Predicting single phase CrMoWX high entropy alloys from empirical relations in combination with first-principles calculations

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ABSTRACT

We use the Hume-Rothery rules and *ab initio* mixing enthalpies to design novel high entropy alloys composed of late $3d$ metal (Mn, Fe, Co, Ni, Cu) and CrMoW. Results predict that CrMoW, CrMoWMn, CrMoWCo and CrMoWNi adopt single body-centered cubic (bcc) crystal structure. The *ab initio* calculations of elastic moduli and ideal strengths indicate that the bcc phase is more stable thermodynamically than the face-centered cubic (fcc) crystal structure for CrMoW, CrMoWMn, CrMoWNi HEAs, but the late $3d$ elements decreases the mechanical stability of the bcc phase. In particular Ni addition increases the intrinsic ductility and decreases the intrinsic strength of CrMoW alloy.

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1. Introduction

During the last decade, considerable research on high-entropy alloys (HEAs) were reported [1–7]. Until now most of the single phase HEAs have been collected and reviewed [1,4]. Except the hexagonal closed-packed (hcp) HEAs composed of early elements or rare earth elements, for instance AlLiMg$_{0.5}$ ScTi$_{1.5}$ [8], DyGdLuTbY [9], DyGdLuTbTm [9], and DyGdHoDyTbY) [10], most of the single phase face centered cubic (fcc) HEAs are composed of near equal-molar late $3d$ transition metals whereas refractory elements give rise to the single phase body centered cubic (bcc) HEAs. With Al addition, the phase of $3d$-HEAs transforms from fcc to bcc. A small mount of refractory metals added to $3d$-HEAs keeps the single fcc phase. As potential high-temperature materials, the HEAs composed of refractory elements remain bcc phase when alloyed with a small amount of Al [11–23].

Based on collected experimental data, the Hume-Rothery rules have been used to investigate the formation of single-phase HEAs.

As key physical parameters, researchers considered the mixing entropy, the atomic size effects, electronegativity, valence electron concentration (VEC), and the mixing enthalpy etc. Actually VEC was used to distinguish the fcc- and bcc-phase HEAs [1,6]. For instance HEAs with VEC > 7.8 often adopt fcc phase, and most of HEAs with VEC < 7.5 are single bcc phase. More recently the formation enthalpy of binary alloys from *ab initio* calculations has been used to successfully reproduce singe-phase HEAs [24], for instance CoCrFeNi, CoCrFeNiPd, CoCrFeMnNi, MoNbTaW, and MoNbTaVW. Our recent work implied that the VEC and the atomic radius difference can be used to estimate the hardness of the single phase HEAs [1]. Researchers attempted to evaluate the un-discovered HEAs via the combination of the above criteria. For instance Gao *et al.* used the *ab initio* molecular dynamics and binary phase diagrams to predict the bcc(fcc)-phase HEAs and search for hcp HEAs [25], Takeuchi *et al.* designed hcp HEAs via the atomic size effect, the formation enthalpy and binary phase diagrams [9].

Considering that the present design of high temperature HEAs focuses on refractory-HEAs or Al doped refractory-HEAs, and very limited reports are about late $3d$ metal doped refractory-HEAs, here we make an attempt to design new refractory-HEAs encompassing late transition metals via the Humer-Rothery rules and *ab initio* formation enthalpy calculations. Next we employ the *ab initio* exact

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muffin-tin orbitals method in combination with the coherent potential approximation (EMTO-CPA) [26] to predict the phase stability and elastic behavior of the proposed refractory HEAs.

The rest of the paper is organized as follows. First we present the Hume-Rothery rules and give the important details of *ab initio* calculations. Second we use the Hume-Rothery rules and *ab initio* formation enthalpy to assess several CrMoWX (X = Mn, Fe, Co, Ni, Cu) alloys. Then based on the calculation schemes in the EMTO-CPA method, we discuss the phase stability, equilibrium properties, elastic moduli, and ideal tensile strength. Finally we draw some conclusions from the present study.

2. Theoretical methodology

2.1. Empirical alloy criteria

We make use of the atomic size effect, Pauling electronegative difference ($\Delta\chi$), valence electron concentration (VEC), the mixing entropy (ΔS_{mix}), the mixing enthalpy (ΔH_{mix}) and the elastic strain energy ($\sqrt{\langle\varepsilon^2\rangle}$) [27] to assess the single phase high-entropy alloys. The atomic size effect includes the average atomic radius (w_{mix}), the maximum of the atomic radius difference (Δw_{max}) [28], atomic radius difference (δ) [6], and the atomic packing misfit ratio (γ) [29].

