Thermodynamic modeling of Al-Co-Cr, Al-Co-Ni, Co-Cr-Ni ternary systems towards a description for Al-Co-Cr-Ni

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1 Introduction

Overlay MCrAlY (M=Ni, Co or NiCo) coatings are critical in the protection of high-temperature Ni- and Co-base superalloys operating in corrosive environments such as gas turbine hot sections. These coatings are used either solely or in conjunction with a ceramic topcoat such as yttria-stabilized zirconia as a part of the thermal barrier coating system [1–4]. Phase fractions and compositions in the coatings change as a result of selective oxidation and interdiffusion during service. It is important to thoroughly understand the thermodynamics of these alloys in order to predict their microstructural evolution, as it affects the corrosion resistance and mechanical properties of the overall system.

In the base Al-Co-Cr-Ni system, there are 6 binaries (Al-Co, Al-Cr, Al-Ni, Co-Cr, Co-Ni, and Cr-Ni) and 4 ternaries (Al-Co-Cr, Al-Co-Ni, Al-Cr-Ni, Co-Cr-Ni) to be studied. In previous work on the Al-Co-Cr system [5], the effectiveness of a computational approach in predicting accurate phase relations by implementing the CALPHAD method (Calculation of Phase Diagrams) has been demonstrated. This method has also been used extensively and successfully to study the thermodynamics of multi-component Ni-base superalloys [6,7]. In the literature, there is no complete description of the Al-Co-Cr-Ni alloy system. The present work focuses on the modeling of the subsystems, especially Al-Co-Ni and Co-Cr-Ni, necessary in building a coherent Al-Co-Cr-Ni quaternary description. Some modifications are made in the description of the Al-Co-Cr [5] system and are discussed in detail later in the manuscript. The quaternary Al-Co-Cr-Ni system is studied in a separate publication [8].

While B2 (β , $Pm\bar{3}m$, simple cubic type) and fcc-A1 (γ , $Fm\bar{3}m$, disordered f.c.c.) are the desired phases in MCrAlY coatings, all other phases must be modeled to give an accurate overall description of phase stability in the system. These include bcc-A2 (α , $Im\bar{3}m$, disordered b.c.c.),

hcp-A3 (ϵ , $P6_3/mmc$, disordered h.c.p.), L1₂ (γ' , $Pm\bar{3}m$, simple cubic type), sigma (σ , $P4_2/mnm$, Frank-Kasper, Figure 1 (a)) and the binary intermetallics.

The present paper focuses on evaluating and modeling the important ternary alloy systems found in the Al-Co-Cr-Ni quaternary in order to produce meaningful extrapolations without the need of excessive higher order parameters. First-principles calculations based on density functional theory (DFT) are performed to supplement the lack of experimentally measured thermochemical data. By effectively combining these results with experimental information from the literature, energetically accurate parameters in the lower order systems are evaluated. Ultimately, this model will be used in the construction of a multicomponent Al-Co-Cr-Ni database in future work.

2 Literature review

2.1 Binary models used in the present work

The **assessment** of the Al-Co binary by Dupin and Ansara [9] reproduces all experimental results available in the literature satisfactorily and is hence adopted in the present work. **The model for B2 in the original Al-Co binary was asymmetrical and was changed to the order-disorder model by Liu et al. in previous work on the system [5], which is adopted here.** The Al-Cr **assessment** by Saunders, which can be found in the COST507 [10] database, is also accepted without modification. The **assessment** for the Al-Ni binary by Ansara et al. [11], (later modified by Dupin et al. [6]) has been used extensively previously and is, therefore, adopted in the present work. There are two descriptions of the Co-Cr binary available which both reproduce certain experiments well, one by Oikawa et al. [12] and another by Kusoffsky et al. [13]. However, it

has been found that the Oikawa description has σ end-member energies which disagree with experiments by Downie and Arslan [14] though it was adopted in the previous modeling of Al-Co-Cr [5]. It is important to have correct energies in the binary subsystems to produce accurate extrapolations to the higher order systems and for this reason, the model by Kusoffsky et al. [13] is used here. The Co-Ni and Cr-Ni binary descriptions are taken from SGTE [15], based on works by Guillermet [16] and Lee [17], respectively. In addition, the present Cr-Ni description includes a metastable description of σ following the work by Gustafson [18] in the ternary Ni-Cr-W system which is later modified by Kattner [7]. Recently, the Al-Co system has been reassessed by Stein et al. [19] with slight improvements in the B2 phase boundaries. Al-Ni has also been reassessed recently by Chen et al. [20] to improve the B2 solidus and liquidus. However, both descriptions offer different values for the substitutional A2 vacancy end-members and cannot be adopted in the current work without significant remodeling of the Al-Cr-Ni system also adopted in the current work.

2.2 Ternary models and experiments

A summary of the experimental techniques from the literature for the ternary systems is shown in Table 1.

2.2.1 Al-Co-Cr

In previous work [5], the Al-Co-Cr description was assessed using experimental findings from Ishikawa et al. [21] supplemented with new phase equilibrium experiments and first-principles data. While the model by Oikawa et al. [12] better reproduces A2+ σ phase boundaries, the model by Kusoffsky et al. [13] better reproduces formation energies for the σ when compared to measurements by Downie and Arslan [14]. Switching to the description by Kusoffsky et al.

[13] will yield better higher order extrapolations for this complex intermetallic. The A2/B2 phases are modeled using a single Gibbs energy function in the previous work [5] and will be retained in the present modeling.

2.2.2 Al-Co-Ni

The Al-Co-Ni ternary system was first modeled by Dupin [22] and reproduces experimental phase equilibria from Schramm [23] and Jia et al. [24] as well as enthalpies from Kek et al. [25]. This system has been remodeled recently by Zhu et al. [26] for incorporation into a Al-Co-Ni-W quaternary database. Since an A2/B2 transition is expected to be present in the quaternary Al-Co-Cr-Ni system, the Al-Co-Ni system will be remodeled with the A2/B2 as one Gibbs energy function in the present work.

We further use new experimental phase equilibria on the γ , γ' and B2 from Kainuma et al. [27] and Albers et al. [28] as well as enthalpies of formation data from Grün et al. [29]. Schramm [23] originally investigated isothermal/vertical sections pertaining to γ , γ' and B2 from room temperature to 1350 °C, and Gödecke et al. [30–33] studied the Al-rich corner of the Al-Co-Ni phase diagram in a series of experiments focusing on Al-rich intermetallics. In addition to the above experimental information available in the literature, first-principles calculations of the solution phases are performed in the present work to aid the modeling.

A complete experimental review of the Al-Co-Ni system was performed by Velikanova et al. [34] which shows the presence of numerous ternary phases in the Al-rich corner of the phase diagram. The current work attempts to address the thermodynamic description of only the Ni-Co

rich section of the Al-Co-Ni ternary system for bond coat alloy applications. Al-rich ternary phases will be studied in future work.

2.2.3 Al-Cr-Ni

The Al-Cr-Ni ternary by Dupin et al. [6] is adopted in the present work. Both the A2/B2 and γ/γ' phases use partitioned Gibbs energy models which is compatible with the Al-Co-Cr ternary model in the present work. All experimental data found in the literature is well reproduced except for the A2/B2 phase boundary near the Cr-rich region of the system at 1423 K compared to EPMA measurements by Oforka and Argent [35]. This was recently investigated, using diffusion couples and EPMA, by Cutler [36] at 1473 K and the A2/B2 phase boundary is found to disagree with those found by Oforka and Argent [35]. More experiments must be performed to determine the phase boundaries in this region at temperatures above 1373 K. A summary of experiments relevant to this ternary can be found in Dupin et al. [6] and is not repeated in detail in the present manuscript. The model by Dupin et al. [6] describes mostly the Cr-Ni rich region of the phase diagram. In order for this system to be compatible with the other ternary subsystems within the Al-Co-Cr-Ni quaternary system, σ is introduced as a metastable ternary phase in the present work with data obtained from first-principles calculations. An earlier description of Al-Cr-Ni by Huang and Chang [37], which is used in the NIST superalloy database by Kattner [7], uses the asymmetrical B2 model is not adopted in the current work.

2.2.4 Co-Cr-Ni

Yang et al. [38] modeled the Co-Cr-Ni ternary using binary descriptions different from those implemented here as well as superfluous ternary interaction parameters. Here, the system is

remodeled using the following binary models due to ternary compatibility with the Al-Co-Cr, Al-Co-Ni and Al-Cr-Ni systems: Co-Cr by Kusoffsky et al. [13], Co-Ni by Guillermet F. [16], and Cr-Ni by Lee B.-J. [17]. As is shown in Table 1, phase equilibrium data by Zhmurko et al. [39], Omori et al. [40], and Zhanpeng J. [41] are accounted for in the evaluation. Additionally, A2, γ , and σ formation enthalpies measured by Kubaschewski and Hack [42] are used. First-principles calculations of the solution phases are performed and accounted for in the modeling work.

3 Thermodynamic models

The thermodynamic modeling methodology remains the same as in previous work on Al-Co-Cr [5]. However, γ' was not modeled as it is not stable in Al-Co-Cr. In the present work γ' is stable in the Al-Co-Ni and Al-Cr-Ni ternary extensions of the Al-Ni binary and hence, γ' must be included as a metastable phase in the Al-Co-Cr and Co-Cr-Ni systems. To account for the A2/B2 order-disorder transition and γ' ordering from γ , each of the bcc and fcc phases is modeled using a partitioning model, which treats the ordered and disordered components separately and with the same Gibbs energy functions [43]. Additionally, in B2-containing systems such as Al-Co [9], Al-Fe [44] or Al-Ni [6], triple-defect mechanisms are especially important and have to be accounted for when considering site ordering. Ordering of the bcc phase was described in Ref. [5]. The ordering of the fcc phase is described in the following Section.

