ZrC-TiC-MoSi₂ ceramic composite by spark plasma sintering

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Abstract. ZrC-TiC-MoSi₂ ceramic composite was consolidated by spark plasma sintering at 1850-1900°C temperature, for 5-10 min of dwell time under 50 MPa of applied pressure. The influence of MoSi₂ addition on the mechanical performance and microstructure of ZrC-TiC composite was investigated. Compared with ZrC-TiC, the sinterability of ZrC-TiC-MoSi₂ was improved, as the latter one achieved relatively fully dense bulk under the same sintering conditions. The hardness and fracture toughness of ZrC-TiC-MoSi₂ composite were increased remarkably manifesting >99% of density, 29.8 GPa of Vicker’s hardness, and indentation fracture toughness of 8.01 MPa·m₁/₂. Under erosion and fracturing conditions, it was shown that solid solutions of (Zr,Ti)C serve an important role in erosion and crack propagation resistance.

Key words: zirconium carbide; titanium carbide; molybdenum disilicide; (Zr,Ti)C solid solution; silicon carbide; spark plasma sintering, Vickers hardness; indentation fracture toughness

1. Introduction
For decades, an extensive research has been focused on the eminent class of ultra-high temperature ceramics (UHTCs) based on the transition metal carbides and their composites, which are considered to be promising candidates for thermal protection system such as, for example, leading edge, nose cones, cowl, struts, etc. in hypersonic vehicles and weapons. Their outstanding properties are associated with unique bonding character constituting covalent, ionic, and metallic nature [1-3].

The silicon based compounds usually possess good oxidation resistance and can be used as sintering additives to materials of intrinsically low sinterability, such as carbides and borides. Manufacturing of the UHTC is a tricky task, as high temperatures and pressure are needed to obtain a fully dense and homogeneous fine-grained bulk. To solve this problem, spark plasma sintering (SPS) technique has been commonly used to densify a wide variety of ceramic composites including, but not limited to TiC-ZrC, SiC-ZrB₂, MoSi₂-ZrB₂, MoSi₂-ZrC, etc. [2-4]. The various sintering reactions with additive materials play a significant role toward achieving the UHTCs with the superior mechanical properties. Particularly, the fracture toughness of carbide-based UHTCs could be improved by the incorporation of a second phase, which can react with the matrix and form a hard new phase. Reaction between ZrC and MoSi₂ at the final stage of sintering results in development of SiC and, therefore, toughen the composite by crack deflection and generation of the compressive stress near the crack tip due difference in coefficient in thermal expansion. This approach is at the core of the present research.

Currently, a new class of the high temperature ceramics designed around MoSi₂ has progressed to meet the demands of advanced high temperature structural applications in the temperature range of 1200-1600°C in oxidizing and aggressive environments. MoSi₂ exhibits excellent oxidation resistance at high temperatures via the formation of a thin protective silica layer, which serves as a barrier against further oxidation of the matrix and acts as a grain boundary lubricant during the initial stage of densification [5-7]. Both zirconium and titanium carbides are intensively studied as promising materials for widespread industrial applications, especially in extreme environments. ZrC is a well-known material for high-temperature aerospace applications due to its high-temperature stability, very
high melting temperature (3530°C), exceptional hardness (> 25.5 GPa) and wear resistance, chemical inertness and imperviousness to hydrogen attack [8, 9]. However, fabrication of a dense ZrC is challenged by a low coefficient of thermal diffusion. Moreover, a low fracture toughness of the pure ZrC (~ 4.0 MPa·m^{1/2}) [10] limits usage of the material for mechanically rigorous applications. The introduction of a second phase, such as TiC or MoSi₂, can facilitate not only the densification of ZrC, but also enhance its room temperature mechanical properties due to refinement of microstructure. The combination of MoSi₂ with ZrC results in improvement of both room-temperature mechanical properties and oxidation resistance of a hot-pressed composite as compared with the monolithic carbides [11, 12]. Improvement in mechanical properties can also be promoted by the formation of solid solution of mixed (Ti,Zr)C carbide, which is primarily acting as a strengthening constituent [13, 14, 15].

