sigma} E_{Re}^{SER} \quad (14)$$

where the letter E represents the DFT calculated endmember energies given per mole of atoms to differentiate from the energy terms in Calphad descriptions denoted by the letter G and the α_i^{σ} represent the sublattice fractions, $\alpha_i^{\sigma} = a_i^{\sigma} / \sum_i a_i^{\sigma}$.

4.2. Treatment of magnetism

As Co and Ni are ferromagnetic elements and Cr is antiferromagnetic, the treatment of magnetism must be adequate to obtain a consistent thermodynamic database for Co-based superalloys. As shown in equation (9), the magnetic contribution to the total energy is given by a separate term $^{mag}\Delta G^{\sigma}$ and the remainder of the Gibbs energy functions describe the paramagnetic state. Spin polarized DFT calculations are used to obtain the energy of the ferromagnetic state, while non-spin-polarized DFT calculations provide the energy of the non-magnetic state. Only complex atomistic calculations can properly describe the paramagnetic state. Thus, a straightforward method introduced in previous papers [20,21,55] was used here to describe the paramagnetic energies of each endmember of the σ phase from DFT results considering spin polarization. However, in contrast to Wang et al. [20,21,55] the contribution of the magnetism is described as composition-dependent and not configuration-dependent to reflect that the present model uses the mean magnetic moment as input. It is important to emphasize that although pure Cr in BCC structure is antiferromagnetic, the magnetic moments obtained from DFT calculations for the Cr-containing σ endmembers are all negligible (see supplementary material A). Therefore, the mentioned method was applied only to describe the σ endmembers containing Co and/or Ni.

Thus, at 0 K and taking the $Co:Re:Co:Re:Co$ endmember as an example, equation (4) can be rewritten:

$$^{mag}\Delta E_{Co:Re:Co:Re:Co}^{\sigma}(0K) = -R \ln(\beta_{Co:Re:Co:Re:Co}^{\sigma} + 1) (\rho_0 T c_{Co:Re:Co:Re:Co}^{\sigma}) \quad (15)$$

where $^{mag}\Delta E_{Co:Re:Co:Re:Co}^{\sigma}$ is the magnetic energy per mole of atoms of the endmember $Co:Re:Co:Re:Co$ in the structure of the σ phase, $\beta_{Co:Re:Co:Re:Co}^{\sigma}$ is the DFT-calculated magnetic

moment of the endmember $Co:Re:Co:Re:Co$ in the structure of σ and the crystal structure constant $\rho_0 = \frac{79}{140D\rho} = 0.86034$ for non-BCC phases. $Tc_{Co:Re:Co:Re:Co}^\sigma$ is the Curie temperature of the endmember $Co:Re:Co:Re:Co$ in the structure of σ and is estimated using the Heisenberg model [21]:

$$\frac{Tc_{Co:Re:Co:Re:Co}^\sigma}{Tc_{Co}^{SER}} = \frac{\beta_{Co:Re:Co:Re:Co}^\sigma}{\beta_{Co}^{SER}} \quad (16)$$

where $Tc_{Co}^{SER} / \beta_{Co}^{SER}$ are the Curie temperatures / magnetic moments of the element Co in the SER state. Note that β_{Co}^{SER} here is the value obtained from DFT while Tc_{Co}^{SER} is the value from SGTE unary database [56].

Finally, the magnetic energies are subtracted from the DFT formation energies of the ferromagnetic state to obtain the energies of the paramagnetic state. Thus, taking the Co-Re system and the $Co:Re:Co:Re:Co$ endmember as an example, the following equations are used to calculate the Gibbs energies of i) the pure elements in the composition-dependent part (*disordered part*) and ii) the endmember compounds:

$$\Delta^\circ G_{Co}^\sigma = \Delta E_{Co:Co:Co:Co:Co}^\sigma - {}^{mag}\Delta E_{Co:Co:Co:Co:Co}^\sigma + {}^{mag}\Delta E_{Co}^{SER} + \Delta^\circ G_{Co}^{SER} \quad (17)$$

$$\begin{aligned} \Delta G_{Co:Re:Co:Re:Co}^\sigma &= n^\sigma \left(\Delta E_{Co:Re:Co:Re:Co}^\sigma - {}^{mag}\Delta E_{Co:Re:Co:Re:Co}^\sigma \right. \\ &\quad - x_{Co}^{\sigma_{Co:Re:Co:Re:Co}} \left(\Delta E_{Co:Co:Co:Co:Co}^\sigma - {}^{mag}\Delta E_{Co:Co:Co:Co:Co}^\sigma \right) \\ &\quad \left. - x_{Re}^{\sigma_{Co:Re:Co:Re:Co}} \left(\Delta E_{Re:Re:Re:Re:Re}^\sigma - {}^{mag}\Delta E_{Re:Re:Re:Re:Re}^\sigma \right) \right) \end{aligned} \quad (18)$$

where $\Delta^\circ G_{Co}^\sigma$ is the term for paramagnetic Co in the structure of σ referred to the enthalpy, H , of the paramagnetic SER at 298 K, $\Delta E_{Co:Co:Co:Co:Co}^\sigma$ is the DFT-calculated Gibbs energy of pure Co in the structure of σ . ${}^{mag}\Delta E_{Co:Co:Co:Co:Co}^\sigma$ is the magnetic energy of pure Co in the structure of σ calculated by equation (15). $\Delta^\circ G_{Co}^{SER}$ represents the Gibbs energy of Co in the paramagnetic SER state at 298 K referred to the H of the paramagnetic SER at 298 K. In equation (18), $\Delta G_{Co:Re:Co:Re:Co}^\sigma$ is the formation Gibbs energy of the paramagnetic endmember $Co:Re:Co:Re:Co$

