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I. Toda-Caraballo¹, Jan S. Wróbel², Duc Nguyen-Manh³,
Pablo Pérez⁴ and P. E. J. Rivera-Díaz-del-Castillo⁵

¹ *Materialia Group - ⁴ Manoeq Group / Physical Metallurgy Dept., National Centre for Metallurgical Research (CENIM-CSIC), Av. de Gregorio del Amo, 8, 28040 Madrid, Spain*

² *Faculty of Materials Science and Engineering, Warsaw University of Technology
ul. Woloska 141, 02-507 Warszawa, Poland*

³ *Culham Centre for Fusion Energy, United Kingdom Atomic Energy Authority, Abingdon,
Oxfordshire, OX14 3DB, United Kingdom*

⁵ *Dep. of Engineering, Univeristy of Lancaster, Lancaster, Engineering building, Lancaster
University, LA1 4YW, United Kingdom*

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I. Toda-Caraballo^{*,1}, Jan S. Wróbel², Duc Nguyen-Manh³,
Pablo Pérez⁴, & P. E. J. Rivera-Díaz-del-Castillo⁵

¹ Materialia Group - ⁴ Manoeq Group / Physical Metallurgy Dept., National Centre for Metallurgical Research (CENIM-CSIC)
Av. de Gregorio del Amo, 8, 28040 Madrid, Spain

¹ E-mail: isaac.toda@cenim.csic.es, ⁴E-mail: zubiaur@cenim.csic.es

² Faculty of Materials Science and Engineering, Warsaw University of Technology
ul. Wołoska 141, 02-507 Warszawa, Poland
E-mail: jan.wrobel@inmat.pw.edu.pl

³ Culham Centre for Fusion Energy, United Kingdom Atomic Energy Authority
Abingdon, Oxfordshire, OX14 3DB, United Kingdom
E-mail: Duc.Nguyen@ukaea.uk

⁵ Dep. of Engineering, Univeristy of Lancaster
Lancaster, Engineering building, Lancaster University, LA1 4YW, United Kingdom
E-mail: p.rivera1@lancaster.ac.uk

Corresponding author: *I. Toda-Caraballo*^{*,1} E-mail: isaac.toda@cenim.csic.es. Tel: +34 915538900 ext. 354

Abstract

High Entropy Alloys (HEAs) is a fascinating field of research, with an increasing number of new alloys discovered. This would hardly be conceivable without the aid of materials modeling and the computational alloy design to investigate the immense compositional space. The simplicity of the microstructure achieved contrasts with the enormous complexity of its composition, which, in turn, increases the variety of property behavior observed. Simulation and modeling techniques are of paramount importance in the understanding of such material performance. There are numerous examples of how different models have explained the observed experimental results; yet, there are theories and approaches developed for conventional alloys, where the presence of one element is predominant, that need to be adapted or re-developed. In this paper, we review of the current state of the art of the modeling techniques applied to explain HEAs properties, identifying the potential new areas of research to improve the predictability of these techniques.

Keywords: High Entropy Alloys, Physical base modeling, Alloy Design, Simulation

Introduction

A traditional alloy design may undergo several iterations to obtain the desired engineering properties [1] and it can take months or even years to optimize its performance. The computational alloy design paradigm is intended to aid in the discovery of novel alloys (or the improvement of existing ones) by describing the microstructure and properties of metallic materials. It replaces the trial-and-error methodology, accelerates the discovery of new materials and dramatically decreases the time, effort and cost of developing new alloys. This is even more crucial in the design of new High Entropy Alloys (HEAs), since the number of compositions having the potential to be a single fcc or bcc solid solution is enormous [2]. This large number of HEAs, is in turn an infinitesimal fraction of all possible combination of elemental mixtures in multicomponent alloys.

In order to analyze such vast compositional space, the use of models and simulations have permeated rapidly in this field, making use of existing techniques and approaches, or adapting and developing new ones. Atomistic simulations

[3, 4, 5, 6, 7], computational thermodynamics [8, 9, 10], lattice distortion description [11, 12, 13], microstructural prediction [14], mechanical properties modelling [15, 16, 17], selection criteria [18, 19, 20, 21, 22, 23], statistical analysis [1] and neural networks combined with optimization techniques such as genetic algorithms [24] applied to multicomponent alloys have combined their efforts to successfully cast and produce new HEAs [25, 26, 27, 28, 29, 30], to cite some of them.

The benefit of using such methods is proven; but there are still many unknowns and unexplored approaches which bring an imperative necessity of developing theories and efficient methodologies to increase the accuracy of the multicomponent properties prediction. The combination of them is of paramount importance to produce robust alloys and scale up the materials produced from the laboratories into industry. This paper explores the current state of the art of different models applied to the design of HEAs and aims at identifying the future challenges in this field. The degree of specialization of the models are such the reader is invited to visit the original references cited for a more detailed expla-

nation.

Key parameters and datamining modeling

Prior to the discovery of HEAs, an experienced metallurgist would predict a microstructure with intermetallics at mixing several elements in similar content. What it is found instead, in some cases, is a single fcc or bcc structure (hcp is also possible but rarely obtained). Physical metallurgy concepts have been reviewed during the last decade to predict this phenomenon. This section describes the modeling efforts to understand how different parameters and approaches can be used to predict HEAs formation.

The first challenge in designing a HEA is to obtain a single phase in solid solution in a multicomponent alloy (two-phases in solid solution is usually frequently considered also a HEA). One of the first approaches to identify which mixtures of elements would potentially produce a single solid solution [18] was adapted from a bulk metallic glasses approach, where it is suggested which atoms are different enough to form a disorder structure. This is done via the parameter δ , the atomic size mismatch, and the use of Miedema's model to estimate the enthalpy of mixing ΔH_{mix} [18]. The combination of these two parameters showed some ability to propose compositions potentially leading to produce a HEA, and more efficiently, which combinations will not produce a HEA. The use of other thermodynamic criteria, μ [19] or Ω [22], or parameters related to atomic characteristics such as electronegativity, valence electron concentration [20], bulk modulus and interatomic spacing mismatches [23] have added higher degree of credibility at proposing new compositions. For detailed description and physical meaning of these parameters, a comprehensive review on HEAs modeling can be found at [31]. The common technique in these selection criteria is to propose a parameter that it is known to be involved in the thermodynamic behavior of alloys, and compare its performance with a database populated with multicomponent alloys, showing then its applicability.

