Influence of the content of Zr$_x$Al$_y$C$_z$ on properties of ZrB$_2$-Zr$_x$Al$_y$C$_z$ Composite Ceramics Fabricated by Spark Plasma Sintering

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Abstract. ZrB$_2$/Zr$_x$Al$_y$C$_z$ composite ceramics with different volume contents of Zr$_x$Al$_y$C$_z$ were fabricated by the spark plasma sintering. The sintering behavior, microstructure, mechanical properties and oxidation resistance were studied. The results indicated that sinterability of the composites was remarkably improved by addition of Zr$_x$Al$_y$C$_z$ compared to the single-phase ZrB$_2$ ceramic. As the content of Zr$_x$Al$_y$C$_z$ increased, both the Vickers hardness and Young’s modulus of the composites first increased and then decreased. The fracture toughness of the ZrB$_2$-40vol% Zr$_x$Al$_y$C$_z$ composite was 3.56 MPa-m$^{1/2}$, which increased by approximately 70% compared to the monolithic ZrB$_2$ ceramic. As increasing the content of Zr$_x$Al$_y$C$_z$, the oxidation resistance of composite ceramics was obviously enhanced. The oxidation-resulted increase in weight of composite ceramic with 20vol% Zr$_x$Al$_y$C$_z$ was the best performance in oxidation resistance at 1500 °C. The high-temperature oxidation resulted in dense and stable Al-B-O glass due to adding Zr$_x$Al$_y$C$_z$ into the composite ceramics, those resulting products effectively blocked the oxygen atoms entering into the ceramic matrix.

1. Introduction
Zirconium diboride (ZrB$_2$) as a member of ultrahigh-temperature ceramics (UHTCs) is currently expected to be a potential candidate material for aerospace applications, owing to its high melting point, high thermal and electrical conductivity, low theoretical density and good chemical inertness [1-4]. Based on these properties, ZrB$_2$ ceramics are attracting more and more attention in ultra-high temperature applications where corrosion-wear-oxidation resistance is demanded[5].

However, the low fracture toughness and poor thermal shock resistance of ZrB$_2$-based composite ceramic restrict its wider application. The widely used toughening approach is making use of the second phase additions with a higher aspect ratio as the toughening materials to improve the fracture roughness of ceramic matrix. On the other hand, oxidation resistance is a well-known bottleneck in the exploration of ZrB$_2$-based ceramics. Recently, it was reported that the oxidation resistance of ZrB$_2$ ceramics could be improved by adding SiC, MoSi$_2$, WC, LaB$_6$, TaB$_2$ and TaC et al[6-8].

The layered structure Zr-Al-C has superior strength, specific stiffness, high fracture toughness and excellent oxidation resistance[9-10]. Our previous works reported that the layered structure Zr-Al-C
materials improved the sinterability and enhanced the toughness of ZrB2-SiC composite ceramics as well as ZrB2 ceramic[11-13]. But, the oxidation resistance of ZrB2-ZrxAlyCz ceramics were rarely reported at high temperatures.

In this study, describe the influence of the ZrxAlyCz content on the densification, mechanical properties and oxidation resistance of the ZrB2-ZrxAlyCz composites. This paper focused on the oxidation behavior of ZrxAlyCz-toughened ZrB2 ceramics using muffle furnace in air. By means of the investigation of microstructure and mass change after oxidation, effect of ZrxAlyCz content on the oxidation resistance of ZrB2-ZrxAlyCz ceramics was newly explored.

2. Experimental Procedure
Commercially available ZrB2 powders (>99.5%, 2 μm), Zr powders (>99.9%, 10 μm), Al powders (>99.99%, 8 μm) and graphite powders (>99.9%, 1 μm) powders were used as starting materials. Zr2Al4C5 was prepared by the spark plasma sintering-reactive synthesis using Zr, Al, and C powders as sintering materials. The ZrB2 and Zr2Al4C5 powders were mixed in an agate mortar, and put into a graphite die with graphite foil and sintered using a SPS system.

The temperature was measured by an optical pyrometer focused on the surface of the graphite die. The samples were heated to 1800 °C at an average heating rate of 100 °C/min, and then the temperature holds constant for 3 min. The sample was cooled naturally after the sintering period finished.