in the structure of σ , $\Delta E_{Co:Re:Co:Re:Co}^\sigma$ is the DFT-calculated formation energy of the endmember $Co:Re:Co:Re:Co$ in the structure of σ and $^{mag}\Delta E_{Co:Re:Co:Re:Co}^\sigma$ is the magnetic energy of the endmember $Co:Re:Co:Re:Co$ in the structure of σ . $\Delta E_{Co:Co:Co:Co:Co}^\sigma$ and $\Delta E_{Re:Re:Re:Re:Re}^\sigma$ are the DFT formation energies of pure Co and Re in the structure of σ and $^{mag}\Delta E_{Co:Co:Co:Co:Co}^\sigma$ and $^{mag}\Delta E_{Re:Re:Re:Re:Re}^\sigma$ are the magnetic energies of pure elements Co and Re in the structure of σ (note that $^{mag}\Delta E_{Re:Re:Re:Re:Re}^\sigma = 0$) and $x_{Co}^{\sigma_{Co:Re:Co:Re:Co}}$ and $x_{Re}^{\sigma_{Co:Re:Co:Re:Co}}$ are the atomic fractions of Co and Re in the endmember $Co:Re:Co:Re:Co$.

The energies $\Delta^\circ G_{Co}^\sigma$ were used directly in the thermodynamic database, while the energies $\Delta G_{Co:Re:Co:Re:Co}^\sigma$ were used to obtain the EBE pairs introduced in the thermodynamic database.

4.3. The matrix inversion method (MIM) and final adjustments

As mentioned above, the EBEF has the potential to play an important role in the development of DFT-supported multicomponent thermodynamic databases. However, how to obtain the EBE pairs from the DFT-calculated formation energies is an important issue. In the EBEF introductory article, Dupin et al. [25] obtained the EBE pairs using the Parrot optimizer module of the Thermo-Calc [49] to adjust the EBE pair parameters to the DFT results. Although this approach is possible, it is also time consuming to assess the EBE pairs in multicomponent systems which can be several hundred parameters for a large database, such as the CHiMaD-Co thermodynamic database. Therefore, using the EBEF method for the purpose of database simplification would not be very attractive. A possible solution to this problem is the use of a Matrix Inversion Method (MIM) to obtain the EBE pairs [57]. The MIM has been successfully applied in the present work for all of the constituent binary systems and is based on a simple matrix operation as shown below for the 5-SL σ phase in the Co-Re binary system:

$$Y = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 1 & 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 1 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 1 & 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 1 & 0 & 1 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 0 \\ 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 1 & 1 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 1 \end{bmatrix}$$

where the Y is a matrix composed of zeros and ones that corresponds to a binary encoding of the list of contributing EBE pair energies, x is a column matrix composed of the EBE pairs to be obtained and the term on the right side of the equation (19) corresponds to a column matrix composed of the endmember formation energies. Since Y is a non-square matrix, it is not directly invertible, and the pseudo-inverse must be obtained. In this work, obtaining the EBE pairs via MIM was automated using the Numpy package from Python [58], where the Penrose-Moore method [59,60] is used to obtain the parameters of the EBE pairs by inverting Y .

Twenty EBE pairs in each binary constituting the Co-Cr-Ni-Re system were obtained and used to build the thermodynamic database. The six binary systems and some of the isothermal

sections of the four ternaries were plotted using the Thermo-Calc software [49]. Finally, to obtain a better consistency between the calculated binary and ternary systems and the experimental phase diagram data available in the literature, entropy terms were added to the description of the pure elements in the structure of σ ($\Delta^\circ G_i^\sigma$ in equation (9)) and composition-dependent interaction parameters ($L_{i,j}^\sigma$ in equation (9)) were introduced.

5. SGTE and DFT-calculated lattice stabilities

Before moving on to the results, it is important to make some comments about the lattice stabilities. The SGTE (Scientific Group Thermodata Europe) compilation of unary Calphad descriptions [56] was an important step forward by allowing the description of higher order systems to be consistent with each other in terms of unary parameters. The SGTE unary database has been successfully applied to describe a wide variety of systems and has helped to spread Calphad databases to industrial applications.

More recently, with the advent of first principles data and the advancement of computer technology, DFT data have become accessible for calculating important input data for Calphad assessments, such as formation energies of endmember compounds. This represented a turning point for Calphad assessments, allowing the construction of physically more meaningful databases and accelerating their development. However, it was noted that in many cases the SGTE lattice stabilities strongly disagree with DFT-calculated lattice stabilities [61,62]. This is shown in Table 2 where the SGTE lattice stabilities for Co, Cr, Ni and Re are compared to first principles results taken from Sluiter [63] and well-known high-throughput DFT databases, i.e., Automatic Flow (AFLOW) [64], the Open Quantum Materials Database (OQMD) [50] and the Materials Project (MP) [65]. Table 2 also lists the lattice stabilities calculated by van de Walle [62] who uses an inflection-detection computational scheme to calculate the energies of structures with mechanical instability. It can be noticed that van de Walle's values are generally closer to the SGTE values, but there is still a significant difference.

This disagreement between DFT and SGTE lattice stabilities makes it difficult to develop more physically meaningful databases without sacrificing the convenience and effectiveness of the Calphad method. It is worth mentioning that the SGTE database is based on empirical models [56] and the 1995 Ringberg workshop [66–68] suggested the use of a physically based approach to

model liquid and solid phases by using physical properties in the expressions of the Gibbs energies. These models are being applied to describe many pure elements [69–75] to develop the third generation of a unary database with more physical meaning that are valid down to 0 K. However, there is a long way to go to obtain a consistent set of third generation unary descriptions and the development of new Calphad databases must move forward to assist the design of new materials. Therefore, the SGTE database [56] is used in the present work.

