Journal of Alloys and Compounds 714 (2017) 668–680

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

An *ab initio* and experimental studies of the structure, mechanical parameters and state density on the refractory high-entropy alloy systems

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ARTICLE INFO

Article history:
Received 1 January 2017
Received in revised form
19 April 2017
Accepted 22 April 2017
Available online 27 April 2017

Keywords:
Ab initio
Refractory
High-entropy alloys
Anisotropy
Density of states

ABSTRACT

The refractory high-entropy alloys (TiZrVMo, TiZrVMoTa, TiZrVMoTaNb, TiZrVMoTaNbCr and TiZrVMoTaNbCrW) possess a single phase solid solutions to the body centered cubic crystal structure. We showed the X-ray diffractograms of the calculation and experimental for refractory high-entropy alloys. However, the results of calculation are basically in agreement with the experimental. The equilibrium volume, thermodynamic stability, elastic constants and anisotropic elastic properties, electronic structures of the refractory high-entropy alloys were employed by the *ab initio* exact muffin-tin orbitals method. Formation enthalpy and cohesive energy were calculated and used to estimate the stability of the refractory high-entropy alloys. The elastic constants and modulus were obtained by the stress-strain method and the Voigt-Reuss-Hill approximation. Meanwhile, all the alloys showed different mechanical anisotropy for bulk modulus and Young's modulus. The total density and partial density of states were analyzed in physical properties of the refractory high-entropy alloys.

1. Introduction

Recently, first-principles calculation has attracted more attentions by lots of material science researchers. *Ab initio* calculation method is also known as the first principle calculation [1]. It is based on adiabatic and single electron approximation, using quantum mechanics theory, starting from the specific requirements. The calculation method of approximate can solve Schrodinger equation directly. This algorithm doesn't need empirical parameters and experimental data in the derivation process.

It mainly can predict the microstructure of atomic scale and all kinds of physical and chemical properties of material [2]. Unfortunately, the limited number of possible host systems limits the properties one could in principle achieve via extended solid solutions [3]. With the fast development of the new technologies and theories for developing advanced materials, the number of constituent principal elements for metallic alloys is increased from one to three or more [4]. Nowadays, as a new system of alloy, high-entropy alloys (HEAs) contain five or more multiple principle metallic elements in equal or near equal atomic percent [5]. These alloys also showed outstanding performance: high hardness, good wear resistance and thermal stability, excellent thermophysical, magnetic and electrical properties, for instance [6–11]. Generally, the atomic fraction of each component is less than 35 at.% and greater than 5 at.% [12]. High-entropy alloy would more likely to produce a simple solid solution rather than generating a complex structure (intermetallic compound phase) in spite containing many components [5]. Most of these single-phase alloys were composed of face centered cubic (FCC), body centered cubic (BCC) or hexagonal close packed (HCP) crystallographic structures. The single-phase solid solutions are stabilized by the high entropy of mixing combined with the relatively low mixing enthalpy [13]. This kind of special alloy is defined by J.W. Yeh et al. [5], and named by Cantor et al. [14,15]. Recently, the refractory HEAs have attracted much attention due to their unique performance under the environment of high temperature. B. Gorr et al. [16] discussed a refractory high-entropy alloy system Mo-W-Al-Cr-x is proposed as a family of candidate materials for structural applications at high temperatures. High temperature oxidation tests show a surprisingly good oxidation resistance. Chien-Chang Juan et al. [17] discussed two new alloys with simple BCC structure, HfMoTaTiZr and HfMoNbTaTiZr. The composition of HfNbTaTiZr is modified with an aim to improve its strength at high temperature. O.N. Senkov et al. [18] studied two refractory HEAs with compositions near NbMoTaW

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http://dx.doi.org/10.1016/j.jallcom.2017.04.237
0925-8388/

and VNbMoTaW. Although under high-temperature conditions, both alloys showed extensive compressive plastic strain that remained not only stable but also disordered.

Nowadays, *ab initio* method by the virtual crystal approximation have become powerful tools for predicting the atomic-level physical properties of multicomponent metallic materials [19]. Although the virtual crystal approximation (VCA) is considered as an overly simplified approach to substitutional solid solutions, many examples have shown that VCA can be reliably used to study the alloys composed of refractory elements [20]. F.Y. Tian et al. [13] used the *ab initio* exact muffin-tin orbitals method in combination with the coherent potential approximation to study the equilibrium bulk properties of the $TiZrNbMo_x$ ($x = 0, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50$). They provided a detailed instructions into the effect of alloying elements on the electronic structure and elastic parameters. Their results indicate that vanadium enhances the anisotropy of the refractory HEAs. Furthermore, they predict that the present HEAs become elastically isotropic for valence electron concentration (VEC) = 4.72. P.Y. Cao et al. [3] employed the equilibrium volume, elastic constants, and polycrystalline elastic moduli of $Al_xMoNbTiV$ HEAs by the *ab initio*. Their results indicate that Al addition decreases the thermodynamic stability of the BCC structure. For the elastically isotropic $Al_{0.4}MoNbTiV$ HEAs, the valence electron concentration (VEC) is about 4.82, which is different from VEC = 4.72 obtained for the isotropic Gum metals and refractory HEAs.

