Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

ZrB_2: Adjusting the phase structure to improve the brittle fracture and electronic properties

Yong Pan*, Bingcheng Zhou

School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, China

ARTICLE INFO

Keywords:
ZrB_2
Crystal structure
Brittle-to-ductile transition
Electronic properties
First-principles calculation

ABSTRACT

Although ZrB_2 is a promising ultrahigh-temperature ceramic, the intrinsic brittleness and low fracture toughness are the main bottlenecks. To solve these key problems, by means of first-principles calculations, we predict ZrB_2 new phases, and investigate the influence of new phase on the mechanical properties and electronic properties of ZrB_2. The calculated results show that two new ZrB_2 phases: RuB_2-type with orthorhombic structure (*Pmmn*, No.59) and ReB_2-type with hexagonal structure (*P63/mmc*, No.194) are dynamical stability at the ground state. Although RuB_2-type and ReB_2-type structures weaken the volume deformation resistance and shear deformation resistance of ZrB_2, it results in brittle-to-ductile transition due to the formation of weak Zr-B bond along the shear direction. Importantly, ReB_2-type structure improves the electronic properties of ZrB_2 because of the strong charge overlap between conduction band and the valence band near Fermi level (E_F). Therefore, our work can open up a new clue to improve the ductility and electronic properties of ZrB_2.

1. Introduction

ZrB_2 is a promising ultrahigh-temperature ceramic (UHTC) due to the high melting point, high-temperature strength, high hardness, low density, better metallic behavior, excellent corrosion and oxidation resistances etc [1–6]. Although the microstructure and mechanical properties of ZrB_2 have been widely investigated over the last years [7,8], the intrinsic brittleness and low fracture toughness (3–4 MPa $m^{1/2}$) [9] are still the great obstacles. To solve these problems, one common approach that the addition of second phase (such as SiC [10,11] and ZrC [12,13]) seems to improve the ductility of ZrB_2. For example, SiC fiber not only improves the oxidation resistance but also enhances the fracture toughness [14,15]. Earlier work has been reported that the measured high-temperature strength and fracture toughness of ZrB_2 with the addition of SiC fiber are about 240 MPa and 12 MPa $m^{1/2}$, respectively [16]. Sha et al. have found that the measured high-temperature strength and fracture toughness of ZrB_2-$ZrSi_2$ ceramic composites with doping of WC are about 585 MPa and 6.87 MPa $m^{1/2}$, respectively [17]. Despite intense investigations, the improvements of intrinsic brittleness and fracture toughness are not completely solved until now. Importantly, the interaction between the fiber phase and substrate forms the strong grain interface, which gives rise to brittle fracture. As a result, it is not beneficial for the improvement of intrinsic brittleness. In addition, the second phase has some shortcomings such as worse interface matching, bad thermal expansion coefficient difference and low mechanical properties etc.

To the best of our knowledge, the mechanical properties and physical properties of a solid mainly derive from the atomic interaction and chemical bonding. To overcome the disadvantages of a second phase, an effective method is to adjust the charge interaction between Zr atom and B atom, and change the chemical bonding and crystal structure. Based on the above design ideal, we assume that the adjustment of ZrB_2 phase structure can improve the brittle fracture and physical properties of ZrB_2. Unfortunately, earlier works have shown that ZrB_2 is a typical MoB_2-type structure with space group of *P6/mmm* (No. 191) [18,19]. Until the present works other phase structures and relevant properties of ZrB_2 are unknown.

In the present work, we apply the first-principles calculations to investigate the influence of phase structure on the mechanical properties, brittle-or-ductile behavior and electronic properties of ZrB_2. Considering the correlation between phase structure and the overall properties, we design and predict three possible new structures: RuB_2-type with orthorhombic structure, ReB_2-type with hexagonal structure and ScB_2-type with cubic structure, respectively. The structural stability of new phase is examined by the dynamically and thermodynamically, respectively. In particular, the elastic properties, brittle-or-ductile behavior, electronic structure and chemical bonding of ZrB_2 with four structures are calculated. Finally, we predict that the new phases can

* Corresponding author.
E-mail address: panyong10@mails.jlu.edu.cn (Y. Pan).

http://dx.doi.org/10.1016/j.ceramint.2017.04.007
Received 23 March 2017; Received in revised form 1 April 2017; Accepted 1 April 2017