First we use Vegard's rule to assess the equilibrium volume of an alloy. Although the lattice parameter is often used to represent the equilibrium volume, here we adopt the Wigner-Seitz (WS) radius in order to be able to compare different lattices and account for elements adopting different parent lattices. Accordingly, the average WS radius of the solid solutions is defined as

$$w_{mix} = \sum_i^n c_i w_i, \tag{1}$$

where w_i is the experimental WS radius of the ith component [26]. Here and in the following, c_i is the atomic percent of the ith component, n stands for the number of alloy component.

The parameter Δw_{max} represents the ratio between the difference between the largest atomic radius (w_i) and average radius and the average atomic radius ($\overline{w} = w_{mix}$), *viz.*

$$\Delta w_{max} = \text{Max}(w_i - \overline{w})/\overline{w}. \tag{2}$$

The atomic size difference δ is expressed as

$$\delta = 100\sqrt{\sum_{i=1}^n c_i\left(1 - \frac{w_i}{\overline{w}}\right)^2}. \tag{3}$$

In order to quantitatively describe the atomic packing effect in multicomponent alloys, Wang *et al*. [29] used the solid angles of atomic packing for the elements with the largest and smallest atomic sizes. The ratio γ between the solid angles of the smallest and largest atoms is defined as

$$\gamma = \omega_s/\omega_l$$
$$= \left(1 - \sqrt{\frac{(w_s + \overline{w})^2 - \overline{w}^2}{(w_s + \overline{w})^2}}\right) \Big/ \left(1 - \sqrt{\frac{(w_l + \overline{r})^2 - \overline{w}^2}{(r_l + \overline{w})^2}}\right), \tag{4}$$

where $\overline{\omega}$, ω_l and ω_s are the radii of the average, largest, and smallest atoms, respectively.

A general self-contained geometric model proposed by Ye *et al*. [27] links the average lattice parameter of the alloy to atomic size, atomic fraction and packing density. This model can be used to

evaluate the intrinsic residual strains around different sized elements in a multi-component alloy and further distinguishes the single-/multi-phase HEAs. Among the model, the root mean square of residual strain is defined as

$$\left\langle\varepsilon^2\right\rangle = \sum_{j=1}^n c_i\varepsilon_j^2, \tag{5}$$

given that average residual strain is zero, *i.e.* $\langle\varepsilon\rangle = \sum_{j=1}^n c_i\varepsilon_j = 0$. Here $\varepsilon = \delta w_i/w_i$ is the residual strain of the ith component.

The electronegative difference $\delta\chi$ is given as

$$\delta\chi = \sqrt{\sum_{i=1}^n c_i(\chi_i - \overline{\chi})^2}, \tag{6}$$

where $\overline{\chi} = \sum_{i=1}^n c_i\chi_i$ and χ_i is the Pauling electronegativity of the ith component.

The mixing enthalpy ΔH_{mix} of a multi-component alloy can be estimated as

$$\Delta H_{mix} = \sum_{i=1, j\neq i}^n \Omega_{ij}c_ic_j, \tag{7}$$

where $\Omega_{ij} = 4\Delta H_{AB}$ and ΔH_{AB} is the mixing enthalpy for binary alloys calculated using the tabulated values by Takeuchi et al. [30]. These data of enthalpy have been improved based on the Miedema macroscopic model [31].

Besides the mixing enthalpy based on the Miedema model, here we also used the first-principles "high-throughput" density functional-theory (DFT) calculations of the energy of formation of binary compounds to evaluate the formation enthalpy of high entropy alloys [24].

For a multi-component alloy, the mixing entropy (ΔS_{mix}) in statistic physics is defined as

$$\Delta S_{mix} = -R\sum_i^n c_i\ln c_i, \tag{8}$$

where R stands for the ideal gas constant (8.314 J/(K mol)).

We can define the average valence electron concentration (VEC) as

$$\text{VEC} = \sum_i^n c_i(\text{VEC})_i, \tag{9}$$

where $(\text{VEC})_i$ is the valence electron number of the ith alloy component. For transition metal elements, VEC represents the number of d electrons.

Yang and Zhang [3] proposed a new parameter to distinguish the solid solutions from the bulk metallic glasses, *i.e.*

$$\Omega = \frac{T_m\Delta S_{mix}}{|\Delta H_{mix}|}, \tag{10}$$

where T_m is the melting temperature of alloy, ΔS_{mix} is the mixing entropy shown in Eq. (8), and ΔH_{mix} for the mixing enthalpy shown in Eq. (7). Here the melting temperature calculated using the linear rule of mixture, *viz.* $T_m = \sum_{i=1}^n c_iT_{m,i}$, where $T_{m,i}$ is the experimental melting temperature of the ith alloy component.

One can use the combination of characteristics given by Eqs.(1)–(10) to predict the solid solution phase or intermetallic compounds of a multi-component alloy. Stabilizing a single phase is important to investigate the correlation between phase and