

Synthesis and characterization of sol-gel derived ZrB_2 -ZrC compounds

Karina S. Campos^{a,*}, Guilherme F. B. Lenz e Silva^b, Eduardo H. M. Nunes^a and Wander L. Vasconcelos^{a,**}

^aFederal University of Minas Gerais Department of Metallurgical and Materials Engineering, Avenida Presidente Antônio Carlos, 6627, Campus da UFMG, Belo Horizonte, MG, CEP: 31270-901, Escola de Engenharia, bloco 2, sala 2230, Brazil

^bUniversity of São Paulo, Department of Metallurgical and Materials Engineering, Av. Mello Moraes 2463, Cidade Universitária, São Paulo/SP, Brazil

In this work ZrB_2 -ZrC compounds were prepared by sol-gel process. These materials were examined by X-ray diffraction (XRD), thermogravimetric (TG) analysis, laser granulometry, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and nitrogen adsorption tests. Thermodynamic calculations were carried out using the FactSage® thermochemical software and databases. XRD revealed that ZrB_2 and ZrC are the major phases present in the materials obtained in this study. It was observed that the relative amount of ZrB_2 and ZrC in these samples can be tailored by controlling the concentration of H_3BO_3 in the starting solution. On one hand, laser granulometry and SEM tests revealed that the ZrB_2 -ZrC compounds prepared in this work show a coarse particle size distribution. On the other hand, they exhibited remarkable specific surface areas (about $150 \text{ m}^2/\text{g}$).

Key words: Sol-gel, ZrB_2 -ZrC compounds, Structural characterization.

Introduction

The major advantages over metals of ceramic compositions based on carbides, nitrides, and borides are related to their outstanding resistance to wear, creep at high temperatures, and oxidation [1-3]. It is well established that metallic elements from the fourth, fifth, and sixth columns of the periodic table give rise to a relatively wide variety of boron- and carbon-based compounds. They constitute a class of promising materials for high temperature applications in several industrial fields, including foundry and refractory industries [4].

Zirconium diboride (ZrB_2) exhibits hexagonal structure typical of transition-metal diborides, belonging to a class of materials known as ultra-high-temperature ceramics (UHTCs) [5, 6]. ZrB_2 has attracted much attention for use in reusable launch and hypersonic vehicles, specially for sharp leading edges and other hot surface applications [7, 8]. It also has been used as molten-metal crucibles, Hall-Heroult cell cathodes, and thermowell tubes for steel refining [9, 10]. Zirconium carbide (ZrC) shows a remarkable hardness, chemical inertness, and low damage under irradiation [11, 12]. In addition, it is highly nonstoichiometric and exhibits an outstanding strength at high temperatures [13, 14]. ZrC has been widely used in structural,

electronic, and nuclear applications [15, 16]. ZrB_2 -ZrC composites have been considered promising materials for high strength, abrasion, and heat resistance applications due to their remarkable properties, such as high melting point, mechanical strength, and chemical inertness [17, 18]. According to Shim *et al.* [19], these composites can also be used as electronic materials because of their good electrical conductivity.

Traditionally, monolithic ZrB_2 , ZrC, and ZrB_2 -ZrC composites can be obtained by various methods, including solid-state reaction, electrochemical, mechanical alloying, and self-propagating high-temperature synthesis (SHS) [20-22]. However, high temperatures and long heating times are commonly used in these processes [23]. In addition, the obtained powders usually show a relatively large crystallite size and poor sinterability [24]. It is well established that the sol-gel process is a powerful method for preparing samples of high purity, homogeneity, and low particle size [25, 26]. Moreover, this method exhibits lower synthesis temperatures and shorter reaction times when compared to other ceramic processing techniques [27, 28]. An array of ceramic materials has been obtained by the sol-gel technique [29, 30]. In this work ZrB_2 -ZrC compounds were prepared by sol-gel process. These materials were examined by X-ray diffraction (XRD), thermogravimetric (TG) analysis, laser granulometry, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and nitrogen adsorption tests. Thermodynamic calculations were carried out using the FactSage® thermochemical software and databases [31, 32].

