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Thermodynamic analysis of the topologically close packed σ phase in the Co–Cr system

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Keywords:	Density functional theory (DFT) calculations show that it is essential to consider the magnetic contribution to the
TCP phase	total energy for the end-members of the σ phase. A more straightforward method to use the DFT results in a
Magnetism Co-Cr CALPHAD DFT σ phase	CALPHAD (Calculation of phase diagrams) description has been applied in the present work. It was found that only the results from DFT calculations considering spin-polarization are necessary to obtain a reliable description of the σ phase. The benefits of this method are: the DFT calculation work can be reduced and the CALPHAD description of the magnetic contribution is more reliable. A revised thermodynamic description of the Co–Cr system is presented which gives improved agreement with experimental phase boundary data for the σ phase.

1. Introduction

The addition of significant amounts of Cr to Co-based superalloys can increase oxidation and wear resistance. However, this may result in formation of the topologically close packed (TCP) σ phase which is detrimental to the alloy properties [1]. Maximizing the Cr content while avoiding the formation of the TCP phases in superalloys is, therefore, of great interest. Superalloys are multi-component alloys, which makes the experimental determination of phase boundaries challenging. The CALPHAD (CALculation of PHAse Diagrams) method is widely accepted as one of the most effective tools for materials design because it can be used for quantitative prediction of the phase relations in multi-component alloys [2,3]. CALPHAD databases provide a set of self-consistent descriptions of the thermodynamic properties of multi-component systems obtained from critical assessments of the relevant elemental, binary and ternary systems [4]. The Co-Cr system is the key system for the addition of Cr to Co-based superalloys and several CALPHAD thermodynamic assessments of the Co-Cr system have been published [5-9]. However, the available thermodynamic descriptions for the Co–Cr system do not provide an accurate description of the σ phase. Quantitative description of complex compounds such as σ is challenging. For the description of ordered phases with the compound energy formalism (CEF) [10], a sublattice is introduced for each of the occupied Wyckoff sites in the crystal structure. For complex phases with many Wyckoff sites, this results in the introduction of many endmember compounds. Most of these are unstable/metastable, e.g., the hypothetical compound where all the sites of the σ structure are fully occupied by Co atoms, cannot be determined by experimental measurements. Thus, simplified thermodynamic models are being used to describe the TCP phases. The availability of data from density functional theory (DFT) calculations permits the use of comprehensive models for the description of the σ phase. However, only a few investigations have addressed the handling of the magnetitic contribution to the Gibbs energy in CALPHAD description using input from DFT calculations [11].

The purpose of the present work is to provide an accurate thermodynamic description for the Co–Cr system. The usage of the results from DFT calculations for compounds with magnetism within the CALPHAD framework is discussed.

2. Thermodynamic modeling

The models that have been used for the description of the σ phase are derived from its crystal structure which is summarized in Table 1. A series of models have been proposed for the description of the σ phase. All these models are based on the 5 Wyckoff sites of the crystal structure of the σ phase. These sites can be combined into a smaller set of sublattices based on site occupation data and coordination numbers for a simplified model description [12–14]. Proper selection of these combinations is essential for reliable extrapolation of the description to

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Table 1

Crystal structure parameters of the σ phase (D8_b), space group P4₂/mnm, species A represents elements with an atomic radius larger than 1.35 Å, while species B represents elements with an atomic radius less than 1.35 Å. The coordinates are averages for σ [12].

Species	Site	x	у	z	CN*
В	2a	0	0	0	12
Α	4f	≈0.399	x	0	15
Α	8i1	≈0.464	≈0.133	0	14
В	8i ₂	≈0.741	≈0.066	0	12
А	8j	≈0.183	≈0.183	≈0.251	14

* CN = coordination number.

multi-component systems. Different models have been used for the thermodynamic description of the σ phase for the Co–Cr system [5–9]. The phase diagram calculated with the description from Kusoffsky and Jansson [9] agrees well with the experimental data. However, the σ phase was modeled with a three sublattice model (Co)₈(Co,Cr)₁₈(Cr)₄ which does not agree with the experimental site occupation data [15]. The same model was used by Havrankova et al. [8] and Oikawa et al. [6] who reassessed the system taking into account more thermochemical data. Houserova et al. [7] used the description from Kusoffsky and Jansson for the disordered solution phases and remodeled the σ phase with two sublattices using DFT data. Li et al. [5] optimized the Co–Cr system using a five sublattice model to describe the σ phase considering data from atomistic calculations (disordered local moment (DLM) approach). However, the calculated σ phase boundaries from Refs. [5–8] show some deviations from the experimental data. All these descriptions have in common that the magnetic contribution to the Gibbs energy of the σ was not considered.