It is important to note that DFT-calculated lattice stabilities of the σ phase are used here along with SGTE lattice stabilities for FCC_A1, BCC_A2 and HCP_A3. However, as mentioned above, the SGTE FCC_A1, BCC_A2 and HCP_A3 lattice stabilities disagree with those predicted by DFT. Thus, in the database, the σ lattice stabilities for Co, Cr and Ni are larger than the lattice stabilities of the other phases, although they should have an intermediate value between FCC_A1/HCP_A3 and BCC_A2 lattice stabilities according to DFT calculations. To generate σ lattice stabilities that have intermediate values between those of FCC_A1/HCP_A3 and BCC_A2, some methods for rescaling the σ lattice stabilities have been tested. However, the as-obtained values did not adequately describe the σ phase in all the subsystems simultaneously. Furthermore, this would be a provisional solution, as a consistent and durable solution must come from a new set of unary descriptions that better match predictions from first principles (FP) calculations.

Therefore, due to this disagreement between SGTE and FP lattice stabilities, even applying a DFT-supported EBEF description and using a thermodynamic model that is more consistent with the real crystallography of the phase, some adjustable parameters may still be needed to describe the σ phase. These adjustable parameters may also be necessary because some of the endmembers may be mechanically unstable and the DFT results for these are likely to be less reliable. However, the number of adjustable parameters used in this work is very low when compared to previous Calphad assessments, as discussed in the next sections.

6. Results and discussion

A thermodynamic description of the σ phase in the Co-Cr-Ni-Re system was obtained by applying a DFT-supported EBEF and using the 5-SL model. The parameters related to the stable disordered solution phases were taken from the literature [13,20,40–42], while the EBE pairs of

the σ phase - for the six constituent binary systems – were calculated in the present work and are listed in Table 3 and Table 4.

It is worth mentioning that new parameters were established here for disordered solution phases in the Co-Re system, as the assessments available in the literature [19,76] for this system are not adequate and prevent a good description of the higher-order systems. The description established by Liu et al. [76] uses the outdated SGTE Re description, while the assessment by Guo et al. [19] has large negative mixing parameters, which is not supported by DFT calculations [50,64] indicating much smaller values.

It is also important to mention that binary parameters were estimated for the metastable disordered phases in each of the constituent binary systems. Thus, the metastable binary parameters of the HCP_A3 phase were assumed to be equal to the FCC_A1 parameters and vice-versa due to the similarity between these two phases. On the other hand, to estimate the metastable binary parameters of the BCC_A2 phase, the Liquid parameters were used due to the similar coordination in these two phases.

The complete thermodynamic database is found in the supplementary material B. The criteria for evaluating the EBE pairs are presented in section 6.1, while the calculated binary and ternary diagrams, in which the σ phase is stable, are discussed in sections 6.2-6.6.

6.1. Criteria for verifying the reliability of the EBE pairs

After obtaining the EBE pairs from the MIM, it is important to study their behavior with respect to the original DFT values and their use in the classical 5 SL-CEF. Ultimately, the EBE pairs must be able to adequately reproduce the features predicted by DFT. In principle ternary formation energies predicted from EBE pairs derived from the binary endmembers could be compared to values from DFT calculations. However, this would require 150 additional DFT calculations for each ternary system. It was shown by Dupin et al. [25] that satisfactory predictions for the ternary endmembers can be obtained and, therefore, other criteria are needed.

With that in mind, a criterion is proposed here to verify the reliability of the EBE pairs based on three evaluations: 1) agreement between the formation energies of the endmember compounds obtained from the EBE pairs and predicted by DFT, 2) concordance between the minimum energies predicted by DFT and the enthalpy and Gibbs energy curves calculated using

the EBEF, 3) ability of the EBE pairs to generate reasonable site occupancy curves and to reproduce those predicted by using the DFT energies in a classical 5-SL CEF description.

The EBEF vs. DFT diagonal plots, found in Figure 1, are important to evaluate whether the obtained EBE pairs can properly reproduce the formation energies calculated by DFT. The fit between DFT and EBEF energies are evaluated here using the coefficient of determination (COD or R^2) and considering the ideal behavior (i.e. function $y = x$). The closer the R^2 is to one, the better the fit. The EBEF energies were calculated by using the EBE pairs (see Table 3) in an equation analogous to equation (12), while the DFT energies were obtained by using the DFT data (see supplementary material A) in equation (18). Taking the R^2 as a reference, it is possible to note that the fit between DFT energy and EBEF energy is very good for the Co-Re, Ni-Re and Cr-Re systems ($R^2 > 0.95$), which is a good indicator that the MIM was able to generate reliable EBE pairs. On the other hand, the R^2 is not as good for the other three systems, especially for the Co-Ni system, where the R^2 is very low (0.00348), indicating that there is no linear relationship between EBEF energy and DFT energy in this system. This can be explained by the fact that Co and Ni are very similar in terms of size and electronic factors leading to a metastable σ phase with a low degree of ordering in this system.

Following the criteria mentioned above to evaluate the obtained EBE pairs, Figure 2 shows the enthalpy and Gibbs energy curves of each binary system at 300 K and 1500 K. Note that these curves were calculated for comparison purposes, taking into account only the DFT formation energies (dashed lines) and the EBE pairs (solid lines). In general, the curves at 300 K reproduce well the lowest DFT energies (calculated at 0 K) and the deviations are due to the fact that the fit between DFT energy and EBEF energy is not perfect, as seen in Figure 1. As expected, better agreements were obtained for the Co-Re, Cr-Re and Ni-Re systems, while larger deviations are observed for Co-Cr and Cr-Ni systems.