These *ad hoc* selection criteria are usually employed to confirm if a specific composition lies inside their limits. If it fails, it is discarded and another one is considered. Successful examples of produced HEAs using the selection criteria methodology, from lightweight to refractory HEAs, can be found at [21, 32, 33, 34, 35]. Their performance is nevertheless limited, although difficult to measure, since the unsuccessful alloys produced may not be completely reported in the literature.

The range of available information so far in the literature for multicomponent alloys, which was used to develop the selection criteria, is in the range of ~ 500 different compositions. It has been mostly gathered at [2, 19, 20, 23, 33, 36, 37], where a visual representation of their families using clustering techniques can be seen at [23]. By using these databases (and forthcoming new compositions), more selection criteria may be developed in the future, but the expected impact on alloy design will probably be in the same range of the existing criteria. Their main advantage is the extremely fast calculation and availability of the informa-

tion of parameters involved, which allows exploring millions of compositions.

It has been proven that using statistics and machine learning techniques to combine the predictability of these criteria, produces more robust approaches to design new HEAs. One of the first successful applications of statistics has been at predicting and developing both single and multiple phases at [25] by using a Principal Component Analysis (PCAs), firstly proposed at [1]. With this technique, the information of several properties (the parameters of the selection criteria in this case) is combined in a new set of variables, called the Principal Components, which gather the maximum variance (direction of maximum information). In this way, properties with some degree of correlation, ΔH_{mix} and Ω for instance, cooperate to refine the information they can provide, while the properties with no correlation, such as ΔH_{mix} and valence electron concentration, re-define the parametric areas where solid solutions can be potentially found. The use of clustering techniques is also useful in data processing [38] which allows at classifying and showing trends in databases for properties prediction. They can be combined with PCAs to better analyze compositional areas of interest.

In a further step, the use of neural networks (NNs) in combination with an optimization algorithm, such as a genetic algorithm, that searches the compositions lying in several of the criteria (or all of them, ideally) is more efficient at using computational resources and exploring a much wider compositional space. Examples of its use in commercial alloys can be found elsewhere [39]. At [24], the selection criteria was combined with predictions on density and solid solution hardening effect to proposed HEAs with enhanced mechanical properties. The necessity of using multi-objective optimization technique is due to the fact that some parameters and properties work in opposite directions. For instance, ΔH_{mix} approximates to 0 when δ decreases, while having a low δ and a very negative ΔH_{mix} is desirable to obtain a solid solution. The stability of such solid solution is in turn decreased if the solid solution hardening effect increases. The challenge in this technique is to find the equilibrium to obtain a HEA with interesting combination of properties, when some of them are somehow inversely correlated. An obvious limitation of using machine learning is that the computational cost of each of the individual criteria and models should be small, to allow the method provide predictions in a reasonable time frame.

On the other hand, the use CALPHAD and computational thermodynamic calculations instead, provides a direct calculation of the Gibbs free energy, which controls phase stability. As in the previous methodologies, CALPHAD approach is also based on databases and available data. The accuracy of its prediction goes concomitantly with the experimental cost of obtaining such information. It is evident that in the field of HEAs, the use of CALPHAD is still far to be competitive with the level of confidence of predictions on steels, Ni-, Al- or Ti-alloys, for instance. Although commercial databases can handle multiple elements with accuracy, which would be convenient to the design of HEAs, they are mainly focused on corners of phase diagrams, with one

principal element. They have already been used to produce successfully new HEAs with good stability [40, 41, 42].

Nevertheless, there are clear indications that the information of binary and some ternary systems is not sufficient to predict the behavior of a multicomponent alloy [43], although all its sub-systems were accurately predicted. Also, the presence of vacancies should be also evaluated in multicomponent alloys [44], which may differ from low-order systems. The calculation of the different entropic contributions, such as the configurational and vibrational entropy, and more recently the magnetic entropy [4] has to be also included for a good prediction of the overall effect of entropy [45]. In this direction new databases for multicomponent alloys have successfully created, providing new tools for alloy discovery [46, 9, 8] in addition to the commercial new developed ones.

Additionally, kinetics of phase transformation is in general well known, but it has been assumed that elements show a much lower diffusivity in multicomponent alloys [5], which will dramatically affect the kinetics of transformation. Studies on HEAs showed [47], nevertheless, that classical kinetics can be applied to HEAs, where the assumed low diffusivity of elements does not play an important role in modifying such approach. Some time-temperature-transformation diagrams have showed that, for instance, B2-phases can form very quickly in a fcc environment, which supports normal-type diffusivity [48]. A deeper analysis on this matter is highly demanded and will definitely provide the tool for control processing routes to obtain the desired microstructure.

Diffusionless transformations are also a key point in alloy design. For instance, the knowledge of stacking fault energy (SFE) is of paramount importance at controlling martensitic transformation, where recent works have provided tools to model this transformation [49]. The calculation of SFE is not an easy task, where two main techniques can be used to predict the SFE. One is the use of the Olson and Cohen model [50] which has shown efficiency at predicting SFE specially in austenitic steels, and the other is the use of atomistic calculations [51], usually employing density functional theory (DFT) method since the availability of accurate potentials is limited, combined with the Axial Next Nearest Neighbor Ising model (ANNNI). Some successful works have proved the use of this methodology in HEAs [52]. Nevertheless, the SFE accuracy required to control the transformation is difficult to achieve due to the large amount of different atomic configurations to be considered, on top of the magnetic contribution to atomic volume and energy, specially if Cr is involved due to its anti-ferromagnetic effect.

DFT and atomistic simulations provide an invaluable tool to examine new compositional areas of interest from the thermodynamic point of view, since it gives proper support to many areas of research on thermodynamics of HEAs. Although the computational cost can be extreme, it shows clear advantages to expand the cited thermodynamic databases, consider the effect of vacancies or calculate energies, for instance. This is discussed in next section

Atomistic modeling: DFT and thermodynamics

The previous section describes the approaches where prior experimental knowledge is used to predict unexplored compositional areas to obtain HEAs. The use of DFT instead provides the possibility of predicting thermodynamic behaviour of multicomponent alloys without such previous experimental information. Although this involves a high computational cost, it adds an immense amount of information to the thermodynamic behaviour of this alloys. In this section, an overview of the use and capabilities of DFT applied to the thermodynamics of HEAs is introduced. The main equations and the parameters more relevant for property predictions are presented.