The Gibbs energy for the solution phases ϕ , liquid, face centered cubic (FCC, α Co), hexagonal close packed (HCP, ϵ Co) and body

Table 2

Phase names, models (sublattice formulae) and parameters of the present thermodynamic description. Gibbs energy is given in J per mole (according to sublattice formula definition), temperature (T) in Kelvin. HSER indicates that the Gibbs energy is relative to the Standard Element Reference, *i.e.*, the enthalpy of the element in its stable state at 298.15 K without magnetic contribution. The parameters for the pure elements in FCC, BCC, HCP and liquid structure where taken form the SGTE (Scientific Group Thermodata Europe) unary database [37,38]. These parameters can be found in the thermodynamic database file (TDB) in the supplemental material.

Liquid: (Co,Cr)1 $L_{Co,Cr}^{0,\text{Liquid}} = -12725.3; L_{Co,Cr}^{1,\text{Liquid}} = -1458.5$ (Cr) (BCC): (Co,Cr,Va)1(Va)3 $L_{Va:Va}^{0,BCC_A2} = 30 \cdot T; L_{Cr,Va:Va}^{0,BCC_A2} = 46912; L_{Co,Va:Va}^{0,BCC_A2} = 126184;$ $L_{C0,Cr}^{0,BCC_A2} = +12652.9 - 11.0201T; L_{C0,Cr}^{1,BCC_A2} = -9092.2$ (αCo) (FCC): (Co,Cr)₁(Va)₁ $L_{Co,Cr}^{0,FCC_A1} = -2256.2 - 7.3908 \cdot T; L_{Co,Cr}^{1,FCC_A1} = -3578.5;$ $TC_{C_0,C_r}^{0,FCC_A1} = -6860; TC_{C_0,C_r}^{1,FCC_A1} = +5216$ (ECo) (HCP): (Co,Cr)1(Va)0.5 $L_{Co,Cr}^{0,HCP_A3} = -8859.4 + 1.3230 \cdot T; L_{Co,Cr}^{1,HCP_A3} = -4432.0; TC_{Co,Cr}^{0,HCP_A3} = -6572;$ $TC_{Co}^{1,HCP}A^{3} = 5811$ σ: (Co,Cr)₁₆(Co,Cr)₄(Co,Cr)₁₀ ${}^{\circ}G_{Co}^{\sigma}(T) = 6958 + {}^{\circ}G_{Co}^{HSER}(T); {}^{\circ}G_{Cr}^{T}(T) = 12291 + {}^{\circ}G_{Cr}^{HSER}(T);$ $\Delta G^{\sigma}_{Co:Co:Co} = 30^{*^{o}} G^{\sigma}_{Co}(T); \ TC^{\sigma}_{Co:Co:Co} = 1400; \ \beta^{\sigma}_{Co:Co:Co} = 1.66;$ $\Delta G^{\sigma}_{Cr:Cr:Cr} = 30^* G^{\sigma}_{Cr}(T);$ $\Delta G_{\rm Cr:Co:Co}^{\sigma} = -150300 - 149.9686 \cdot T + {}^{\circ}G_{\rm Co}^{\sigma}(T) + 16^{*\circ}G_{\rm Cr}^{\sigma}(T);$ $\Delta G_{Co:Co:Cr}^{\sigma} = +20*^{\circ}G_{Co}^{\sigma}(T) + 10*G_{Cr}^{\sigma}(T);$ $\Delta G^{\sigma}_{Co:Cr:Co} = 14040 + 26^{*\circ} G^{\sigma}_{Co}(T) + 4 * G^{\sigma}_{Cr}(T);$ $\Delta G_{Cr;Co;Cr}^{\sigma} = 126570 + 4^{*} G_{Co}^{\sigma}(T) + 26 * G_{Cr}^{\sigma}(T);$ $\Delta G^{\sigma}_{Cr:Cr:Co} = -298659 - 51.5880 T + 10*^{\circ}G^{\sigma}_{Co}(T) + 20*G^{\sigma}_{Cr}(T);$ $\Delta G^{\sigma}_{\text{Co:Cr:Cr}} = -130290 + 16^{*\circ} G^{\sigma}_{\text{Co}}(T) + 14 * G^{\sigma}_{\text{Cr}}(T); L^{\sigma}_{Co,Cr:Cr:Co} = -395592.2;$ $L^{\sigma}_{Cr:Cr:Co,Cr} = -295397.4; L^{\sigma}_{Cr:Co,Cr:Cr} = -549595.8$

