The FCC to BCC transition and atomic ordering in the $Al_xCoCrFeNi$ high entropy alloy

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Abstract

The transition between a face-centred cubic (FCC) and body-centred cubic (BCC) solid solution in the $Al_xCoCrFeNi$ high-entropy alloy system has been investigated using static density functional theory calculations. Ordering in the FCC system was investigated and an order-disorder transition temperature was predicted at ∼600 K. It was found that at low temperature an ordered lattice is favoured over a truly random lattice - a simple Cu_3Au-type ordering was investigated although others may form. We expect that a more favourable ordering is expected to increase the order-disorder transition temperature. The fully disordered BCC was found to be unstable, instead showing preference for a FCC structure during relaxation at high Al concentrations. When a partial ordering was imposed, with Al and Ni limited to the centre and corner sites of the BCC system (lowering the symmetry), respectively, the BCC structure was stabilised. Decomposition of the ordered BCC phase into a Al-Ni-rich and Fe-Cr-rich phase is also considered and compared to experimental observations.

I. INTRODUCTION

The Al-Co-Cr-Fe-Ni system, and its variations, is one that has attracted a lot of interest since it was first studied at the turn of the century by Huang and Yeh et al.[1–3]. Since then, it has been the focus of nearly a quarter of all high entropy alloy (HEA) studies to date. This is due to its interesting properties such as hardness[4], corrosion resistance[5,6], wear resistance[7] and fatigue behaviour[8].

Interestingly, the Al_xCoCrFeNi system is known to transition from a face centred cubic (FCC) crystal structure to a body centred cubic (BCC) crystal structure, as the Al content is increased. Extensive studies into the alloying of Al have been performed and it has been identified that when there is an Al content of approximately $0 \leq x \leq 0.5$ in the Al_xCoCrFeNi HEA, the crystal structure will remain a single phase disordered FCC[3,9]. Increasing the Al content to $0.5 \leq x \leq 0.9$ the system is observed to simultaneously form a BCC structured phase as well as the FCC structure. Further increases in Al content $0.9 \leq x \leq 1.0$, only a single phase BCC structure is observed.

A number of papers differentiate the BCC phases observed into two types: disordered A2 and ordered B2 forms (the B2 being analogous to the NiAl phase although the extent of the ordering is not clear)[4]. This effect has been related to the valence electron concentration by Guo et al.[10]. Wang et al.[9] confirmed the existence of the ordered B2 structure in their arc melted samples. The distinctive ordering peak in the XRD-pattern of the HEA, attributed to [100], can actually be seen to some degree in all patterns containing the BCC phase. The [111] peak is clearly observed in the higher Al content alloys.

Two phase BCC?

Currently, a quantitative understanding of the energetics of this system are lacking. One specific study by Zhang et al.[11] utilised the CALPHAD program to thermodynamically aid in alloy design. The purpose of the current study is to use atomic scale simulation techniques to support the experimental evidence and understand the role of ordering and configurational entropy in the alloys.

II. METHODOLOGY

Past work[6] utilised a method by which randomly populated FCC supercells were relaxed within the VASP program[12] to understand the drive for Cr segregation in the CoCrFeNi system. The results of the work compared well with experimental results for the system and previous atomic scale methods using special quasi-random structures (SQS) supercells[13]. This work employs the same random population method as the past work, with the added complexity of modelling the FCC to BCC transition as well as partial ordering of the sub-lattice.

The stability of the HEA phases are calculated by computing the formation enthalpy from the alloy's constituent metals in their low temperature structures (i.e. FCC Al, HCP Co, BCC Cr, FCC Fe and FCC Ni). The FCC HEA supercell is the same size as the one used in past work[6]: a 2×2×2 supercell of the FCC unit-cell, containing 32 atoms. The BCC supercell is slightly larger: a 3×3×3 supercell of the BCC unit-cell, containing 54 atoms. In both cases a 4×4×4 γ-centred k-point grid was used with a Methfessel-Paxton smearing method (0.125 eV) providing a suitably low error of $<10^{-3}$ eV per supercell. The pseudopotentials provided as part of the VASP package[14] were used with the GGA-PBE exchange correlation (using the highest valence electron number available).

