Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Review article

Effects of carbon additives on the properties of ZrB_2–based composites: A review

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ARTICLE INFO

Keywords:
Carbon
Ceramic
Composite
Nanomaterial
Ultrahigh temperature
Zirconium diboride

ABSTRACT

This review presents the recent achievements on carbon additives incorporated in ZrB_2 ceramics, improved properties, and their advancements. Monolithic ZrB_2 ceramics have broad potential applications, but their critical drawbacks such as poor damage tolerance, and weak oxidation and ablation resistance confines their applicability. It is an important issue to resolve these shortages in physiochemical properties by engineering the composite ingredients and process design of the ceramic counterparts for an extensive production and applications, which are especially essential in high–tech industries and products. Carbon additives have exceptional characteristics including low density, low cost, and excellent thermo–mechanical stability. These materials have been incorporated in ZrB_2 ceramics to enhance their efficiency and form practical composite ceramics. Although addition of the secondary carbonaceous phases is generally supposed to improve the mechanical properties of ZrB_2 composites, it may also result in a decrease in other aspects of performance, comparing with monolithic ZrB_2 ceramics. In this work, we reviewed the methods and strategies for the preparation of carbon modulated ZrB_2 ceramic composites. Moreover, the advantages, disadvantages, and the productivity of the introduced composite ceramics have been explored and featured.

1. Introduction

There are a few natural elements with high melting points exceeding 3000 °C, including carbon (C) and metals such as rhenium (Re), osmium (Os), tungsten (W) and tantalum (Ta). In addition, the manufactured components possessing such a property are not so many. Among them, ultrahigh temperature ceramics (UHTCs) feature prominently, which are comprised of thorium dioxide (ThO_2), diboride composites (*e.g.* tantalum diboride (TaB_2), hafnium diboride (HfB_2) zirconium diboride (ZrB_2)), carbide composites (*e.g.* tantalum carbide (TaC), hafnium carbide (HfC), niobium carbide (NbC), zirconium carbide (ZrC), titanium carbide (TiC)), and nitride composites (*e.g.* tantalum nitride (TaN), hafnium nitride (HfN), boron nitride (BN)) [1]. Numerous opportunities and advanced practical applications have been arisen for these materials. Accordingly, in the last decade, many efforts have been devoted to developing the elaborated UHTCs with improved properties and performances [2–4]. Among the aforementioned ceramics, due to their fascinating physicochemical properties and broad potential applications, zirconium diboride ceramics have been intently studied. However, to this point, some issues remain undealt with, e.g. poor sinterability and low fracture toughness [5–8]. Not only does ZrB_2 have a high melting temperature (3245 °C), but also has a relatively low density (6.1 g/cm^3). These characteristics make it a very appropriate candidate for cutting–edge technologies such as aerospace refractory, and cutting tools. However, due to the poor fracture resistance and damage tolerance, its use is limited someway [1,9–11]. To pursue the improved developments, pertinent composites have been fabricated by combining diverse materials with ZrB_2, aiming ideal products [12–14].

Carbon additives with special characteristics, *e.g.* low density, low cost, and excellent thermo–mechanical stability have been incorporated in the designed ZrB_2 structures to modulate their efficiencies and form practical composites [15]. It should be noted that the fracture toughness of the carbonaceous admixed composites is higher than that of the un–reinforced ceramics.

This review article describes the effects of carbonaceous additives on the properties of ZrB_2 composites. Discussions will concentrate on

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https://doi.org/10.1016/j.ceramint.2018.01.214
Received 8 August 2017; Received in revised form 25 January 2018; Accepted 25 January 2018

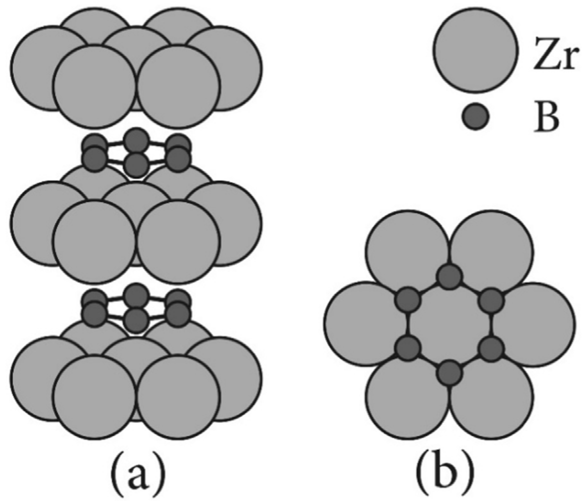

Fig. 1. Projections of ZrB_2 structure: (a) 3 dimensional view and (b) top view.

the recent major achievements of the relevant composites with enhanced efficiencies. Finally, the perspective carbonaceous modifications of ZrB_2 composites, advantages and challenges of the introduced composites will be presented.