centered cubic (BCC, Cr), are described by the substitutional solution model with Redlich–Kister polynomials [16]:

$$G^{\varphi} = x_{Co} \cdot {}^{\circ}G^{\varphi}_{Co} + x_{Cr} \cdot {}^{\circ}G^{\varphi}_{Cr} + R \cdot T \cdot (x_{Co} \cdot \ln x_{Co} + x_{Cr} \cdot \ln x_{Cr}) + x_{Co} \cdot x_{Cr} [L^{0,\varphi}_{Co,Cr} + L^{1,\varphi}_{Co,Cr} (x_{Co} - x_{Cr})] + {}^{mag} G^{\varphi}_{m}$$
(1)

where x_{Co} and x_{Cr} represent the mole fractions of the elements Co and Cr, respectively. ${}^{\circ}G_{Co}^{\varphi}$ and ${}^{\circ}G_{Cr}^{\varphi}$ are the Gibbs energies of the pure elements in the structure of phase ϕ . *R* is the gas constant ($R = 8.3145 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$) and $L_{Co,Cr}^{\nu,\varphi}$ are the Redlich-Kister parameters representing the interaction of order ν between components Co and Cr in the ϕ phase. A linear temperature dependence was used for each of the interaction parameters:

$$L_{C_0,C_r}^{\nu,\varphi} = A_\nu + B_\nu \cdot T \tag{2}$$

 ${}^{mag}G_m^{\varphi}$ is the magnetic contribution to the Gibbs energy of the solution phase using the Hillert-Jarl formalism [17]. The temperature dependence uses the magnetic transformation temperature and magnetic moment as input parameters. The composition dependence of these parameters is described by a formalism similar to Eq. (1).

For the description of the σ phase, the (Co,Cr)₁₆(Co,Cr)₄(Co,Cr)₁₀ model was selected because it closely reflects the crystallography of σ phase while keeping the number of end-member parameters reasonably small, i.e., in addition to the 2 unary end-members 6 binary endmembers compared to 30 in a model with five sublattices and substitution on each. This model is based on the recommendation by Ansara et al. [14] who recommended a (A,B)₁₆(A)₄(A,B)₁₀ model for the description of the σ phase. However, experimental site occupancy data [15] indicate that substitution occurs on all sublattices. Cieslak et al. [15] found that the 2a and 8i₂ sites are preferentially occupied by Co while the 4f, 8i₁ and 8j sites are preferentially occupied by Cr. A similar distribution was also observed in the first-principles study by Kabliman et al. [18]. Therefore, substitution needs to be allowed on all sublattices. The elemental distribution found in both studies actually supports the use of the 2 sublattice model proposed by Joubert [12] where the 2a and 8i2 sites and the 4f, 8i1 and 8j sites are combined, respectively. Yet, the occupation of the 4f site is in many systems significantly different from that of the 8i1 and 8j sites and this needs to be considered when selecting a model if the description will be included in a thermodynamic database for multi-component alloys.

The CEF [10] was used to describe the Gibbs energy of the σ phase:

$$\begin{aligned} G_{\rm m}^{\sigma}(y_i^{(s)}) &= \sum_i \sum_j \sum_k y_i^{(1)} y_j^{(2)} y_k^{(3)} G_{i;j;k}^{\sigma} + RT \sum_s a^{(s)} \sum_i y_i^{(s)} \ln y_i^{(s)} \\ &+ \sum_{s1} \sum_i y_i^{(s)} \left(\sum_{s2 \neq s1} \sum_i y_i^{(s2)} \left(\sum_i \sum_{j>i} y_i^{(s3)} y_j^{(s3)} L_{i,j}^{0,s3,\sigma} \right)_{s3 \neq s2 \neq s1} \right) \end{aligned}$$
(3)

where $y_i^{(s)}$ is the fraction of site *s* occupied by element *i*, $a^{(s)}$ is the total number of sites corresponding to site *s*. $G_{i;j:k}^{\sigma}$ is the molar Gibbs energy of the stoichiometric end-member. Contributions from the magnetism can be included as contribution to $G_{i;i;k}^{\sigma}$.