Each arrangement was repeated 10 times with any erroneous high energy supercells discounted and the calculation repeated. In all cases, the energies of similar supercells varied by less than ± 0.02 eV per atom, suitable for this study.

An added complexity is also investigated in this work whereby we understand the impact of Al ordering, and subsequently Al-Ni-ordering, on the stability of the BCC phase in comparison to the completely disordered BCC structure. In the ordered B2 structure, the AlNi intermetallic for example, Al can be thought of as occupying the centre site of a body centred unit-cell[15] whilst Ni occupies the other site (when the simultaneous ordering of both species is investigated).

Ordering of the CoCrFeNi FCC phase in a Cu_3Au type structure[16] (devoid of Al) was investigated, whereby the Au site is fully occupied by one of the constituent elements (e.g. Fe) and the Cu sites are randomly populated by the remaining species. The Cu_3Au structure has $Pm\bar{3}m$ symmetry where the Au takes the 1a (0,0,0) site and the Cu occupies the 3c $(0.0,\frac{1}{2},\frac{1}{2})$ site.

To investigate the role of configurational entropy on the systems' stabilities, we use Boltzmann's equation[17] for the configurational entropy (entropy of mixing):

$$\Delta S_{conf} = k_B ln\Omega \tag{1}$$

whereby k_B is Boltzmann's constant and:

$$\Omega = \frac{N_{tot}!}{N_1!N_2!...N_j!} \tag{2}$$

where:

$$N_{tot} = (\sum_{i=1}^{j} N_i) \tag{3}$$

for N number of atoms of element i in a j element system.

Applying Stirling's approximation[18] for $lnN!$ when N$\gg$1:

$$\Delta S_{conf} = -k_B \sum_{i=1}^{j} N_i ln(\frac{N_i}{N_{tot}}) \tag{4}$$

Since N_i/N_{tot} corresponds to the atomic concentration, x, of element i, $k_B = R/N_A$ where N_A is Avagadro's number and $N_{tot} = nN_A$, where the n is the number of moles.

$$\Delta S_{conf} = -nR \sum_{i=1}^{j} x_i ln(x_i) \tag{5}$$

For a system with partial ordering we can expand $n_{tot} = \Sigma_{k=1}^{l} n_k$ whereby the total number of moles n_{tot} is the sum of the number of moles n of sublattice k for l number of sublattices. Therefore:

$$\Delta S_{conf} = -R \left[\sum_{k=1}^{l} n_k \sum_{i=1, i\neq m}^{j} x_{i,k} ln(x_{i,k}) \right] \tag{6}$$

where m is any element that is not included on that sublattice.

To explore the impact of the ordering on the expected experimental observations, the Crystal Maker® software was used to generate simulated X-ray diffraction patterns[19]. The relaxed structures are mixed with equal weighting within the program and given an instrumental broadening value of 0.02°.

III. RESULTS

A. Relaxed structures

The disordered supercells that were built with FCC symmetry kept their structure through the atomic scale optimisation routine, regardless of Al content. The lattice param-

eter was observed to vary with Al concentration, as is expected given the larger metallic radius of Al (1.43 Å[20]) compared to the other constituent elements (1.25 Å, 1.36 Å, 1.26 Å and 1.24 Å for Co, Cr, Fe and Ni, respectively[20]). The lattice parameter variation for the FCC Al_xCoCrFeNi was predicted to increase from 3.519 Å to 3.556 Å from x=0→0.57, a difference of 0.037 Å. The experimental variation in lattice parameter, observed by Wang et al.[9] was 0.025 Å between x=0→0.5.