The PARROT module [45] within Thermo-Calc [46,47] is used to assess all model parameters for each phase in the system using phase equilibrium data from the experimental measurements listed in Table 1 as well as first-principles data obtained in the present work.. Discrepancies in higher order systems can sometimes stem from inappropriate parameter choices

in lower order systems in which distinct sets of parameters can describe phase equilibria equally well [48]. Therefore, the optimized ternary parameters are systematically extrapolated to the quaternary Al-Co-Cr-Ni system to ensure consistency and agreement with quaternary data from Ref. [8]. Finalized parameters included in the Appendix are those that reproduce the ternary as well as the quaternary system best.

3.1 Modeling of fcc- γ and L1₂- γ'

The γ and γ' phases are modeled with a single Gibbs energy function using a partitioned two sublattice model (2SL) (Al,Co,Cr,Ni)₃(Al,Co,Cr,Ni) to be compatible with the Al-Cr-Ni binary by Dupin et al. [6]:

$$\text{Eq. 1:} \quad G_m^{\gamma/\gamma'} = G_m^\gamma(x_i) + \Delta G_m^{\text{Order}}(y_i^{(s)})$$

where $y_i^{(s)}$ denotes the site fraction of element i on sublattice s , $G_m^\gamma(x_i)$ describes the contributions from the disordered solution with only mole fractions taken into account and $\Delta G_m^{\text{Order}}(y_i^{(s)})$ describes the site-fraction dependent ordering energy. The ordering term can be expressed as the difference of two terms with one dependent only on mole fraction:

$$\text{Eq. 2:} \quad G_m^{\gamma/\gamma'} = G_m^\gamma(x_i) + G_m^{\gamma'(O)}(y_i^{(s)}) - G_m^{\gamma(O)}(y_i^{(s)} = x_i)$$

When $G_m^{\gamma'(O)}(y_i^{(s)})$ and $G_m^{\gamma(O)}(y_i^{(s)} = x_i)$ are equal, the ordering terms cancel out and the phase is completely disordered. The term $G_m^{\gamma(O)}(y_i^{(s)})$ takes on the partitioned form, as described by Dupin et al. [6], and is expressed as

$$\text{Eq. 3:}$$

$$\begin{aligned}
G_m^{\gamma'(O)}(y_i^{(s)}) = & \sum_i \sum_j (y'_i y''_j \circ G_{i,j}^{\gamma'(O)}) + RT \left[\frac{3}{4} \sum_i y'_i \ln(y'_i) + \frac{1}{4} \sum_j y''_j \ln(y''_j) \right] \\
& + \sum_i \sum_j \sum_k \left\{ y'_i y'_j y''_k \left[\sum_k {}^v L_{i,j;k}^{\gamma'(O)} (y'_i - y'_j)^v \right] \right\} \\
& + \sum_i \sum_j \sum_k \left\{ y'_k y'_i y''_j \left[\sum_k {}^v L_{k:i,j}^{\gamma'(O)} (y''_i - y''_j)^v \right] \right\} \\
& + \sum_i \sum_j \sum_k \sum_l (y'_i y'_j y'_k y''_l {}^v L_{i,j,k;l}^{\gamma'(O)} + y''_i y''_j y''_k y'_l {}^v L_{l:i,j,k}^{\gamma'(O)})
\end{aligned}$$

Here i, j, k , and l represent Al, Co, Cr, or Ni. Ansara et al. [49] proposed a set of constraints for this equation for both end-members and interaction parameters that must fulfilled for the phase to disorder correctly even in the case of a non-partitioned model. This is best illustrated in the mathematically equivalent four sublattice model (4SL) (A,B,...) (A,B,...) (A,B,...) (A,B,...) for the L1₂. While not true for the 2SL model, the 4SL model has all sites equivalent, and consequently, two species can be interchanged on sublattices without changing the energy of the system. This can be represented by, for the L1₂, as

$$\text{Eq. 4: } G_{A:A:A:B}^{4SL-\gamma'} = G_{A:A:B:A}^{4SL-\gamma'} = \dots = G_{A_3B}^{4SL-\gamma'}$$

In addition, interactions between species A and B in any sublattice are equivalent if site occupancy in the other sublattices remains the same. As described by Ansara et al. [11] and Dupin et al. [6], the mathematical equivalence of the 4SL and 2SL models for L1₂ (when $y_i^{4SL-(1)} = y_i^{4SL-(2)} = y_i^{4SL-(3)} = y'_i$ and $y_i^{4SL-(4)} = y''_i$) allows 2SL parameters to be represented in terms of 4SL parameters for the binary, ternary, and the quaternary systems. However, the L1₀ ordering is lost in the conversion of the 4SL to the 2SL fcc model because the

$G_{A:A:B:B}^{4SL-\gamma'}$ end-member in the 4SL model has no equivalent in the 2 SL model. End-members with L1₂ ordering, $G_{A_3B}^{4SL-\gamma'}$ and $G_{AB_3}^{4SL-\gamma'}$, can be expressed as G_{A_3B} and G_{AB_3} in the 2SL model, respectively. A detailed descriptions of the constraints and conversions can be found in Ref. [50] in the case that no 4SL reciprocal interactions, or so called approximations to short-range ordering [51], exists ($L_{A,B:A,B:*,*}^{4SL-\gamma'}$). Though this is outside the scope of the present work, Yuan et al. [52] and Franke [53] has presented the conversion from 4SL to 2SL with the inclusion of the reciprocal interactions for the binary case. The 2SL expressions for the binary and ternary cases concerned in the present work are given by Ref. [6] as

$$\text{Eq. 5: } G_{A:B}^{\gamma'} = G_{AB_3}$$

$$\text{Eq. 6: } G_{B:A}^{\gamma'} = G_{A_3B}$$

$$\text{Eq. 7: } {}^0L_{A,B:A}^{\gamma'} = -\frac{3}{2}G_{AB_3} + \frac{3}{2}G_{A_2B_2} + \frac{3}{2}G_{A_3B}$$

$$\text{Eq. 8: } {}^0L_{A,B:B}^{\gamma'} = +\frac{3}{2}G_{AB_3} + \frac{3}{2}G_{A_2B_2} - \frac{3}{2}G_{A_3B}$$

$$\text{Eq. 9: } {}^1L_{A,B:A}^{\gamma'} = +\frac{1}{2}G_{AB_3} - \frac{3}{2}G_{A_2B_2} + \frac{3}{2}G_{A_3B}$$

$$\text{Eq. 10: } {}^1L_{A,B:B}^{\gamma'} = +\frac{3}{2}G_{AB_3} + \frac{3}{2}G_{A_2B_2} - \frac{1}{2}G_{A_3B}$$

$$\text{Eq. 11: } {}^0L_{*:A,B}^{\gamma'} = {}^0L_{A,B}^{\gamma'}$$

$$\text{Eq. 12: } {}^1L_{*:A,B}^{\gamma'} = {}^1L_{A,B}^{\gamma'}$$

$$\text{Eq. 13: } {}^0L_{A,B:*}^{\gamma'} = 3 {}^0L_{A,B}^{\gamma'}$$

$$\text{Eq. 14: } {}^1L_{A,B:*}^{\gamma'} = 3 {}^1L_{A,B}^{\gamma'}$$

$$\text{Eq. 15: } {}^0L_{A,B:C}^{\gamma'} = -\frac{3}{2}G_{A_3C} - \frac{3}{2}G_{B_3C} + \frac{3}{2}G_{AB_2C} + \frac{3}{2}G_{A_2BC}$$

$$\text{Eq. 16: } {}^0L_{A,C:B}^{\gamma'} = -\frac{3}{2}G_{A_3B} - \frac{3}{2}G_{BC_3} + \frac{3}{2}G_{ABC_2} + \frac{3}{2}G_{A_2BC}$$

$$\text{Eq. 17: } {}^0L_{B,C:A}^{\gamma'} = -\frac{3}{2}G_{AB_3} - \frac{3}{2}G_{AC_3} + \frac{3}{2}G_{ABC_2} + \frac{3}{2}G_{AB_2C}$$

$$\text{Eq. 18: } {}^1L_{A,B:C}^{\gamma'} = -\frac{1}{2}G_{A_3C} + \frac{1}{2}G_{B_3C} - \frac{3}{2}G_{AB_2C} + \frac{3}{2}G_{A_2BC}$$

$$\text{Eq. 19: } {}^1L_{A,C:B}^{\gamma'} = -\frac{1}{2}G_{A_3B} + \frac{1}{2}G_{BC_3} - \frac{3}{2}G_{ABC_2} + \frac{3}{2}G_{A_2BC}$$

$$\text{Eq. 20: } {}^1L_{B,C:A}^{\gamma'} = -\frac{1}{2}G_{AB_3} + \frac{1}{2}G_{AC_3} - \frac{3}{2}G_{ABC_2} + \frac{3}{2}G_{AB_2C}$$

$$\text{Eq. 21: } {}^0L_{A,B,C:A}^{\gamma'} = +G_{AB_3} - \frac{3}{2}G_{A_2B_2} - \frac{3}{2}G_{A_3B} + G_{AC_3} - \frac{3}{2}G_{A_2C_2} - \frac{3}{2}G_{A_3C} - \frac{3}{2}G_{ABC_2} - \frac{3}{2}G_{AB_2C} + 6G_{A_2BC}$$

$$\text{Eq. 22: } {}^0L_{A,B,C:B}^{\gamma'} = -\frac{3}{2}G_{AB_3} - \frac{3}{2}G_{A_2B_2} + G_{A_3B} + G_{BC_3} - \frac{3}{2}G_{B_2C_2} - \frac{3}{2}G_{B_3C} - \frac{3}{2}G_{ABC_2} + 6G_{AB_2C} - \frac{3}{2}G_{A_2BC}$$

$$\text{Eq. 23: } {}^0L_{A,B,C:C}^{\gamma'} = -\frac{3}{2}G_{AC_3} - \frac{3}{2}G_{A_2C_2} + G_{A_3C} - \frac{3}{2}G_{BC_3} - \frac{3}{2}G_{B_2C_2} + G_{B_3C} + 6G_{ABC_2} - \frac{3}{2}G_{AB_2C} - \frac{3}{2}G_{A_2BC}$$