Optimization of the Co–Cr system was carried out using the PARROT module in Thermo-Calc software [19].¹ Table 2 lists the phases, names, models, and parameters used in the present work. Detailed literature reviews of the experimental data are available from Ishida and Nishizawa [20] and Li et al. [5] and will not be repeated here. The same set of experimental data was accepted in the present work: phase equilibrium data [6,15,21–34] and thermochemical data [8,35,36]. No attempt was made to fit the available experimental data for the Néel temperature of the Cr solid solution. The antiferromagnetism of Cr is very complex and cannot be properly modeled using current CALPHAD models. The absolute value of a linear function

¹ Commercial products are identified in this paper for reference. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

between the negative Néel temperature and the Curie temperature of hypothetical BCC Co agrees qualitatively with the experimental values and because the effect on the Gibbs energy is very weak and the magnetic transformation occurs at fairly low temperatures this agreement was deemed satisfactory.

The unary descriptions from Dinsdale [37,38] were used for the description of the temperature dependence of the Gibbs energy of the pure elements. Efforts are underway to develop new, physically more accurate descriptions of the unaries and new description have been developed for Co [39,40]. However, such descriptions are currently available only for a few elements which makes them at the moment not feasible for the development of a multicomponent database.

3. DFT calculations

It has become customary to use data from DFT calculations for the parameters of the end-members and to supplement the experimental information [41]. In the present work, the total energies for all the 32 end-members of the σ phase were calculated by DFT [42] with and without spin-polarization. The total energies were calculated using the Projector Augmented Wave method [43], implemented in the Vienna Ab initio Simulation Package (VASP) [44,45]. The exchange-correlation energy of electrons was described in the generalized gradient approximation (GGA) using functionals of Perdew, Burke, and Ernzerhof (PBE) [46]. These calculations treat the $4s^23d^7$ and $4s^13d^5$ electrons as valence in Co and Cr, respectively. Structures were allowed to relax with a maximum cutoff energy of 520 eV and a gamma centered $9 \times 9 \times 18$ kpoint mesh [47]. Lattice parameters and atomic positions were allowed to relax until energy convergence reached 0.1 meV and a final static calculation was performed to determine the total energy.

The CALPHAD description of a magnetic phase without considering the magnetic contribution to the Gibbs energy describes the paramagnetic state rather than the non-magnetic state (this term is used to describe a state for which the contribution of the magnetism to the energy is not considered). Atomistic calculations, such as the DLM approach that is based on the coherent potential approximation (CPA), treating the paramagnetic state properly are more complex than DFT calculations with or without spin-polarization. Therefore, data from DFT calculations without spin-polarization is frequently used in lieu of data from atomistic calculations. However, this is not correct since the magnetic phase disorders to the paramagnetic state rather than the nonmagnetic state represented by calculations without spin polarization. In the present work, a straightforward method was used to describe the magnetic contribution and it was found that only the DFT results considering spin-polarization are needed to obtain a reliable description of the σ phase. The non-spin polarized calculations were carried out to demonstrate the large deviations that occur for the Co rich region when data from such DFT calculations are used for phases with magnetic elements.

The enthalpies of formation for all 32 end-members ($\Delta G_{ij;k:l:m}^{\sigma}$ and $\Delta G_{l:j:k:l:m}^{\sigma,nsp}$) were obtained from the following equations:

$$\Delta G_{i;j;k;l;m}^{\sigma} = E_{i;j;k;l;m}^{\sigma} - x_{Co} E_{Co}^{HCP} - x_{Cr} E_{Cr}^{BCC}$$
(4)

$$\Delta G_{i;j;k;l;m}^{\sigma,nsp} = E_{i;j;k;l;m}^{\sigma,nsp} - x_{Co} E_{Co}^{HCP} - x_{Cr} E_{Cr}^{BCC}$$
(5)

where $E_{i;j:k:l:m}^{\sigma}$, E_{Co}^{HCP} and E_{Cr}^{BCC} are the total energies for the endmember *ijklm*, pure HCP Co, and pure BCC Cr calculated with spinpolarization, respectively, and *nsp* represents that no spin-polarization was used in the calculation. In the present work, only the values of $\Delta G_{i;j:k:l:m}^{\sigma}$ were used for CALPHAD assesment. $\Delta G_{i;j:k:l:m}^{\sigma,nsp}$ was only used for comparsion, all values are listed in Table 3. For the parameter optimization of in the CALPHAD assessment only DFT values of the 5 sublattice configurations corresponding to 3 sublattice configurations, e.g., $Co_2Cr_4Cr_8Co_8Cr_8 \equiv Cr_{16}Cr_4Co_{10}$, were used as enthalpy values at 298.15 K.