The simulated X-ray diffraction patterns for the four FCC Al_xCoCrFeNi systems simulated are reported in Figure 1. The wavelength of the simulated X-rays was set to 1.5406 Å (to match with the majority of the experimental data). The main [111] peak (at ∼45°) shifts from higher angles to lower angles as the Al content is increased, as expected, whilst the [200] peak (at ∼50°) diminishes in intensity compared to the [111] peak to the theoretical composition of x=2.40 (experimentally, the two higher Al content systems are not observed to be FCC).

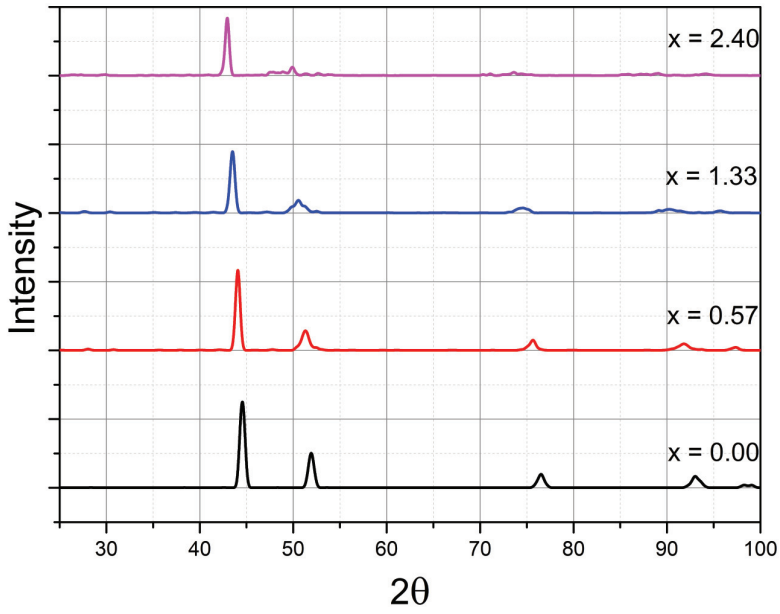

FIG. 1. Simulated X-ray diffraction patterns of FCC Al_xCoCrFeNi with x=0.00, 0.57, 1.33 and 2.40.

When the pseudo-Cu_3Au-type structure of the CoCrFeNi phase is considered, there are no significant differences to the XRD patterns produced, apart from a very small ordering peak observed at ∼36° related to the [110] direction, when each of the constituent four elements are ordered on the Au site. The lattice parameter for the Fe ordered system

(energetically the most stable, as discussed in the following section) is slightly increased to 3.521 Å compared to 3.519 Å in the fully disordered system.

Somewhat surprisingly, the supercells that were built with the BCC symmetry without ordering relaxed to a wide variety of simple structures, normally markedly different from the initial BCC arrangement. At low Al concentrations of x=0.00 and x=0.15, more than 50 % of the structures relaxed to a R$\bar{3}$m symmetry (hexagonal not cubic). At intermediate Al contents of x=0.50 and x=0.91, the structures again relaxed to a range of structures: 40 % remained BCC with a Im$\bar{3}$m symmetry, 25 % relaxed to the R$\bar{3}$m symmetry observed for lower Al contents, 10 % transformed to a FCC Fm$\bar{3}$m symmetry, while the remainder transformed to lower symmetry Fmmm and IA$\bar{3}$d symmetries. At high Al concentrations, the majority (70 %) of the structures relaxed to an FCC Fm$\bar{3}$m symmetry with the remainder taking up the R$\bar{3}$m and Im$\bar{3}$m. It is clear that the simple, disordered BCC phase is not the predicted stable structure using static DFT.