It is worth mentioning that the DFT results presented by Palumbo et al. [77] and Crivello et al. [78] are superimposed on the curves of the Cr-Ni, Cr-Re and Ni-Re systems for comparison purposes. It can be noted that the agreement between our DFT data and their data is very good for the Cr-Re system. However, for the Cr-Ni and Ni-Re systems, the agreement is not as good for the Ni-rich endmembers, which is explained by the different magnetic treatment adopted for each DFT dataset. As explained in the section 4.2, this work uses paramagnetic formation energies by subtracting calculated magnetic energies from spin polarized DFT energies. On the other hand,

Palumbo's data were obtained from spin polarized DFT calculations (ferromagnetic formation energies) [77], while Crivello used calculations without spin-polarization which led to non-magnetic formation energies [78]. The DFT dataset of the Co-Cr system is compared with the results of Wang et al. [20], Pavlů et al. [79] (adapted to paramagnetic energies using equations presented in section 4.2) and Korzhavyi et al. [80], who calculated the energies for the paramagnetic state using the Disordered Local Moment (DLM) method which is based on the Coherent Potential Approximation (CPA). It can be seen that our DFT data agree well with those of Wang et al. [20] and Pavlů et al. [79]. On the other hand, Korzhavyi et al. [80] obtained more negative values, which can be explained by the different DFT method used. While our DFT dataset is based on GGA calculations, Korzhavyi et al. [80] used Local Density Approximation (LDA), which can overestimate the calculated energies [81]. To the best of our knowledge, no DFT data are available in the literature for the σ phase in the Co-Ni and Co-Re systems.

Finally, Figure 3 shows the site occupancy curves at 300 K and 1500 K for each of the binary systems. At first glance, it can be noted that most of the curves are reasonable. However, unusual, and undesirable behavior of the curve for the 2a site is observed in the Co-Cr (on the Cr-rich side) and Cr-Ni (around 0.5 mole fraction of Ni) systems, i.e., systems with $R^2 < 0.95$. These artifacts in the site fraction curves were caused by the conversion of the DFT energies into EBE pairs and must be corrected. All the site fraction curves (including those obtained using DFT-CEF) are found in the supplementary material C. It is interesting to note that for the Co-Re system, an increase in the 2a site occupancy at approximately 0.7 molar fraction of Re at 300 K occurs in both the EBEF and DFT-CEF descriptions.

Therefore, new EBE pairs were obtained for the Co-Cr and Cr-Ni systems, by increasing the weight of the most negative formation energies in the MIM, as the phase features are mainly defined by the negative formation energies. Therefore, the values of the five most negative formation energies and the corresponding rows of the Y matrix were doubled. The compositions of these doubled values are 0.4, 0.53333, 0.6, 0.66667 and 0.73333 mole fraction of Cr for the Co-Cr system and 0.26667, 0.33333, 0.53333, 0.6 and 0.73333 mole fraction of Ni for the Cr-Ni system. The new EBE pairs (Table 4) are able to better describe the σ phase and the description of the site occupancies has been particularly improved and seems more reasonable, as observed in Figure 4. Thus, this second set of EBE parameters are used in our database. A better description of the most negative energies was essential to achieve these better results, although the overall R^2

improved only slightly (Co-Cr from 0.90464 to 0.90689) or even worsened (Cr-Ni from 0.74153 to 0.6831).

Regarding the Co-Ni, Co-Re, Cr-Re and Ni-Re systems, EBE pairs obtained from a regular MIM were used to describe the σ phase. It is important to emphasize that although the fit between DFT and EBEF energies in the Co-Ni system is poor, they have been used here as obtained from a regular MIM. This decision was made based on the fact that all the Co-Ni σ formation energies are very low ($-1 \text{ kJ/mol} < \Delta G_{endmember}^{\sigma} < 1 \text{ kJ/mol}$), not significantly affecting the site fraction plots and phase equilibria.

6.2. The Co-Cr system

The Co-Cr system shows the σ phase as its only stable intermediate compound, while large stability regions of FCC_A1, BCC_A2 and HCP_A3 are observed. The thermodynamic assessment developed by Wang et al. [20] was used as a starting point for the present work.

The description of the σ phase has been modified by implementing the EBEF. However, the use of EBE pairs and addition of entropy coefficients in the pure elements were not sufficient to stabilize the σ phase. This is possibly due to the use of DFT-calculated lattice stabilities for the σ phase along with SGTE lattice stabilities for FCC_A1, BCC_A2 and HCP_A3, as explained in section 5. Therefore, the addition of one single adjustable composition-dependent parameter (${}^0L_{Co,Cr}^{\sigma,dis}$) was needed to properly describe the σ phase. It is worth noting that the use of this parameter does not change the site occupancies predicted by DFT. Furthermore, this still represents a significant reduction in the number of adjustable parameters since Wang et al. [20] used three excess terms (${}^0L_{Co,Cr:Cr:Co}^{\sigma}$, ${}^0L_{Cr:Cr:Co,Cr}^{\sigma}$, ${}^0L_{Cr:Co,Cr:Cr}^{\sigma}$), that affect the site occupancies of the phase. As mentioned in section 4.2, in contrast to Wang et al. [20] the present work describes the magnetism in the composition-dependent part of the σ phase. The magnetic moment obtained from DFT is adopted for pure Co in the structure of the phase, while the Curie temperature is obtained from equation (16). Therefore, the compositional dependence of magnetism of the σ phase, discussed by Wang et al. [20], is described here by using Curie temperature and magnetic moment excess terms.