According to the basic thermodynamic equation of state the free energy of formation of an alloy is given by:

$$F_{form}(T) = H_{form}(T) - T(S_{conf}(T) + S_{vibr}(T) + S_{elec}(T) + S_{mag}(T)) \quad (1)$$

where $H_{form}(T)$ is the enthalpy of formation, $S_{conf}(T)$, $S_{vibr}(T)$, $S_{elec}(T)$ and $S_{mag}(T)$ are the configurational, phonon, electronic and magnetic entropies, respectively. At higher temperatures, the product $TS_{conf}(T)$ for a disordered alloy is larger than for an ordered alloy, like for example an intermetallic phase. The disordered structures of multicomponent HEAs possess significantly larger configurational entropy in comparison with the traditional alloys, for example for equimolar 5-component solid solutions S_{conf} reaches the value of $1.61 R$, where R is the gas constant, which could even maintain the solid solution stable at relatively low temperatures. The other entropy terms have a significantly smaller influence on the stability of alloys, especially in the case of non-magnetic systems. Even though the vibrational entropy is bigger than the configurational one, the vibrational entropy difference between two structures is usually not larger than approx. $0.2 R$, which means that it is an order of magnitude smaller than the maximum configurational entropy difference between ordered and disordered structures of HEAs [2, 53]. The excess of magnetic contribution to entropy between solid solution and ordered phases is also believed to be smaller than the configurational one [54]. However, this small contribution of excess magnetic entropy can play an important role in the phase stability of multi-component alloys. For example, the magnetic excitations stabilize the fcc phase of Fe and the austenitic Fe-Cr-Ni alloys in a comparison with ferritic bcc phase [55, 3]. In multi-principal Co-Cr-Fe-Ni alloys, there are experimental observations of a distinct magneto-volume coupling. This effect can be explained theoretically that the ordered fcc CoCrFeNi phase possesses larger magnitudes of magnetic moments and consequently a larger volume per atom than the corresponding disordered phase [56].

Both the enthalpy of formation and the configurational entropy can be investigated using the Cluster Expansion (CE) method, where the effective interactions between different kind of atoms are determined from the number of ab-

initio calculations, combined with Monte Carlo (MC) simulations. In the CE formalism the enthalpy of mixing of a binary or multicomponent alloy is defined in the form of Ising-like Hamiltonian as

$$\Delta H_{CE}(\vec{\sigma}) = \sum_{\omega} m_{\omega} J_{\omega} \langle \Gamma_{\omega'}(\vec{\sigma}) \rangle_{\omega} \quad (2)$$

where an atomic configuration is specified by a vector of the configurational variables $\vec{\sigma}$. The summation is performed over all the clusters ω distinct under group symmetry operations of the underlying lattice. The parameters m_{ω} are multiplicities indicating the number of clusters equivalent to ω by symmetry, J_{ω} are the effective cluster interaction parameters (ECIs) and $\langle \Gamma_{\omega'}(\vec{\sigma}) \rangle$ are the cluster functions defined as products of point functions of occupation variables on a specific cluster averaged over all the clusters ω' that are equivalent by symmetry to cluster ω .

ECIs can be obtained from DFT using either the structure inversion method (SIM), based on the Connolly-Williams approximation [57], or the coherent potential approximation used in combination with the generalized perturbation method (CPA-GPM) [57]. In SIM, applied in this study, energies are computed using DFT for a series of ordered structures, the cluster functions are calculated for these structures and a set of linear equations is constructed, from which the unknown ECIs can be obtained through least-squares fitting. The exchange MC simulations with ECIs obtained from DFT enable to investigate the enthalpy of mixing ($H_{mix}(T)$) and enthalpy of formation ($H_{form}(T)$) that are defined as the energy of a structure in reference to the energies of pure elements underlying the same lattice and the energy of these elements in their ground states, respectively. The configurational entropy, which is the key parameter responsible for the formation of disordered high entropy alloys, can be calculated from MC simulations using the equation:

$$S_{conf}(T) = \int_0^T \frac{C_{conf}(T)}{T} dT \quad (3)$$

where the configurational contribution to the specific heat is C_{conf} is related to fluctuations of enthalpy of mixing at a given temperature [55, 58] through

$$C_{conf}(T) = \frac{\langle H_{mix}(T)^2 \rangle - \langle H_{mix}(T) \rangle^2}{T^2} \quad (4)$$

where $\langle H_{mix}(T) \rangle$ and $\langle H_{mix}(T)^2 \rangle$ are the mean and mean square average enthalpies of mixing, respectively, computed by averaging over all the MC steps at the accumulation stage for a given temperature.

As an example of the method capabilities, the configurational entropies for the equimolar four- and five-component alloys in Mo-Nb-Ta-V-W system obtained from MC simulations are shown in Figure 1(b). In the high-temperature limit they approach the values of configurational entropy of ideal random solid solution $S_{random}(T) = -k_B \sum_i c_i \ln(c_i)$ where c_i is the concentration of i -th element and k_B is the Boltzmann constant.

It is important to note that the calculated S_{conf} varies as a function of temperature. For example, for the alloys in

Mo-Nb-Ta-V-W system, it decreases rapidly below temperature ~ 1000 K. It means that the configurational entropy of these alloys can be approximated by the value for ideal random solid solution only at relatively high temperatures. The profiles at Figure 1a) show that the fast increase regime of $S_{conf}(T)$ varies with composition. This is related to the fact that for these alloys the temperatures of ordering between pairs of atoms appear at different temperatures. With the decrease of temperature, the largest decrease of $S_{conf}(T)$ possesses the Mo-Nb-Ta-V alloy whereas the smallest one is observed for Mo-Nb-Ta-W and Mo-Nb-V-W alloys. Similar results were obtained by Widom in his review of atomistic simulations applied to HEAs [31]. For the quaternary Mo-Nb-Ta-W alloy, using special quasi-random structures (SQS), a fast decaying S_{conf} below ~ 1000 K, and very close values to ideal S_{conf} of a random solid solution at temperatures higher than 1200 K, are also observed.