Past work has experimentally suggested that when the Al positions in the BCC phase were limited to the centre site of the unit cell (preventing Al-Al nearest neighbours) the BCC structure is stabilised. When limiting the positions of the Al we find that at low Al concentrations of x=0.15 and x=0.50, the hexagonal (R$\bar{3}$m) phase continued to form for 30 % of the supercells with the remainder remaining BCC (Im$\bar{3}$m). For the three higher concentrations of Al considered, all supercells remained in the BCC (Im$\bar{3}$m) symmetry. This is a significant finding that suggests that the atomic scale ordering (or at least partial ordering of the constituent elements, in this case Al) is a pivotal property required in the formation of the single phase BCC Al_xCoCrFeNi HEA.

The simulated X-ray diffraction patterns for the Al-ordered ordered BCC systems with the three highest Al concentrations (that showed no relaxations to an alternate symmetry) are shown in Figure 2: The peaks normally associated with the BCC phase are highlighted with • symbols and remain for all patterns. A peak at ∼31° is prominent in the pattern with the higher Al content (highlighted with the ∗ symbol). This peak is present in the two systems with lower Al content but the peak is weaker. Wang et al.[9] attribute this peak to the [100] and another peak at ∼55° to [111], peaks that only form in the ordered structure.

When the simultaneous ordering of Al and Ni on two separate sub-lattices is considered, the high Al concentration systems remain BCC in nature for the three higher Al content systems with the two lower Al content phases morphing into the hexagonal system in 30 % of

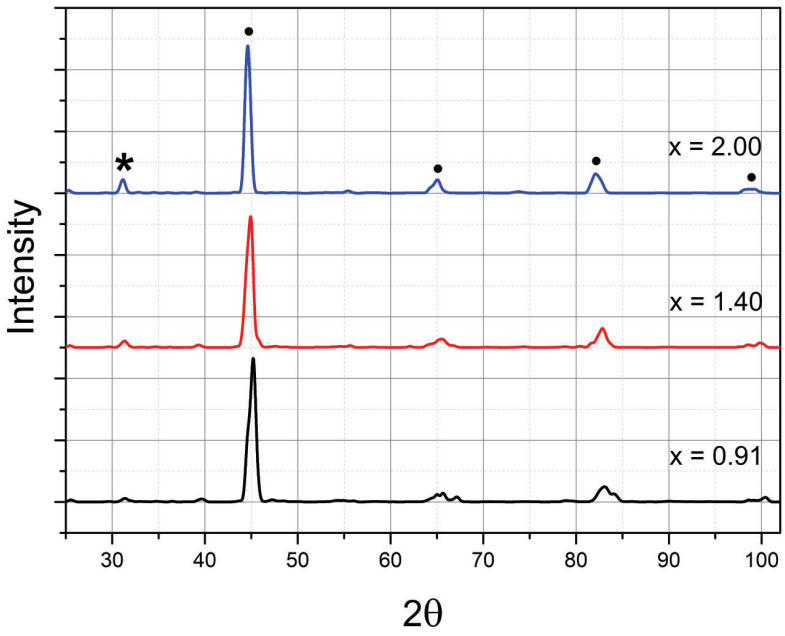

FIG. 2. Simulated X-ray diffraction patterns of BCC $Al_xCoCrFeNi$ with x=0.91, 1.40 and 2.00.

cases (similar to the Al-only ordered systems). The XRD pattern for the highest Al content Al-Ni-ordered system is shown in Figure 3: The compositions with x=1.4 and x=0.9 were similar to the x=2.0 composition, except for the small shift associated with the change in lattice parameter (0.02 Å between x=0.9 and x=2.0). The ordering peak associated with the [100] that was observed in the Al-ordered systems remains in these systems in addition to the experimentally observed peak at ∼55°, which is clearly visible in all of the Ni-Al-ordered systems.

