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# Role of configurational entropy in body-centred cubic or face-centred cubic phase formation in high entropy alloys

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ABSTRACT

This study examines the comparative phase stability of transition and late transition element based high entropy alloys in body-centred cubic (BCC) or face-centred cubic (FCC) forms using a combined classical molecular dynamics and statistical mechanics based approach. Multi-configurational sampling was carried out using a hybrid genetic algorithm-molecular dynamics (GA-MD) based method. The calculations demonstrate that comparative BCC or FCC phase stability is influenced by configurational entropy. The present study also provides a theoretical explanation of the recently reported occurrence of BCC phase in CoCrFeNi HEA, where the high temperature structure may be retained.

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High entropy alloys (HEAs) are a class of multicomponent metallic alloys [1], which exhibit simple crystal structures such as body-centred cubic (BCC), face-centred cubic (FCC), hexagonal cubic phase (HCP) or orthorhombic [2–4] crystal structures. The stabilisation of a solid solution phase over intermetallic and amorphous alloy formation in such multicomponent systems was initially attributed to the high configurational entropy of mixing [5]. The prediction of the comparative phase stability of BCC and FCC phases for HEAs remains a major debate in the literature. For example, CoCrFeNi shows the FCC structure [6], but addition of Al causes its transformation to the BCC crystal structure [6]. The phase transformation and existence of HEAs in two main types of crystal structures was initially rationalised in terms of the conventional metallurgical concept of FCC and BCC stabilising elements [7]. Traditionally, phase stability in alloys has been understood in terms of the number of electrons per atom (*e*/*a*) [8], which has been extensively used for Hume-Rothery electron phase stabilisation. In the case of HEAs, which are mostly composed of transition metals, the accurate determination of the *e*/*a* ratio is problematic. Hence, the valence electron concentration (VEC) has been employed to rationalise FCC and BCC formation, where higher VEC ($\geq 8.0$) leads to FCC phases, while lower VEC ($\leq 6.87$) causes BCC formation, leaving a mixture of BCC and FCC phase for $6.87 \leq \text{VEC} \leq 8.0$ [9]. This criterion, however, does not apply to HEAs containing Mn [10], and in certain cases the effect of cooling conditions dominates the phase formation, i.e., alloys with the same composition but subjected to different processing conditions produce different phase occurrence characteristics [11]. Therefore phase selection remains an open debate. Computationally expensive ab-initio approaches, such as coherent potential approximation [12] and special quasi-random structures with density functional theory (DFT) [13] have been used to study HEAs. Given the potential significance of (configurational) entropy in the phase stability in HEAs, there is a need for an extensive sampling of configurations, which cannot be achieved easily with ab-initio methods that are limited to small cells. The present study attempts to address this issue by a using atomistic simulation with a genetic algorithm (GA) as the sampling strategy followed by a statistical mechanics technique for the calculation of the configurational entropy.

The DL_POLY code was employed to carry out Molecular Dynamics (MD) simulations [14]. Position, velocity and acceleration of the atoms were updated via the velocity-verlet integration algorithm [15]. The GULP code [16] was used to generate $7 \times 7 \times 7$ (FCC) and $9 \times 9 \times 9$ (BCC) cubic supercells for starting configurations. The disordered structures of the alloys were generated by randomising the elements on the lattice sites. The simulations were performed with a 1 fs time-step. The long-range interaction cut-off was set to be 6 Å. The MD simulations were carried out for 10 ps, where the system was equilibrated for first 5000 time steps. The configurational energy was shown to converge over this time (see Fig. A1 in supplementary information). A Nóse-Hoover NPT ensemble with thermostat and barostat relaxation times of 0.01 ps and 0.1 ps, respectively, was used to keep temperature (300 K) and pressure (1 atm) constant. The initial lattice parameters for the BCC and the FCC variant of AlCoCrFeNi, CoCrFeNi and CoCrFeNiTi were taken from first-principle calculations, while for $Al_{0.5}CoCrFeNi$, the equilibrium lattice parameter was calculated from finding the minimum of the energy-volume curve in NVT calculation. The initial lattice

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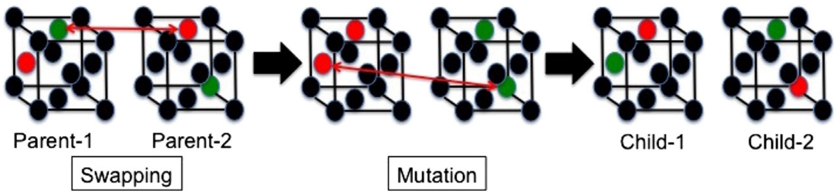

**Fig. 1.** Schematic representation of two-step swapping process for generation of new configurations.

parameters used in MD simulations are tabulated in Table A1 in the supplementary information.

The embedded atom method (EAM) potential for elements (Al, Co, Fe, Ni and Ti) were taken from Zhou et al. [17] and the interatomic potentials of Cr was taken Lin et al. [18]. Although, Lin et al. used a similar parameter model as of Zhou et al., it was found that the parameterisation followed a different rule-set. This resulted in substantial instabilities in the alloys. Therefore, the Cr potential was modified as per ref. [17] (detailed discussion can be found in supplementary information).