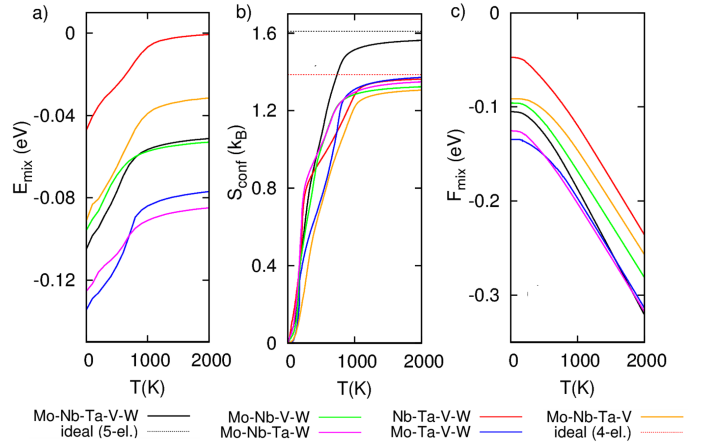


Figure 1: a) Enthalpy of mixing, b) configurational entropy and c) free energy of mixing of the quinary and quaternary equimolar alloys in the Mo-Nb-Ta-V-W system as a function of temperature.

The configurational entropies have a clear impact on the free energies of mixing. For example, at 2000 K the enthalpy of mixing of the equimolar five-component alloy is higher than the enthalpies of some equimolar four-component alloys, whereas the five-component alloy is the most stable one according to the criterion of free energy of mixing, as observed in Figures 1a)c).

Chemical ordering in alloys can be investigated by analysing Warren-Cowley short-range order (SRO) parameters. For atoms i and j being in the n -th nearest neighbor shell in either binary or multicomponent alloys they can be defined as:

$$a_n^{ij} = 1 - \frac{y_n^{ij}}{c_i c_j} = 1 - \frac{P_n^{i-j}}{c_j} \quad (5)$$

where c_i and c_j are the concentrations of i 's and j 's atoms, and $P_n^{(i-j)} = (y_n^{ij})/c_i$ is the conditional probability of finding atom i in the n -th coordination sphere of atom j . As in the binary alloy case, segregation gives rise to positive a_n^{ij} , a negative value of a_n^{ij} indicates ordering, and the values of

a_n^{ij} close to zero mean that there is no (positive or negative) preference for a given atom to be surrounded by atoms of any other type. SRO parameters can be expressed also in terms of average point and pair correlation functions. The analytical formulas for SRO parameters in quaternary and quinary alloy are given in [59].

The SRO parameters between pairs of atoms in the 1st nearest neighbour (1NN) and 2nd nearest neighbour (2NN) coordination shell obtained from MC simulations for equimolar Mo-Nb-Ta-V-W alloy as a function of temperature are shown in Figures 2a)b).

The strongest chemical ordering is observed for Mo-Ta pairs of atoms. Their SRO parameters in the first and second coordination shells are the most negative and the most positive, respectively, of all considered SRO parameters in Mo-Nb-Ta-V-W alloys. This indicates a strong probability of having Ta atoms around a Mo atom in the 1NN coordination shell and the same chemical species, Mo-Mo or Ta-Ta, in the 2NN coordination shell. As a consequence, such SRO parameters favor the formation of Mo-Ta B2 phase in the Mo-Nb-Ta-V-W alloy. Another strong chemical ordering in the five-component alloy is visible for V-W pairs of atoms. In that case the SRO parameters are strongly negative both in the 1NN and 2NN coordination shell. This indicates the presence of unlike V-W pairs in the alloy. Finally, strongly positive SRO parameters in both 1NN and 2NN shells are observed for V-Ta and V-Nb pairs, which shows that V atoms in the considered alloy repel Ta and Nb atoms.

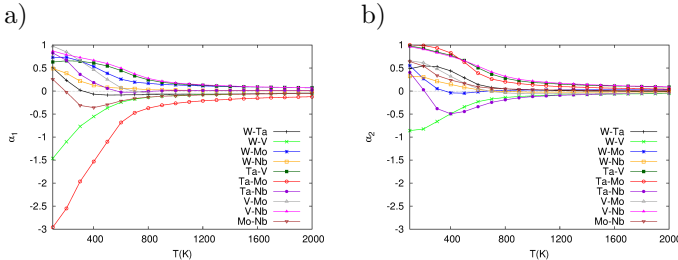


Figure 2: Enthalpy of mixing (a) and free energy of mixing (b) of the quinary and quaternary equimolar alloys in the Mo-Nb-Ta-V-W system as a function of temperature.

Magnetic properties and magnetic entropy of alloys can be investigated using Magnetic Cluster Expansion (MCE) method in which additional magnetic interactions have been included. The MC simulations using MCE parameters enabled to investigate the Curie, Neel and structural phase-transition temperatures in magnetic binary and ternary alloys [55, 3, 60].

Since the above CE and/or MCE methods are conventionally developed within the underlying lattice (bcc or fcc), it is not easy to use them for investigating the presence of complex phases present in HEAs such as the phase in CrMnFeCoNi as it has been recently observed experimentally [61]. The phase stability between simple (fcc and/or bcc) and complex phases can be analysed by using the Rigid Band Approximation (RBA) combined with the frozen potential approach [61]. For magnetic alloys, the RBA model

can be generalised using the Stoner model of magnetism. The energy difference between two magnetic structures can be given by:

$$\Delta E^{(1-2)} \approx \Delta E_{Spin-Band}^{(1-2)} + \frac{1}{4} [I_{eff}^{(1)} m_{av}^{2(1)} - I_{eff}^{(2)} m_{av}^{2(2)}] \quad (6)$$

where the first term is related to the spin-polarised band energy difference and the second term is the double-counting contribution coming from magnetic interactions, which is calculated from the effective Stoner parameters, I_{eff} , and the average atomic magnetic moments, m_{av} , of considered structures. Both terms can be computed as a function of valence electron concentration, n , from the spin-polarised densities of states of considered phases. For example, as shown in Figure 3 the region of stability of sigma phase is for n values between 5.3 and 7.6, where $\Delta E^{(\sigma-bcc)}$ is negative and smaller than $\Delta E^{(fcc-bcc)}$ [4].