B. Phase stability

The energy of the disordered CoCrFeNi FCC phase, compared to the partially ordered (Cu_3Au-like) phase, is initially considered. It was found that when Fe was ordered (fully occupying the 1a site), the formation energy per atom dropped to ∼0.00 eV, 0.03 eV lower than the fully disordered FCC arrangement. Ni and Cr ordering also lowered the formation enthalpy relative to the fully disordered system by 0.02 eV and 0.01 eV, respectively. The preference in formation enthalpy for the ordered structure, although significant, may be negated by the variation in entropy with temperature. Although vibrational entropy and other forms of entropy will play a role on the phase stability, the configurational entropy is

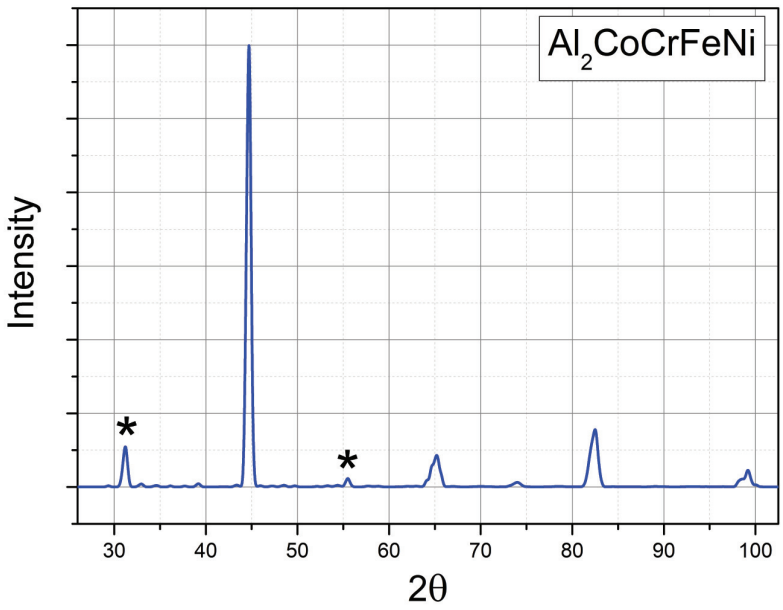

FIG. 3. Simulated X-ray diffraction pattern of BCC $Al_2CoCrFeNi$ with simultaneous ordering of Al and Ni on separate sublattices.

expected to dominate the discrepancy between the fully disordered and the partially ordered phase as other forms of entropy are expected to cancel out between products and reactants to a greater extent.

A δS_{mix}=7.19×10^{19} eV/K/mol was calculated for the fully disordered system while the δS_{mix} for the partially ordered system is 4.28×10^{19} eV/K/mol. The partially ordered system's entropy term was calculated by averaging the configurational entropy over both sublattices (i.e. the completely filled Fe sublattice giving an entropy of 0 eV/K/mol and the disordered Co/Cr/Ni lattice). Combining the enthalpies of formation with the configurational entropy term allows the estimation of the Gibb's free energy. Figure 4 reports the Gibb's free energy variation with temperature for the fully disordered and partially ordered CoCrFeNi system. There is a clear cross-over at ∼600 K indicating a change in preferential formation. At high temperatures the fully disordered high entropy alloy is predicted to be favoured over the partially ordered system.

The ordering we have considered in this work is very basic and there are many other forms of atomic ordering that should be considered including investigating structures with increased periodicity and complexity. It would be foolish to assume that the Cu_3Au structure considered in this work was the most favourable in reality, however, we have shown that an

