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Reactive sintering of tungsten-doped high strength ZrB_2–SiC porous ceramics using metastable precursors

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ABSTRACT

Tungsten-doped porous ZrB_2-20 vol.% SiC specimens with a high strength skeleton were fabricated by reactive sintering using metastable reactants, i.e., as-synthesized amorphous hydrous ZrO_2–WO_3/ZrO_2, amorphous boron, nanocarbon, and β-SiC. Doping with tungsten clearly promoted sintering and improved mechanical properties; the optimum tungsten concentration to obtain high mechanical properties was investigated. A single-phase solid solution (Zr,W)B_2 was formed in the specimens with tungsten. We suggest that sintering was promoted by self-accelerated diffusion owing to the formation of point defects caused by doping with tungsten. The improvement of mechanical properties could be attributed to solid solution strengthening.

1. Introduction

Porous ceramics have shown many potential applications in the last few decades because of their excellent mechanical and chemical stabilities even in high-temperature environments, and corrosive media. However, only a few research articles about ZrB_2-based porous ceramics have been reported. One of the most promising candidates for high-temperature structural applications, ZrB_2–SiC composites exhibit many excellent properties, such as high strength, high hardness [1–4], moderate fracture toughness, and relatively good oxidation/ablation resistance [5–8].

Reactive hot pressing has been identified as an efficient route to produce ZrB_2-based ceramics with low impurity levels and high density at lower temperatures [9]. There are two processes that occur in reactive hot pressing: *in situ* reaction of precursor powders, and densification. The former process could provide cleaner and stronger interfaces between the component phases, which would be beneficial for densification of the materials [5,10–12].

Based on our previous study, ZrB_2 powder could be synthesized via borothermal/carbothermal reduction as described by the following reactions [13,14]:

$$ZrO_2(s) + 4B(s) \rightarrow ZrB_2(s) + B_2O_2(g) \quad (1)$$

Actually, B_2O_2 is known to be unstable and may decompose to B_2O_3 and boron, which can then react further [15]:

$$3B_2O_2(g) \rightarrow 2B_2O_3(l) + 2B(s) \quad (2)$$

$$3ZrO_2(s) + 10B(s) \rightarrow 3ZrB_2(s) + 2B_2O_3(l) \quad (3)$$

Initially, ZrO_2 can react with boron to form B_2O_3/B_2O_2 and ZrB_2 during heating. We added a small amount of carbon into the initial binary ZrO_2/boron reaction system. With increasing temperature, B_2O_3 and residual ZrO_2 react with the carbon to form ZrB_2, as shown in Reaction (4):

$$ZrO_2(s) + B_2O_3(l) + 5C(s) \rightarrow ZrB_2(s) + 5CO(g) \quad (4)$$

The gaseous products (B_2O_2 and CO) of this reaction system provide a potential way of fabricating ZrB_2-based porous ceramics.

In addition, many studies on the positive effects of tungsten or WC on the properties of ZrB_2-based ceramics have been published. Because of this, we attempted to prepare porous ZrB_2–SiC ceramics

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with a high strength skeleton by reactive hot-pressing along with tungsten doping.

The possible reactions of WO_3 in the W-B-C system are shown in Reactions (5) and (6):

$$2WO_3(s) + 9B(s) \rightarrow W_2B_5(s) + 2B_2O_3(l) \quad (5)$$

$$WO_3(s) + 4C(s) \rightarrow WC(s) + 3CO(g) \quad (6)$$

Because it is a stronger reductant than carbon, boron can more readily form strong covalent bonds with tungsten. Additionally, the excess boron in this system favors the production of W_2B_5.

In the present work, porous ZrB_2-20 vol.% SiC ceramic composites with different tungsten contents were prepared by reactive sintering from a powder mixture of as-synthesized amorphous hydrous ZrO_2–WO_3/ZrO_2, amorphous boron, nanocarbon, and β-SiC. The sintering characteristics, the properties of the final composites, and the mechanism of the enhancement of these properties in the ZrB_2-20 vol.% SiC composites were investigated.

2. Experimental

Commercially available zirconyl nitrate ($ZrO(NO_3)_2$), tungsten hexachloride (WCl_6), amorphous boron (B), nanocarbon (C), and β-SiC were used as raw materials. The properties and suppliers are listed in Table 1. The composite-manufacturing process consists of two main steps: (1) synthesis of amorphous hydrous ZrO_2–WO_3/ZrO_2 and (2) sintering. In a typical synthesis, the hydrous ZrO_2–WO_3 precursor was prepared by adding a mixture of 0.5 M $ZrO(NO_3)_2$ aqueous solution and 0.1 M WCl_6 alcohol solution dropwise into a stirred ammonia solution. Details of the processes were shown in our previous study [14]. Precursors with W:Zr molar ratios of 0, 0.05, and 0.1 were synthesized. The as-synthesized precursor was dried at 60 °C and then blended with amorphous boron, and nanocarbon to give a molar ratio of Zr:B:C = 1:4:1, and finally β-SiC with a volume ratio of ZrB_2:SiC = 80%:20%. They were wet mixed in ethanol for 4 h and then dried. Finally, the mixed powder was loaded into a graphite hot press die with a BN coating, and heated in vacuum ($\sim 10^{-1}$ Pa). The heating rate was 10 °C min^{-1}. To promote the reaction, the specimen was held for 30 min at 1550 °C. Then, an axial pressure of 30 MPa was gradually applied as the specimen was heated further to 1800 °C. After 30 min at 1800 °C, the specimens were cooled within the furnace, and the pressure was released gradually.