The energy difference for HCP Co between results from calculations

Table 3

DFT calculated total energies and enthalpies of formation for all end-members of the σ phase. β is given in $\mu_{\rm B}$ /atom, $E^{\sigma, nsp}_{i;j:k:l:m}$ and $E^{\sigma, nsp}_{i;j:k:l:m}$ in eV/atom and $\Delta G^{\sigma}_{i;j:k:l:m}$ in kJ/mol (mole of atoms). The end-members used for the parameter assessment of the three sublattice description are indicated in bold.

Wyckoff Sites			β	$E_{i:j:k:l:m}^{\sigma}$	$E_{i:j:k:l:m}^{\sigma,nsp}$	$\Delta G_{i:j:k:l:m}^{\sigma}$	$\Delta G^{\sigma,nsp}_{i:j:k:l:m}$		
2a	4f	8i ₁	8i ₂	8j	_				
Со	Co	Co	Co	Co	1.67	-211.47	-202.52	5.692	13.155
Cr	Cr	Cr	Cr	Cr	0.00	-281.47	-281.47	12.291	12.294
Cr	Co	Co	Co	Co	1.37	-215.13	-208.78	9.381	9.897
Co	Cr	Co	Co	Co	1.30	-219.88	-215.62	9.567	4.758
Cr	Cr	C0	Co	Co	1.20	- 224.22	- 220.72	11.055	5.227
C0	Co	Cr	C0 Cm	Co	1.00	- 228.89	- 227.30	11.478	0.944
C0	Co	Co	Cr	C0	0.08	- 22/.88	- 220.48	14.724	3.301
C0	Co	Cu Cr	Co	Co	1.20	- 229.33	- 227.12	11 966	1.310
Cr	Co	Co	Cr	Co	0.72	- 233.37	- 233.29	15.018	-1.433 5.052
Cr	Co	Co	Co	Cr	0.73	- 232.31	- 231.27	10 569	0.876
Co	Cr	Cr	Co	Co	0.45	-238.56	- 238 21	11 271	-0.402
Co	Cr	Co	Cr	Co	0.10	- 238.08	- 237.92	12.825	0.521
Co	Cr	Co	Co	Cr	0.51	-239.46	-238.99	8.380	-2.919
Cr	Cr	Cr	Co	Co	0.21	-243.62	-243.56	10.444	-0.729
Cr	Cr	Co	Cr	Co	0.42	-242.71	-242.44	13.365	2.848
Cr	Cr	Co	Co	Cr	0.60	-243.87	-243.23	9.633	0.332
Co	Co	Cr	Cr	Co	0.42	-246.81	-246.48	15.643	6.740
Со	Со	Cr	Со	Cr	0.49	-248.95	-248.56	8.745	0.041
Со	Co	Co	Cr	Cr	0.18	-247.89	-247.69	12.168	2.854
Cr	Co	Cr	Cr	Co	0.31	-251.43	-251.26	16.229	8.233
Cr	Co	Cr	Co	Cr	0.23	-254.15	-254.08	7.483	-0.827
Cr	Co	Co	Cr	Cr	0.14	-252.34	-252.27	13.293	4.988
Со	Cr	Cr	Cr	Co	0.12	-257.14	-257.14	13.310	6.185
Со	Cr	Cr	Со	Cr	0.16	-259.95	-259.89	4.252	-2.641
Co	Cr	Co	Cr	Cr	0.17	-258.29	-258.19	9.597	2.810
Cr	Cr	Cr	Cr	Co	0.01	-261.87	-261.87	13.529	7.837
Cr	Cr	Cr	Со	Cr	0.16	-264.43	-264.39	5.311	-0.253
Cr	Cr	Co	Cr	Cr	0.00	-262.83	-262.83	10.459	4.759
Со	Co	Cr	Cr	Cr	0.20	-266.25	-266.17	14.913	10.885
Cr	Со	Cr	Cr	Cr	0.15	-270.41	-270.32	16.968	14.410
Со	Cr	Cr	Cr	Cr	0.01	-277.16	-277.16	10.699	9.274

with spin-polarization (-7.108 eV/atom) and without spin-polarization (-6.887 eV/atom) is -0.22 eV/atom. The energies for Cr-BCC are the same from both calculations (-9.5098 eV/atom).