Furthermore, the Gibbs energy of each stoichiometric compound can be expressed as the sum of the bond energies (U):

$$\text{Eq. 24: } G_{A:B:C:D} = U_{AB} + U_{AC} + U_{AD} + U_{BC} + U_{BD} + U_{CD} + \alpha_{ABCD}$$

and for binary and ternary compounds, the Gibbs energies are given by

$$\text{Eq. 25: } G_{AB_3} = 3U_{AB} + 3\alpha_{AB_3}$$

$$\text{Eq. 26: } G_{A_2B_2} = 3U_{AB}$$

$$\text{Eq. 27: } G_{A_3B} = 3U_{AB} + 3\alpha_{A_3B}$$

$$\text{Eq. 28: } G_{A_2BC} = 2U_{AB} + 2U_{AC} + U_{BC} + \alpha_{A_2BC}$$

The correction terms, α_i , are applied for the Gibbs energies when the results $\alpha_{ABCD} = 0$ are not satisfactory, as is shown by Kusoffsky et al. [51]. However, this introduces additional parameters and is preferably not implemented unless first-principles results show strong dissimilarity between G_{AB_3} and G_{A_3B} . Some bond energies are fixed from the binary and ternary assessments including U_{AlNi} , U_{AlCr} , and U_{CrNi} from the Al-Cr-Ni description by Dupin et al. [6]. The bond energies U_{AlCo} and U_{CoNi} are assessed in the present work by utilizing first-principles calculations and experimental results.

3.2 Sigma (σ)

When adding Ni to the Al-Co-Cr system, the σ phase modeling needs to be modified accordingly. The model for σ is adapted to accommodate Ni in the first and second sublattices: $(Al,Co,Ni)_8(Al,Co,Cr,Ni)_{18}(Cr)_4$, and the ternary end-members that describe σ now include: σ -(Al)₈(Co)₁₈(Cr)₄ and σ -(Co)₈(Al)₁₈(Cr)₄ in Al-Co-Cr, σ -(Al)₈(Ni)₁₈(Cr)₄ and σ -(Ni)₈(Al)₁₈(Cr)₄ in Al-Cr-Ni, as well as σ -(Co)₈(Ni)₁₈(Cr)₄ and σ -(Ni)₈(Co)₁₈(Cr)₄ in Co-Cr-Ni. No σ end-members exist for the Al-Co, Al-Ni, and Co-Ni binary systems in the confines of the present model.

The sublattice model implemented here for σ does not offer the best description of this CoCr-base σ , as discussed in detail by Joubert [54]. In the current model, Cr can take on a maximum composition of 73.3 at. % at the end-member $(A)_8(Cr)_{18}(Cr)_4$ (where A is Al or Co). A non-simplified σ model would include 5 distinct sublattices relating to Wyckoff positions with all four Al, Co, Cr, and Ni allowed to occupy each sublattice: $(Al,Co,Cr,Ni)_2(Al,Co,Cr,Ni)_4(Al,Co,Cr,Ni)_8(Al,Co,Cr,Ni)_8(Al,Co,Cr,Ni)_8$ [54,55]. Within this model, 1024 end-members would have to be defined. Simplifications made in Refs. [5] by combining certain sites and restricting site occupation, which are commonly made [54], were thus retained here. A model based on a better suited site combination exists [54], which would lead to a maximum Cr concentration of 66.7 at. % at the end-member $(A)_{10}(Cr)_{16}(Cr)_4$. With similar site occupations, this would yield Cr concentrations closer to experimental results. Changing sublattice models would require remodeling the Co-Cr binary and associated ternaries; this was outside the scope of the current work but will be investigated in the future. The resulting discrepancy is limited (1-5 at. %) and the compositional trends are respected, such that the rest of the system is little affected.

4 First-principles methodologies

A detailed description of the first-principles methodology implemented in this work is given in Ref. [5]. The Helmholtz energy $F(V,T)$ of the condensed phases is calculated using the quasiharmonic approach. A four-parameter Birch-Murnaghan (BM4) equation of state (EOS) [56,57] is used in the fitting to obtain the Helmholtz energy. For the calculations of the elastic stiffness constants, the method proposed by Shang et al. [58] is applied. The lattice vibration model utilized is the Debye-Grüneisen model using a scaling factor in order to both increase accuracy and efficiency. Details about this model have been published previously [59,60].

Special quasirandom structures calculations (SQS) [61] are performed to predict enthalpies of mixing in the A2, B2, γ and γ' phases. The calculations for γ utilizes binary 16-atom cells developed by Wolverton [62] and ternary 24/32-atom cells by Shin et al. [63]. The supercell generated by Jiang [64], is used for the B2 ternary calculations of the $A_{0.5}B_{0.5}C$ composition sections, see Figure 1 (b). To enable the γ' SQS calculations along certain composition sections, such as Ni_3Al to Co_3Al , a 24-atom ternary SQS supercell (Figure 1 (c)) is generated using the Alloy Theoretic Automated Toolkit (ATAT) [65] together with the Monte Carlo method developed recently by van de Walle et al. [66]. Other cell sizes are tested to ensure that the selected cell size is sufficient. Other SQS settings for these calculations and the relaxation requirements in obtaining a final structure remain the same as in previous work [5]. To obtain the scaling factors to be used in the Debye-Grüneisen model for finite-temperature thermodynamic properties of B2, γ' and σ end-members, elastic constant calculations are performed. The effectiveness and accuracy of using a scaling factor for the Debye-Grüneisen model has been demonstrated previously [67].

First-principles DFT calculations are performed using the Vienna *ab-initio* Simulation Package (VASP) [68] with spin-polarization due to the ferromagnetic nature of Co and Ni as well as the antiferromagnetic nature of Cr. The Project augmented-wave (PAW) method is used to describe electron-ion interactions while the Perdew, Burke, and Ernzerhof (PBE) [69] implementation of the generalized gradient approximation (GGA) is used to describe electron exchange and correlation. To ensure that enough basis sets are included in the calculation, a plane-wave cutoff energy of 400 eV is consistently used for all calculations. Reciprocal k -meshes used for fcc-Al/Co/Cr/Ni, hcp-Co, and bcc-Al/Co/Cr/Ni are $21 \times 21 \times 21$, $23 \times 23 \times 12$ and

$17 \times 17 \times 17$, respectively. For the intermetallic B2, γ' and σ , the reciprocal k-meshes $15 \times 15 \times 15$, $21 \times 21 \times 21$, and $6 \times 6 \times 11$ are used, respectively.

5 Results and discussion

5.1 First-principles results

The results of the first-principles calculations for the B2 and γ' end-members are shown in Table 2. This includes elastic stiffness constants (C_{ij}), volume/atom (V_0), bulk modulus (B_0), Poisson's ratio (Voigt-Reuss-Hill effective medium), the Debye model scaling factor as well as the Debye temperatures for each end-member. These results are crucial properties necessary for accurate finite temperature predictions. End-members B2-CoNi and γ' -Cr₃Al are shown to be mechanically unstable due to the stability criteria $C_{11} > |C_{12}|$, $C_{44} > 0$, and $C_{11} + 2C_{12} > 0$ for cubic structures [70]. B2-CoAl, NiAl and γ' -Ni₃Al are the only stable end-members, and experimental results for these are included in Table 2. Present C_{ij} and B_0 results for B2-CoAl and NiAl agree well with experimental findings [71–75] at various temperatures as well as other first-principles calculations [76,77]. It should be noted that C_{ij} decreases as a function of temperature. The C_{ij} and B_0 results for γ' -Ni₃Al [78,79] also are shown to agree with experimental data and other calculations [77,80]. Elastic and equation of state calculations for other end-members are not available in the literature.

In Table 3, the elastic stiffness constants for the end-members of σ are listed. The end-member σ -(Al)₈(Al)₁₈(Cr)₄ can be concluded to be mechanically unstable as its $C_{44} < 0$ breaks the necessary elastic stability requirements for a tetragonal (I) crystal class [70].

Table 4 includes the enthalpies ($\Delta_f H^{298}$, kJ/mol-atom), entropies ($\Delta_f S^{298}$, J/mol-atom/K) and Gibbs energies ($\Delta_f G^{298}$, kJ/mol-atom) of formation at 298 K relative to standard reference states for the pure elements. The enthalpies of formation for B2-CoAl and NiAl from fcc-Al, hcp-Co, bcc-Cr and fcc-Ni are in good agreement with experiments at 298 K and other temperatures. The enthalpy of formation of B2-CoAl predicted in the present work at 1100 K is -59.911 kJ/mol-atom, between the experimental value of -59.5 by Henig et al. [81] at 1100 K and the compilation value of -60.7 ± 0.5 by Rzyman and Moser [82] at 1073 K. The experimental enthalpy of formation of B2-NiAl varies from -58.3 to -67 kJ/mol-atom according to Rzyman et al. [83] while the value at 298 K predicted in the present work is -64.211 kJ/mol-atom. Present results also agree with previous DFT predictions by Arroyave et al. [84] at 298 K. In the case of Ni_3Al , the calculated enthalpy of formation ($\Delta_f H^{298}$) of -42.126 kJ/mol-atom agrees with the measured values -40.6 ± 1.0 by Kek et al. [25] and -41.3 ± 1.3 by Rzyman et al. [85]. Additional experimental values compiled by Rzyman et al. [85] indicate enthalpies of formation between -47 and -37.6 kJ/mol-atom at various temperatures for Ni_3Al . Other first-principles calculations by Ohtani et al. [86] and Arroyave et al. [84] produced values of -42.38 and -46.39 kJ/mol-atom. Results for the entropy of formation (-3.252 J/mol-atom/K) and Gibbs energy (-39.809 kJ/mol-atom) agree with measured values by Róg et al. [87] at 900 K for Ni_3Al . Additionally, the Gibbs energy of formation at 900 K vary between -34.2 to -47.5 kJ/mol-atom according to other experiments compiled by Róg et al. [87]. Al_3Co , Al_3Ni , Co_3Al end-member enthalpies of formation calculated by Ohtani et al. [86] at 0 K are also in agreement with the present results. The overall good agreement reported above validates the method of the present work for prediction of finite temperature thermodynamic properties by Shang et al. [56].

