Elastic and thermal properties of refractory high-entropy alloys from first-principles calculations

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ABSTRACT

We present a study of the elastic and thermal properties of single-phase ternary and quaternary Al-Ti-V-Cr-Nb-Mo refractory high-entropy alloys based on the first-principles calculations. The exact muffin-tin orbitals (EMTO) method in combination with the coherent potential approximation (CPA) is employed to calculate the equilibrium bulk properties and elastic parameters. The calculated Young's moduli are in good agreement with the available experiments. Based on the thermal equation of state we use the quasi-harmonic Debye model to study the thermal properties such as the Gibbs free energy, Debye temperature, thermal expansion coefficient, and specific heat capacity. The elastic moduli at finite temperature are also discussed.

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1. Introduction

Metallic alloys with superior mechanical and functional properties remain in high demand for elevated temperature applications. Recently, a novel concept of high-entropy alloys (HEAs) proposed by Yeh et al. [1–3], has been applied to produce several metallic alloys consisting of refractory elements [4–8]. HEAs, also known as multi-principal element alloys, are composed of four or more alloying elements with nearly equiatomic concentrations [6,9]. Because of their high entropy of mixing, relatively small atomic radius difference, less negative enthalpy of mixing and sluggish diffusion of atoms, HEAs may form a simple solid-solution structure, such as face-centered cubic (fcc), body-centered cubic (bcc), or hexagonal closed-pack (hcp) structure [10–12], rather than a complicated intermetallic phase.

Since refractory elements have relatively high melting points (Ti (1946 °C), V (2202 °C), Cr (2133 °C), Mo (2895 °C), Nb (2750 °C), Zr (2128 °C), Hf (2504 °C), Ta (3293 °C), W (3695 °C)), it is reasonable to explore HEAs composed of such elements for high-temperature applications. Using the vacuum arc melting technique, Senkov et al. studied some HEAs composed of refractory elements (Ti, V, Cr, Mo, Nb, Zr, Hf, Ta, or W), for instance WMoNbTa and WNbMoTaV [4], TaNbHfZrTi [11], NbCrMo$_{0.5}$Ta$_{0.5}$TiZr [8], CrNbTiVZr [5,6], TiZrNbMoV$_x$ (x = 0–1.5) [13,14], and TiZrHfNbX (X = V or Cr) [9]. It was found that, compared to the individual

element of the constituents, WNbMoTa, WNbMoTaV and TaNbHfZrTi HEAs exhibit exceptional microhardness and highly compressive yield strength, derived from the solid-solution strengthening mechanism [4,11]. The TiZrNbMoV$_x$ alloys possess excellent mechanical properties [15] and their anisotropy enhances with the increase of V content [13]. TiZrHfNbV shows high strength and homogeneous deformation under compression near room temperature. The addition of equimolar Cr to TiZrHfNb HEAs induces an increase of yield strength and hardness [9].

In addition to the experimental efforts mentioned above, theoretical studies have been performed to predict the formation energy, structure, stability, and intrinsically elastic mechanics of serval single-phase refractory HEAs [13,16–18]. Among the theoretical activities in the past, only few efforts were made to investigate the thermodynamic properties of the alloys [19,20]. Considering that the ternary (MoNbTi, MoNbV, MoTiV, CrMoTi) and quaternary (AlMoTiV, CrMoTiV, MoNbTiV) alloys all exhibit a single bcc solid solution phase in experiment, in the present work, we focus on the elastic constants and thermal parameters of the equimolar ternary and quaternary Al-Ti-V-Nb-Mo refractory HEAs, and we investigate the effect of the addition of equimolar alloying element on the intrinsic ductility and thermodynamic properties of the alloys.

The structure of this paper is as follows. In Section 2, we briefly describe the computational methodology. In Section 3, we present the results and discussion of the elastic and thermodynamic properties. And finally, we give conclusions in Section 4.

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2. Methodology

In the present work we resort to the exact muffin-tin orbitals (EMTO) method [14,21–23] combined with the coherent potential approximation (CPA) [24,25] within the framework of density functional theory (DFT) [14]. The EMTO technique is an improved screened Korringa–Kohn–Rostoker approach, employing large overlapping potential spheres for an accurate description of the exact single-electron potential, and the full charge density method further improves the accuracy of full potential total energy [14]. And it is an efficient *ab initio* approach to solving the Kohn–Sham equation [26]. The CPA is a powerful tool to treat the substitutional disorder, in both chemical and magnetic degrees of freedom [24,25], using an effective medium in single site approximation. The one-electron Kohn–Sham equation in the scalar-relativistic form was solved for the valence states using the Green's function method. Since the EMTO is an all electron method, the core states were solved explicitly. For the self-consistent calculations, the Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) was used for the exchange correlation functional [27]. The Green's function was calculated for 24 complex energy points, which are Gaussian points for the energy contour integration, on a semicircular contour, from the bottom of the valence bands to the Fermi energy, in the upper half of complex energy plane. In the irreducible wedge of the bcc Brillouin zone, we used 285 inequivalent k points, allowing to maintain a 10^{-2} mRy/atom accuracy in the total energy. For the alloys in the present study, we used the same screen impurity model (SIM) parameter $\alpha_{SIM} = 0.902$. After performing a set of *ab initio* calculations with different α_{SIM}, we found that the SIM parameter has almost no effect on the equilibrium and bulk modulus. For a detailed discussion of the screen impurity model parameter, readers are referred to Ref [28]. We employed the disordered local magnetic moment (DLM) picture [29] to describe the paramagnetic CrMoTi and CrMoTiV HEAs. Cr reveals the vanishing local magnetic moments.