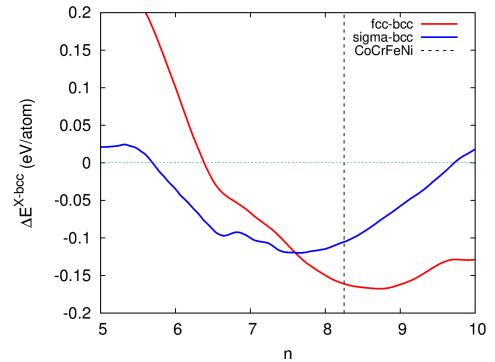


Figure 3: The magnetic energy difference, $\Delta E^{(X-bcc)}$ ($X = \text{fcc}, \sigma$), of CCFN-based alloys as a function of valence electron concentration, n [4].

The knowledge that this method can provide is of paramount importance and it could complete the experimental thermodynamic databases where they lack of information.

Molecular Dynamics modeling and interatomic potentials

A molecular dynamics (MD) simulation is not generally intended to model thermodynamics within the scope of HEAs. The existence of interatomic potentials capable to model phase transition in such mixture of elements is limited. Nevertheless, MD simulations are very useful at providing information of the crystal behaviour, their atomic coordinates and stress fields. This is particular useful since, in general, the HEAs are characterized not only by high values of entropy but also by high atomic-level stresses originating from mixing of elements with different sizes. Therefore, there are still many fundamental questions that need to be addressed to understand local atomic structure in the terms order and disorder of HEAs. Each element in HEAs will tend to occupy the position that minimizes its site energy and bond energies which in turn depend on preferred local chemical

environments, inter-atomic interactions and atomic volumes of different constituent species.

In order to perform MD simulations on HEAs, one needs various models of total energy and interatomic force calculations which can describe not only fcc, bcc, hcp structures of elements but also intermetallic phases in multi-component alloys. There is some physical model of interatomic forces which may be based on something as simple as a pair interaction, such as the Lennard Jones model, or as complex as self-consistent, all-electron solution from the quantum mechanical problem [62]. In the Ab-Initio Molecular Dynamics (AIMD) scheme, due to the treatment of the electronic degrees of freedom including spin-polarization within DFT calculations, the computational cost is far higher than classical dynamics. The Bond-Order Potentials (BOP) model [63, 64] based on the chemically intuitive tight-binding approximation to the quantum mechanical electronic structure, is a bridging scheme between AIMD and classical MD in describing interatomic forces of large and complex systems including magnetic ones [65]. During the last three decades the most commonly used have been central-force many-body potentials, in particular, Finnis-Sinclair (FS) potentials [66], embedded-atom method (EAM) [67] or modified EAM (MEAM) potentials [68]. Note that a magnetic version of FS potentials has also been proposed for molecular dynamic simulations in iron [69] but it is really challenging to develop magnetic potentials for HEAs due to quantum mechanical description of electron spins. For that, as far as we are aware from literatures, only non-magnetic EAM potentials have been used to perform MD simulations for equiatomic multi-component Co-Cr-Ni systems [70] while MEAM interatomic potentials constructed for binary systems were being used for describing HEAs CrCoFeMnNi [71].

To theoretically determine the distribution of nearest neighbor distances between atoms of different species in HEAs, multibody interatomic potentials derived from DFT are desirable for accurate prediction in the order of pm over all the compositions and temperatures considered. The average value of interatomic distances between atom species i and j can be determined by matrix $S(\{s_{ij}\})$ which is related to the mean interatomic spacing in multi-component alloys s_{ij} by frequency of occurrence of each i - j interactions, U_{ij} . In general, the total potential energy of considered system is written as

$$U_{lat} = \frac{1}{2} \sum_{i=1}^n \sum_{j \neq i}^n U_{ij} \quad (7)$$

where n denotes the number of components in HEAs. In order to analyze the dependence of lattice spacing distribution in HEAs on the atomic bonding for any compositions X_i and X_j of element i and j , respectively, the potential for the binary system can be modeled from potential energies of pure elements, U_{ii} and U_{jj} , as

$$U_{ij} \approx X_i U_{ii} + X_j U_{jj} \quad (8)$$

where the energy dependence on lattice parameter of pure elements can be obtained from DFT calculations. Using (7), the total potential energy (6) of n -component alloy in solid solution reads

$$U_{lat} = \sum_{i=1}^n X_i U_{ii} \quad (9)$$

Locally, the behavior of lattice potentials for multi-component alloys around their corresponding equilibrium positions is approximately quadratic. This stems from the elastic properties of the corresponding pure elements where the equilibrium interatomic distance a_{ii} and bulk modulus K_{ii} are well-known from DFT or experimental data. The element of matrix $S(\{s_{ij}\})$ can be then computed by the following formula [11]:

$$S_{ij} = f \frac{K_{ij} a_{ij}^2 + K_{lat} a_{lat}^2}{K_{ij} a_{ij} + K_{lat} a_{lat}} \quad (10)$$

where $f = (\sqrt{3})/2$ for bcc and $f = (\sqrt{2})/2$ for fcc lattice. The lattice cell parameter, a_{lat} , the lattice bulk modulus for multi-component alloys are determined, respectively, by

$$a_{lat} = \frac{\sum_{i=1}^n X_i K_{ii} a_{ii}^2}{\sum_{i=1}^n X_i K_{ii} a_{ii}} \quad (11)$$

and

$$K_{lat} = \frac{(\sum_{i=1}^n X_i K_{ii} a_{ii}^2)^2}{\sum_{i=1}^n X_i K_{ii} a_{ii}^2} \quad (12)$$

Fig. 4 shows the calculated S matrix by Eq. (9) versus the S'DFT obtained from the relaxed DFT calculations for 128-atom relaxed configurations generated by applying Special Quasi-Random Structures (SQS) for equiatomic quinary bcc alloys Mo-Nb-Ta-V-W as well as for the corresponding five quaternary systems. It is found that the mean error in the atomic coordinates predicted by DFT in a comparison with atomistic simulations is in the order of 1-2 pm over all compositions and temperatures considered.