Figure 5 presents the Co-Cr system obtained in this work with the experimental results from [82–89] superimposed on the calculated phase diagram. The phase diagram established by

Wang et al. [20] is shown in dashed lines. The main difference between the description established in this work and the description by Wang et al. [20] is the Cr-rich solvus line of the σ phase, since Wang's description establishes a slightly larger stability region of the σ phase. Figure 5 also presents the enthalpy curves of the σ phase calculated with and without interaction parameters in comparison with the curve calculated with the database developed by Wang et al. [20]. It can be seen that the use of ${}^0L_{Co,Cr}^{\sigma-dis}$ was important to stabilize the σ phase. This figure also represents the enthalpy of the terminal solution phases established by Wang et al. [20]. Some lattice stabilities from ab initio studies are also represented on this figure. The previously discussed differences with the SGTE descriptions of the pure elements are clearly noticeable. Our choice to base the description of the pure elements in the σ phase on DFT values induces different relative stability of the metastable phases than expected according to DFT calculations. Note that the endmember energies superimposed in Figure 5b are the spin-polarized values as obtained from DFT calculations.

It can be noted that both descriptions are generally in good agreement with the experimental results. However, the experimental data on the extend of the σ phase are somewhat scattered. None of the descriptions of this system have been able to properly reproduce the tie-lines reported for the Cr-rich side at low temperatures. The available Calphad studies of this system show different stability of the σ phase at temperatures below 900. It is highly desirable to obtain better knowledge of the phase diagram at lower temperatures and in particular of the decomposition temperature of the σ phase.

6.3. The Cr-Re system

Like the Co-Cr system, the Cr-Re system has the σ phase as its only intermediate compound. The thermodynamic parameters of the terminal phases established by Palumbo et al. [13] were used as a starting point. The Cr-Re system calculated using the database developed in this work is shown in Figure 6 along with Palumbo's description (in dashed lines). Although the available experimental data are somewhat contradictory [90–93] and further experimental study is needed, it is possible to say that a reasonable agreement was reached. The enthalpy curves of the σ phase at 298.15 K calculated with our database and with the database developed by Palumbo et al. [13] are also shown in Figure 6.

The description of the σ phase obtained here is very similar to that established by Palumbo et al. [13], which was expected as the authors also used the 5-SL model and their DFT data are similar to ours as can be observed in Figure 2e. However, it can be noted that the description established in this work has a larger stability region of the σ phase. Thus, Palumbo's assessment better describes some experimental points around 0.5 mole fraction of Re at different temperatures [90,92]. On the other hand, our description better describes the single-phase experimental points at approximately 0.6 mole fraction of Re [92] and the compositions of the solid phases in the invariant reactions [93]. These differences can be explained by the fact that Palumbo et al. [13] used a composition-dependent interaction parameter (${}^0L_{Cr,Re}^{dis,\sigma}$) to describe the σ phase, while in the present work, this parameter was successfully replaced by the addition of entropy coefficients for the pure elements. To do this, the value of $-1.205T$ for pure Re was taken from the original EBEF article [25], since the enthalpy term used there is similar to the value used in this work (+9331 and 9315.75, respectively). Thus, the value of $-3T$ was assessed during this work for pure Cr in order to describe the Cr-Re system. A better agreement could be achieved if the terminal solution phases would be reassessed. This is out of the scope of the present work where the objective is to compare the extrapolation ability of the CEF and EBEF by changing only the description of the σ phase.

Moreover, it is important to emphasize that the EBEF was used to describe the σ phase in our database while Palumbo et al. [13] used the two-term CEF. Therefore, the main advantage of our approach is the fact that only DFT-calculated binary formation energies are required to describe higher-order systems, while additional ternary formation energies would be needed using Palumbo's database.

6.4. The Co-Cr-Ni system

Experimental data of the Co-Cr-Ni system have been reported by Omori et al. [94]. The authors showed that the σ phase dissolves around 0.20 mole fraction of Ni at 900 °C, 1000 °C and 1100 °C. More recently, Wang et al. [23] carried out a thermodynamic assessment of the Co-Cr-Ni using the two-term CEF and a 3-SL model - $(Co,Cr,Ni)_{10}(Co,Cr,Ni)_4(Co,Cr,Ni)_{16}$ - to describe the σ phase. Wang et al. [23] used two ternary interaction parameters

(${}^0L_{Cr:Co,Ni:Co}^\sigma$ and ${}^0L_{Cr:Co,Ni:Cr}^\sigma$) and two formation energies of the ternary endmembers (${}^0G_{Cr:Ni:Co}^\sigma$ and ${}^0G_{Cr:Co:Ni}^\sigma$) to describe the σ phase.

On the other hand, a good description of the Co-Cr-Ni ternary system is obtained in the present work without any ternary interaction parameters for any of the phases. Therefore, the ternary parameters established by Wang et al. [23] for the sigma phase as well as the disordered solution phases are no longer needed after the implementation of the EBEF. A binary composition-dependent adjustable parameter (${}^0L_{Cr,Ni}^{dis-\sigma}$) for the metastable σ phase in the Cr-Ni system is used here. As previously discussed, this parameter is needed to adjust the stability of the σ phase due to the inconsistency between the SGTE lattice stabilities with those predicted by DFT. Furthermore, an entropy coefficient of +6T was estimated for pure Ni in the structure of the σ phase. To do this, the value of +3T used by Dupin et al [25] was considered, but their enthalpy value (non-magnetic) is much higher than the paramagnetic value used in this work (+13582 and +9302.69, respectively). Therefore, the value of +6T was estimated so that the parameter ${}^0G_{Ni}^{dis-\sigma}$ has a similar effect at temperatures around 1000 °C to 1200 °C.

