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Fabrication of non-oxide ceramic powders by carbothermal-reduction from industrial minerals

Ljiljana Kljajević [1], Aleksandra Šaponjić *,[1], Svetlana Ilić, Snežana Nenadović, Maja Kokunešoski, Adela Egelja, Aleksandar Devečerski

Laboratory of Materials Science, Institute of Nuclear Science Vinča, University of Belgrade, Belgrade, Serbia

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ABSTRACT

The most promising method for obtaining a large variety of non-oxide products having important technical uses is carbothermal-reduction reaction (CRR). By using this procedure, SiC and ZrC/SiC powders are obtained from diatomaceous earth and zircon powder. In this way the synthesized powders are obtained at a relatively low temperature due to good homogenization. Starting C/$ZrSiO_4$ admixtures having different molar ratios (3:1, 4:1, 5:1 and 7:1) and C/SiO_2 having ratios 1:1, 3:1, 4:1, and 7:1 were heated at temperatures between 1300 and 1600 °C in a controlled Ar flow atmosphere. The phase evolution was a function of the raw materials molar ratios and sintering temperature. The optimal parameters for the synthesis of SiC and ZrC/SiC powders were obtained. The results obtained by EDS analysis are in good agreement with those obtained by XRD analysis for the synthesized carbide powders.

1. Introduction

In the recent years, significant progress has been done in the development of engineering ceramic materials. A new generation of ceramics which is expected to find a wide use in high temperature applications has been developed. Non-oxide ceramics based on the carbides, nitrides, and borides of group IVB and VB transition metals have received a considerable attention due to their unique combination of properties, such as high melting temperature, hardness, high electrical and thermal conductivities, as well as chemical inertness [1]. Silicon carbide is an important engineering material due to its high temperature strength, thermal shock resistance, and resistance to wear and corrosion [2]. Many authors have studied the formation of SiC powders from the commercially mined geological materials known as industrial minerals, such as high purity quartz sand, aluminosilicates, diatomaceous earth, zircon, mulite, clay as a SiO_2 source [3–7]. These minerals may be used in their natural state or after beneficiation as raw materials in a wide range of applications. The required quality of a final product depends on the starting materials and processing technology. Among the most utilized industrial minerals are diatomaceous earth and zircon [7]. The admixture of carbon and diatomaceous earth yields SiC in the temperature range from 1480 °C to 1700 °C [5]. Among the raw materials that may be used for SiC powder production, the above mentioned diatomaceous earth has some advantageous properties such as high specific surface area, high silica content, and low price [8]. Beside SiC, zirconium carbide is one of the most promising ceramics for ultrahigh temperature applications due to its high melting point (up to 3540 °C), ability to form refractory oxide scales at high temperatures, and a relatively low density (6.7 g/cm^3) compared to HfC (12.2 g/cm^3) [9]. Also, ZrC powders can be produced by using naturally occurring minerals, mainly zircon beach sands ($ZrSiO_4$) and badeleyite (ZrO_2) [9].

Various routes for preparing homogenous ceramic powders have been developed so far. Good homogenization and high purity of produced powders are obtained by chemical routes, but these methods are expensive in terms of industrial manufacturing in comparison with the conventional milling techniques. One of the most promising methods for production of the non-oxide ceramic powders with important technical uses is carbothermal-reduction reaction (CRR) [10]. This procedure offers the possibility of an economically attractive production route from naturally occurring materials and the obtained powders are well homogenized. This method has been used as a preferred route to process oxidic ores and for elimination of the silica component from mineral silicates [11–14].

During the carbothermal reduction reaction between two solids, oxide and carbon, one solid (carbide) and one gaseous (CO)

* Corresponding author.
E-mail address: acavuc@vinca.rs (A. Šaponjić).
[1] Contributed equally to this article.

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reaction product are formed. This indicates the importance of mass transport mechanisms in these reactions [15]. The possible ways for the mass transport and formation of reaction products are:

1. Reduction of the oxide by CO and regeneration of CO from the resulting CO_2 and solid carbon – the mass transport of carbon to the oxide particle is realized by the CO/CO_2 gas couple. The oxide particle is the precursor for the carbide particle in this case.
2. Formation of gaseous oxide intermediates or formation of the solid reaction product in the gas phase by reaction with CO. The precursor for the carbide particle is the carbon particle during this path.
3. Reaction between the oxide and carbon by solid state reaction, in which CO appears as a gaseous reaction product without any mass transfer function [15–17].

The overall process of experimentally confirmed carbothermal reduction of SiO_2 is presented by general equation [15–17].

$$SiO_2(s)+3C(s)\rightarrow SiC(s)+2CO(g) \quad (1)$$

Formation of the final product is more complex and requires series of solid–solid, solid–gas and gas–gas reactions [15–17]. During heat treatment, Si, or SiO in gaseous form, is liberated and further reacts with excess of carbon to form SiC. Reaction of carbothermal reduction of zircon and diatomaceous earth, or any other source of SiO_2, strongly depends on amount and shape of particles of the starting materials as well as on specific surface of the added carbon [10,11,18–23].

Formation of ZrC from zirconia is usually represented by the following general reaction [18]:

$$ZrO_2+3C=ZrC+2CO(g) \quad (2)$$

Eq. (2) is also an over simplified view of the far more complex mechanism of ZrO_2 carbothermal reduction which comprises the steps that are very similar to those of SiO_2 carbothermal reduction. Variations of $C/ZrSiO_4$ ratio obtain different zircon carbothermal reduction reaction products [19,23,24].