As is shown in Table 5, calculated formation enthalpy at 0 K by Pavlů et al. [88] for both σ -CoCr end-members are more positive than the predictions in the present work. This is due to the use of LMTO energies for σ end-members and discrepant DFT energies for the magnetic elements by Pavlů et al. [88]. Unfortunately, calorimetric experiments for σ -CoCr prove to be unreliable as enthalpies of formation range from -3 to +10 kJ/mol-atom [14,88,89]. Downie and Arslan [14] studied the formation enthalpy of one σ -CoCr sample close to the composition of the end-member σ -(Co)₈(Cr)₁₈(Cr)₄ at 473 K and measured enthalpies of formation of 6.77 kJ/mol-atom. While no direct comparison can be made due to the different compositions, the predicted value of 6.19 kJ/mol-atom for σ -(Co)₈(Cr)₁₈(Cr)₄ is in good agreement with the measured value for a similar composition. It can be seen that all binary σ end-members have rather positive enthalpies of formation at 298 K with (Al)₈(Al)₁₈(Cr)₄ being mechanically unstable. In the Co-Cr case, positive entropies of formation can be seen for both end-members indicating potential stabilization of σ at higher temperatures as it is not stable on the convex hull at 0 K [88].

SQS calculations from A2, γ , B2 and γ' are shown in Table 6, Table 7, Table 8, and Table 9, respectively. In the case of Cr-containing systems, the huge difference in Cr lattice stability between DFT and CALPHAD makes SQS calculations for γ difficult to interpret. Wolverton and Ozolins have noted similar problems for calculations involving Cr in fcc structures [90]. By and large, taking the fcc reference state for Cr will produce enthalpies of mixing that are too negative near the Cr-rich portion of the phase diagram as any addition to fcc-Cr produces great stability.

Ternary SQS calculations provide guidance towards modeling of the energetics in the systems shown here and are therefore weighted accordingly during optimization. It is often the case that binary SQS calculations differ in energies compared to adopted binary models. In this case, strictly fitting to the coupled ternary SQS calculations can produce ill results and poor

descriptions. This is akin, then, to the adopting of SQS calculations when DFT and CALPHAD lattice stabilities are very different [55]. Therefore, the trends, rather than absolute energies, provide more meaning in this context.

It can be seen in Table 6 that Al-rich B2-CoAl and NiAl, have the largest ordering and enthalpies of formation relative to their respective A2 disordered states. This is unexpected given the high melting points and large composition ranges of B2 in both the Al-Co and Al-Ni systems. It can also be concluded that B2-CrAl has a much lower ordering energy compared to CoAl and NiAl. Furthermore, B2-CoNi and CrNi all have positive ordering energies relative to their disordered states with CoNi being mechanically unstable which can be attributed to the almost ideal mixing behavior in the A2 for Co-Ni; between -0.81 and 0.2 kJ/mol-atom. B2-CoCr also presents an interesting case as its ordering energy is nearly 0. Much like with B2, in the γ/γ' case, γ' -Al₃Co, Co₃Al, Al₃Ni, and Ni₃Al have the largest ordering tendencies, see Table 7. In the Al-Cr system, γ' -Al₃Cr has a large ordering energy while Cr₃Al is mechanically unstable based on its elastic stiffness constants. For Co-Cr and Cr-Ni, small ordering energies are seen for γ' -Co₃Cr, Cr₃Co, Cr₃Ni, and Ni₃Cr end-members. Interestingly, the present results for ordering in the Cr-Ni binary is in agreement with the bond energy assessed by Dupin et al. [6]. The calculations for γ Co-Ni demonstrate its similarity with A2 of which mixing behavior almost is ideal. Ordering energies in the Co-Ni binary are negligible from the present results.

5.1.1 CALPHAD modeling results

5.1.1.1 Al-Co-Cr

The previous modeling of the Al-Co-Cr system included the Co-Cr binary by Oikawa et al. [12]. While a satisfactory phase diagram was obtained, the enthalpy of formation of one σ end-member, $\sigma\text{-(Co)}_8\text{(Cr)}_{18}\text{(Cr)}_4$, was -6.27 kJ/mol-atom. This corresponds to enthalpies of formation much lower than those measured by Downie et al. at 473 K [14], which range between +2 to +7 kJ/mol-atom around the composition range where σ is present. Present DFT calculations indicate that the enthalpies of formation of the end-members $\sigma\text{-(Co)}_8\text{(Co)}_{18}\text{(Cr)}_4$ and $\sigma\text{-(Co)}_8\text{(Cr)}_{18}\text{(Cr)}_4$ are 9.62 and 6.29 kJ/mol-atom at 298 K, respectively. The modeling by Kusoffsky et al. [51] resulted in end-member enthalpies of 9.83 and 0.003 kJ/mol-atom at 298 K for $\sigma\text{-(Co)}_8\text{(Co)}_{18}\text{(Cr)}_4$ and $\sigma\text{-(Co)}_8\text{(Cr)}_{18}\text{(Cr)}_4$, which are both positive and in agreement with findings by Downie et al. [14]. Using the model by Oikawa et al. [12], the same end-member enthalpies are 8.70 and -6.27 kJ/mol-atom. While this produces correct phase boundaries, its disagreement with the current DFT calculations and measurements by Downie et al. [14] could extrapolate poorly in higher order systems. This justifies the selection of the Co-Cr description by Kusoffsky et al. [51] in the present work.

The A2/B2 partitioned model is still retained in the present work for B2 but with fewer, decoupled A2/B2 interaction parameters, such as in the modeling of Al-Fe-Ni by Zhang et al. [91]. As seen in **Figure 2** (a) and (b), the 1173 and 1273 K isotherms remain nearly identical to previous work. The important A2+B2, B2+ γ , and B2+ γ + σ regions are described well with the new models when compared to measurements from Liu et al. [5], Mosktivina et al. [92] and Ishikawa et al. [21].

At 1373 K (Figure 2 (c)) the new assessment reproduces B2+ γ , and A2+B2+ γ regions better than previous calculations. It should be noted that Gómez-Acebo et al. also performed diffusion couple studies of Al-Co-Cr alloys at 1373 K [93] but used relatively short heat treatment times and their results are thus not included in the current assessment. Results at 1473 K for the A2+ γ and B2+ γ regions are also improved (Figure 2 (d)). These improvements will prove crucial in the quaternary system as most MCrAlY alloys are of the B2+ γ variety. Previous modeling efforts also attempted to capture the complex A2+B2 phase boundary curvature seen especially at 1473 K (Figure 2 (d)), and it has been determined that additional asymmetrical B2 interaction parameters were needed to reproduce the curvature. This is omitted in the present model as more experiments are needed to confirm these phase boundaries, and over-fitting may produce unreliable results in the quaternary extrapolation. Even without the asymmetrical parameters, the A2+B2 regions are reproduced well at 1373, 1473, and 1573 K, respectively (Figure 2 (c), (d), and (e)). Figure 3 shows the Co_{0.5}Al_{0.5}-Cr vertical section at 298 K with predicted SQS solution enthalpies of mixing for A2 and the enthalpy of formation for B2-CoAl. Figure 4 depicts a similar calculated Co_{0.5}Cr_{0.5}-Co_{0.5}Al_{0.5} vertical section in comparison to SQS results (Table 6 and Table 8). It can be seen that in both cases the present, calculated CALPHAD results coordinate well with first-principles predicted results. In Figure 5 the calculated γ and γ' enthalpies of formation for the (Cr_xCo_{1-x})_{0.75}Al_{0.25} vertical section at 298 K are compared to their respective SQS calculations (Table 7 and Table 9). The Cr₃Al end-member (Figure 5) is not mechanical stable, as shown by present elastic constant calculations, indicating that its true enthalpy of formation is not well-defined. Given the instability, the ordered state has the same energy as a disordered γ at this composition since any ordering energy contribution is not to be expected. The bond energy term U_{CoCr} is not assessed in the present ternary modeling as it is

metastable in all ternaries. It will be modeled using quaternary data alongside with the present DFT calculations.

5.1.1.2 Al-Co-Ni

The binary subsystems adopted in the present work produces a ternary extrapolation of the Al-Co-Ni system that agrees quite well with B2+ γ , B2+ γ' , and γ + γ' phase boundaries as well as enthalpies [23–25,27–29]. Bond energies U_{AlCo} and U_{CoNi} are modeled using experimental information as well as first-principles calculation results, including SQS enthalpies of mixing. Al-Co-Ni isotherms at 1173 up to 1573 K are shown in Figure 6 (a) through (e). The important phase regions of B2, γ and γ' appear at all temperatures. Good agreement with measurements from Jia et al. [24], Kainuma et al. [27] and Schramm [23] (Figure 6 (a) to (e)) is seen at all temperatures. Data on single-phase γ' and two-phase γ' +B2 and γ + γ' alloys equilibrated at 1473 K by Albers et al. [28] also match the present results (Figure 6 (d)). No composition measurements in the γ + γ' +B2 phase region have been performed at any temperatures for comparison. However, given the good agreement for the single and two-phase regions around the ternary region, it is expected to be accurate. Figure 7 shows calculated Co_xNi_y -Al vertical sections at Ni:Co ratios of 90:10, 80:20, 50:50, and 20:80 in comparison to experimental data by Schramm [23]. Good agreement is seen at all Ni:Co ratios for single-, two- and three-phase regions.