3.1. The magnetic contribution of the σ phase

Significant differences between the results from calculations with and without spin-polarization indicate a strong magnetic contribution to the energy of the Co-rich end-members. This suggests that it is essential to consider the magnetic contribution for the description for the σ phase in the thermodynamic assessment of the Co-Cr system. However, no clear strategy has been proposed for importing DFT data for magnetic phases into CALPHAD descriptions. The results from such DFT calculations are the sum of the chemical and magnetic energy while in a CALPHAD description these contributions are separated. In their investigation of the Fe-Re system, Breidi et al. [11] used DFT data calculated with and without spin-polarization. The results were used to develop five sets of CALPHAD descriptions, one set employing the results from the calculations with spin-polarization and the remaining sets using the results from the calculations without spin-polarization. Phase diagrams for the first set and three sets with ideal, regular and quasi-regular solution descriptions are shown in the article. Breidi et al. found that the phase diagrams calculated with these sets reproduced the experimental phase diagram more or less qualitatively and that those using the results from calculations without spin-polarization tended to give a better phase diagram at higher temperatures. The fifth set was only used to show the effect of the magnetic contribution to the enthalpy of the σ phase compared to the two other sets of DFT calculations. For this a CALPHAD magnetic contribution was added to the results calculated without spin-polarization.

The strategy derived in the present work is to evaluate the CALPHAD Gibbs energies of the end-members of the σ phase using only the results form DFT calculations considering spin-polarization. As mentioned above, the magnetic contribution to the total energy is described by a separate term, $m^{ag}G_{m}^{\phi}$, in CALPHAD descriptions where the magnetic moment (β) and Curie temperature (T_c) are the only two parameters to be assessed:

$${}^{mag}G^{\varphi}_m = RT \ln(\beta + 1)g(\tau) \quad \text{with } \tau = \frac{1}{T_C}$$

and

$$g(\tau) = 1 - \frac{p_0}{\tau} + p_1 \left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \qquad \tau \le 1$$

$$g(\tau) = -p_2 \left(\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right) \qquad \tau \ge 1$$
(6)

where T_C is the Curie temperature, β is the average magnetic moment, and p_0 , p_1 and p_2 are crystal structure specific constants which are $p_0 = 0.86034$, $p_1 = 1.04695$ and $p_2 = 0.42690$ for crystal structures other than bcc [37]. From Eq. (6) the magnetic contribution at 0 K is obtained:

$${}^{mag}G_m^{\varphi}(0\,K) = -R\,\ln(\beta+1)(p_0\,T_C) \tag{7}$$

The value of the magnetic moment is obtained from the DFT calculations with spin-polarization but significant effort would be required to obtain the Curie temperature from first principles calculations. Therefore, the Curie temperature is estimated using the magnetic moment from the DFT calculations with spin-polarization using the experimental magnetic moment and Curie temperature of the stable element. The DFT magnetic moment and the estimated Curie temperature are then used with Eq. (7) to evaluate the contribution of the magnetism to the Gibbs energy. This contribution is then subtracted from the DFT energy that was calculated with spin-polarization to obtain the energy of the paramagnetic state:

$$G^{\varphi,p} = E^{\varphi} - {}^{mag}G^{\varphi}_m(0\ K) \tag{8}$$

The Gibbs energy of formation of the paramagnetic phase from the paramagnetic pure elements is:

$$\Delta G^{\varphi,p} = G^{\varphi,p} - x_1 G^{1,p} - x_2 G^{2,p} \tag{9}$$

Alternatively, the DFT values calculated with spin-polarization were used in the present work fitting the model parameters of sub-lattice model with magnetic contribution.

The magnetic moment for pure Co in σ structure was set to 1.66 $\mu_B/$ atom (Bohr magneton per atom) according to the present DFT results which is consistent with the literature values of 1.64 μ_B /atom [48,49] and 1.67 $\mu_{\rm B}$ /atom [48,49]. Considering that this value is close to the experimental and calculated magnetic moment of pure Co in HCP structure, the Curie temperature of pure Co in HCP structure [50] was used as guide to estimate this temperature for pure Co in σ structure, it was set to 1400 K $^{\circ}\!G^{\sigma}_{Co}$ and $^{\circ}\!G^{\sigma}_{Cr}$ were then evaluated as 6958 J/mol + $G_{Co}^{HSER}(T)$ and +12291 J/mol + $G_{Cr}^{HSER}(T)$, respectively, to reproduce the DFT enthalpy of formation from the calculations with spin-polarization (Table 3, column $\Delta G^{\sigma}_{i;i;k;l;m}$) at 298 K. However, to reproduce the non-linear change in the average magnetic moment from DFT calculations the magnetic contribution is added to the Gibbs energy of the endmember $\Delta G^{\sigma}_{\text{Co:Co:Co}}$. The remaining temperature independent terms of $\varDelta G^{\sigma}_{i:j:k}$ were then evaluated to fit the DFT values from the spin-polarized calculations.