The aim of this study is the investigation and development of a low cost synthesis route for production of carbide powders directly from industrial raw minerals, diatomaceous earth, and zircon powders, involving a minimum number of process steps.

2. Experimental

2.1. Preparation of SiC and ZrC/SiC powders

Non-oxide ceramic powders were synthesized from raw materials and commercially available powder.

The raw materials used for synthesis of SiC were diatomaceous earth (Kolubara mine, Serbia) and active carbon (Miloje Zakic, Krusevac) with a specific surface area BET=46 $m^2 g^{-1}$ and 99% purity, as a reducing agent. The diatomaceous earth was previously purified by acid treatment using 1 M HCl solution in order to remove iron oxide from material. Chemical composition of the as-received and chemically treated samples is given in Table 1. The C/SiO_2 mixtures were prepared by mixing diatomaceous earth with appropriate amounts of carbon black (C/SiO_2=3:1, 4:1, 5:1 and 7:1) and homogenized by vibro milling in the presence of distilled water. The green bodies were formed into specimens of 10 mm in diameter and 10 mm in thickness by the cold uniaxially pressing at the pressure of 100 MPa. After the compact formation/pressing, the specimens were heated at temperatures between 1300 and 1500 °C in the controlled argon-flow atmosphere.

Table 1
Chemical composition of the as-received diatomaceous earth and chemically treated diatomaceous earth (in wt%).

Element, wt%	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	SiO_2
Clay [13]	6.05	2.06	0.48	0.35	0.18	1.05	1.76	88.00
Diatomite [14]	12.28	3.29	–	0.44	0.70	0.12	1.01	73.68

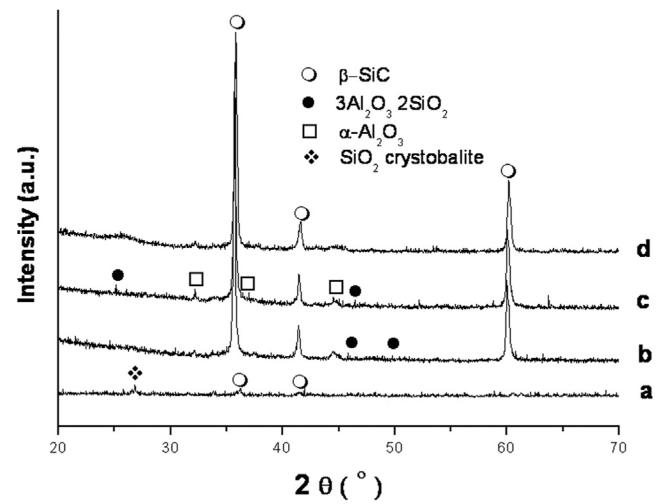

Fig. 1. XRD patterns of samples heat treated for 4 h at 1400 °C, having different C/SiO_2 molar ratios 1:1 (a), 3:1 (b), 4:1 (c), and 7:1 (d).

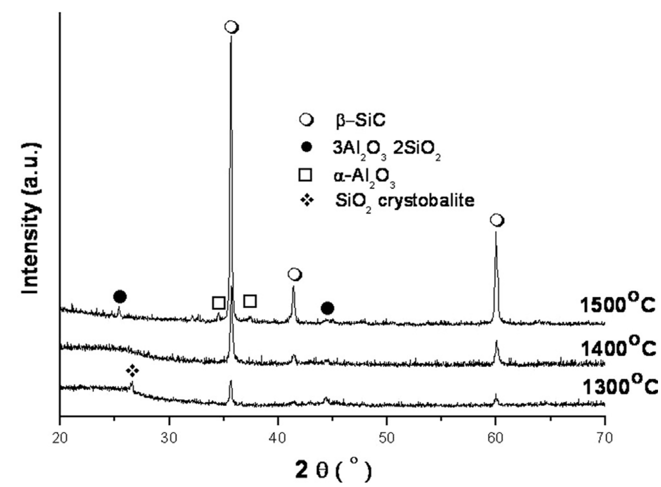

Fig. 2. XRD patterns of samples having C/SiO_2 3:1 molar ratio, heat-treated at different temperatures in range 1300–1500 °C.

Heating of the alumina reactor was carried out in a water-cooled vertical graphite furnace ("ASTRO", Santa Barbara, USA) by a SiC heating element. Temperature was measured by Pt-(Pt-10 wt% Rh) thermocouple (±5 °C). The argon flow was kept until 200 °C during cooling. The sintered samples were crushed into powder for further analysis.

Commercially available zircon powder ($ZrSiO_4$, "Trebol", USA, ~40 μm) was used as the starting material for the synthesis of ZrC and ZrC/SiC powder. Chemical analysis of the powder, given by the manufacturer, is as follows: ZrO_2 – 65%, SiO_2 – 33%, Al_2O_3 – 2%, TiO_2 – 0.35%, Fe_2O_3 – 0.05%. Activated carbon ("Trayal", Serbia, ~10 μm, ashes ≤ 1%) dried at 110 °C (2 h) was used as a reducing agent. The $C/ZrSiO_4$ mixtures were prepared by mixing $ZrSiO_4$ powder with appropriate amounts of the activated carbon in order to obtain samples with the various molar ratios $C/ZrSiO_4$=3, 4, 5, and 7. Carbothermal reduction of powder admixtures is performed