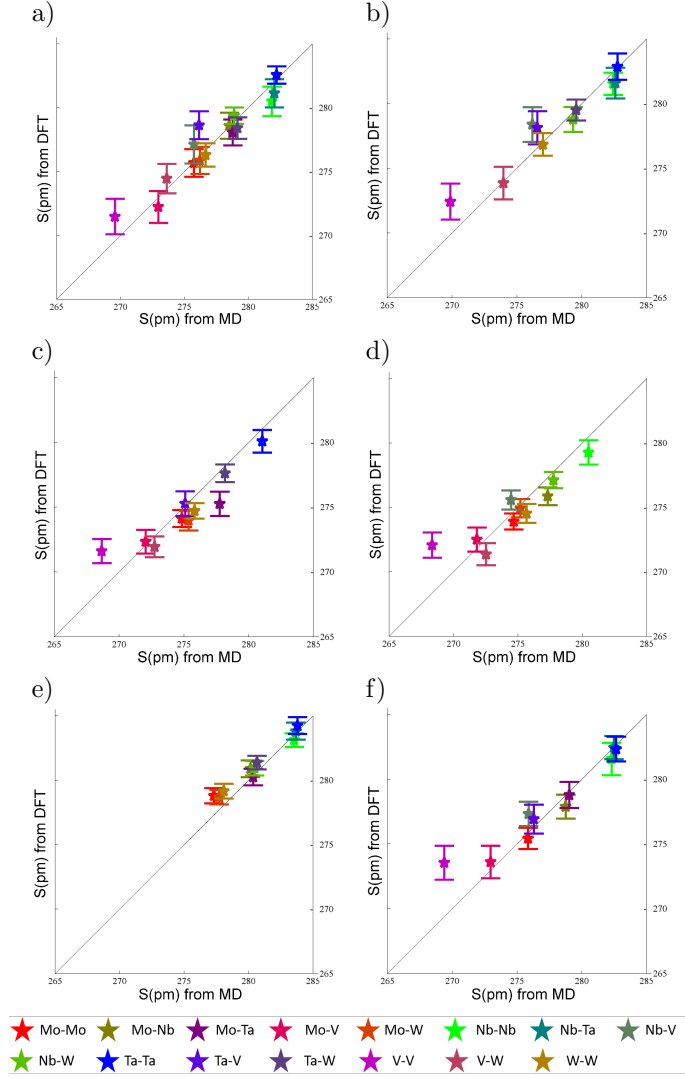


Figure 4: The comparison of interatomic distances obtained using DFT and MD between pairs of atoms in high-entropy alloys: a) Mo-Nb-Ta-V-W, b) Nb-Ta-V-W, c) Mo-Ta-V-W, d) Mo-Nb-V-W, e) Mo-Nb-Ta-W, f) Mo-Nb-Ta-V.

Mechanical properties prediction

As exposed previously, there important advances in thermodynamic prediction (from numerous approaches) of HEAs and stability of single phases. From a designing point of view, there are many other considerations to be taken at proposing new compositions. Mechanical properties prediction is reviewed in this section, where the physical-based modeling is commonly used. The factors affecting their mechanical behaviour are starting to be analyzed and there have been already a number of publications on its modeling. The effects of alloying additions have shown to display a rather dramatic effect on said properties, e.g. the variations in Al content in $Al_xCoCrFeNiTi$ system, which can lead to excellent properties even at elevated temperatures [72]. HEAs display a variety of deformation mechanisms owing to the complexity of their lattice distortions. They may exceed properties displayed by commercial superalloys

[5]. The work by Suarez Anzorena *et al.* [73] constitutes an attempt to model, based upon lattice parameters variations, phase stability which is related to mechanical properties, although a direct correlation with experiments is not established. Based on Labush's approach, a model for predicting solid solution strengthening was proposed [15] based upon variations in shear modulus and atomic size, and refined later at [16]. On a similar line of thought, for the MoNbTaTiV Yao *et al.* [29] have developed a model to predict yield stress following a similar approach which was able to recover the solid solution strengthening conditions consistent with strengthening improvement.

Following methods more typically inspired in mechanics approaches, Stepanov *et al.* [74] have produced a simple rule of mixtures model to predict mechanical properties. These are adjusted based upon experimental measurements on certain systems, and working back the strength of Laves phases with knowledge of the volume fraction. This work highlights the need to predict strength based upon composition. It also highlights the importance of concentration fluctuations in strengthening. On the other hand, CrFeCoNiMo_{0.2} has recently been studied by Wang *et al.* [75]; they derived constitutional equations to describe the strain-dependent warm and hot deformation of said alloy. The work is very useful in describing mechanisms already observed, but a tool to predict mechanical behavior is still missing in their work.

The first combined detailed measurements on critical resolved shear stress (CRSS) with first principles calculations have been provided by Patriarca *et al.* [76]. They have been able to recover the value of the CRSS for experimentally observed crystallographic orientations, as well as its variation with temperature for FeNiCoCrMn. In a first step towards multiscale modeling, they obtained from atomistic calculations the unstable stacking fault energy and the intrinsic stacking fault energy values for the first time.

The formation of precipitate intermetallic phases is regarded as of importance for high-temperature alloys, especially those aiming to replace nickel superalloys. One example is $L1_2$ Co₃(Al,Mo,Nb) formation in Co alloys. Yao *et al.* [77] have performed a first principles study on the phase stability, elastic and thermodynamic properties of such phase. The input of such can be valuable for modeling the precipitate contribution to the mechanical properties of such alloy. A similar approach has also been applied by the authors to $L1_2$ (Co,Ni)₃(Al,Mo,Nb) in [78].

Making a critical analysis of the literature on mechanical properties modeling, we highlight the presence of five key types of contributions: (1) solid solution, (2) stacking fault energy, (3) Peierls stress, (4) constitutive equations and (5) precipitate contributions. The future of HEAs design, especially for improved mechanical properties, demands the combination of those techniques. This is a true challenge as it requires information not available at present. Much of the work has focused on predicting the compositional conditions for phase stability, but mechanical properties prediction requires a wealth of information concerning the formation of secondary phases, their composition and, importantly, the size, number density and composition of concentration fluctuations across the microstructure. One of the first attempts

to quantify this is by Toda-Caraballo *et al.* [11]. A quantification of such concentration fluctuations and their temperature dependence, combined with their temperature effects as well as phase separation conditions, is essential for a robust prediction of properties, and for designing HEAs for improved mechanical behavior.

Oxidation

While the research on mechanical properties for HEAs is showing some advance in the literature, the oxidation phenomenon, probably due to its complexity, is still practically unexplored in HEAs. But it is irrefutable that for a complete HEA design, oxidation resistance is a mandatory requirement that must be fulfilled before a new alloy can be used in applications since their properties can be seriously affected by long-term exposure in aggressive atmospheres. In this section, the main results observed in the literature of multicomponent alloys are described and comprehensively analyzed to provide a designing guide at considering oxidation aspects at developing new HEAs. Although atomistic simulations could aid at understanding oxidation in HEAs, its extreme complexity limits the simulation capability.