Figure 7 shows the isothermal section of the Co-Cr-Ni system at 1000 °C calculated using the CEF and EBEF without any ternary parameters. Since the binary composition-dependent adjustable parameter (${}^0L_{Cr,Ni}^{dis-\sigma}$) is used in both CEF and EBEF descriptions, the better results shown in Figure 7b is exclusively attributed to the use of the EBE pairs. The comparison of the two isothermal sections clearly demonstrates the advantage of the EBEF, which produces a good ternary homogeneity range for the sigma phase while the homogeneity range obtained using the CEF barely extends into the ternary system.

6.5. The Co-Cr-Re system

The experimental information on the Co-Cr-Re system available in the literature was established by Sokolovskaya et al. [95]. The authors produced 36 samples and identified the stable phases after heat-treatment at 1000 °C, 1150 °C and 1300 °C. The σ phase forms a continuous solution between the Co-Cr and the Cr-Re systems. However, the experimental procedure is strongly questionable as the results show important inconsistencies with the accepted Co-Cr binary subsystem. For this reason, a thermodynamic assessment of this system cannot be performed

adequately. Ostrowska and Cacciamani [43] described the σ phase in this system by using the traditional CEF and the 3-SL model. They used six ternary interaction parameters in addition to the Gibbs formation energy of six ternary endmembers, four of them expressed as linear combination of GHSER, in order to describe the continuous solution of the σ phase reported by Sokolovskaya et al. [95]. They also compare their description with the site occupancies measured by Joubert et al. [96] showing poor agreement due to the limited number of sublattices used.

In the present work, the mentioned continuous solution is obtained without any ternary parameters for the σ phase (see Figures 8b and 8c), which can be attributed to the use of the EBEF. Moreover, the use of the 5-SL model allows the calculated site occupancies to reasonably agree with those measured by Joubert [96], as shown in Figure 9. Regarding the disordered phases, one single ternary parameter is used here to better describe the solubility of the BCC_A2 phase. The need to use this parameter is highly correlated to the binary interaction parameter used for the metastable BCC_A2 phase in the Co-Re system. Thus, a better assessment of this binary parameter is desirable. More experimental information is needed to obtain a better description of this system.

Figure 8 shows the isothermal section of the Co-Cr-Re system at 1150 °C calculated without any ternary parameters for any of the phases, using the CEF and EBEF and the EBEF with the mentioned ternary interaction parameter for the BCC_A2 phase. The comparison of the two isothermal sections calculated without any ternary parameters shows again the advantage of the EBEF, which produces the continuous solution of the σ phase, while this behavior is not observed using the CEF. The binary interaction parameters were kept in the CEF description, thus the better description with the EBEF cannot be attributed to them. Further, the use of the ternary parameter for the BCC_A2 phase slightly improved the description of the Cr-rich side of the isothermal section, but it should be noted that the extrapolation from the binary descriptions predicts this ternary section very well.

6.6. The Cr-Ni-Re system

The Cr-Ni-Re system has been experimentally studied by Slyusarenko et al. [97] and later by Saito et al. [98,99]. More experimental results are needed to perform a complete thermodynamic description of the system as both works only present results of the isothermal section at 1150 °C. According to the results, the σ phase dissolves around 0.2 mole fraction of Ni at 1150 °C.

Huang et al. [36,37] performed a preliminary thermodynamic assessment of the system and a reasonable agreement with the experimental results was obtained. Their assessment was based on the old Re lattice stabilities and their description of the Ni-Re system is not in agreement with the experimental information currently available for this system. They used the traditional CEF applied to the $(\text{Ni,Re})_8(\text{Cr})_4(\text{Cr,Ni,Re})_{18}$ thermodynamic model. The values of the σ endmembers in the Cr-Re binary are based on their assessment of this system. Those for the Cr-Ni system were taken from other previous ternary assessments where Cr-Ni is a constituent system. The ternary endmembers were defined as a linear combination of the FCC_A1, BCC_A2 and HCP_A3 lattice stabilities of the pure elements.

In the present work, a DFT-supported EBEF-type description of the σ phase applied to the 5-SL model is used. Figure 10 shows the isothermal section of the Cr-Ni-Re system at 1150 °C calculated without any ternary parameters for any of the phases, using the CEF and EBEF and the EBEF with ternary parameters. It should be noted that the binary interaction parameters were also used to calculate the CEF isothermal section. The EBEF proved again to be effective in obtaining the correct phase topology and reasonably predicting the phase solubility in the ternary system without the use of ternary parameters, while the description of the σ phase using CEF is very poor. Since the EBEF description of the σ solubility is somewhat overestimated when ternary parameters are not considered, a single positive ternary composition-dependent adjustable parameter was needed to fit the experimental data (${}^0L_{\text{Cr,Ni,Re}}^{\text{dis-}\sigma}$). Note that the binary parameters ${}^0L_{\text{Cr,Ni}}^{\text{dis-}\sigma}$ and ${}^0L_{\text{Ni,Re}}^{\text{dis-}\sigma}$ are also affecting the phase equilibria in this system. As previously discussed, these parameters are needed due to the inconsistency between the SGTE lattices stabilities and those predicted by DFT.

6.7. The Co-Cr-Ni-Re system

Figure 11 shows the isothermal section at 1150 °C and a constant mole fraction of 0.20 Ni using the present description for the extrapolation of the quaternary system. This section also demonstrates the power of the EBEF for the extrapolation of higher component systems as the σ phase has a noticeable quaternary homogeneity range. This is particularly important as experimental data for quaternary system are rarely available.

7. Conclusion/Summary

The recently introduced Effective Bond Energy Formalism (EBEF) allows the use of thermodynamic models consistent with the real crystallography of complex phases, since the input data can be reduced to DFT formation energies of the binary endmembers. The Matrix Inversion Method used to determine the EBE pairs is described in this work. It allows reducing the subjectivity and time required to obtain the EBE pairs in the initial introduction of the formalism.