Figure 8 shows the Gibbs energies of formation for B2-CoAl, initially modeled by Dupin and Ansara [9] but modified in the present work, and for B2-NiAl modeled by Dupin et al. [6]. First-principles predictions using the Debye-Grüneisen model are also included and good

agreement is seen for both B2 end-members. Figure 9 shows the calculated A2 and B2 enthalpies of formation compared to enthalpy measurements by Grun et al. [29] at 1073 K as well as first-principles SQS results (Table 6 and Table 8). Satisfactory agreement is obtained although the metastable A2 enthalpy of mixing at $\text{Ni}_{0.5}\text{Al}_{0.5}$ deviate slightly from the present SQS results. This can be attributed to the sublattice model conversion of the Al-Ni system by Dupin et al. [6] which was performed without the availability of these new SQS calculations. Due to the metastable nature of the A2, such a deviation does not prompt the re-assessment of Al-Ni binary.

Figure 10 shows γ and γ' enthalpies of formation compared with measurements by Kek et al. [25] at 298 K and present SQS results (Table 7 and Table 9). Similar to A2 in Al-Ni, good agreement is seen for γ' at $\text{Ni}_{0.75}\text{Al}_{0.25}$ but not for the metastable γ at this composition. Lack of information on the mixing behavior of γ in the Al-Co description by Dupin and Ansara [9] also creates an uncertainty in energy compared to present SQS results for $\text{Co}_{0.75}\text{Al}_{0.25}$. Calculations in the present work give a Co_3Al ordering energy of -5.09 kJ/mol-atom, which is different than that produced by Dupin [22] due to differences in bond energy parameters U_{AlCo} and U_{CoNi} . Dupin assessed values of $U_{\text{AlCo}} = -9870 + 3.068 \times T$ and $U_{\text{CoNi}} = 4000$. Using these bond energies, the enthalpy of formation for Co_3Al at 298 K is -28.64 kJ/mol relative to the disordered solution, which is -21.24 kJ/mol (order energy of -7.4 kJ/mol). Present DFT calculations yield values of -18.62 kJ/mol for the ordered Co_3Al relative to the SQS disordered solution (energy of -13.54 kJ/mol), as seen in Table 4. It can be seen that the calculated DFT values are smaller in magnitude compared to the CALPHAD energies. Our results also agree with first-principles results in Ref. [86], where the enthalpy of formation of Co_3Al was found to be -19.9 kJ/mol.

Therefore, the updated value for $U_{\text{AlCo}} = -4872$ is smaller in magnitude and omits the temperature dependence by the addition of a $U_{\text{AlCo}} = 3023$ term, similar to that in the Al-Ni

system [6,11]. Using this new value, the enthalpy of formation of Co_3Al at 298 K is calculated to be -23.77 kJ/mol. Additionally, U_{CoNi} is set to 0 due to small differences in energies between the ordered and disordered states of Co_3Ni and Ni_3Co calculated in the present work, as is shown in Table 4 and Table 7.

5.1.1.3 Co-Cr-Ni

The ternary extrapolation produced with the Co-Cr binary by Kusoffsky et al. [13] is better than that produced with that by Oikawa et al. [12]. If the description by Oikawa et al. [12] is used, ${}^0\text{L}$, ${}^1\text{L}$ and ${}^2\text{L}$ interaction parameters are required for the A2 and γ phases in order to reproduce the enthalpies of formation measured by Kubaschewski and Hack [42] as well as first-principles predictions. Additional excess entropy terms and ternary σ end-members are then required to reproduce phase boundary data from Zhmurko et al. [39], Omori et al. [40], and Zhanpeng [41]. On the other hand, with the binary description by Kusoffsky et al. [13], enthalpies of formation [42] and phase boundaries [39–41] are well produced at 1073-1373 K without the introduction of any ternary interaction parameters. Symmetrical ternary interaction parameters are simply used to improve the phase boundary agreement at 1473-1573 K.

As seen in Figure 11 (a) and (b), the present description agrees well with EPMA measurements by Omori et al. [40] at 1173 and 1273 K. Tie-line compositions and directions match measured values well for the A2+ σ , γ + σ , and A2+ γ regions. Figure 11 (c) and (d) show the rapid decomposition of σ in accordance with data by Omori et al. [40] and Zhanpeng [41] at 1373 to 1473 K. The agreement is good between the calculated phase boundaries and EPMA measurements from both experiments, especially at 1473 K where the calculated A2+ σ boundary

is similar to the loop measured by Zhanpeng [41]. Attempts at fitting this phase boundary resulted in σ becoming too stable at 1573 K which disagrees with results from the more self-consistent data set by Omori et al. [40]. At 1573 K (Figure 11 (e)), only the A2+ γ region remains as σ has decomposed at this temperature. Calculated tie-lines in this region are in good agreement with measurements by Omori et al. [40]. Figure 12 shows the calculated liquidus and solidus temperatures at 10-40 % Cr compared with DSC measurements by Omori et al. [40]. Disagreement arises primarily from the Co-Cr binary where melting temperatures suggested by Omori et al. [40] are consistently about 20 K higher than the model by Kusoffsky et al. [13]. It should be noted that liquidus and solidus measurements by Omori et al. [40] disagree slightly with the binary model by Kusoffsky et al. [13]. Given the small amount of melting data in the Co-rich region of the Co-Cr phase diagram, more experiments need to be performed in order to adjust the parameters in the Co-Cr model by Kusoffsky et al. [13].

In Figure 13, the calculated enthalpies of formation for the A2 and γ at 1523 K are compared to measured enthalpies by Kubachewski and Hack [42] and to SQS calculations for the solution phases (Table 6 and Table 7). Reference states are taken to be γ -Co, A2-Cr and γ -Ni in order to enable direct comparison with calorimetric values. Enthalpies of formation values for A2 agree with experiments as well as the "s" shape predicted by first-principles which reaches a maximum at 50 % Cr. Agreement for γ compared to the measured values are also good. However, first-principles results show some deviation. This can be attributed to the large difference in lattice stability for γ -Cr between CALPHAD and DFT, which is 31 kJ/mol-atom. Overall, this work has produced a thermodynamic description of the Co-Cr-Ni system that agrees well with measured and first-principles predicted energies in addition to experimental phase equilibria.

5.2 Conclusions

The Al-Co-Cr, Al-Co-Ni, and Co-Cr-Ni ternary systems are reviewed and investigated thoroughly in the present work. Due to the lack of thermochemical data and the metastability of phases in the ternary systems, first-principles calculations are performed. SQS calculations and Debye-Grüneisen predictions are used to predict energies for the important A2, B2, γ , and γ' phases. These results are used to produce CALPHAD models that agree well with experimental results in the literature including a number of isotherms at temperatures ranging from 1173 to 1573 K. The ternary systems modeled in this work are to be combined into a Al-Co-Cr-Ni quaternary description for use in predicting the thermodynamics of MCrAl coatings.

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Tables

Table 1: Summary of relevant experimental information used in the modeling

References	Exp. method	Exp. data
Al-Co-Cr		
Moskvitina et al. [92]	XRD	Isothermal section at 1173 using cast alloys; no phase compositions
Ishikawa et al. [21]	EDS, TEM	Isothermal sections at 1273, 1473, 1573 and 1623 K determined using cast alloys and diffusion couples, order-disorder transition; phase compositions given
Liu et al. [5]	XRD, EPMA	Isothermal sections at 1173, 1273 and 1373 K
Al-Co-Ni		
Schramm [23]	OM, XRD	Isothermal sections at 1173, 1273, 1373, 1473, 1573 K and room temperature using cast alloys. Vertical sections at Ni:Co concentrations of 90:10, 80:20, 50:50, and 20:80; no phase compositions
Kek et al. [25]	Calorimetry	γ' enthalpies of formation for various Co additions
Jia et al. [24]	SEM, EDS, TEM, XRD	B2, γ , and γ' phase boundaries near γ' at 1073, 1173, 1273, 1373, 1473, and 1573 K; phase compositions given
Kainuma et al. [27]	SEM, EDS, TEM, XRD, DSC	Isothermal sections at 1173, 1373, and 1573 K; phase compositions given
Albers et al. [28]	SEM, KEMS	Solubility of Co in γ' at 1473 K, activities from 1326 to 1581 K; phase compositions given
Grün et al. [29]	DSC	B2 enthalpies of formation at 1073 K
Co-Cr-Ni		
Kubaschewski and Hack [42]	Adiabatic calorimetry	Enthalpies of formation for A2, γ , and σ alloys at 1523 K, some at 1523-1648 K
Zhanpeng J. [41]	EPMA	Isothermal section at 1473 K; phase compositions given
Zhmurko et al. [39]	SEM, EDS, XRD	Isothermal section at 1073 K using cast alloys; phase compositions given
Omori et al. [40]	EPMA, XRD, DSC	Isothermal sections at 1073, 1173, 1273, 1373, 1473, and 1573 K, liquidus and solidus temperatures at 10-40 % Cr concentrations; phase compositions given

Table 2: Calculated DFT elastic stiffness constants and various properties of the end-members of B2 and γ' compared to experimental data and calculations available in the literature. Stable end-members CoAl, NiAl, and Ni₃Al are bolded while mechanically unstable CoNi and Cr₃Al are italicized.