ZrC is also considered as a material for tribological applications due to a unique combination of properties. In particular, it is not only harder and stiffer (modulus of elasticity 392 MPa) as compared to the common advanced ceramics (Al₂O₃, ZrO₂, Si₃N₄, etc.), but also has a high chemical resistance to corrosive and caustic agents, and a good thermal conductivity (~ 40 W m⁻¹ K⁻¹) and thermal stability. Therefore, ZrC can advantageously alleviate and resist the frictional heating during tribo-related processes, which makes it particularly useful for the fabrication of a great variety of tribo-components (bearings, wear parts, valves, seals, rollers, etc.). Another feature that distinguishes ZrC from the majority of the commonly used tribo-ceramics is its relatively high electrical conductivity (~ 10⁶ S m⁻¹) [13] allowing the exploitation of materials for electrical contacts, such as brushes, microelectromechanical devices, circuit breakers, motor vehicle starters, etc. Therefore, the purpose of this contribution is to develop the route of consolidation of the ZrC-20wt%TiC-10%wt.%MoSi₂ composite via spark plasma sintering (SPS) technique utilizing the synergistic influence of the constituent phases.

2. Experimental

The commercially available powders used to prepare the composites are listed in Table 1. The raw ZrC was mixed with 20wt.% TiC and 10wt.% MoSi₂ powders and milled in acetone following a conventional approach of ball milling for 2 hours in a stainless steel mill using Si₃N₄ milling media and ball-to-powder ratio of 4:1 at a fixed rotation speed of 100 rpm. The mixture was then dried for 1 h at 30 °C and sieved to 20 μm.

| Powder | Particle size, μm | Mark | Purity, % |
|--------|------------------|------|-----------|
| ZrC    | 2–3              | Pacific Particulate Materials, (PPM), ZrC-7643 | 99.0 |
| TiC    | 2–3              | PPM, TiC-2088 | 99.0 |
| MoSi₂  | 0.5 - 3          | Aldrich | 99.0 |

The mixture of ZrC-20%TiC-10%MoSi₂ was sintered by SPS technique (KCE®-FCT HP D 10-GB, FCT System GmbH, Germany) in vacuum at the temperature range of 1800 - 1900°C with simultaneous application of 50 MPa uniaxial pressure for the dwell time of 5 - 10 min employing a heating rate of 100 °C/min. The powder was loaded into a 20 mm inner diameter graphite die with a sheet of graphitic paper placed between the punch and the powder.

The samples were polished with the diamond abrasives down to 0.5 μm finish. The Archimedes' technique was used to measure the bulk density of as-produced samples. Distilled water (Mettler Toledo ME204, Switzerland) was utilized as an immersion medium. The theoretical density was calculated applying the rule of mixtures considering the theoretical density of ZrC (6.73 g·cm⁻³), TiC (4.93 g·cm⁻³) and MoSi₂ (4.93 g·cm⁻³) and assuming no spurious phases formation during sintering. Therefore, the calculated theoretical density of ZrC-20%TiC-10%MoSi₂ composite was estimated as 6.27 g·cm⁻³.

The Vickers hardness (HV10) and the indentation fracture toughness (IFT) were measured on the polished surfaces applying a load of 98 N using a Vickers hardness tester (Indentec 5030 SKV) at a
room temperature. The IFT (the critical stress intensity factor) was calculated from the length of emanating cracks according to following equations:

- Palmqvist crack system- \( K_{IC} = 0.0515 \frac{P}{l^{3/2}} \) [16]
- Median crack system- \( K_{IC} = 0.0726 \frac{P}{c^{3/2}} \) [16]
- Evans and Charles method \( K_{IC} = 0.16 \left( \frac{c}{a} \right)^{-1.5} \left( \frac{H}{10} \right) \) [17]

Where \( K_{IC} \) - fracture toughness (MPa·m\(^{1/2}\)); \( H \) - Vickers hardness (MPa); \( P \) - applied load (N); \( c \) - average length of the cracks (μm); \( a \) - half average length of the diagonal of the indents (μm); \( l \) - length of a single crack (μm). The reported properties are derived from the average values of 10 indentations.