Oxidation of pure metals is a complex phenomenon as it involves many physical, chemical and mechanical properties of the metallic substrate and the oxide scale. The ideal case is that the material can generate itself a protective scale or barrier that could minimise further attack. Otherwise, the material should be protected by applying proper coatings which could act as effective barriers against the aggressive species. Moreover, the type of the atmosphere and the concentration of aggressive species are decisive factors that need to be taken into account for the correct analysis of the oxidation phenomena as it can be observed in Figure 5a, where it is shown the effect of nitrogen or moisture in titanium oxidation.

The complexity of the oxidation phenomenon is considerably increased in the case of multicomponent alloys, because the nature of the oxide scale formed over the pure metal can be dramatically changed with the presence of additional elements. Fig 5 depicts this effect on some Ni- and Ti-based alloys [79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89]. In the case of titanium oxidized in air, the beneficial effect of niobium additions is related to the formation of a continuous nitride layer which prevents oxygen solution into the matrix. In the case of nickel, the development of protective chromia or alumina layers reduces noticeably the oxidation kinetics compared to pure nickel, but this only happens when the content of both elements exceeds a critical value. Otherwise, the alloy cannot generate the protective layer, occurring instead accelerated mass gain due to internal oxidation of chromium or aluminum. In the case of HEAs or multicomponent alloys, understanding the oxidation phenomenon reaches an extraordinary complexity, where the presence of one or two single phases deeply affect its behavior.

While considerable efforts have been made in the HEAs field to understand their chemical and thermodynamic properties, as well as the modeling of mechanical properties to a lesser extent, less attention has been paid on their oxida-

tion behavior, in spite of their potential applications at high temperature, not only as monolithic materials but also as coatings. A review on the oxidation resistance of HEAs, specially in transition metals [90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105] and refractory [106, 107, 108, 109, 110] based HEAs, evidences that their oxidation resistance is inferior to that reported for conventional oxidation-resistant alloys, whose excellent oxidation behavior derives from the rapid establishment of thin, adherent, slow-growing alumina, chromia or silica scales [111]. Differently, most of HEAs are unable to form such protective scales, developing instead less protective complex oxide scales. A careful analysis on the reported results reveals common features during the oxidation of HEAs:

- 1) Protection is conferred, generally, by alumina and/or chromia layers. As a general rule, the highest the contents of both elements the highest the oxidation resistance of the HEAs [97, 98, 99, 102, 105].

- 2) Most of the oxidation research regards equiatomic HEAs [90, 91, 93, 95, 96, 98, 100, 101, 103, 104, 110]. Only very few of them are single-phase HEAs [90, 91, 93, 103], especially those belonging to the FeCoNiCr family [90, 91, 93, 103]. Single phase HEAs exhibit the best oxidation behavior if the single-phase contains enough aluminium and/or chromium to form their corresponding oxides [98].

- 3) Most of non-equiatomic HEAs consists of two or more phases [92, 94, 97, 98, 99, 102, 105, 108, 109], which cannot establish scales as protective as conventional oxidation-resistant alloys [89, 92]. As suggested above, only those alloys with high aluminium/chromium contents have good oxidation resistance [98].

- 4) A protective scale is generally developed when the alloy consisted of a single phase [94] or a matrix embedding a fine dispersion of second phases [98, 99, 105]. In some alloys, a depleted zone in the element building up the protective layer, usually aluminium, is generated in the course of the oxidation beneath the scale [92, 94, 98, 99, 105]. This behavior is similar to that found during the oxidation of intermetallic-based alloys [86] and it denotes slow diffusivity in the alloy which cannot supply from the bulk the aluminium flow needed for replacing the amount of this element consumed for the formation of the alumina on the surface of the alloy. In the case of HEAs, the Al-depleted zone appears as a continuous layer beneath the oxide scale and it could have a positive effect since it would favor the continuous development of an alumina scale while the aluminum content in this region is above a critical value [94, 98, 99, 105].

- 5) A protective scale can be developed in multiphase HEAs, when each phase is enriched in elements such as chromium or aluminum whose concentrations are enough high in each phase to develop alumina/chromia layers [94, 99, 105, 110]. If only one of the phases can lead to the formation of a protective layer but the second phase is unable for that, the overall scale is not protective because oxidation should proceed preferentially through this phase [109]. If no protective layer is formed, thick non-protective scales consisting of a mixture of different oxides are generated throughout the oxidation process [93, 94].

- 6) Severe internal oxidation is found in most of the HEAs

during the oxidation process [94, 98, 99, 101, 102, 107]. Occasionally, the protective oxide layer cannot prevent internal oxidation of the alloy [92].

7) Single phase structure of some HEAs can be affected during long-term exposure at high temperatures [97], induced directly by the oxidation process if the composition of the alloy, for instance an Al-depleted zone, reaches a compositional space where more phases are thermodynamically stable [95]

8) If the different phases constituting a multiphase alloy cannot generate a protective layer, the oxidation penetrates into the alloy at different rates depending on the individual oxidation resistance of each phase. Large stresses induced by large volume changes induce cracking in the scale and accelerated oxidation [108].

9) Oxide scales are prone to undergo spalling during cooling [95, 98, 110]. Their adherence could be improved by adding a fine dispersion of oxides [96].

Preceding points evidence many discrepancies in the oxidation behavior of HEAs, even with close chemical compositions. Thus, it is precise to gain understanding how the peculiarities of HEAs can affect their oxidation resistance. Prediction of the oxide scales that could be developed in HEAs through the proper design of the composition and microstructure of the alloy would constitute a relevant advance in the design of oxidation resistant HEAs. Numerous models have been proposed as attempts for offering chemical or thermodynamical approaches which can describe suitably the oxidation behavior of materials. The first general theory about oxidation was given by Wagner [112]. The model considers the growth of a single-phase oxide scale is controlled by diffusion processes (ions, electrons or punctual defects) across a dense scale well adhered to the metallic substrate under the assumption that chemical reactions proceeds very quickly. According to this model the oxide growth obeys a parabolic law. Deviation from Wagner's theory results from the non accomplishment during the oxidation of the assumptions used in the theory. Development of porosity, the formation of more than one oxide, microcracking events, spalling, large contribution of grain boundary diffusion or short-circuit diffusion paths (especially at low/intermediate temperatures), growth stresses into the scale, the presence of more than one reactive agent in the atmosphere or high solubility of the reactive agent in the metallic substrate deviate kinetics from Wagner's theory.