*Corresponding author:

Tel : +55-31-3409-1813

Fax: +55-31-3409-1815

E-mail: *karinaespanhol@hotmail.com, **wlv@demet.ufmg.br

Experimental

Sol-gel syntheses

Initially a solution of zirconium (IV) oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ - $\geq 99.5\%$ -Aldrich), boric acid (H_3BO_3 - $\geq 99.8\%$ -Aldrich), and absolute ethanol (EtOH -F. Maia Chemicals) was prepared. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and H_3BO_3 were used, respectively, as sources of zirconia (ZrO_2) and boron oxide (B_2O_3). The solution pH was adjusted by adding ammonium hydroxide (NH_4OH -28-30%-Quimex). Next, phenolic resin (PR) with about 60 wt% carbon loading (Crios Resinas Sintéticas / SI Group) was added to the solution. The molar ratio of the prepared solution was kept at 1 $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$: 2 EtOH : 5 PR. The obtained sol was aged at room temperature for 04 hours and then dried in air at 80 °C for 12 hours. Next, it was placed in a graphite crucible and heat treated under argon atmosphere at 1500 °C for 01 hour, using a heating rate of 10 °C/min.

Characterization

XRD was carried out with a Philips PANalytical X' Pert Pro diffractometer, using $\text{CuK}\alpha$ radiation and a scan velocity of 0.127 °/s. The identification of the crystalline phases was performed using the JCPDS file numbers 34-0423, 11-0110, 24-1165, 18-1492, and 25-0284 for ZrB_2 , ZrC , ZrO_2 , ZrCl_2 , and C phases, respectively. Morphological studies were carried out with a JEOL JSM-6360 LV scanning electron microscope. Compositional analyses were performed using a NORAN EDS system available in the SEM equipment. Particle size distribution tests were carried out in a CILAS 1064 laser granulometer using water as dispersing medium. Samples were deagglomerated in an agate mortar before these tests.

Nitrogen adsorption tests were performed in a Micromeritics ASAP 2020 apparatus, using samples degassed at 150 °C for up to 48 hours under vacuum. The specific surface area and pore size distribution were assessed by the BET and NLDFT methods, respectively. TG tests were carried out with a Netzsch STA 409 thermoanalyzer. They were performed under argon flow (50 ml/min) and using a heating rate of 10 °C/min. Thermodynamic calculations were carried out using the FactSage 6.4 thermochemical software.

Results and Discussion

Fig. 1 exhibits a typical XRD pattern of the samples prepared in this work. We observed that ZrB_2 and ZrC are the major phases present in these materials. ZrO_2 was detected in significant amounts, whereas ZrCl_2 and C were observed as minor components. The ZrCl_2 and C phases observed in the XRD patterns seem to be related to the use of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and PR in the synthesis step. The formation of ZrB_2 could be related to the following reaction [33, 34]:

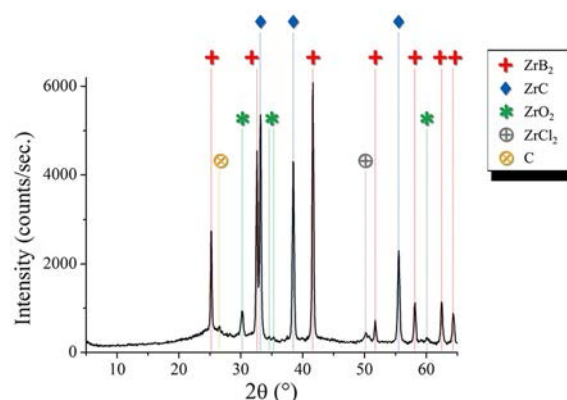
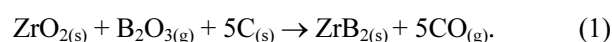
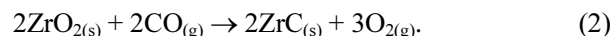


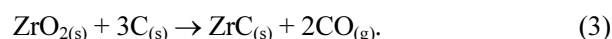
Fig. 1. Typical XRD pattern of the samples prepared in this work.