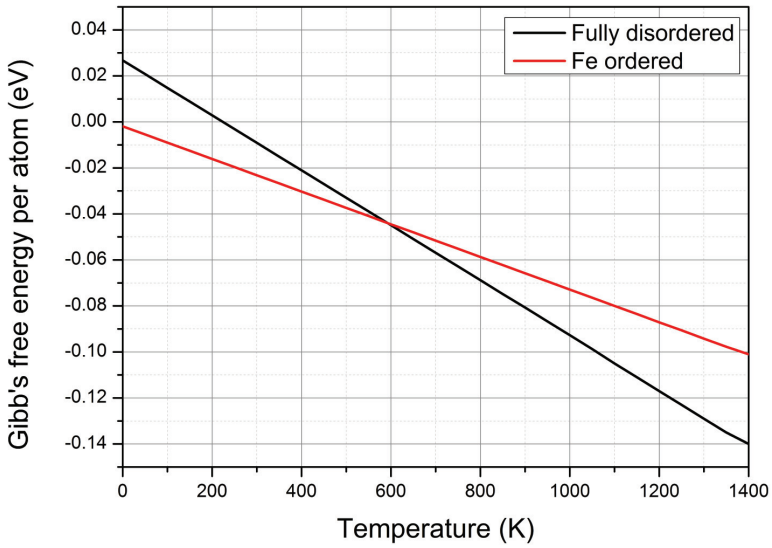

FIG. 4. The calculated variation in Gibb's free energy of the disordered and partially ordered (Fe ordered) CoCrFeNi systems.

ordered structure is more favoured at low temperature, compared to the fully disordered 'high entropy alloy'. Any structure found with a lower enthalpy of formation may still form a completely disordered structure at high temperature (as we predict for the Cu_3Au structure), the transition point may, however, be higher.

Now the formation energy of the Al_xCoCrFeNi phases is investigated. Figure 5 reports the formation energies of the disordered FCC phase and the ordered BCC phases (both Al and Al-Ni-ordered) as a function of Al content. There is a clear change in behaviour associated with increasing the Al content that matches extremely well with experimental observations. Between x=0.57 and x=0.91, the calculations predict that preferred symmetry changes from FCC to an ordered BCC phase and work by Wang et al.[9] observed this transformation to occur between x=0.5 and x=0.9. As the transition is not observed to be very energetically sharp, the formation of a dual phase (FCC and BCC) can be expected (and is experimentally observed).

The enthalpies of formation for the Al-ordered and the Al-Ni-ordered BCC phases were very similar at low Al concentrations (and combined in Figure 5). At higher Al contents there is a notable divergence in stability (although both are more stable that the associated FCC system). The configurational entropy of the Al-Ni-ordered system is similar to the Al-ordered system and the enthalpy difference is large enough to prevent the a predicted

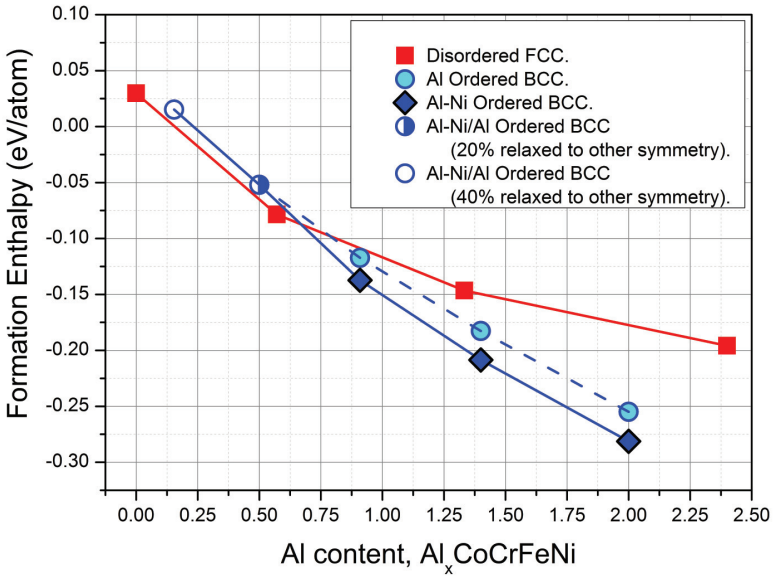

FIG. 5. Variation in formation enthalpy of $Al_xCoCrFeNi$ from the constituent elements. Completely disordered face-centred cubic (red), Al-ordered body-centred cubic (light blue) and Ni-Al-ordered body-centred cubic (blue) are plotted. The values for completely disordered body-centred cubic are not included as the simulation predicted this phase to be unstable at all Al contents.

change in preference between the formation of the systems with temperature.