End-member	Temp (K)	C_{11}	C_{12}	C_{44}	V_0 (Å ³ /atom)	B_0 (GPa)	ν	Scaling factor	Θ_D (K)	Ref.
B2										
CoAl	298	305.6	121.1	140.4	11.615	178.2	0.233	0.893	640	This work
CoAl	298	268.8	107.2	139.2						Expt. [71]
CoAl	298	320	108	140		175	0.213			Calc. [76]
AlCr	298	262.4	146.6	126.4	14.031	124.6	0.269	0.822	722	This work
NiAl	298	218.2	141.4	117.6	12.129	157.8	0.301	0.756	523	This work
NiAl	73	210	135	117						Expt. [72]
NiAl	298	211.5	143.2	112.1						Expt. [73]
NiAl	296	197	119	110		145				Expt. [74]
NiAl	295	205	135	117		159				Expt. [75]
NiAl									470-560	Expt. [95]
NiAl		202	129	113						Calc. [77]
NiAl		233	121	114	12.069	159				Calc. [76]
CoCr	298	306.6	179.8	148.6	11.600	214.0	0.294	0.772	537	This work
<i>CoNi</i>	298	<i>119.7</i>	<i>239.3</i>	<i>142.5</i>	<i>11.107</i>	<i>190.9</i>				This work
CrNi	298	185.3	157.5	125.0	12.175	148.5	0.325	0.705	429	This work
γ'-L1₂										
Al ₃ Co	298	196.6	88.1	66.4	13.663	125.5	0.288	0.783	527	This work
Al ₃ Co					12.932					Calc. [86]
Co ₃ Al	298	190.6	162.7	97.1	11.472	172.4	0.362	0.622	396	This work
Co ₃ Al					10.857					Calc. [86]
Al ₃ Cr	298	190.1	62.5	73.2	14.838	105.3	0.230	0.900	579	This work
<i>Cr₃Al</i>	298	<i>184.3</i>	<i>238.9</i>	<i>107.9</i>	<i>12.431</i>	<i>198.7</i>				This work
Al ₃ Ni	298	191.8	75.9	32.1	14.222	110.7	0.341	0.670	437	This work
Ni₃Al	298	248.1	158.1	129.0	11.385	178.4	0.302	0.755	503	This work
Ni₃Al	90	227	148	129						Expt. [78]
Ni₃Al	300	224.5	148.6	124.4						Expt. [79]
Ni₃Al									470	Expt. [96]
Ni₃Al		242.2	151.8	125.4	11.365	180				Calc. [80]
Ni₃Al		231	142	124						Calc. [77]
Co ₃ Cr	298	434.7	213.5	193.9	10.560	258.0	0.271	0.818	627	This work
Cr ₃ Co	298	272.9	223.1	125.1	11.367	245.9	0.365	0.614	449	This work
Co ₃ Ni	298	287.8	165.5	143.1	10.927	203.6	0.287	0.786	506	This work
Ni ₃ Co	298	287.3	164.8	138.5	10.947	196.1	0.290	0.779	501	This work
Cr ₃ Ni	298	278.2	218.5	152.7	11.440	238.0	0.338	0.676	494	This work
Ni ₃ Cr	298	281.4	147.6	137.7	11.261	188.1	0.272	0.816	518	This work

Table 3: Calculated DFT elastic stiffness constants and various properties of the end-members of σ .

End-member	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	V_0 ($\text{\AA}^3/\text{atom}$)	B_0 (GPa)	ν	Scaling factor	Θ_D (K)
$(Al)_8(Al)_{18}(Cr)_4$	118.4	110.8	50.6	175.2	-18.4	27.6	15.704	86			
$(Al)_8(Cr)_{18}(Cr)_4$	460.6	156.5	139.2	469.0	108.6	147.9	12.369	199	0.273	0.815	674
$(Co)_8(Co)_{18}(Cr)_4$	354.5	134.7	129.1	342.8	53.9	75.7	11.121	197	0.333	0.689	446
$(Co)_8(Cr)_{18}(Cr)_4$	503.1	211.9	167.1	534.1	103.1	132.7	11.333	249	0.305	0.748	603
$(Ni)_8(Ni)_{18}(Cr)_4$	351.5	155.8	114.2	355.2	35.5	59.6	11.109	198	0.358	0.631	409
$(Ni)_8(Cr)_{18}(Cr)_4$	427.8	159.2	141.0	475.2	92.4	106.5	11.451	240	0.298	0.763	566
$(Al)_8(Co)_{18}(Cr)_4$	301.6	113.6	93.6	365.3	57.6	88.3	11.648	174	0.298	0.764	499
$(Co)_8(Al)_{18}(Cr)_4$	286.0	125.7	73.5	277.2	65.7	63.3	13.072	141	0.289	0.781	553
$(Al)_8(Ni)_{18}(Cr)_4$	297.2	120.5	78.4	332.4	41.9	64.5	11.834	173	0.329	0.696	452
$(Ni)_8(Al)_{18}(Cr)_4$	301.3	135.5	78.5	245.0	75.3	78.1	13.249	135	0.277	0.806	580
$(Co)_8(Ni)_{18}(Cr)_4$	367.0	146.4	106.7	385.9	36.1	81.3	10.974	209	0.342	0.667	432
$(Ni)_8(Co)_{18}(Cr)_4$	361.9	124.8	116.7	387.5	57.3	74.8	10.757	233	0.320	0.717	461

Table 4: Calculated enthalpies, entropies and Gibbs energies of formation of B2 and γ' end-members at 298 K with respect to the standard reference states from DFT. Experiments and calculations at various temperatures, including 298 K, are included for comparison; experimental temperature information is given in the second column when available. Mechanically unstable end-members have 0 K enthalpies of formation shown in italics. Asterisks denote data from compilations by other authors.

End-member	Temp. (K)	$\Delta_f H^{298}$ (kJ/mol-atom)	$\Delta_f S^{298}$ (J/mol-atom/K)	$\Delta_f G^{298}$ (kJ/mol-atom)	Ref.
B2					
CoAl	298	-57.673	-8.231	-55.220	This work
CoAl	1100	-59.5			Expt. [81]
Co Al	1073	-60.7±0.5			*Expt. [82]
AlCr	298	-2.776	-6.449	-0.854	This work
NiAl	298	-64.211	-4.241	-62.947	This work
NiAl	298	-66.1±1.3			Expt. [83]
NiAl	Various	-66.4±2.0, -67.0, -62.0, -67.4±2.55, -66.0±0.13, -58.3±1.1			*Expt. [83]
NiAl	298	-67.18			Calc. [84]
CoCr	298	16.597	1.031	16.289	This work
CoNi	298	5.66			This work
CrNi	298	24.262	5.925	22.497	This work
γ'-L1₂					
Al ₃ Co	298	-20.035	-5.627	-18.358	This work
Al ₃ Co	0	-22.6			Calc. [86]
Co ₃ Al	298	-17.345	4.043	-18.550	This work
Co ₃ Al	0	-19.9			Calc. [86]
Al ₃ Cr	298	-9.197	-6.699	-7.200	This work
Cr ₃ Al	298	-12.94			This work
Al ₃ Ni	298	-21.175	-1.268	-20.798	This work
Al ₃ Ni	0	-22.9			Calc. [86]
Ni ₃ Al	298	-42.126	-2.187	-41.474	This work
Ni ₃ Al	298	-40.6±1.0			Expt. [25]
Ni ₃ Al	298	-41.3±1.3			Expt. [85]
Ni ₃ Al	Various	-37.6±4.2, -38.2±5, -40.6±1, -47.0			*Expt. [85]
Ni ₃ Al	900	-45.6±1.1	-4.05±1.2	-41.9±0.2, -47.5±1.1, -34.2±0.33, -36.2	*Expt. [87]
Ni ₃ Al	298	-46.39			Calc. [84]
Ni ₃ Al	0	-42.38			Calc. [86]
Co ₃ Cr	298	6.475	-2.176	7.123	This work
Cr ₃ Co	298	18.079	4.662	16.690	This work
Co ₃ Ni	298	0.390	-0.303	0.480	This work
Ni ₃ Co	298	1.321	-0.192	1.378	This work
Cr ₃ Ni	298	14.291	2.291	13.609	This work
Ni ₃ Cr	298	-0.719	-1.520	-0.266	This work

Table 5: Calculated enthalpies, entropies and Gibbs energies of formation of σ end-members at 298 K from DFT. Energies taken with respect to the standard reference states. Experiments and calculations at various temperatures, including 298 K, are included for comparison. Mechanically unstable end-members have 0 K enthalpies of formation shown in italics.

End-member	$\Delta_f H^{298}$ (kJ/mol-atom)	$\Delta_f S^{298}$ (J/mol-atom/K)	$\Delta_f G^{298}$ (kJ/mol-atom)	Ref.
<i>(Al)₈(Al)₁₈(Cr)₄</i>	<i>10.976</i>			This work
(Al) ₈ (Cr) ₁₈ (Cr) ₄	1.736	-2.624	2.518	This work
(Co) ₈ (Co) ₁₈ (Cr) ₄	9.615	3.597	8.543	This work
¹ (Co) ₈ (Co) ₁₈ (Cr) ₄	11.65			Calc. [88]
(Co) ₈ (Cr) ₁₈ (Cr) ₄	6.193	0.157	6.146	This work
¹ (Co) ₈ (Cr) ₁₈ (Cr) ₄	8.39			Calc. [88]
² Co _{39.3} Cr _{60.7}	6.77±0.05			Expt. [14]
(Ni) ₈ (Ni) ₁₈ (Cr) ₄	8.981	5.048	7.476	This work
(Ni) ₈ (Cr) ₁₈ (Cr) ₄	8.339	-2.663	9.133	This work
(Al) ₈ (Co) ₁₈ (Cr) ₄	-13.385	-1.127	-13.049	This work
(Co) ₈ (Al) ₁₈ (Cr) ₄	-24.582	-4.048	-23.375	This work
(Al) ₈ (Ni) ₁₈ (Cr) ₄	-29.500	-0.119	-29.208	This work
(Ni) ₈ (Al) ₁₈ (Cr) ₄	-33.053	-4.952	-31.578	This work
(Co) ₈ (Ni) ₁₈ (Cr) ₄	16.647	3.533	15.594	This work
(Ni) ₈ (Co) ₁₈ (Cr) ₄	23.057	1.456	22.608	This work

Note: ¹0 K, ²473 K

Table 6: Calculated enthalpies of mixing for A2 from DFT. The results are based on binary and ternary SQS calculations at 0 K with reference states taken as bcc-A2 for Al, Co, and Cr, and Ni. B2 end-members with the same reference states are included. Energies for mechanically unstable ordered structures are shown in italics. Values for Al-Co, Al-Cr, Co-Cr, and Al-Co-Cr and adapted from previous work [5] and are indicated with an asterisk *.