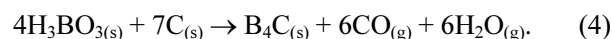
Thus, from equation (1) it is clear that the lower the concentration of B_2O_3 in the starting solution, the lower the amount of ZrB_2 in the prepared material. The formation of ZrC could be associated with the lack of B_2O_3 in the reaction medium [35, 36]. As a result, the relative amount of ZrB_2 and ZrC in the obtained materials can be tailored by controlling the concentration of H_3BO_3 in the starting solution. One could suggest that the formation of ZrC could be ascribed to the reaction between ZrO_2 and CO:



Nonetheless, the change in Gibbs free energy associated with this reaction is highly positive for a wide temperature range. Thus, under atmospheric pressure CO is unlikely to react with ZrO_2 to form ZrC [37]. The formation of ZrC could be related to [38, 39]:



The Gibbs free energy associated with the reaction (3) is highly negative at temperatures about 1500 °C [40]. The formation of B_4C could also be expected [41]:



The Gibbs free energy for reaction (4) is negative at temperatures above 1400 °C. However, B_4C was not detected in the XRD tests. We believe that it could be present in the samples at concentrations below the detection limit of XRD (about 5%) [42, 43]. Khanra *et al.* [40] reported that the reaction (4) is kinetically unfavorable, suggesting that it would require a long period of time for this reaction to complete. Fig. 2 exhibits the phase diagram for the Zr-B-C-O system at 1400 °C. We noticed that the formation of ZrB_2 , ZrC , and ZrO_2 was also predicted in the equilibrium diagram obtained using FactSage®.

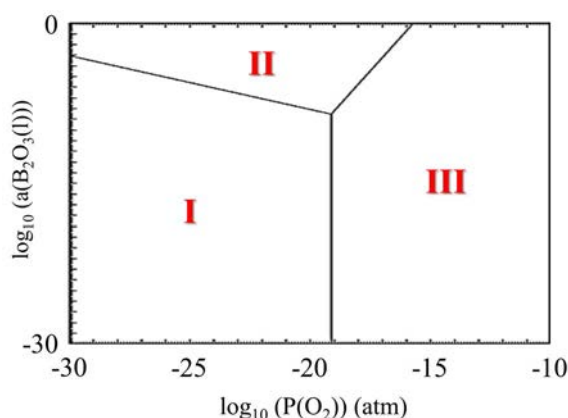


Fig. 2. Equilibrium diagram obtained from FactSage® for the Zr-B-C-O system at 1400 °C. I: ZrC(s) / II: ZrB₂(s) / III: ZrO₂(s).

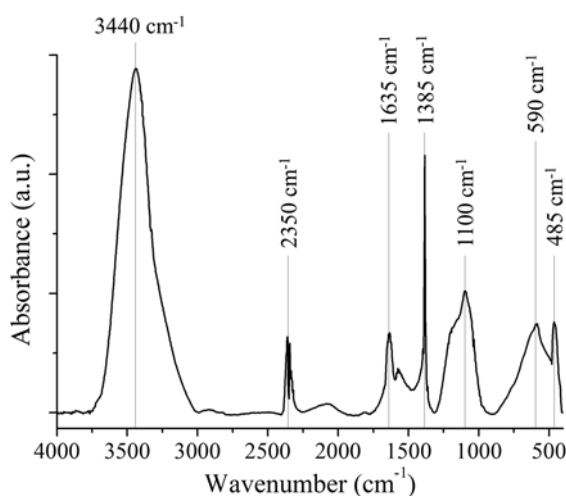


Fig. 3. FTIR spectrum of the samples obtained in this study.

