

Combined sol–gel and carbothermal synthesis of ZrC–TiC powders for composites



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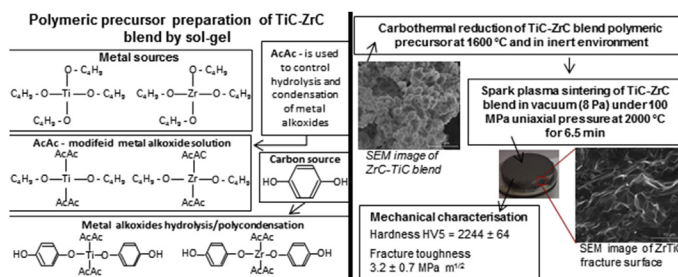
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HIGHLIGHTS

- A polymeric precursor of TiC–ZrC blend was synthesised by sol–gel process.
- The polymeric precursor synthesis was studied by infrared spectroscopy.
- TiC–ZrC powder blend was carbothermally reduced from polymeric precursor.
- TiC–ZrC powder blend was sintered to ZrTiC₂ solid solution by spark plasma sintering.
- Sintered ZrTiC₂ have good mechanical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

The TiC–ZrC binary compound of nanostructured powders was synthesised by combination of sol–gel and carbothermal reduction. The polymeric precursor of the blend was produced by sol–gel process from titanium tetrabutoxide, zirconium tetrabutoxide and benzene-1,4-diol; then carbothermally reduced to the TiC–ZrC blend at 1600 °C in an inert environment. The chemical reactions occurring in the system were monitored by infrared spectrometry. Stable alkoxide solution was obtained by adding acetylacetonate to avoid premature gelation of the metal alkoxide mixture. A solid solution of ZrTiC₂ was produced by spark plasma sintering at temperature of 2000 °C.

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1. Introduction

The need for high temperature (HT) materials that can operate at temperatures efficiently above 2000 °C has driven the development of new compounds consisting of materials with melting points above or around 3000 °C. The transition-metal carbides can

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be considered as candidates for HT applications due to their high melting temperatures, high hardness, low thermal expansion and potentially tailorable thermo-mechanical and thermo-physical properties [1]. In addition, monocarbides, such as zirconium carbide (ZrC) and titanium carbide (TiC), are widely used as reinforcing phases in the materials of cutting tools, wear-resistant coatings and aerospace materials, as well as structural components in chemical and electronic industries [2–4]. However, full densification of undoped ZrC is a challenge and low fracture toughness is a limiting factor for a wide use of zirconium carbide [5–7]. One of the promising approaches for improving sinterability and compound reliability includes the use of sintering additives. Improvement in the mechanical endurance of the materials is achieved through the design of controlled technological processes and introducing a second phase into ZrC matrix. The means to improve the fracture toughness are explored by addition of controlled amount of refractory metal molybdenum as a binder metal [7,8], and/or toughening compounds, such as tetragonal zirconia (*t*-ZrO₂), which undergoes phase transformation from its tetragonal polymorph into monoclinic one under stress [5], [9]; and/or refractory titanium carbide, which is known as additive improving densification [10], [11].

Several methods for preparation of ZrC, TiC powders and ZrC–TiC mixture have been reported, among them there are carbothermal reduction of the corresponding metals and/or metal oxides at elevated temperature [12–14]; sol–gel process [15–18]; chemical vapour deposition [19]; self-propagating high-temperature synthesis (SHS) [20], etc. Carbothermal reduction of metal oxides (ZrO₂ and TiO₂) mixed with amorphous carbon in controlled atmospheres at temperatures between 1700 and 2100 °C is a conventional method for synthesis of metal carbides. Combination of sol–gel chemical process with carbothermal reduction provides novel routine to synthesize metal carbides [2]. When prepared by a sol–gel technique, the polymeric precursor reactants are homogeneously distributed at a molecular level that reduces the kinetic barriers between the developed metal oxides and carbon particles created in pyrolysis of a metal alkoxide polymer precursor. Increased contact area of the nanoparticles results in carbothermal reduction of metal oxide and carbon at lower temperature and shorter time as compared to conventional methods of carbide synthesis. Moreover, the use of molecular precursors and the control of the process conditions allow preparation of homogeneous and pure multicomponent systems [2–4], [18], [11].