System	Al	Co	Cr	Ni	SQS prototype	ΔH_{mix} (kJ/mol-atom)	$\Delta_f H$ B2- β (kJ/mol-atom)	ΔH^{order} (kJ/mol-atom)
*Al-Co	0.75	0.25			16	-8.99		
	0.5	0.5			16	-21.58	-67.75	-46.17
	0.25	0.75			16	-18.42		
*Al-Cr	0.75		0.25		16	0.93		
	0.5		0.5		16	1.41	-7.96	-9.37
	0.25		0.75		16	1.42		
Al-Ni	0.75			0.25	16	-25.52		
	0.5			0.5	16	-39.83	-73.80	-33.97
	0.25			0.75	16	-31.83		
*Co-Cr		0.75	0.25		16	9.99		
		0.5	0.5		16	11.98	11.99	0.01
		0.25	0.75		16	9.59		
Co-Ni		0.75		0.25	16	0.20		
		0.5		0.5	16	-0.81	5.66	6.47
		0.25		0.75	16	-0.37		
Cr-Ni			0.75	0.25	16	10.02		
			0.5	0.5	16	9.15	20.12	10.97
			0.25	0.75	16	4.98		
*Al-Co-Cr	0.5	0.25	0.25		32	-9.42		
	0.25	0.5	0.25		32	-6.69		
	0.25	0.25	0.5		32	-0.86		
	0.33	0.33	0.33		36	-7.46		
Al-Co-Ni	0.5	0.25		0.25	32	-25.81		
	0.25	0.5		0.25	32	-20.43		
	0.25	0.25		0.5	32	-23.59		
	0.33	0.33		0.33	36	-25.82		
Co-Cr-Ni		0.5	0.25	0.25	32	0.86		
		0.25	0.5	0.25	32	11.95		
		0.25	0.25	0.5	32	8.03		
		0.33	0.33	0.33	36	3.83		

Table 7: Calculated enthalpies of mixing for γ from DFT. These calculations are based on binary and ternary SQS calculations at 0 K with references taken as fcc- γ for Al, Co, and Cr, and Ni. γ' end-members with the same reference states are also shown. Energies for mechanically unstable ordered structures are shown in italics.

System	Al	Co	Cr	Ni	SQS prototype	ΔH_{mix} (kJ/mol-atom)	$\Delta_f H_{L1_2-\gamma'}$ (kJ/mol-atom)	ΔH^{order} (kJ/mol-atom)
Al-Co	0.75	0.25			16	-9.28	-20.80	-11.51
	0.5	0.5			16	-18.00		
	0.25	0.75			16	-13.54	-18.62	-5.09
Al-Cr	0.75		0.25		16	-2.52	-19.04	-16.52
	0.5		0.5		16	-6.86		
	0.25		0.75		16	-7.08	<i>-12.94</i>	<i>-5.86</i>
Al-Ni	0.75			0.25	16	-17.05	-21.15	-4.10
	0.5			0.5	16	-30.54		
	0.25			0.75	16	-27.86	-42.22	-14.37
Co-Cr		0.75	0.25		16	-0.90	-5.04	-4.15
		0.5	0.5		16	-5.46		
		0.25	0.75		16	-6.86	-10.48	-3.62
Co-Ni		0.75		0.25	16	-0.48	-0.94	-0.46
		0.5		0.5	16	-0.67		
		0.25		0.75	16	-0.77	0.90	1.67
Cr-Ni			0.75	0.25	16	-12.69	-13.88	-1.19
			0.5	0.5	16	-9.03		
			0.25	0.75	16	-5.79	-10.03	-4.24
Al-Co-Cr	0.5	0.25	0.25		32	-11.66		
	0.25	0.5	0.25		32	-11.39		
	0.25	0.25	0.5		32	-18.06		
	0.33	0.33	0.33		24	-15.33		
Al-Co-Ni	0.5	0.25		0.25	32	-21.66		
	0.25	0.5		0.25	32	-17.13		
	0.25	0.25		0.5	32	-21.68		
	0.33	0.33		0.33	24	-22.62		
Co-Cr-Ni		0.5	0.25	0.25	32	-3.20		
		0.25	0.5	0.25	32	-8.14		
		0.25	0.25	0.5	32	-5.04		
		0.33	0.33	0.33	24	-5.90		

Table 8: Calculated enthalpies of mixing for B2 from DFT. The results are based on ternary SQS calculations at 0 K with reference states taken as bcc-A2 for Al, Co, and Cr, and Ni. Energies for mechanically unstable binary ordered structures are shown in italics. Values for Al-Co, Al-Cr, Co-Cr, and Al-Co-Cr and adapted from previous work [5] and are indicated with an asterisk *.

	Section	Al	Co	Cr	Ni	SQS prototype	ΔH_{mix} (kJ/mol-atom)
*Al-Co-Cr	(Al)(Co,Cr)	0.5		0.5			-7.96
		0.5	0.25	0.25		8	-32.77
		0.5	0.5				-67.75
	(Co)(Al,Cr)	0.5	0.5				-67.75
		0.25	0.5	0.25		8	-27.20
			0.5	0.5			11.99
	(Cr)(Al,Co)		0.5	0.5			11.99
		0.25	0.25	0.5		8	8.22
Al-Co-Ni		0.5		0.5			-7.96
	(Al)(Co,Ni)	0.5			0.5		-73.80
		0.5	0.25		0.25	8	-68.64
		0.5	0.5				-67.75
	(Co)(Al,Ni)	0.5	0.5				-67.75
		0.25	0.5		0.25	8	-26.94
			0.5		0.5		5.66
	(Ni)(Al,Co)		0.5		0.5		5.66
Co-Cr-Ni		0.25	0.25		0.5	8	-33.61
		0.5			0.5		-73.80
	(Co)(Cr,Ni)		0.5		0.5		5.66
			0.5	0.25	0.25	8	10.80
			0.5	0.5			11.99
	(Cr)(Co,Ni)		0.5	0.5			11.99
			0.25	0.5	0.25	8	17.62
				0.5	0.5		20.12
	(Ni)(Co,Cr)			0.5	0.5		20.12
			0.25	0.25	0.5	8	16.02
			0.5		0.5		5.66

Table 9: Calculated enthalpies of mixing for γ' from DFT. The results are based on ternary SQS calculations at 0 K with reference states taken as fcc- γ for Al, Co, and Cr, and Ni. Energies for mechanically unstable binary ordered structures are shown in italics.

	Section	Al	Co	Cr	Ni	SQS prototype	ΔH_{mix} (kJ/mol-atom)
Al-Co-Cr	(Al)(Co,Cr) ₃	0.25	0.75				-18.62
		0.25	0.375	0.375		24	-12.37
		0.25		0.75			-12.94
	(Co)(Al,Cr) ₃	0.75	0.25				-20.80
		0.375	0.25	0.375		24	-25.57
			0.25	0.75			-10.48
	(Cr)(Al,Co) ₃	0.75		0.25			-19.04
		0.375	0.375	0.25		24	-14.04
			0.75	0.25			-5.04
Al-Co-Ni	(Al)(Co,Ni) ₃	0.25	0.75				-18.62
		0.25	0.375		0.375	24	-29.84
		0.25			0.75		-42.22
	(Co)(Al,Ni) ₃	0.75	0.25				-20.80
		0.375	0.25		0.375	24	-28.12
			0.25		0.75		0.90
	(Ni)(Al,Co) ₃	0.75			0.25		-21.15
		0.375	0.375		0.25	24	-25.03
			0.75		0.25		-0.94
Co-Cr-Ni	(Co)(Ni,Cr) ₃		0.25		0.75		0.90
			0.25	0.375	0.375	24	-5.64
			0.25	0.75			-10.48
	(Cr)(Ni,Co) ₃			0.25	0.75		-10.03
			0.375	0.25	0.375	24	-3.87
			0.75	0.25			-5.04
	(Ni)(Co,Cr) ₃		0.75		0.25		-0.94
			0.375	0.375	0.25	24	-5.61
				0.75	0.25		-13.88

Figure captions

Figure 1: Atomic structures for the σ (a), the SQS 8-atom B2 (b) and the SQS for the 24-atom γ' (c). The different colors denote different atomic species and some bonds have been added to aid in the visualization of the unit cell crystal structures. Structures shown are used for ternary DFT calculations: σ - $(B)_8(A)_{18}(C)_4$, B2 - $(A)_4(B)_2(C)_2$, γ' - $(B)_9(C)_9(A)_6$.

Figure 2: Calculated Al-Co-Cr isothermal sections (solid lines) at 1173 (a), 1273 (b), 1373 (c), 1473 (d) and 1573 K (e). Experimental phase equilibrium data by Moskvitina et al. [92] is included for comparison: single phase ($\square$), 2-phase (∇), and 3-phase ($+$). and by Ishikawa et al. [21]: 2-phase ($\circ$), order-disorder transition ($*$). Phase equilibria data from the Ref. [5]: 2-phase ($\bullet$), 3-phase ($\blacktriangle$). The calculated order-disorder transition is also shown ($\cdot \cdot \cdot$).

Figure 3: Calculated CALPHAD A2 (- - -) and B2 (—) enthalpies of formation of the $Co_{0.5}Al_{0.5}$ -Cr vertical section compared to first-principles results for the A2 ($\circ$) and B2 phases ($\bullet$) at 298 K. Reference states are taken as A2 for Al, Co and Cr.

Figure 4: Calculated CALPHAD A2 (- - -) and B2 (—) enthalpies of formation of the $Co_{0.5}Cr_{0.5}$ - $Co_{0.5}Al_{0.5}$ vertical section compared to first-principles results for the A2 ($\circ$) and B2 phases ($\bullet$) at 298 K. Reference states are taken as A2 for Al, Co and Cr.