Fig. 3 depicts the FTIR spectrum of the samples obtained in this study. The wide band centered at 3440 cm⁻¹ has been related to OH⁻ groups [44]. The duplet at 2350 cm⁻¹ is ascribed to atmospheric CO₂ [45]. The features at 1635 cm⁻¹ and 1385 cm⁻¹ reveal the presence of ZrC in the samples [46]. The band at 1100 cm⁻¹ is associated with CH₂-OH bonds [47], whereas those at 590 cm⁻¹ and 485 cm⁻¹ could be related to ZrO₂ [44, 48]. It is worth mentioning that ZrB₂ do not show infrared-active modes in the spectral range used in this work [48]. The presence of the band at 1100 cm⁻¹ could reveal that PR was not fully consumed during reaction (1). As already mentioned, C was also observed in minor amounts in the XRD tests. Features ascribed to B₂O₃ were not observed in the obtained FTIR spectra, revealing that B₂O₃ was fully consumed in the reaction (1).

Fig. 4 displays a typical TG curve of the materials obtained in this study. The first derivative of this curve is also shown in this figure. The mass loss at temperatures of up to 200 °C is ascribed to the removal of water [24]. The thermal event from 200 °C to 400 °C seems to be associated with the decomposition of the

residual PR present in the samples [49]. The sharp decrease in weight at temperatures above 1100 °C could be related to the carbothermal reaction that leads to the formation of ZrC [49]. It is worth highlighting the low total mass loss observed in these tests (about 6%). Opeka *et al.* [50] investigated the oxidation behavior of monolithic ZrB₂, ZrC, and ZrB₂-ZrC-based composites by performing TG under air flow. ZrC showed a complete oxidation at temperatures about 700 °C. Its oxidation products were ZrO₂ and carbon oxides. In case of ZrB₂, the oxidation products were ZrO₂ and liquid B₂O₃. Liquid boria formed in the initial stages of oxidation filled the porosity and grain boundaries of ZrB₂, leading to the formation of a continuous protective coating around it. This material showed a complete oxidation at temperatures about

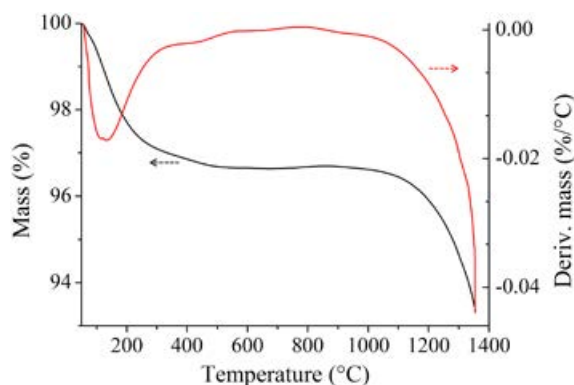


Fig. 4. Typical TG curve of the ZrB₂/ZrC compounds obtained in this work.

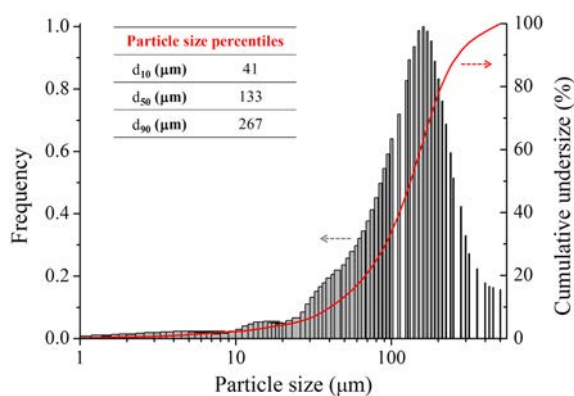


Fig. 5. Particle size distribution of the materials prepared in this study.

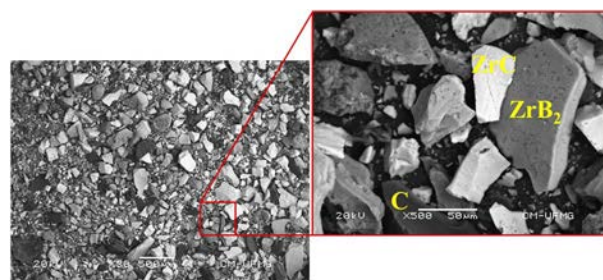


Fig. 6. SEM micrographs of ZrB₂/ZrC compounds.