The microstructure of the materials was examined with the help of a field-emission scanning electron microscope (Zeiss Evo MA15, Germany) equipped with an energy dispersive spectroscopy (EDS). The phase composition of the synthesized powder was examined by X-ray diffraction (XRD; D5005, Bruker, USA). Step-scan data were collected with CuK\( \alpha \) radiation (\( \lambda = 1.5406 \) Å) at a step size of 0.02°(2θ) and a scanning rate of 4°min\(^{-1}\).

3. Results and discussion

3.1. Mechanical properties

ZrC-20%TiC-10%MoSi\(_2\) mixture was sintered at various temperatures to find the most suitable conditions for production of the mechanically reliable composite. Table 2 summarizes the parameters of SPS and the mechanical properties associated with the materials sintered at these conditions.

Density of > 99% was achieved when the composite sintering was realized at 1850 °C for 5 min; the further increase either of the temperature up to 1900 °C or the dwell time to 10 min does not promote densification. The Vickers hardness can be favorably compared with the hardness reported in the literature for the monolithic ZrC (~25 GPa) [9] despite the presence of toughening agent MoSi\(_2\) of a lower hardness. The highest fracture toughness was measured for the sample consolidated at 1800 °C for 5 min. For example, the composites of ZrC and Mo, which were sintered at 2100 °C and a pressure of 50 MPa, exhibited the hardness of around 21 GPa (HV10) and the IFT of 5.5 MPa·m\(^{1/2}\) (Palmqvist approach). The hardness values reported for many ZrC-based composites are ranged between 15 and 19 GPa [8, 9].

| Sample designation | Dwell (min) | Temperature (°C) | Relative density (%) | Hardness (HV10) GPa | Toughness \( MPa\cdot m^{1/2} \) Median | Palmqvist | Evans’s method |
|--------------------|------------|------------------|----------------------|---------------------|--------------------------------------|----------|----------------|
| Z1                 | 5          | 1800             | 93.26                | 24.1±2.3            | 6.22±0.4                            | 8.4±1.0  | 7.5±0.2        |
| Z2                 | 5          | 1850             | 99.16                | 25.8±2.42           | 4.37±0.3                            | 5.21±0.3 | 5.21±0.3       |
| Z3                 | 5          | 1900             | 98.1                 | 26±2.76             | 5.23±1.3                            | 8.1±0.5  | 5.9±0.3        |
| Z4                 | 10         | 1850             | 98.41                | 29.8±1.95           | 5.2±0.8                             | 6.22±0.3 | 5.7±0.6        |

Fig. 1 demonstrates the crack propagation from the corner of indentation imprint. Cracks deflection and branching are evident and can be regarded as operating toughening mechanisms in the composites.

![Figure 1. SEM image of indent: (a, c) the cracks from the indent; (b) the common view of the imprint in Z3.](image-url)
Room temperature indentation fracture toughness does not vary much among the composites, but it is a bit larger for a less dense Z1, which is understandable due to enhanced porosity and stress relaxation when the crack tip meets a pore. The enhanced hardness values (up to 30 GPa HV10) of the ZrC–20%TiC-10%MoSi2 composite can be explained by the formation of new phases, particularly, due to ultra-hard solid solutions and SiC [24].

3.2. Phase composition and microstructural analysis

Figures 2 and 3 demonstrate the SEM images of the processed materials revealing overall relatively homogeneous distribution of phases throughout the composite. The samples consolidated at 1750 and 1800 °C contain the well-recognizable undersintered areas (Figs 2c and f). Increase in the compaction temperature and dwell time provides materials with no detectable pores.