The bulk density and porosity of the ceramic samples were measured through the Archimedes’ immersion method using water as the immersing medium. The phase composition of samples was analyzed by X-ray diffraction (XRD) using a Rigaku Ultima III diffractometer (Cu Kα radiation, operation at 40 KV and 40 mA). The surface and fracture morphologies of bulk ceramics were observed by using a scanning electron microscopy (SEM, Hitachi S-3400, Japan). A detailed description of the measurement of mechanical properties, including Young’s modulus (E), Vickers’ hardness (HV) and fracture toughness (KIC), was reported in previous work [13].

Cubes 2mm×3mm×4mm were cut out from the hot pressed materials, oxidation tests on these cubes were performed in a muffle furnace at a fixed temperature for 30 min in air. Specimens were heated to the designated temperature at a heating rate of 10 °C/min.

3. Results and Discussion
Figure 1 shows the curve of the open porosity and density versus ZrxAlyCz content in ZrB2-ZrxAlyCz composites. It can be seen that the open porosity firstly decreased and then gradually increased with

![Figure 1. The curve of the open porosity and density of multiphase ceramics with different volume content of ZrxAlyCz.](image)

![Figure 2. The XRD patterns of multiphase ceramics with different volume contents of ZrxAlyCz: (a) 0vol%, (b) 10vol%, (c) 20vol%, (d) 30vol%, (e) 40vol%.](image)
the increase of Zr₅Al₃C₂ volume content. Compared to the open porosity (10.8%) of as-received powder compacts, the open porosity of 20 vol% Zr₅Al₃C₂ is relatively low, only 0.14% open porosity. The morphology observation also shows that there are more pores in the monolithic ZrB₃ than in 20vol%, and the pores in the monolithic ZrB₂ are larger and distributed un-uniformly (Figure 3). This indicates that the presence of Zr₅Al₃C₂ improves the densification of the material.

In the formation of Zr₅Al₃C₂ compounds, a reaction is similar to that in the decomposition of Ti₃AlC₂. YC Zhou et al. [14] used Ti₃AlC₂ as a sintering aid to improve the sintering property of TiB₂ due to the reason that the Ti₃AlC₂ decomposed into TiCₓ and Al at high temperature to promote the sintering. Zr₂Al₄C₅ compound also decomposes at high temperatures[15], our experimental results also show that when Zr₂Al₄C₅ is added in a small amount, it is converted into Zr₂Al₄C₆ (see Figure 2). Although there is no direct evidence that Al precipitates, it can be inferred that the Zr₂Al₄C₅ compound is decomposed and its decomposition products have a certain promoting effect on densification.

Figure 2 shows the XRD patterns of the composites with different volume contents of Zr₅Al₃C₂. It can be seen from the figure that when adding different contents of Zr₅Al₃C₂ compounds, the major phases of the samples after sintering by SPS1800°C are ZrB₂ and Zr₂Al₄C₅, which show the same diffraction peaks as that of the raw material powder. While the content is less than 20 vol%, the diffraction peaks of Zr₂Al₄C₆ and ZrC appear, this is because the Zr₂Al₄C₅ compound is susceptible to the impurity phase and decomposes at high temperature to form Zr₂Al₄C₆ and ZrC compounds. Although the Zr₂Al₄C₅ compound has a higher decomposition temperature, this experiment uses SPS sintering technology that is different from the conventional sintering, the local and transient high temperature leads to the decomposition of Zr₂Al₄C₅ compound [15].

![Figure 3](image_url)

**Figure 3.** The SEM micrographs of fracture surface of multiphase ceramics with different volume contents of Zr₅Al₃C₂, (a) 0vol%, (b) 10vol%, (c) 20vol%, (d) 30vol%, (e) 40vol%.
Figure 3 shows the SEM micrographs of fracture surface of ZrB$_2$-Zr$_x$Al$_y$C$_z$ composites with different Zr$_x$Al$_y$C$_z$ contents. It can be seen that porosity is hardly observed on the crosssection of composites with Zr$_x$Al$_y$C$_z$ particle, only some small pores trapped into the ZrB$_2$ grains can be observed. Meanwhile, no trace of layered Zr$_x$Al$_y$C$_z$ grain pullout is observed. Compared to the monolithic ZrB$_2$ (Figure 3(a)), the grains size of composites with Zr$_x$Al$_y$C$_z$ particle is rather uniform and fine little. Therefore, the Zr$_x$Al$_y$C$_z$ suppressed the growth of ZrB$_2$ grains. The monolithic ZrB$_2$ exhibited a rather smooth fracture surface, and some pores were detected in Figure 3 (a). The fracture surfaces of composites with Zr$_x$Al$_y$C$_z$ particle show a concave-convex appearance (shown in Figure 3 (b)-(e)), and are much rougher than that of the monolithic ZrB$_2$, which indicated that the fracture modes of the ZrB$_2$-Zr$_x$Al$_y$C$_z$ composites changed from transgranular modes to mixed transgranular and intergranular ones.