In a cubic lattice, the elastic properties can be described by three independent elastic constants, c_{11}, c_{12}, and c_{44}. In our study, the elastic constants c_{11} and c_{12} were determined from the bulk modulus $B = (c_{11} + 2c_{12})/3$ and the tetragonal shear modulus $c' = (c_{11} - c_{12})/2$. The bulk modulus and equilibrium volume were extracted from the equation of state by fitting the Birch-Murnaghan (BM) function to the total energy as a function of the unit cell volume. The shear elastic constants c' and c_{44} were calculated by using a standard method [14].

To study the thermodynamic properties, we used the quasi-harmonic Debye model implemented in the Gibbs program [30]. This method allows to derive the thermal behaviors from the calculated energy versus volume data [30] and is less expensive, compared to the methods using lattice dynamics and molecular dynamics.

Here, we give a brief description of the quasi-harmonic Debye model [31]: The vibrational Helmholtz free energy A_{Vib} is given by

$$A_{Vib}(\Theta, T) = nk_B\left[\frac{9\Theta}{8T} + 3\ln(1 - e^{-\Theta/T}) - D(\Theta/T)\right], \quad (1)$$

where n, k_B and $D(\Theta/T)$ represent the number of atoms in per formula, Boltzmann constant, and the Debye integral, respectively. For an isotropic solid with Poisson ratio v, Θ is expressed as

$$\Theta = \frac{\hbar}{k_B}[6\pi^2 V^{1/2}n]^{1/3}f(v)\sqrt{\frac{B_s}{M}}, \quad (2)$$

where M is the molecular mass per formula unit, and adiabatic bulk modulus B_s is approximated by

$$B_s \cong B(V) = V\left(\frac{d^2E(V)}{dV^2}\right). \quad (3)$$

In Eq. (2) $f(v)$ is given by

$$f(v) = \left\{3\left[2\left(\frac{2}{3}\frac{1+v}{1-2v}\right)^{3/2} + \left(\frac{1}{3}\frac{1+v}{1-v}\right)^{3/2}\right]^{-1}\right\}^{1/3}. \quad (4)$$

Accordingly one can obtain the minimized value of the non-equilibrium Gibbs functions and obtain further the thermal equation of state (EOS), $V(P, T)$. Combining the isothermal bulk modulus with the Grüneisen parameter, one can compute the heat capacities, C_v and C_p, the entropy S, containing both vibrational and electronic contributions, and the thermal expansion coefficient α. Note that the present calculations of the electronic contribution are based on the Sommerfeld model of free and independent electrons. It should be acknowledged that electronic contributions, also for refractory HEAs as considered here, are nowadays computed with methods going beyond the Sommerfeld approximation (see, e.g., Ref. [32]). For further details of the quasi-harmonic Debye model, readers are referred to Refs. [20,33–37].

3. Result and discussion

3.1. Elastic properties

Table 1 lists the theoretical Wigner–Seitz (WS) radius ω_t, elastic constants c_{11}, c_{12} c_{44}, the tetragonal shear modulus c', Zener ratio A_Z, and Cauchy pressure $(c_{12} - c_{44})$ at different temperatures. Since no experimental lattice parameter data for the alloys in the table are available, we evaluated the average WS radius w_e from the experimental WS radii of alloying elements via Vegard's law [38]. From Table 1 we can see that the WS radius values calculated by EMTO-CPA are in good agreement with the average data. The criteria of mechanical stability condition of the elastic constants are known as to be $c_{44} > 0$, $c_{11} > |c_{12}|$ and $c_{11} + 2c_{12} > 0$ for the cubic crystal. According to Table 1, the calculated elastic constants of the alloys considered in this work satisfy these criteria, and therefore these alloys are expected to be mechanically stable. The Cauchy pressure $(c_{12} - c_{44})$ is often used to characterize materials bonding properties. In general, a positive value of $(c_{12} - c_{44})$ suggests that the material is dominated by metallic bonding, while a negative value of $(c_{12} - c_{44})$ suggests covalent bonding. Since the calculated Cauchy pressure $(c_{12} - c_{44})$ shows large positive values, we conclude that these refractory HEAs have strong metallic bonding character. From Table 1 we can see that Al (Cr, V, or Nb) reduces (strengthens) the metallic character of the bonding in the present alloys. This may be due to the large negative formation enthalpy ΔH for atomic pairs between Al and refractory metal elements, for instance $\Delta H = -30$ kJ/mol for Al-Ti, $\Delta H = -5$ kJ/mol for Al-Mo, $\Delta H = -18$ kJ/mol for Al-Nb, and $\Delta H = -16$ kJ/mol for Al-V [39]. Whereas ΔH is less negative for atomic pairs between refractory elements, for instance $\Delta H = -2$ kJ/mol for Ti-V, $\Delta H = -1$ kJ/mol for V-Nb, $\Delta H = -2$ kJ/mol for V-Cr, and $\Delta H = -4$ kJ/mol for Ti-Mo [39].

The elastic constant $c' = (c_{11} - c_{12})/2$ is the tetragonal shear modulus. For a bcc crystal, a decreasing c' suggests that the stability of the bcc phase decreases. Compared to the tetragonal elastic modulus $c' = 100.2$ GPa for MoNbV, the addition of Al (Ti) reduces the c' value of the quaternary alloys, for instance $c' = 62.0$ GPa for AlMoNbV and $c' = 74.8$ GPa for MoNbTiV. It suggests that both Al and Ti decreases stability of bcc structure of MoNbV. Whereas the comparison of c' between MoTiV and CrMoTiV indicates that Cr increases the stability of the bcc phase of MoTiV. Both V and Nb alloying elements have almost no effect on the stability of