The present work conveys a DFT-supported EBEF 5-SL description of the σ phase in the Co-Cr-Ni-Re system using previous descriptions of the different terminal solution phases available in literature assessments of the subsystems. The extension of the σ phase was successfully described in the subsystems where it is reported. The most important result is that good descriptions of the ternary systems are obtained with the EBEF without considering any ternary parameters, which is not the case when the CEF is used. The ability of the EBEF to extrapolate properly is thus confirmed here in ternary subsystems, which show very different extensions of the σ phase. A few ternary parameters were eventually introduced to better fit the experimental data even if the reliability of some of these data is weak. It shows the possibility to use excess parameters in the EBEF when needed. The excellent extrapolation behavior of the EBEF makes it very suitable for the development of large databases and the methodology presented here is used by some of the authors (JCPS and URK) to describe complex TCP phases in a database for Co-base γ/γ' superalloys.

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Figure captions

Figure 1 – Comparison between DFT energy and EBEF energy in the constituent binary systems: a) Co-Cr, b) Co-Ni, c) Co-Re, d) Cr-Ni, e) Cr-Re and f) Ni-Re.

Figure 2 – Enthalpy and Gibbs energy curves of each binary system: a) Co-Cr, b) Co-Ni, c) Co-Re, d) Cr-Ni, e) Cr-Re and f) Ni-Re. Solid lines represent the EBEF curves and dashed lines represent the DFT-CEF curves.

Figure 3 – Calculated site occupancies at 300 K and 1500 K of each binary system: a) Co-Cr, b) Co-Ni, c) Co-Re*, d) Cr-Ni, e) Cr-Re and f) Ni-Re.

* DFT data predicted a miscibility gap on the Re-rich side at 300 K.

Figure 4 – Results for Co-Cr and Co-Ni using EBE pairs obtained from MIM by increasing the weight of the most negative energies a) DFT vs EBEF diagonal plots, b) enthalpy curves, c) Gibbs energy curves, d) site occupancies at 300 K and e) site occupancies at 1500 K.

Figure 5 – The Co-Cr system: a) calculated phase diagrams and b) calculated enthalpy curves. The enthalpy curves of the σ phase: this work with interaction parameters (solid line), this work without interaction parameters (dotted line) and Wang et al. (dashed line).

Figure 6 – The Cr-Re system: a) calculated phase diagrams and b) calculated enthalpy curves. The enthalpy curves of the σ phase: this work (solid line), and Palumbo et al. (dashed line).

Figure 7 – The calculated isothermal section of the Co-Cr-Ni system at 1000 °C using a) two-term CEF without ternary parameters and b) EBEF without ternary parameters.

Figure 8 – The calculated isothermal section of the Co-Cr-Re system at 1150 °C using a) two-term 5SL-CEF without ternary parameters, b) EBEF without ternary parameters and c) EBEF with ternary parameters.

Figure 9 – Calculated site occupancies of the σ phase in the Co-Cr-Re system at 1150 °C along the composition $\text{Cr}_{42}\text{Re}_{58}$ - $\text{Co}_{21}\text{Cr}_{39}\text{Re}_{39}$ - $\text{Co}_{33.5}\text{Cr}_{47.5}\text{Re}_{19}$ - $\text{Co}_{43}\text{Cr}_{57}$.

Figure 10 – The calculated isothermal section of the Cr-Ni-Re system at 1150 °C using a) two-term 5SL-CEF without ternary parameters, b) EBEF without ternary parameters and c) EBEF with ternary parameters.

Figure 11 – The calculated isothermal section of the Co-Cr-Ni-Re system at 1150 °C and a constant mole fraction of 0.20 Ni.

Table 1 - Crystallographic data of σ phase.

Phase	Prototype	Strukt.	Space group	Pearson symbol	Wyckoff position	Coordination number	Point symmetry
					2a	12	mmm
					4f	15	mm
σ	CrFe	$D8_b$	$P4_2/mnm$	$tP30$	8i ₁	14	m
					8i ₂	12	m
					8j	14	m

Table 2 - Comparison between SGTE and DFT lattice stabilities. The lattice stability, ΔG_{Para}^{ϕ} , is relative to the GHSER function. DFT values are from spin-polarized calculations and, therefore, reflect the ordered magnetic state.

Element	Phase	Lattice stability (J/mol)*						
		SGTE [56] / This work		vdWalle [62]	AFLOW [64]	MP [65]	OQMD [50]	Sluiter [63]
		ΔG_{Para}^{ϕ}	$^{mag} \Delta G_i^{\phi/SER}$ (0K) **					
Co	FCC_A1	427.59-0.61525·T	0	1737	1737	1930	1640	0
	BCC_A2	2938-0.7138·T	-793.17	5114	9456	8684	9746	8700
	HCP_A3	-	0	0	0	0	0	-
	σ	6010.18+0.5·T	-1296.97	-	-	-	5693	4700
Cr	FCC_A1	7284+0.163·T	-1564.84	21421	37535	38596	38114	38100
	BCC_A2	-	0	0	0	0	0	0
	HCP_A3	4438	-1564.84	13412	38596	40526	39175	-
	σ	12299.3-3·T	0	-	-	-	12254	13200
Ni	FCC_A1	-	0	0	0	0	0	0
	BCC_A2	8715.084-3.566·T	-766.64	9070	9360	9649	9070	8800
	HCP_A3	1046+1.2552·T	0	2412	2316	2895	2219	-
	σ	9302.69+6·T	-80.44	-	-	-	9456	16600
Re	FCC_A1	11000-1.5·T	0	6079	5982	5789	5982	0
	BCC_A2	17000-3.7·T	0	15245	30587	30877	30491	23400
	HCP_A3	-	0	0	0	0	0	-
	σ	9315.75-1.205·T	0	-	-	-	9360	4900

*It should be noted that results from DFT calculations generally have the accuracy of 10 J/mol to 100 J/mol.