To evaluate the reliability of the current description the enthalpies of formation with respect to HCP Co with different magnetic states and BCC Cr are shown in Fig. 1. The blue solid line in Fig. 1 is the CALPHAD



Fig. 1. CALPHAD calculated enthalpy of formation in Joule per mole of atoms for the σ phase at 298.15 K compared with DFT results. For comparison with the DFT results the interaction parameters were removed from the description of the σ phase. The data from Ref. [51] are referred to ferromagnetic HCP Co and BCC Cr. See text for details of the different CALPHAD calculations.

calculated enthalpy of formation of σ phase with magnetic contribution referred to magnetic HCP Co at 298.15 K and is compared with the DFT enthalpy of formation calculated with spin-polarization referring to HCP Co at 0 K which are shown as filled blue circles. The results obtained from the present description agree well with lowest values from the DFT calculations.

For further evaluation of the present description, additional sets of CALPHAD and DFT results are also shown in Fig. 1. The orange dashed line represents the enthalpy of formation of the σ phase calculated with the present description but without any magnetic contribution, i.e. the paramagnetic state, from magnetic HCP Co and BCC Cr. Significant differences can be seen between the orange dashed line and DFT results from calculations without spin-polarization referred to HCP Co where spin-polarization was considered (purple squares, Eq. (5)). The origin for these differences may be manifold: e.g., current thermodynamic CALPHAD descriptions are designed for temperatures above 298.15 K. The "magnetic moment" for the Co (both HCP and FCC) in CALPHAD descriptions was set to 1.35 μ_B /atom by fitting the heat capacity and enthalpy data above 298.15 K [50], which is not in agreement with the experimentally observed magnetic moment value of 1.7 $\mu_B/atom.$ Using the current CALPHAD description of Co [50], the magnetic contribution to the total Gibbs energy of the HCP Co, ${}^{mag}G^{HCP}_{Co}$, is -8.531 kJ/mol at 0 K and -6.417 kJ/mol at 298.25 K compared to -9.917 kJ/mol at 0.1 K if the experimental magnetic moment is used. In contrast, the energy difference form DFT calculations with and without spin-polarization is ΔG_{Co}^{sp-nsp} is -21.23 kJ/mol. This difference is too large to be attributed solely to the difference in the CALPHAD and experimental magnetic moment. These differences clearly indicate that results from non-spin-polarized DFT calculations do not represent the paramagnetic state of magnetic elements and their use in the parameter assessment may adversely affect the quality of the description that is obtained. Korzhavyi et al. [51] and Breidi et al. [11] pointed out that spin-polarized treatment of the paramagnetic state of the strong magnetic elements (Fe, Co, Ni) is necessary. Korzhavyi et al. [51] performed atomistic DLM calculations considering the paramagnetic contribution (orange solid stars in Fig. 1). The calculated orange dashed line agrees

well with these data. It should also be noted that the orange dashed line and solid blue line only differ from each other when the Co-rich σ phase is ferromagnetic.

An important conclusion can be drawn from Fig. 1 and the poor agreement of the CALPHAD calculated enthalpies with the results from DFT calculations without spin-polarization which clearly indicates that results from DFT calculations without spin-polarization should not be used for phases with magnetic elements. The ideal case for obtaining a high-quality description of phases with magnetic elements would be to perform atomistic calculations to obtain the energy for the paramagnetic state and DFT calculation with spin-polarization to obtain the magnetic moment. However, atomistic calculations of the energy of the paramagnetic state are more challenging than DFT calculations with or without spin-polarization. The present study demonstrates that results from DFT calculations without spin-polarization for magnetic elements should be avoided because they do not represent the paramagnetic state and that only DFT calculations in which spin-polarization are needed to obtain a reliable CALPHAD description. The advantages of the approach taken in the present work are twofold: avoiding unnecessary DFT calculations for unstable compounds and obtaining a more accurate description of the magnetic contribution to the Gibbs energy.

As shown in Fig. 1, the DFT enthalpy of formation from the pure element in their SER state are positive whatever the composition, Thus, the σ phase is not stable at low temperatures. However, the lower temperature limit for the stability of the σ phase is unknown.

DFT calculations of the σ phase end-members considering spin-polarization were also carried out by Pavlů et al. [49] (Fig. 1, empty circles). These values show the same trend as the values from calculations with spin-polarization from the present work, but their energies are generally larger than the values from the present work. Both datasets used the GGA, but different k-point meshes and cut-off energies.