Even so, the Wagner's theory has been successfully extended to alloys under certain approaches [113, 114, 115]. A Thermodynamical model for the oxidation of ternary NiAlCr has been also proposed [116]. Assuming a sequence of local equilibria and based on thermodynamic calculations, the model can predict the oxides constituting the scale and the phases which could form in the diffusion zone. Other models have been addressed to calculate the stresses developed within the oxide scale and the strains induced on the metallic substrate which could result in its detachment or failure [117]. Also, finite element modeling has been used to demonstrate that plastic deformation of the substrate occurs if the scale becomes undulated [118]. Other models have tried to gather the different aspects involving the oxidation pro-

cess, i.e., thermodynamics and kinetics of the evolution of film thickness, diffusion of all components, oxidation reaction rates and the effects of stresses [119]. The use of first principles calculations is not usually considered for modeling the overall oxidation phenomenon because they need huge computational resources to simulate complex systems, like those involving reaction dynamics. Occasionally, quantum chemical molecular dynamics (QCMD) have been used to model specific aspects of the oxidation as, for instance, the atomic transfer at the scale/metal during the early stages of oxidation [120].

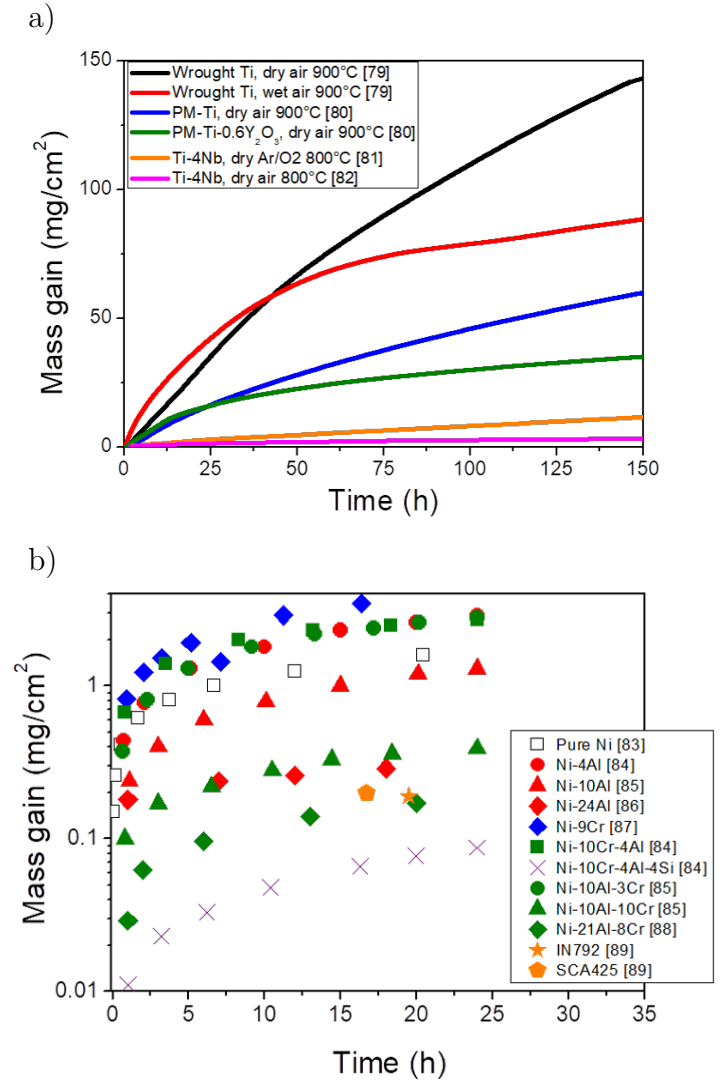


Figure 5: a) Influence of the composition of the atmosphere on the oxidation behavior of pure Ti and Ti-4Nb alloy. b) Influence of alloying additions on the oxidation behaviour of pure nickel in air and pure oxygen. Data taken from [79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89]. Symbols in red correspond to binary Ni-Al alloys, in blue to a binary Ni-Cr alloy, in green to ternary Ni-Cr-Al alloys, in orange to commercial Ni-based superalloys.

The preceding review evidences problems associated with the thermodynamical, kinetics, chemical and mechanical aspects in the oxidation model. Such complexity is exacer-

bated in the HEAs, especially if they are multi-phase alloys, because the high number of elements included in their composition makes harder the correct prediction of the oxides constituting the scale. In addition, the stability of the HEA solid solution beneath the scale could be lost if outward flow diffusion of that element from the bulk of some of the elements being preferentially oxidized cannot be kept as oxidation proceeds. Although such task is not easy, modeling of HEAs oxidation should be initially addressed regarding both aspects.

Summary

In this paper, we have presented an overview of the modeling state of the art for HEA design, the main techniques and its limitations, which allows at identifying the principal challenges for the future development of new approaches for predicting properties in these alloys.

It is clear that the thermodynamics of HEAs are much more studied than other material properties of multicomponent alloys. This is due to the fact that obtaining a single phase solid solution multicomponent alloy is not such a simple task, while good properties are generally assumed to arise naturally from obtaining such particular alloy. Even though, concerning phase stability, there are still many unknowns, and different techniques have been applied and adapted to HEAs. Data analysis, CALPHAD and atomistic simulations have been employed to aid in its understanding. Nevertheless, the magnetic contribution to phase stability, kinetics or stacking fault energies, for instance, still need to be properly revised. The very common molecular dynamics technique applied in materials science, has serious difficulties to formalize the complexity of the HEA composition. Since most of the HEA produced are Fe- Co- or Cr-based alloys, a proper magnetic description of the interatomic forces is demanded.

It has been exposed previously how properties depend on the obtained phases and respective composition homogeneity. Symmetrically, the behavior of such properties can affect phase stability, as for instance the appearance of compositionally depleted zones close to protective scales or layers, or the induced stresses due to non-homogeneous oxidation, which in turn affects mechanical performance. Hence, the approaches to predict HEA properties cannot work in isolation, but should collaborate to provide a complete description of each of them. New theoretical results and studies are still needed to optimize the prediction of HEAs properties, from which a good alloy design can be performed.

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