



Full length article

Probing the entropy hypothesis in highly concentrated alloys

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ABSTRACT

High Entropy Alloys (HEAs) designate a class of multicomponent metallic alloys in nearly equiatomic compositions. According to the constituting postulate, a larger number of constituents in a solid solution increases its configurational entropy, which has a maximal value when constituents exist in equiatomic concentrations and this is sufficient to overcome enthalpic contributions between the alloy components which would otherwise favor compound formation or phase separation. This entropy effect would, thus, stabilize disordered, crystallographically simple, solid solutions. Since then, numerous HEA candidate systems have been experimentally studied. It is unclear, however, if, and to which extent, the configurational entropy can be accessed by the system in the way it is suggested. The present work deals with this question using theoretical/computational methods. First, a series of model Body Centered Cubic (BCC) systems involving strong symmetric interactions between unlike atom pairs (referred to as “equinteracting” systems), containing up to five components, is investigated using the Cluster Variation Method in the irregular tetrahedron approximation. The symmetry of interactions, though artificial, allows for the straightforward presentation of phase diagram sections even for quaternary and quinary systems. Next, a “real” HEA candidate system, VNbTaMoW, which presents the BCC structure, is investigated by *ab initio* calculations, allowing to extend the conclusions to a realistic case with asymmetric interactions. The results show that configurational entropy has a small, even marginal, effect on phase transitions and the competition between conflicting interactions in the solid solution (*i.e.* frustration) seems to be the relevant factor behind the observed stabilization in the disordered states in HEA systems.

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1. Introduction

High Entropy Alloys (HEAs), Multi-principal Component Alloys (MCA), or Compositionally Complex Alloys (CCAs)—here we will refer to them uncritically as HEAs—are alloys containing multiple (typically more than four) principal alloying elements that, in contrast to more conventional alloy systems, lie relatively close to the center of the composition space [1,2].

In the early years since the first reports on the now-canonical HEAs based on the CrMnFeCoNi system, it was posited that the apparent remarkable (phase) stability of that and potentially other equiatomic alloys was due to the configurational entropy arising from the mixing of a concentrated solution in a single sublattice. Assuming complete random mixing, such entropy would grow

with the number components, N , as $\Delta S_{mix} = -k_B \sum_i x_i \ln x_i$. The so-called *entropy hypothesis* prescribed alloys consisting of a large number of constituents (typically above 4) at stoichiometric compositions, $x_i = \frac{1}{N} \forall i$, as likely to be rather stable (at elevated temperatures), resulting in microstructures consisting of single phase solid solutions.

We note here that ΔS_{mix} assuming random mixing is nothing but an upper bound to the configurational entropy in a mixture that does not account for short-range-order (SRO) effects (that would necessarily reduce the total entropy in the mixture) or non-configurational entropy sources [3] arising from other thermally-excited degrees of freedom, such as phonons or electrons. While the absolute value of the non-configurational contributors to the entropy of a random solution are high, higher even than the absolute value of the upper configurational entropy bound, what matters is the comparison between these contributions and those for competing phases and in this case the change in non-configurational entropy tends to be rather small. As an example, typically $\Delta S_{non-conf} < k_B$, while $\Delta S_{mix} \sim 1.6k_B$ for an $N = 5$ stoichiometric alloy, assuming comparison with a fully ordered state with

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zero configurational entropy. The configurational entropy is, however, not only used to justify this phase stability, but also to explain other “abnormal” properties these alloys would have. One example is the postulated “sluggish diffusion”, which would affect some of these HEA systems [4].

Regardless of whether single-phase random solid solutions were desirable from the perspective of the properties that could be achieved [5,6] – design specifications for structural alloys always tends towards more compositional and microstructural complexity over time – the vast majority of alloys with equiatomic concentrations synthesized to date have been shown to be rather complex from the phase stability stand point [7]. The lack of correlation between the *maximum* configurational entropy achievable and the existence of stable random solutions over a wide temperature range has led the community to develop other alloy selection guidelines [8–13] to identify regions in the vast multi-composition space that were likely to form stable single phase solid solutions. Needless to say, neither of the rules developed to date have been shown to be effective, when considered alone [14,15]. While it is possible that the lack of sufficient training data impacts the performance of such indicators, there is a more fundamental problem as phase stability is not an intrinsic material property and instead is determined from the competition of multiple phases as defined from the need to minimize, under isothermal/isobaric conditions, the *total* Gibbs energy of the system, subject to mass conservation and other appropriate constraints. Indeed, perhaps the most promising approaches to date when it comes to exploration of the HEA alloy space have been based [16,17] on so-called CALPHAD approaches towards predictive phase stability.