V.I. Ivashchenko et al. has theoretically demonstrated that ZrC–TiC composites can exhibit better mechanical properties as compared to the single-phase ceramics of TiC and ZrC and the micro-hardness of the ZrC–TiC system reaches a maximum at intermediate composition; moreover, the ZrC–TiC composite requires a lower sintering temperature, [21].

The present study is aimed at (i) elaboration of a novel way for synthesis of the binary solid carbide blend of ZrC and TiC using polymeric precursors of the corresponding metal alkoxides and hydroquinol; and (ii) densification of ZrC–TiC powder mixture to single phase solid solution by spark plasma sintering.

2. Experimental details

2.1. Powder preparation

Precursors of titanium tetrabutoxide, Ti(OC₄H₉)₄ (≥97.0%, Aldrich), and 80% solution of zirconium tetrabutoxide, Zr(OC₄H₉)₄ (80%, in butanol, Aldrich) were used as metal sources. The benzene-1,4-diol C₆H₆O₂ (≥99.0%, Aldrich) was used as a carbon source. Acetylacetone C₅H₈O₂ (AcAc) (≥99.0%, Aldrich) was added as a chelating ligand to reduce reactivity of the metal alkoxides, i.e. to

prevent a rapid self-condensation reaction. The precursors were dissolved in 1-butanol C₄H₉OH (>99%, Aldrich).

In the present work, the ZrC–TiC polymeric precursor was synthesized by sol–gel method following a procedure described in detail elsewhere [4], [16]. The ZrC–TiC polymeric precursor was synthesized under argon (Ar) flow in a specially designed teflon cell to prevent a premature gelation of a metal alkoxide. As the first step of preparation of the polymeric precursor 1 mol Ti(OC₄H₉)₄ and 1 mol Zr(OC₄H₉)₄ were dissolved in 2 ml butanol. Then 4 mol of AcAc was dropped to the solution heated to 50 °C and stirred for 30 min. The next step was increasing the temperature of the solutions up to 80 °C and addition of dissolved 0.5 mol benzene-1,4-diol in 2 ml butanol. The solution turned deep red and was further heated up to a reaction temperature of 125 °C for 2 h. Afterwards, the solvent was evaporated leaving a neat precursor, which was then pyrolysed and carbothermally reduced. The sketch of the process of synthesis is illustrated in Fig. 1.

The neat ZrC–TiC precursors were pyrolysed in graphite boats using an alumina tube furnace (Nabertherm HTRH) at 900 °C in argon for 1 h. The pyrolysed ZrC–TiC precursors were carbothermally reduced at 1450 °C in argon environment and the carbothermal reduction time at the maximum temperature was 90 min. The heating rate was adjusted to 200 °C per 1 h. The mechanism of the carbothermal reduction up to 1450 °C of the pyrolysed ZrC–TiC precursors was monitored with mass spectrometer (CIS SRS 200) to detect carbon monoxide (CO) content in an effluent gas. The total gas flow rate was 0.084 NL/min. The samples were further heat-treated at 1600 °C in vacuum of 7–8 × 10^{−2} mbar in a furnace (WEBB 107) to complete the carbothermal reduction.

2.2. Sintering

The powder mixture of 1 mol TiC + 1 mol ZrC was consolidated by spark plasma sintering (SPS) using FCT HP D25/2 equipment. The temperature was measured by a vertically located optical pyrometer through a hole in the upper graphite punch and from the graphite surface of the punch 5 mm above the powder. The material was compacted at room temperature and subsequently sintered in graphite mould/punch parts. Graphite foil was used between the material and the graphite mould to reduce a contact resistance and avoid carburisation on the compact surface. In order to prevent heat losses during processing and maintain a homogeneous heat distribution throughout the mould/material system, a graphite felt was used around the cylindrical graphite mould. The powder

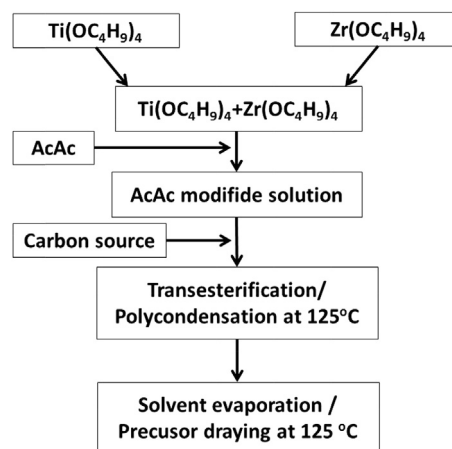


Fig. 1. Flow chart of synthesis of ZrC–TiC precursor.

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