1500 °C. However, the $\text{ZrB}_2\text{-ZrC}$ -based composites obtained by the authors showed an oxidation resistance higher than those exhibited by ZrB_2 and ZrC .

Fig. 5 shows the particle size distribution of the samples obtained in this study. One observes that these materials exhibit a nearly unimodal particle size distribution centered at about 160 nm, with 50% of the particles showing sizes below 133 nm. Fig. 6 depicts SEM micrographs of these samples. We observed coarse particles of C, ZrC , and ZrB_2 in these images. It is worth mentioning that the identification of the phases detected in the SEM micrographs was also based on EDS microanalysis. We believe that the particle size distribution of these materials could be decreased by milling them in a high-energy ball mill.

Fig. 7a shows a typical nitrogen adsorption isotherm of the prepared composites. According to IUPAC [51], this isotherm is related to mesoporous materials. The BET specific surface area of these samples is about $150 \text{ m}^2/\text{g}$. Fig. 7b shows their pore size distribution. It was observed that these samples show a significant volume fraction of pores with sizes between 20 Å and 400 Å, which are the lower and upper limits established by IUPAC for mesopores. The high specific surface area exhibited by the materials obtained in this work could be an issue of great importance since this large contact area could improve their reactivity [52]. For instance, this behavior could lead to a more effective prevention of oxidation when they are used as antioxidants in refractory compositions [53, 54]. Commercial grade antioxidants usually show specific surface areas much

lower than those observed for the samples obtained in this work [55].

Conclusions

In this work $\text{ZrB}_2\text{-ZrC}$ compounds were prepared by sol-gel process. XRD revealed that ZrB_2 and ZrC are the major phases present in these materials. It was observed that the relative amount of ZrB_2 and ZrC in the obtained samples can be tailored by controlling the concentration of H_3BO_3 in the starting solution. ZrO_2 was detected in significant amounts, whereas ZrCl_2 and C were observed as minor components.

Absorption bands ascribed to ZrC , ZrO_2 , and PR were observed in the FTIR tests. Features ascribed to B_2O_3 were not observed, revealing that B_2O_3 was fully consumed in the synthesis step. The thermal behavior of the materials obtained in this work was observed by performing TG tests under argon flow. On one hand, laser granulometry and SEM revealed that they show a coarse particle size distribution. It is important recalling that these samples were not subjected to milling procedures. On the other hand, these materials exhibited a remarkable specific surface area (about $150 \text{ m}^2/\text{g}$).

Acknowledgments

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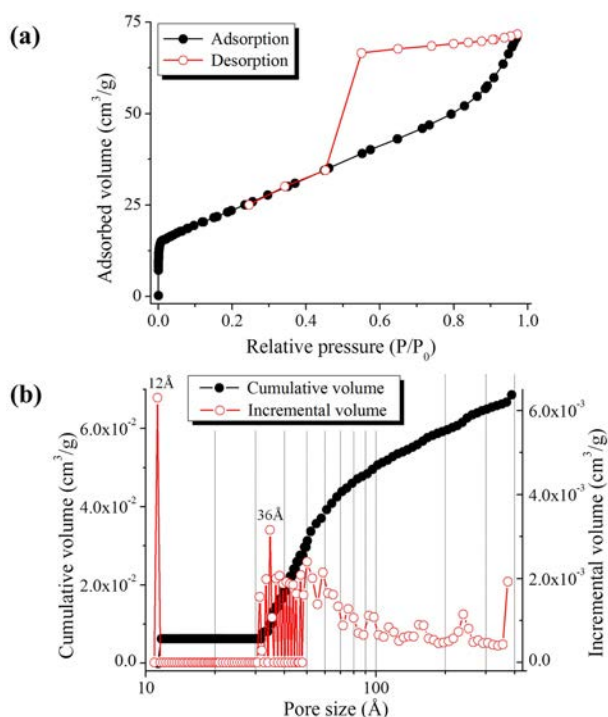


Fig. 7. Typical nitrogen adsorption isotherm (a) and pore size distribution (b) of the samples prepared in this work.

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