Some experimental compositions, mainly studying thermally aged compositions, have notable co-segregation of Ni with the Al leaving a Cr-Fe-rich phase[24]. This is briefly investigated by considering the following reaction from the single phase x=1.4 composition forming an Al-Ni-rich and corresponding poor phase in similar stoichiometries to those reported by Wang et al.[24]:

$$Al_{28}Co_{20}Cr_{20}Fe_{20}Ni_{20} \rightarrow \ Al_7Co_{14}Cr_{14}Fe_{14}Ni_5 + Al_{21}Co_6Cr_6Fe_6Ni_{15} \tag{7}$$

The Al atoms are once again limited to the body centred site, maintaining the B2 structure, while the Ni atoms are limited to the other site of the BCC unit cell (providing the additional ordering calculated to be favourable). The energy released as a result of the partition is 0.01 eV per atom meaning a dual phase is stable with regards to the enthalpy of the system. The temperature that we predict the configurational entropy of the single phase to overcome the enthalpy advantage of the dual phase for the x=1.4 composition is 1250 K. Experimental observations by Wang et al.[24] show a dual phase when quenching from 1373 K, therefore our predictions, which do not consider the other forms of entropy, should be treated with caution

(although a transition from single to dual phase can be expected before the melting point at ∼1650 K).

IV. CONCLUSIONS

Ordering of the FCC phase was found to be preferable at lower temperatures; our simulations suggesting a Cu_3Au-type structure with Fe ordering being preferred over Co, Cr and Ni ordering. The XRD-patterns obtained from the simulated supercells match well with experimental data, the ordered systems showing a small ordering peak at ∼36°, not observed experimentally. The transition between ordered and disordered FCC formation was predicted by taking account of the difference in the two systems' configurational entropy. The transition temperature was estimated to be ∼600 K. Other forms of ordering in the CoCrFeNi system may, in reality, be preferred. Future work using a combination of experimental and simulation methods could investigate this. A more stable structure is likely to result in a higher order-disorder transition temperature.

It is clear that the fully disordered BCC system (termed the A2 configuration in other work) is not stable as the geometry optimisation process relaxed >50 % of the simulated structures to $R\bar{3}m$ and $Fm\bar{3}m$ symmetries (amongst others), a result that would be experimentally obvious. This work predicts that for a phase of BCC packing to be stabilised, it is necessary for the system to be partially ordered. Here we have shown that Al occupying a single site of the BCC lattice stabilises the BCC phase and that further ordering of the Ni in the same structure further stabilises the system further. The associated XRD-patterns for the ordered BCC systems match well with experimental results, the Al-Ni-ordered system clearly presenting the two experimentally observed ordering peaks at ∼31° and ∼55°.

The decomposition of the single phase ordered-BCC structure to a dual phase structure was investigated for the x=1.4 composition. The calculations predict that the enthalpy to form a dual phase structure is preferential compared to the single phase structure. When the configurational entropy terms are considered, estimating the Gibb's free energy of the system, a transition temperature of is predicted, above which a single phase structure is expected. This may be related to the observed transition in the hardness of BCC alloys observed by Wang et al[24]. The simulated transition is extremely indistinct (the entropy terms for the single and duel phases are similar) and therefore the error on the temperature

is high and should be treated with some caution.

Importantly, our calculations predict the a transition between an FCC based structure from $0 \geq x \geq 0.75$, to the partially ordered BCC structure with greater Al content. This result closely agrees with the experimentally observed transition from FCC to BCC with Al content in a number of works.

ACKNOWLEDGEMENTS

This research was undertaken with the assistance of resources provided at the NCI National Facility systems at the Australian National University through the National Computational Merit Allocation Scheme supported by the Australian Government. This work was supported by the Multi-modal Australian ScienceS Imaging and Visualisation Environment (MASSIVE) (www.massive.org.au).

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