Entropy maximization alone will never define equilibrium in a material system (except for when the system itself is isolated from the rest of the universe), although the quantification of entropic contributions to the Gibbs energy of a phase is a necessary condition towards an understanding of the competition towards equilibrium with other phases. While the topic of the accelerated exploration of the HEA phase stability space is important – one of the present co-authors and collaborators has already presented a promising approach [18,19] – this work instead focuses exclusively on exploring the so-called *entropy hypothesis* in HEAs.

Specifically, we propose to use a well understood theory – the Cluster Variation Method in the irregular tetrahedron approximation (CVM-IT) – to probe in an explicit manner the different contributions to phase stability in model multi-component systems of $q = 3, 4$ and 5 constituents (in what follows, the symbol q will be employed to designate the number of components in the system). The CVM-IT model is applied on a BCC-lattice with symmetric positive and negative interaction parameters between unlike atoms (henceforth designated “equinteracting systems”). The CVM-IT approximation is then used to examine the relative effects of entropy and enthalpy on the competition between phase separated/ordered states and disordered single phase solid solutions. In a later part of the work we employ the proposed framework on the V – Nb – Ta – Mo – W system,² which has already been investigated both theoretically [20,21] and experimentally [22,23], since this constitutes the basis of potentially promising so-called Refractory Concentrated Alloys (RCAs). Here we use DFT-based calculations to estimate the CVM interactions in the (VNbTaMoW) BCC lattice and then proceed to investigate its phase stability at finite temperatures within the CVM-IT theoretical formalism. In particular we will also investigate the thermodynamics of diffusion in this alloy, to verify if

this could justify the so called “sluggish diffusion” effect.

In the remaining of the present paper we will provide some short review of prior related work, present the CVM framework, the alloy theoretic results with model systems and proceed to apply the CVM framework to the V – Nb – Ta – Mo – W BCC RCA system. We will then provide some discussions on the general outlook on the implications of the present work to studies of intrinsic thermodynamic properties of concentrated mixtures, synthesizing the results.

2. Prior experimental and theoretical work on the entropy of HEAs

Singh et al. [24] used an electronic-structure based thermodynamic theory of the Short Range order (SRO) in disordered substitutional single phase solid solutions with the objective of probing its electronic origin. Their formalism allowed them to interpret SRO within a concentration-wave framework and through the use of KKR-CPA-based electronic structure methods they were able to investigate the SRO in the AlCoCrFeNi system. The Korringa-Kohn-Rostoker (KKR) is a theoretical framework to solve the electronic structure of a lattice occupied by different atomic species. Combined with the Coherent Potential Approximation (CPA), the KKR-CPA enables a mean-field technique to address the assemble average of disordered systems. Khan et al. [25] also used the KKR-CPA formalism to investigate a series of concentrated alloys. Their formalism provided a framework to derive the free energy of a system with arbitrary fluctuations in site occupancies, again within the concentration wave framework.

Ma et al. [26] introduced the so-called Cluster-plus-glu-atom (CPGA) model to describe solid solutions with SRO. The CPGA model was initially developed to examine topological and chemical SRO in amorphous and quasicrystalline alloys and consists of describing a system as consisting of a 1st-neighbor coordination polyhedral cluster plus a chemical environment termed “glue atoms”. This model was used by Ma et al. to investigate two Al-containing HEAs based on the NiCoFeCr system. Notably, using different variants of the CPGA model for FCC lattices, the authors were able to reproduce satisfactorily the pair distribution functions (PDFs) for the first two coordination shells as measured by neutron scattering experiments. Addition of Al was shown to de-stabilize the FCC lattice, with the CSRO parameters involving Al-TM (transition metal) interactions eventually de-stabilizing the FCC lattice in favor of BCC-like atomic environments. Wang et al. [27] also used the CPGA model to examine SRO in WMoTM₁TM₂ (TM = Ta, Nb, V) BCC RCAs.

On the experimental front, several groups have recently focused on probing the local structure and SRO in concentrated solid solutions. Zhanget al. [28] used x-ray total scattering and extended x-ray absorption fine structure (EXAFS) techniques to examine SRO behavior in NiCoCr alloys. While PDF analysis for this system did not show any noticeable local lattice distortion induced by chemical disorder, EXAFS analysis revealed SRO involving Cr-Ni/Co interactions. Tong et al. [29] used a similar approach to investigate SRO in FeCoNiCrPD HEA, showing a moderate degree of local lattice distortion as inferred from PDF analysis.

Virtually all theoretical/experimental attempts to probe the nature of the solid solutions in HEAs have focused on characterizing the SRO. SRO itself is important as its presence limits the total configurational entropy in a solution phase. Probing directly the so-called *entropy hypothesis* requires the explicit calculation of the configurational entropy. Few works have addressed this issue directly in HEAs. Widom's work [30] is the exception as he recently used a combination of Monte Carlo and Molecular Dynamics to examine the diffuse scattering and entropy evolution in NbTiVZr

² The order of presentation of the elements in a HEA is somewhat arbitrary, in the present work we will adopt the natural order corresponding to the periods in the periodic table of the elements.

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