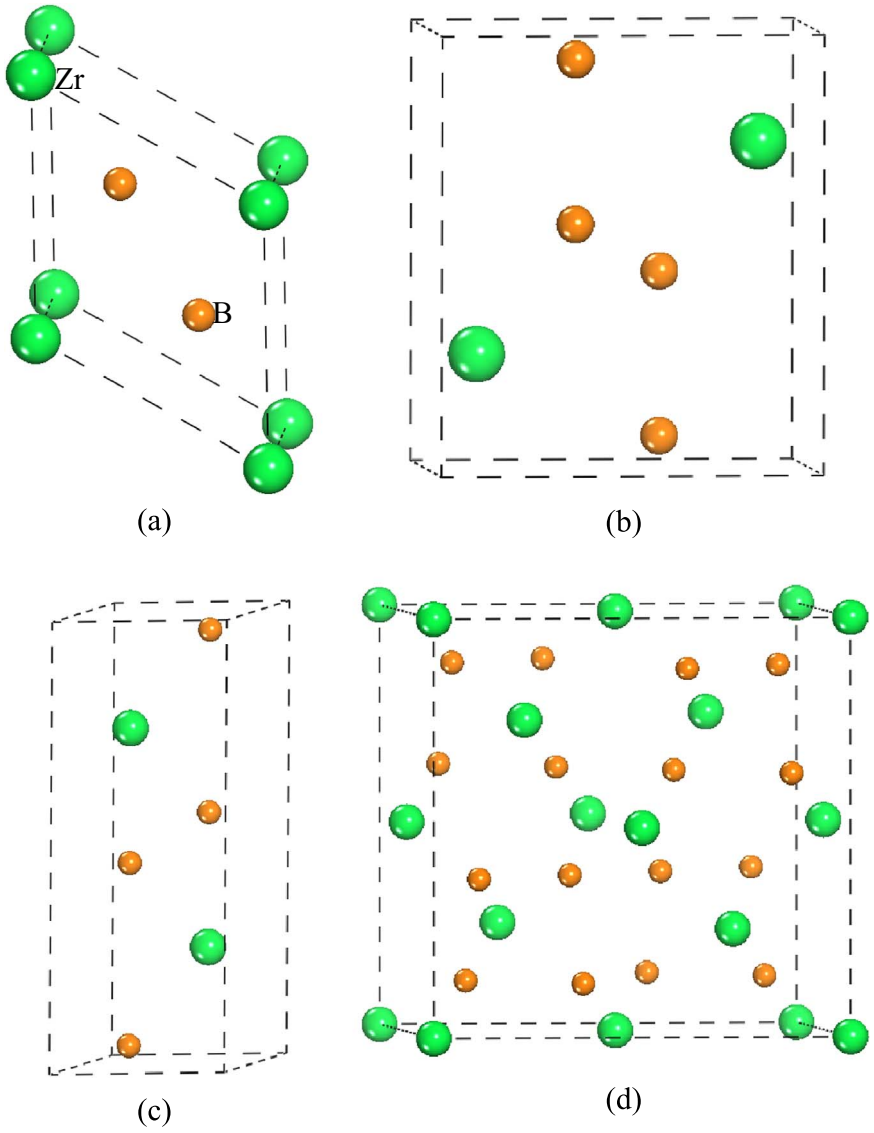

Fig. 1. Structural model of ZrB_2. (a) MoB_2-type with hexagonal structure, (b) RuB_2-type with orthorhombic structure, (c) ReB_2-type with hexagonal structure and (d) ScB_2-type with cubic structure, respectively.

effectively improve the intrinsic brittleness and electronic properties of ZrB_2.

2. Theoretical methods

As we known, ZrB_2 is a typical hexagonal structure (space group: *P6/mmm*, No. 191) within lattice parameters a=3.169 Å and c=3.530 Å [20], respectively. To explore the influence of phase structure on mechanical and physical properties of ZrB_2, we design three possible crystal structures: RuB_2-type with orthorhombic structure (space group: *Pmmn*, No. 59), ReB_2-type with hexagonal structure (space group: *P63/mmc*, No. 194) and ScB_2-type with cubic structure (space group: *Fd-3ms*, No. 227), respectively. The structural models of ZrB_2 are shown in Fig. 1.

All calculations in this paper were carried out by using the first-principles approach, as implemented in the CASTEP code [21]. To treat the electronic interaction, the exchange correlation function was adopted by using the generalized gradient approximation (GGA) with PBE functional [22]. The interaction between ion and the electron was treated by the Ultrasoft pseudopotentials [23]. After converged test, the cut-off energy of all systems was 350 eV. The Monkhorst Pack k meshes of 18×18×14, 12×17×12, 19×19×7 and 12×12×12 were selected for MoB_2-type, RuB_2-type, ReB_2-type and ScB_2-type structures, respectively. During the structural optimization, lattice parameters, internal coordinates and all atomic positions in a system were fully relaxed. Importantly, the elastic properties of ZrB_2 were calculated by using the stress vs strain method [24,25]. To examine the dynamical stability, we calculated the phonon dispersion curves of ZrB_2 based on the PHONON code [26].

3. Results and discussions

To explore the correlation between phase structure and the mechanical properties, the structural stability is examined firstly. Generally, the structural stability of a solid is determined by the thermodynamically and dynamically, respectively. The thermodynamic stability of ZrB_2 is measured by the formation enthalpy (ΔH), which is given by:

$$\Delta H = \frac{E(ZrB_2) - E(Zr) - 2E(B)}{3} \quad (1)$$

where E(ZrB_2), E(Zr) and E(B) are the calculated total energy of ZrB_2, Zr atom and B atom at the ground state, respectively. On the other hand, the dynamical stability of the predicted structure is measured by