**Value relative to the magnetic Gibbs energy in the SER state, i.e., $^{mag} \Delta G_i^{\phi/SER} = ^{mag} \Delta G_i^{\phi} - ^{mag} \Delta G_i^{SER}$.

Table 3 - Calculated EBE pairs for the six constituent binary systems (in J/mol, referring to one mole of formula).

EBE pairs (A-B system)	Co-Cr	Co-Ni	Co-Re	Cr-Ni	Cr-Re	Ni-Re
$\Delta G_{A:B:***}^{\sigma}$	-26961.12	-6192.39	-44235.00	26285.58	-47246.10	-51299.40
$\Delta G_{A:*:B:**}^{\sigma}$	-6743.55	253.49	-22876.35	-15736.68	-48408.00	-40315.50
$\Delta G_{A:**:B:*}^{\sigma}$	-3962.34	-1452.91	-27655.17	-9225.15	-2319.57	-24853.89
$\Delta G_{A:**:*:B}^{\sigma}$	-16292.67	7833.23	-2130.91	-20273.34	-13150.14	-4259.76
$\Delta G_{*:A:B:**}^{\sigma}$	74171.37	-3484.17	33663.75	17482.48	-68399.70	-5320.08
$\Delta G_{*:A:**:B}^{\sigma}$	-10573.80	18336.16	55362.39	-41008.50	32703.69	97461.84
$\Delta G_{**:A:**:B}^{\sigma}$	54470.22	-14167.35	86410.38	6671.65	39790.29	26744.06
$\Delta G_{**:*:A:B**}^{\sigma}$	-31929.00	4081.97	18930.21	-48292.50	30625.20	55375.14
$\Delta G_{**:**:A:*:B}^{\sigma}$	-30663.30	-5391.48	147348.63	64763.52	-11230.47	134502.72
$\Delta G_{**:**:*:A:B}^{\sigma}$	-101664.00	3006.21	-69796.50	-53398.20	-40918.80	-75200.40
$\Delta G_{B:A:***}^{\sigma}$	13091.16	-7217.91	41040.99	1682.77	31279.17	17195.86
$\Delta G_{B:**:A:**}^{\sigma}$	46790.82	3439.58	75171.66	-38368.50	58455.87	51666.87
$\Delta G_{B:**:*:A**}^{\sigma}$	-33642.60	1051.58	-55779.00	5886.05	-28768.80	-48572.40
$\Delta G_{B:**:**:A}^{\sigma}$	-15090.54	-1740.58	10073.61	10428.89	-7502.52	-44169.90
$\Delta G_{**:B:A:**}^{\sigma}$	-30607.20	3271.66	5247.16	38489.34	-22925.97	2448.35
$\Delta G_{**:*:B:A**}^{\sigma}$	50927.34	-18409.41	17899.36	13026.85	-40823.40	-49206.00
$\Delta G_{**:**:B:A**}^{\sigma}$	2646.94	15015.74	-21409.20	28619.38	-81669.60	-11488.53
$\Delta G_{**:**:B:A**}^{\sigma}$	-115143.60	3400.37	-107241.60	-10549.62	-102687.90	-60325.80
$\Delta G_{**:**:B:**:A}^{\sigma}$	3927.83	7853.55	94414.35	-71388.30	3245.01	65041.59
$\Delta G_{**:**:**:B:A}^{\sigma}$	47478.93	-11616.30	11720.65	-56843.10	-25957.11	-75673.50

Table 4 - Calculated EBE pairs from increasing the weight of the most negative formation energies for the Co-Cr and Cr-Ni binary systems (in J/mol, referring to one mole of formula).

EBE pairs (A-B system)	Co-Cr	Cr-Ni
$\Delta G_{A:B:***}^{\sigma}$	-24874.19	21081.62
$\Delta G_{A:*:B:***}^{\sigma}$	-4756.93	-9124.49
$\Delta G_{A:***:B:***}^{\sigma}$	1305.06	761.78
$\Delta G_{A:***:***:B}^{\sigma}$	-19347.86	-21716.06
$\Delta G_{*:A:B:***}^{\sigma}$	75635.20	23951.96
$\Delta G_{*:A:*:B:***}^{\sigma}$	-9765.80	-35489.69
$\Delta G_{*:A:***:B}^{\sigma}$	51513.38	1721.74
$\Delta G_{*:***:A:B:***}^{\sigma}$	-37065.36	-44384.31
$\Delta G_{*:***:A:***:B}^{\sigma}$	-20426.41	69872.83
$\Delta G_{*:***:***:A:B}^{\sigma}$	-106162.26	-61963.56
$\Delta G_{B:A:***:***}^{\sigma}$	14204.81	-3836.22
$\Delta G_{B:***:A:***:***}^{\sigma}$	41367.27	-32077.48
$\Delta G_{B:***:***:A:***}^{\sigma}$	-31589.51	9812.81
$\Delta G_{B:***:***:***:A}^{\sigma}$	-10004.90	3252.53
$\Delta G_{*:B:A:***:***}^{\sigma}$	-25216.91	33133.10
$\Delta G_{*:B:***:A:***}^{\sigma}$	40944.75	25080.99
$\Delta G_{*:B:***:***:A}^{\sigma}$	6990.51	17790.06
$\Delta G_{*:***:B:A:***}^{\sigma}$	-116084.13	-12380.31
$\Delta G_{*:***:B:***:A}^{\sigma}$	-625.21	-73280.53
$\Delta G_{*:***:***:B:A}^{\sigma}$	43972.58	-53262.29