The density and porosity were measured by the Archimedes method. The mass and heat flow of the specimens were monitored by thermal analysis (TG-DSC, Netzsch STA449F3). The crystallographic structure was identified by X-ray diffractometry (XRD, D/MAX 2200 PC). The microstructure and morphology of the particles were investigated using scanning electron microscopy (SEM, JEOL JSM-6700F). Three point bending strength was measured on bars with a span of 10 mm using a crosshead speed of 0.5 mm min^{-1}. The dimensions of the bars were 2 × 3 × 18 mm. Hardness was measured by Vickers' indentation on polished surfaces using a 50 N load with a dwell time of 10 s. Each value was an average of five measurements. Fracture toughness (K_{IC}) was calculated by the indentation fracture (IF) technique, as shown in Eq. (7):

$$K_{IC} = P\left[\pi\left(\frac{C_1 + C_2}{4}\right)\right]^{-3/2}(\tan\beta)^{-1} \quad (7)$$

where, P is the load (50 N), C_1 and C_2 are the measured diagonal crack lengths (m), and β is an angle constant (68°).

Table 1
Details of the starting materials.

Starting material	Particle size (D50)	Purity	Supplier
Zirconyl nitrate	*N/A*	AR	Lanyi Reagents Co., Ltd., Beijing, China
Amorphous boron	0.85 μm	95%	Dandong Chemical Co., Ltd., Beijing, China
Nanocarbon	30 nm	99.5%	Shanghai Jingchun Reagents Co., Ltd., Shanghai, China
Tungsten hexachloride	*N/A*	99%	Shanghai Jingchun Reagents Co., Ltd., Shanghai, China
β-SiC	60 nm	99%	Kaier Reagents Co., Ltd., Hefei, China

3. Results and discussion

The characteristics of the as-sintered specimens are summarized in Table 2. Specimens with W:Zr (mol) = 0 and 0.1 had porosities of 10 and 9%, respectively. On the other hand, the specimen with W:Zr (mol) = 0.05 showed the highest porosity, 17%. However, the mechanical properties of the specimens do not simply correlate with their porosities. The specimen with W:Zr (mol) = 0.05 had the highest values of bending strength (480 ± 36 MPa), hardness (17.3 ± 1.8 GPa), and fracture toughness (3.6 ± 0.2 MPa $m^{1/2}$); these values are comparable to those of dense ZrB_2-20 vol.% SiC ceramics. In general, the porosity should have a major influence on the mechanical properties of materials. Thus, the enhancement mechanism was investigated further.

Generally, there are two routes to speed up sintering of ceramic materials. One is to apply an external pressure to allow the particles to approach one another more closely, and also to reduce the activation barrier to melting. The other is to add sintering aids to provide a diffusional short-cut. Both approaches were used in this study to prepare porous ZrB_2–SiC ceramics.

Sintering occurs by atom and/or ion diffusion when an atom or ion gains sufficient energy to leave its site and migrate. There are essentially three mechanisms by which atoms will diffuse. The first one is the vacancy mechanism, which involves the jump of an atom or ion from a regular site into an adjacent vacant site. The second one is interstitial diffusion, which requires the presence of interstitial atoms or ions. The third (and least common) one is the interstitialcy mechanism, *i.e.*, an interstitial atom pushes an atom from a regular site into an interstitial site. Accordingly, the sintering process will be enhanced through increasing the amount of vacancies; meanwhile, the presence of interstitial atoms can also improve diffusion during heating.

For ZrB_2, it is possible to tailor point defects by doping with differently charged species, such as W^{5+}. When it is accommodated into the ZrB_2 structure, both vacancies and interstitial ions are formed for charge compensation. It is expected that these defects can enhance diffusion by the first and second diffusion mechanisms. Moreover, the promotion of sintering by introducing W^{5+} may also be because of enhancement of the thermal vibration of the atoms by partial substitution of the smaller W^{5+} for the larger Zr^{4+} [16].

Table 2
Characteristics of specimens sintered at 1800 °C under 30 MPa for 30 min in vacuum.

W:Zr (mol)	0	0.05	0.1
Density (g cm^{-3})	5.1	4.9	5.6
Porosity (%)	10	17	9
Phase composition	ZrB_2, SiC	W-doped ZrB_2, SiC	W-doped ZrB_2, SiC, W_2B_5
Three-point bending strength (MPa)	316 ± 60	480 ± 36	184 ± 40
Fracture toughness (MPa $m^{1/2}$)	3.0 ± 0.6	3.6 ± 0.2	1.6 ± 0.5
Vickers hardness (GPa)	14.9 ± 1.7	17.3 ± 1.8	14.6 ± 1.6