Compared with the experimental results, the calculating data and theoretical results on HEAs by *ab initio* are still extremely confined [3]. The lack of such works is due to the calculating results associated with an awful lot of alloy constituent elements involved in HEAs [13]. As an *ab initio* alloy theory, the muffin-tin orbitals (EMTO) [21] method in combination with the coherent potentials approximation (CPA) [22,23] has verified to be an effective equipment to research the equilibrium properties of $MoNbTiV_xZr$ [13], TiVNbMo [24], HfNbTaTiZr [25], NiFeCrCo [26], and CoCrFeMnNi [27]. The traditional first principles calculation method is only applicable to the materials with regular crystal type and atomic arrangement. The atoms of HEAS are randomly arranged and the atoms can appear in any position of the crystal lattice. Therefore, the application of the traditional first principles calculation method to calculate the properties of HEAS will be very limited, and the results are not accurate. Next, most of the HEAS exist in the form of solid solution. The traditional calculation method is mainly used in the calculation of intermetallic compounds. However, the application of EMTO method can completely solve the limitations of the traditional calculation method [28]. In this paper, the X-ray diffractograms, the equilibrium volume, thermodynamic stability, elastic constants and anisotropic elastic properties, electronic structures of the refractory high-entropy alloys have been calculated by the *ab initio* exact muffin-tin orbitals method as performed. The contribution to this work would help to design the high entropy alloy with excellent properties.

2. Experimental and details of calculations

2.1. Material and methods

Experiments choose Ti, Zr, V, Mo, Ta, Nb, Cr and W elemental powders, five kinds of powder combinations (TiZrVMo, TiZrVMoTa, TiZrVMoTaNb, TiZrVMoTaNbCr and TiZrVMoTaNbCrW) that the ratio of powders by equal atomic percent, with purity more than 99.9%. The alloys were prepared by arc melting under argon atmosphere. The alloys were melted together at least three times. After melting, the specimen cut into many small pieces by wire-electrode cutting. The phase constitution of the samples were analyzed by an X-ray diffraction analysis system (D/MAX-3BX) with Cu target, voltage 40 kV, current 40 mA, the scanning angles ranging from 35° to 100°, scanning speed is 1°/min. The microstructure of specimens were investigated by field emission scanning electron microscope. SEM investigations were performed utilizing the scanning electron microscope (Holland PHILPS XL30ESEM-TM) equipped with energy dispersive detector (EDAX-Phoneix) used for chemical composition measurements.

2.2. Computational methods

In this calculation, using *ab initio* based on density functional theory which is implemented in Cambridge Sequential Total Energy Package (CASTEP) codes [29,30], and the crystal structure was built with the Virtual Crystal Approximation (VCA) [31–33]. Within the EMTO theory the single-electron equations are solved for the optimized overlapping muffin-tin potential and the full charge density technique is used to calculate the total energy [3]. The exchange and correlation functional is calculated by generalized gradient approximation under Perdew-Burke-Ernzerh of functional (GGA-PBE) [34,35]. The EMTO basis set included *s*, *p*, *d* and *f* orbitals. In the irreducible wedge of the BCC Brillouin-zone [36], we used 285 inequivalent k-points. For all atoms, the valence electrons considered are following: $3d^24s^2$(Ti), $3d^34s^2$(V), $3d^54s^1$(Cr), $4d^25s^2$(Zr), $4d^45s^1$(Nb), $4d^55s^1$(Mo), $5d^36s^2$(Ta) and $5d^46s^2$(W), respectively. These atoms are distributed randomly among the supercells. The potential sphere radii were chosen to be equal to the corresponding average atomic sphere radius of all alloy components. The calculations were performed for static lattice neglecting all thermal contributions.

Under the condition of this calculation, the accuracy of the calculation results are verified. By verifying calculation, body centered cubic structure Fe crystal lattice constant is 2.83 Å, and this is very similar to the experimental value, 2.87 Å [37]. Therefore, this study selected calculation setting is quite reasonable.

3. Results and discussion

3.1. Phase structure

Fig. 1 shows the metallographic photos for (a)-TiZrVMo, (b)-TiZrVTaMo, (c)-TiZrVTaMoNb, (d)-TiZrVTaMoNbCr and (e)-TiZrVTaMoNbCrW refractory high-entropy alloys by arc melting. The micro-area EDS which including dendrite and inter-dendrite analysis results of refractory high-entropy alloys (TiZrVMo, TiZrVMoTa, TiZrVMoTaNb, TiZrVMoTaNbCr and TiZrVMoTaNbCrW) under vacuum are showed in Table 1. From Table 1 we can see, the dendrite of the TiZrVMoTa alloy is rich in high-melting-point elements: Ta (2996 °C) and Mo (2610 °C). In contrast, the inter-dendrite region is rich in low-melting-point elements: Ti (1668 °C), Zr (1852 °C) and V (1895 °C). Similarly, the dendrite region of the TiZrVMoTaNb alloy is rich in Ta, Mo and Nb(2415 °C). The dendrite region of the TiZrVMoTaNbCr alloy is rich in Ta, Mo and Nb, too. The dendrite region of the TiZrVMoTaNbCrW alloy is rich in Ta, Mo, Nb and W (3407 °C). This is consistent with the report of Chien-Chang Juan et al. [17] on refractory high entropy alloys. The main reason has been attributable to the strong tendency foe elements with higher melting point to form the first solid phase [18]. But, the dendrite region of the TiZrVMo alloy is rich in Mo and V. It does not comply with the above rules. It can be seen from Table 1, uniform distribution of each element between the dendrite and inter-dendrite region except the, basic accord with the requirement of forming high entropy alloy solid solution (molar content of 5%-35%). The X-ray diffractograms of the calculation and experimental for refractory HEAs are displayed in Fig. 2. For multicomponent alloy, many of the complex phases or intermetallic compounds would normally form