Figure 5: Calculated CALPHAD γ (- - -) and γ' (—) enthalpies of formation for the $(Cr_xCo_{1-x})_{0.75}Al_{0.25}$ vertical section compared at 298 K compared to first-principles SQS results for γ ($\circ$) and γ' ($\bullet$). Reference states are taken as γ for Al, Co and Cr.

Figure 6: Calculated Al-Co-Ni isothermal sections (solid lines) at 1173 (a), 1273 (b), 1373 (c), 1473 (d) and 1573 K (e). Experimental data from Jia et al. [24] ($\triangle$), Kainuma et al. [27] ($\circ$), and Albers et al. [28] (1-phase $\diamond$, 2-phase $\square$) are included for comparison. Equilibrated alloys from Schramm [23] are also shown: 1-phase ($*$), $\gamma'+B2(\times)$, $\gamma+\gamma'(+)$, and $\gamma+B2(\nabla)$.

Figure 7: Calculated Al-Co-Ni vertical sections at Ni:Co ratios of 90:10, 80:20, 50:50, and 20:80 compared to equilibrated alloys from Schramm [23]: 1-phase ($*$), $\gamma'+B2(\times)$, $\gamma+\gamma'(+)$, $\gamma+B2(\nabla)$, 3-phase ($\diamond$), and Curie temperature ($\times$). The γ ferromagnetic-paramagnetic transition is also shown with ($\cdot \cdot \cdot$).

Figure 8: CALPHAD Gibbs energies of formation for B2-CoAl (—) and B2-NiAl (- - -) from the CALPHAD modeling compared to their respective results from the Debye-Grüneisen model ($\circ$ and $\triangle$).

Figure 9: Calculated CALPHAD B2 (—) enthalpies of formation for the $(\text{Ni}_x\text{Co}_{1-x})_{0.5}\text{Al}_{0.5}$ vertical section compared to measurements from Grun et al. (▲) [29] at 1073 K (error bars approximately size of symbols). Experimental reference states are liquid Al, solid γ -Co, and solid γ -Ni. CALPHAD Enthalpies of formation for A2 (- · -) and B2 (- - -) with all A2 reference states at 298 K are shown in comparison to first-principles SQS results for A2 (○) and B2 (●).

Figure 10: Calculated CALPHAD γ' (—) enthalpies of formation for the $(\text{Ni}_x\text{Co}_{1-x})_{0.75}\text{Al}_{0.25}$ vertical section compared to measurements from Kek et al. (▲) [25] at 298 K. Experimental reference states are solid γ for Al, Co, and Ni. The CALPHAD enthalpy of formation for the γ (- - -) with all γ reference states at 298 K are shown in comparison to first-principles SQS results for γ (○) and γ' (●).

Figure 11: Calculated Co-Cr-Ni isothermal sections (solid lines) at 1173 (a), 1273 (b), 1373 (c), 1473 (d) and 1573 K (e). Experimental results of investigations of the 2-phase equilibria by Omori et al. [40] (○) and Zhanpeng J. [41](△) are included as comparison. A2/ σ phase boundaries measured by Zhanpeng J. [41] are also shown (+).

Figure 12: Calculated CALPHAD liquidus and solidus temperatures (—) in the Co-Cr-Ni ternary compared to measurements from Omori et al. [40] at various Cr concentration levels: 0.1Cr (○), 0.2Cr (△), 0.3Cr (□), 0.4 (◇)

Figure 13: Calculated CALPHAD γ (—) and A2 (- - -) enthalpies of formation of the $\text{Co}_{0.5}\text{Ni}_{0.5}$ -Cr vertical section compared to measured γ (●) and A2 (▲) enthalpies from Kubachewski and Hack [42] at 1523 K. Experimental reference states are solid γ -Co, A2-Cr and γ -Ni. First-principles SQS results for the γ (○) and A2 phases (△) at 298 K with the same reference states as the experimental measurements are also included.

Appendix

Parameters for the binary systems not shown except for where modifications are made

Phase	Model	Parameter	System	References
Liquid	(Al,Co,Cr,Ni) ₁	${}^0L_{Al,Co,Cr}^{Liq} = +30000$	Al-Co-Cr	Liu et al. [5]
		${}^0L_{Al,Co,Ni}^{Liq} = +20000$	Al-Co-Ni	This work
		${}^0L_{Co,Cr,Ni}^{Liq} = -16000$	Co-Cr-Ni	This work
fcc-A1	(Al,Co,Cr,Ni) ₁	${}^0L_{Al,Co,Cr}^{fcc-A1} = +990 + 8.278 \times T$	Al-Co-Cr	This work
		${}^0L_{Al,Co,Ni}^{fcc-A1} = 0$	Al-Co-Ni	This work
		${}^0L_{Co,Cr,Ni}^{fcc-A1} = -40710 + 13.533 \times T$	Co-Cr-Ni	This work
$\gamma'/L1_2$	(Al,Co,Cr,Ni) _{0.75} (Al,Co,Cr,Ni) _{0.25} Ordered part of fcc-A1	$G_{Al:Co}^{\gamma'} = G_{Co:Al}^{\gamma'} = AL3CO = ALCO3 = 3U1ALCO$	Al-Co	This work
		$U1ALCO = -4872$	Al-Co	This work
		${}^0L_{Al,Co:*}^{\gamma'} = 3U3ALCO, {}^0L_{*:Al,Co}^{\gamma'} = U3ALCO$	Al-Co	This work
		$U3ALCO = 0$	Al-Co	This work
		${}^1L_{Al,Co:*}^{\gamma'} = 3U4ALCO, {}^1L_{*:Al,Co}^{\gamma'} = U4ALCO$	Al-Co	This work
		$U4ALCO = +3023$	Al-Co	This work
		$G_{Co:Ni}^{\gamma'} = G_{Ni:Co}^{\gamma'} = CO3NI = CONI3 = 3U1CONI$	Co-Ni	This work
		$U1CONI = 0$	Co-Ni	This work
		Other interactions shown in Eq. 1.5-1.28		
bcc-A2	(Al,Co,Cr,Ni,Va) ₁	${}^0L_{Al,Co,Cr}^{bcc-A2} = -28128$	Al-Co-Cr	This work
		${}^1L_{Al,Co,Cr}^{bcc-A2} = +123468 - 61.879 \times T$	Al-Co-Cr	This work
		${}^2L_{Al,Co,Cr}^{bcc-A2} = -12107 - 32.267 \times T$	Al-Co-Cr	This work
		${}^0L_{Al,Co,Ni}^{bcc-A2} = -15483$	Al-Co-Ni	This work
		${}^0L_{Co,Cr,Ni}^{bcc-A2} = -60134 + 17.700 \times T$	Co-Cr-Ni	This work
B2	(Al,Co,Cr,Ni,Va) _{0.5} (Al,Co,Cr,Ni,Va) _{0.5} Ordered part of bcc-A2	$G_{Al:Co}^{B2} = G_{Co:Al}^{B2} = 0.5GB2ALCO - 0.5LB2ALCO$	Al-Co	Liu et al. [5]
		$GB2ALCO = -138500 + 34.620 \times T$	Al-Co	Dupin & Ansara [9]
		$LB2ALCO = +56531 - 37.040 \times T$	Al-Co	Liu et al. [5]
		$G_{Co:Cr}^{B2} = G_{Cr:Co}^{B2} = -3.074 \times T$	Co-Cr	This work
		$G_{Co:Ni}^{B2} = G_{Ni:Co}^{B2} = +3864 - 1.664 \times T$	Co-Ni	This work
		${}^0L_{Al:Co,Cr}^{B2} = {}^0L_{Co,Cr:Al}^{B2} = -11069$	Al-Co-Cr	This work
		${}^0L_{Cr:Al,Co}^{B2} = {}^0L_{Al,Co:Cr}^{B2} = -30895$	Al-Co-Cr	This work
		${}^0L_{Ni:Al,Co}^{B2} = {}^0L_{Al,Co:Ni}^{B2} = -21769$	Al-Co-Ni	This work
σ	(Al,Co,Ni) ₈ (Al,Co,Cr,Ni) ₁₈ (Cr) ₄	$G_{Al:Ni:Cr}^{\sigma} - 8G_{Al}^{fcc} - 18G_{Ni}^{bcc} - 4G_{Cr}^{bcc} = -1045169$	Al-Cr-Ni	This work
		$G_{Ni:Al:Cr}^{\sigma} - 8G_{Ni}^{fcc} - 18G_{Al}^{bcc} - 4G_{Cr}^{bcc} = -1169367$	Al-Cr-Ni	This work
		$G_{Ni:Co:Cr}^{\sigma} - 8G_{Ni}^{fcc} - 18G_{Co}^{bcc} - 4G_{Cr}^{bcc} = 0$	Co-Cr-Ni	This work
		$G_{Co:Ni:Cr}^{\sigma} - 8G_{Co}^{fcc} - 18G_{Ni}^{bcc} - 4G_{Cr}^{bcc} = 0$	Co-Cr-Ni	This work
		Al-Co-Cr σ parameters remain same as Liu et al. [5]		

Fig1

(a) T=1173 K

(b) T=1273 K

(c) T=1373 K

(d) T=1473 K

(e) T=1573 K

Intermetallics:

Al-Co

1. Al_9Co_2
2. $\text{Al}_{13}\text{Co}_4$
3. Al_3Co
4. Al_5Co_2

Al-Cr

5. $\text{Al}_{11}\text{Cr}_2$
6. Al_4Cr
7. Al_9Cr_4 (LT)
8. Al_8Cr_5 (LT)
9. Al_9Cr_4 (HT)
10. Al_8Cr_5 (HT)

Fig3

Fig4

Fig5

(a) T=1173 K

(b) T=1273 K

(c) T=1373 K

(d) T=1473 K

(e) T=1573 K

Intermetallics:

Al-Co1. Al_9Co_2 2. $\text{Al}_{13}\text{Co}_4$ 3. Al_3Co 4. Al_5Co_2 Al-Ni5. Al_3Ni_2

Fig7

Fig8

Fig9

Fig10

Fig12

Fig13