1.1. Structure and properties of ZrB_2

ZrB_2 has a hexagonal crystal lattice with a prototype structure of P6/mmm, and unit–cell parameters of a: 3.17 Å and c: 3.53 Å. As shown in Fig. 1, this structure contains layers of boron (B) atoms in two–dimensional graphite–like plates in sp^2 hybridization with hexagonal close packed (hcp) Zr arrays alternation [1]. The structure of ZrB_2 is composed of Zr–Zr metallic bonds, B–B covalent bond, and Zr–B covalent/ionic bonds. The presence of free electrons in Zr–Zr bonds provides high electrical and thermal conductivities. B–B bonds elevate the stiffness, hardness and chemical inertness properties. The strong Zr–B bonds increase the melting point of ZrB_2 [16].

In addition to its high melting point, ZrB_2 has a combination of exceptional characteristics such as chemical inertness against molten metals and slags, retention strength at high temperatures, erosion and corrosion resistance in adverse atmosphere, low coefficient of thermal expansion, high thermal and electrical conductivities and great thermal shock resistance [1,17,18]. ZrB_2 is also reported to be favorably resistive to plasma arcs and sparks [17].

1.2. Applications of ZrB_2 composites

There has been growing interest in ZrB_2 development and applications in recent years all around the world. This UHTC ceramic has been applied successfully in cutting tools, microelectronics, plasma–arc electrodes, solar absorbers, electric discharge machining electrodes, Hall–Heroult cells, refractory crucibles, and furnace elements. Because ZrB_2 is resistant to molten metals and slags, it can be used in steel continuous casting as refractory protective linings/sleeves in submerged entry nozzles and re–usable atmospheric re–entry vehicles. Although carbide materials typically have high melting points, ZrB_2 and its related composites are special candidates for ultrahigh–temperature thermomechanical structural applications, owing to their unique properties. In addition, relatively low cost and low theoretical density make ZrB_2 a fascinating UHTC for aerospace applications, hypersonic vehicles, wing leading edge, jet vanes, and nozzle components [1,16–19].

1.3. Limitations and challenges of ZrB_2

The use of monolithic ZrB_2 ceramics for ultrahigh temperature industrial applications is restricted by its poor damage, oxidation, and ablation tolerances. Therefore, several methods have been investigated to resolve this drawback. For instance, ZrB_2 compositing technique produces the materials with enhanced densification behavior, improved physical and mechanical properties as well as ablation and oxidation resistance [18]. The nature of ZrB_2 is covalent with a low self–diffusion coefficient. Furthermore, the presence of oxide contaminations *e.g.* zirconia (ZrO_2) and boria (B_2O_3) on the surface layers of ZrB_2 powder decreases the sinterability [20]. Dense ZrB_2 ceramics are fabricated by hot pressing (HP) or hot isostatic pressing (HIP) routes at elevated temperatures under externally applied pressures. Such sintering procedures require long preparation time, post–processing procurement, costly electrical energy, and sophisticated encapsulation technology. Complementary cutting and tooling are generally required to resolve the shortages of the imperfect shaped materials incidental to these products. Subsequently, high manufacturing costs effects on the integrity of the products arise out of such modification processes. Moreover, long dwelling time during sintering process leads to the grain growth and microstructure coarsening causing deficiencies in the structural properties [16,21]. Furthermore, to improve the corresponding composites properties such as oxidation resistance, mechanical strength and fracture toughness, silicon carbide particles are frequently added. Despite its positive attributes, ZrB_2 is brittle, which may limit its use in critical applications, in particular, for hypersonic aerospace vehicles.

2. Synthesis of zirconium diboride composites

Producing ZrB_2 composites highly depends on the characteristics and intrinsic properties of the additives and raw materials. The components' morphology, purity, particle size, surface areas, and *etc*. are important factors with remarkable influence in the preparation process and products properties [17]. Although the characteristics of ZrB_2 composites can generally be modulated during the production process, they are mainly determined by engineering the synthetic steps and ingredient properties. Accordingly, it is an important issue to study the synthesis routes of ZrB_2–based ceramics comprehensively. Such studies may provide detailed understanding about the effect of the utilized materials in manufacturing processes and potential properties of the final products. Synthetic routes of ZrB_2 ceramics are generally classified in three main categories [45]. In this section, published literatures with innovative production procedures are highlighted. Discussions elucidate the strategies and designs to prepare carbon incorporated ZrB_2 composites with improved properties, which will lead to the development of efficient and effective ceramics. It is noteworthy that one can develop a new synthesis path by combining and modifying the previously verified synthetic procedures.

2.1. Direct synthesis by pure elements utilization

Zirconium diboride ceramics can be synthesized via direct reaction of boron and Zr metal, based on the following reaction: [22]

$$2B + Zr \rightarrow ZrB_2 \quad \Delta G_{2000K} = -279.6 kJ.\ mol^{-1} \tag{1}$$

The reaction is favorably achieved at 1700 °C and easily initiated with a relatively low activation energy. Recently, several successful attempts have been reported based on self–propagating high temperature synthesis (SHS) of zirconium diboride and traditional synthesis using the basic elements [17]. Camurlu et al. successfully synthesized nano–ZrB_2 powders (particle size < 200 nm) via SHS using NaCl as binder [22]. SHS process was also applied on a mixture of Zr, B, and C powders by Tsuchida and Yamamoto [23]. In another study, Licheri et al. synthesized dense ZrB_2 composite using a mixture of zirconium