Initially, MD calculations on the 2500 randomly generated configurations of each alloy were carried out. It was noticed that energy distribution of these randomly generated configurations did not necessarily follow the Maxwell-Boltzmann distribution suggesting that our distribution did not include many important lower energy configurations. This provided the motivation for the development of the hybrid GA-MD based methodology to ensure the sampling low energy configurations.

The systematic generation of a new configuration of atoms on the lattice is two-step process, as represented schematically in Fig. 1. In the first step, the swapping is carried out between two supercells (Parent-1 and Parent-2) at the same equivalent position (so that child-1 and child-2 inherit certain atomic positions from parent-2 and parent-1 respectively). In next step, the constant composition of the supercell is maintained by the swapping of random positions. This process is repeated randomly for 10–30% of the total number of atoms in the supercell. These children are then used as input configurations for MD simulations. After these simulations are completed the new configurations act as parent configurations for the next generation etc. The selection of parents is performed with reference to their energy, with the probability of selection for a low energy configuration higher than high-energy configurations. This process represents the iterative cycle of two-step swapping-MD calculation-selection of configurations.

It is important to note that, once the energy variation in the population had reached zero (all configurations had the same energy) and the thermodynamic values (such as enthalpy and entropy) had reached a constant value, then further sampling was unlikely to improve the population in terms of finding lower energy configurations. Therefore, this provided the rationalisation to stop the GA-MD cycle.

Fig. 2(a) shows that 61 and 71 generations of GA-MD cycle are required for BCC and FCC variants of $Al_{0.5}CoCrFeNi$ are required to reach the state, when all the configurations have equal energy. For AlCoCrFeNi, the BCC and FCC phases both required 77 cycles. For BCC-CoCrFeNi, 71 generations were required, while 82 cycles were required for the FCC variant. 55 and 56 generations were required for BCC and FCC variants of CoCrFeNiTi, respectively (a pictorial representation of these data can be found in the supplementary material). It should be noted that the BCC variant reaches the state when all the configurations have same energy before the FCC variants in all the cases, which is surprising since the number of atoms simulated in the BCC (1458 atoms) was slightly higher than the FCC (1372 atoms).

Thermodynamic quantities such as, enthalpy ($H$) and Gibbs free energy ($G$) were calculated using the configurational energy ($E_i$) of the atomic configurations, $i$. H can be calculated using Eq. (1) as:

$$H = \frac{\sum_{i=1}^{N} E_i.\, exp\left(\frac{-E_i}{k_B T}\right)}{\sum_{i=1}^{N} exp\left(\frac{-E_i}{k_B T}\right)} \tag{1}$$

where $N$ in Eq. (1) represents the total number of atomic configurations sampled. $k_B$ and $T$ are the Boltzmann constant and temperature respectively.

$G$ can similarly be calculated using Eq. (2), as:

$$G = -k_B T.\, \ln \sum_{i=1}^{N} \exp\left(\frac{-E_i}{k_B T}\right) \tag{2}$$

It should be noted that, as the GA-MD cycle progresses with each generation, the energy values of configurations generated in that particular generation and energy values from prior generations are used are used to calculate the thermodynamic quantities. Therefore as the GA-MD cycle progresses, we are adding further configurations to the thermodynamic average.

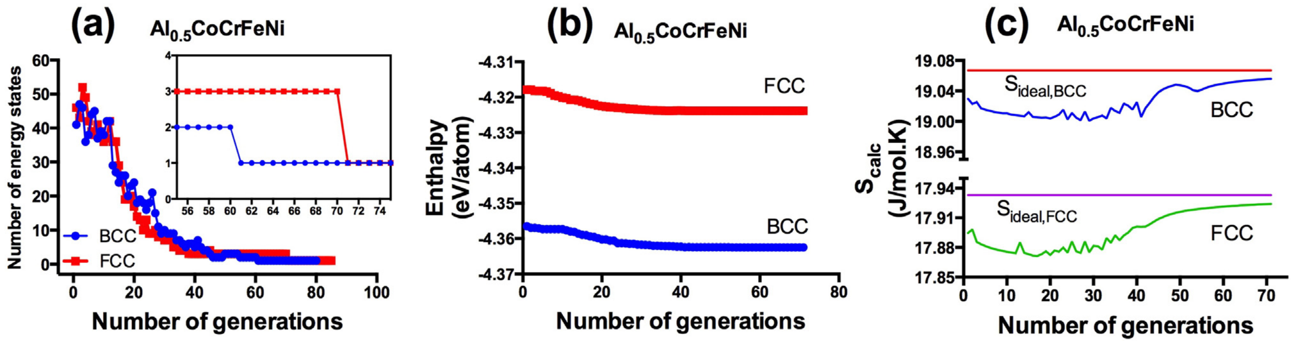

**Fig. 2.** (a): Number of energy states with a unique value, (b) enthalpy and (c) entropy with successive GA-MD cycle.

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