The calculated magnetic moment and Curie temperature of the σ phase at 298 K using the current full description of the σ phase with interaction parameters are shown in Fig. 2 together with the magnetic moments from DFT calculations. The black solid line represents the calculated magnetic moment using the present description. While the red dashed line represents the calculated magnetic moment with a description that includes the magnetic moment for all the 8 end-members from the corresponding DFT calculations. The red dashed line agrees with the higher values of the DFT data while black solid line, where only the pure Co end-member has a magnetic contribution,



Fig. 3. Calculated site fractions of Co in the σ phase at 1273 K compared with experimental data [15].

agrees with the lower DFT data. The calculated Curie temperature falls below 298 K for the composition regime of stable σ phase which is in accord that no magnetism has been reported for it. However, for magnetic phases with high Curie temperatures it may be necessary to consider the magnetic contribution for all end-members for an accurate description.

The calculated site fractions of Co in the σ phase are compared with experimental data [48] in Fig. 3. The site occupation in all the 5 sites is well described by the current description, which indicates that the three sublattice model (Co,Cr)₁₆(Co,Cr)₄(Co,Cr)₁₀ selected here is very appropriate.

4. Results

The calculated Co–Cr phase diagram is shown in Fig. 4a. The present calculation agrees well with the experimental data except for the Cr-rich side. It is obvious that the σ +BCC_A2 phase boundary data from



Fig. 2. Calculated magnetic moment (a) and Curie temperature (b) of the σ phase at 298.15 K (solid lines). The symbols show the average magnetic moment from the DFT calculations for the individual end-members. The dashed line shows the magnetic moment calculated with description of the magnetic contribution for all end-member compounds taken from the corresponding end-member values from the DFT calculation. The full description from Table 2 was used for the solid lines.



Fig. 4. Calculated Co-Cr phase diagram (a) with experimental phase diagram data and (b) with Curie temperature data.



Fig. 5. Calculated activity of Co and Cr at 1673 K (solid line) compared with experimental data [8]. The reference state is: FCC Co; BCC Cr.

Allibert et al. [25] at high temperatures (above 1373 K) are in conflict with their low temperature data (below 1373 K) as shown in Fig. 4a. Considering that the alloys annealed at higher temperature are likely to reach equilibrium faster, only the experimental data above 1173 K were considered for the Cr-rich side. Further experimental research is necessary, particularly for phase equilibria at temperatures below 1000 K. Fig. 4b shows the calculated Co-rich side of the phase diagram with the Curie temperatures for FCC and HCP phases. The calculated and experimental Curie temperatures agree well. Figs. 5 and 6 show the calculated activities of Co and Cr at 1673 K and 1800 K, respectively, compared with experimental data [8]. The results from the present calculation are in agreement with the experimental data. It should be pointed out that the activity data from Ref. [8] were determined by the Knudsen cell mass spectrometry. The derived excess Gibbs energy and excess enthalpy from activity data [8], which were used as experimental data during optimization by previous assessments [5,6], were not used in the present work.

Standard enthalpies of formation are shown in Fig. 7. In Fig. 7a the calculated enthalpy of formation at 298.15 K using the full description



Fig. 6. Calculated activity of Co and Cr at 1800 K (solid line) compared with experimental data [8]. The reference state is: liquid Co; liquid Cr.

of the σ phase is compared with the data from 0 K DFT calculations with spin-polarization and atomistic calculations of the paramagnetic state. The agreement is not as good as in Fig. 1 where the interaction parameters were not used but this present description also provides an accurate description of the phase equilibria with the σ phase. Fig. 7b shows the enthalpies of formation of the α Cr and Cr phases at 1623 K and 1673 K. The calculated enthalpies are consistent with the experimental data [35].

5. Conclusions

A critical review of the Co–Cr system showed that a thermodynamic re-assessment of the Co–Cr system was necessary to improve the description of the σ phase. Two sets of DFT calculations with and without spin-polarization were performed for the 32 end-member compounds of the σ phase. A straightforward method was used to describe the magnetic contribution and it was found that only the DFT results considering spin-polarization are needed to obtain a reliable description of the σ phase. However, for improved accuracy first-principles data are



Fig. 7. Calculated standard enthalpies of formation in Joule per mole of atoms (a) of the σ phase at 298.15 K using the full description is compared with computation data (present work, [49,51]) (b) of α Cr and (Cr) at 1623 K and 1673 K compared with experimental data [35].

needed for paramagnetic pure Co.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.intermet.2018.11.004.

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