At least three distinct phases, related to different colors in the SEM images, were detected on the polished surfaces of the compacted samples. The EDS examination confirms the formation of Zr-rich (Zr,Ti)C phase with a trace amount of MoC (the light grey area), which holds the largest space throughout the composite (Fig. 3e, spectrum 1). The dark grey area corresponds to Ti-rich. (Zr,Ti)C, MoC and some amount of MoSi2 (Fig. 3e, spectrum 2). The black particle-like zones, which are spread over the surface, testify the formation of a new phase of SiC along with Zr- and Ti-rich phases (Fig. 3e, spectrum 3). The EDS analysis performed on the fractured surfaces confirms the presence of all phases detected on the surface as justified in Fig. 4.

Figure 2. SEM images of ZrC-20%TiC-10%MoSi2 sample spark plasma sintered for 5 min at 1750°C (a-c), 1800°C (d-f), 1850°C (g-i), 1900°C (j-l)
Figure 3. SEM images (a-d) and EDS spectra (e) of Z4

The XRD pattern of the fractured samples, presented in Figure 5, reveals the formation of Zr-rich and Ti-rich (Zr,Ti)C solid solutions, as well as MoC and SiC reaction phases along with MoSi2.

Figure 4. Secondary electron SEM images (a,c), back scattered electron SEM images (b,d), and EDS analysis of the fractured (e-g) Z4.

Figure 5. XRD patterns of the ZrC-20%TiC-10%MoSi2 mixture (a); Z1 (b); and Z3 (c)
The XRD pattern taken from Z1 and given in Fig. 5b indicates shift of the ZrC peak to higher 2θ values, and disappearance of the TiC peaks, which points to the formation of Zr-rich solid solution $(Zr_{0.6}Ti_{0.4})C$ reflected by the strong peaks at 33.64° and 39.07°, and the formation of $(Zr_{0.7}Ti_{0.3})C$ Ti-rich phase observed at 35.69° and 41.15°. Fig. 5c shows the coexistence of SiC and MoC along with Zr- and Ti-rich solid solutions. The development of SiC occurs due to reaction of MoSi$_2$ with surface oxides forming silica around 500 °C and the presence of a carbon-rich environment, which promotes the carbo-thermal reduction of SiO$_2$ into Si–O–C or SiC species [23]. Sintering of the composites is reflected by new reaction phases development and possible local melting phenomena. Zr-Ti-C phases have a variable stoichiometry and formation of MoC carbides may be due to some excess of C from a graphite-rich environment and carbides themselves. Development of SiC phase at 35.69° and 41.15° points to the interaction between C and MoSi$_2$ during solidification [25]. Final MoSi$_2$ content is decreased due to partial or complete decomposition of MoSi$_2$ during sintering. Decomposition can supply Mo necessary for the formation of the MoC phase.

The in-situ developed SiC phase incorporated into the composite matrix may improve the oxidation resistance of ZrC by forming a protective SiO$_2$-containing oxide scale. Such behavior requires a homogenous microstructure in terms of chemical composition and grain size distribution. According to the SEM images of the SPS-ed samples (Figs. 2 and 3), the SiC particles are in a submicron range not exceeding 2 µm being homogeneously spread throughout the bulk. The spherical SiC grains coexisting within (Zr,Ti)C solid solutions have perspective to improve behavior of the composite for structural and wear applications.

4. Conclusions

The spark plasma sintering technique was successfully utilized for the consolidation of ZrC-20%TiC-10%MoSi$_2$ composite of the relative density 98-99%, the Vickers hardness in the range of 25 - 30 GPa (HV10) and the indentation fracture toughness up to 8.0 MPa·m$^{1/2}$. The effect of sintering temperature on the mechanical properties has been evaluated revealing the optimum conditions for complete densification to be of 1850 °C applied for 5 min at the pressure of 50 MPa. The dominant feature of the sintered materials is the development of the Ti- and Zr-rich solid solutions along with SiC secondary phase.

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