SEM images of the polished surfaces of the composites with different Zr$_x$Al$_y$C$_z$ contents are shown in Figure 4. It was confirmed by EDS analyses the large columnar or plate-like gray grains are identified as Zr-Al-C composite (including Zr$_x$Al$_y$C$_z$ and Zr$_3$Al$_4$C$_6$), the fine bright particles are ZrB$_2$, and the black phases in the microstructure are the residual porosity. With the increase of Zr$_x$Al$_y$C$_z$ volume content, the columnar or plate-like gray Zr$_x$Al$_y$C$_z$ grains dispersed homogenously in all these composites, which not only located at the grain boundaries, but are also contained within them. However, the agglomeration of Zr$_x$Al$_y$C$_z$ grains is observed in Figure 4 (c)-(e).

![Figure 4](image1)

**Figure 4.** The BESEM micrographs of polished surfaces of multiphase ceramics with different volume contents of Zr$_x$Al$_y$C$_z$, (a)0vol%, (b) 10vol%, (c) 20vol%, (d) 30vol%, (e) 40vol%.

The Young’s modulus and Vickers’ hardness measured for the various the ZrB$_2$-Zr$_x$Al$_y$C$_z$ compositions consolidated by SPS are summarized in Figure 5. From this figure, it can be seen that the Young’s modulus and Vickers’ hardness firstly increased and then decreased with increasing the Zr$_x$Al$_y$C$_z$ content. The composites with 20 vol% Zr$_x$Al$_y$C$_z$ show a maximum value of hardness of 16.4 GPa, and a maximum value of Young’s modulus of 406 GPa.
The fracture toughness values of the compositions are depicted in Figure 6. It can be seen that the ZrB₂-based composites including ZrₓAlᵧC₀ grains have markedly higher fracture toughness than the monolithic ZrB₂ material, and the fracture toughness increased with the content of ZrₓAlᵧC₀ grains. For a monolithic ZrB₂ ceramic fabricated under the same conditions, the fracture toughness is only 2.11 MPa·m₁/₂. While the maximum value of fracture toughness reaches 3.56 MPa·m₁/₂ for ZrB₂-40vol% ZrₓAlᵧC₀, which is about 70% larger than that of the monolithic ZrB₂ material.

Figure 7 shows the weight gain of ZrB₂/ZrₓAlᵧC₀ multiphase ceramics with different ZrₓAlᵧC₀ volume fractions under 30 min oxidation at different temperatures. It can be seen from the figure that the ceramic oxidation weight gain increases as increasing oxidation temperature. When the temperature is lower than 1000°C, the weight gain of the composite ceramics is not obvious. While the temperature exceeds 1000°C, the oxidation weight gain is apparent and tends to decrease first and then increase as increasing volume fraction of ZrₓAlᵧC₀. When the content of ZrₓAlᵧC₀ is 20vol%, the weight gain after oxidation is smaller and ceramic’s oxidation resistance is the best. Because the higher the oxidation temperature is, the more active the reaction is between oxygen and ZrB₂ and ZrₓAlᵧC₀, the faster the diffusion rate of oxygen is in ceramics and the higher the weight gain of oxidation is.

Figure 7. The Mass gain curve of ZrB₂/ZrₓAlᵧC₀ multiphase ceramics with different volume contents of ZrₓAlᵧC₀ at different temperature for 30min.

Figure 8. XRD patterns of multiphase ceramics after oxidation with different volume contents of ZrₓAlᵧC₀ at 1200°C (a) 0vol%, (b) 10vol%, (c) 20vol%, (d) 30vol%, (e) 40vol%.
Figure 8 shows the XRD patterns of the surface of the multiphase ceramics with different Zr\(_x\)Al\(_y\)C\(_z\) contents after oxidation at 1200°C for 30min. It can be seen from the figure that after oxidation the single-phase ZrB\(_2\) ceramic shows a major phase of ZrO\(_2\) on the surface and a small amount of B\(_2\)O\(_3\). After adding Zr\(_x\)Al\(_y\)C\(_z\) compounds, Al\(_4\)B\(_2\)O\(_9\), Al\(_9\)B\(_2\)O\(_{11}\) and Al\(_2\)O\(_3\) compounds formed in addition to ZrO\(_2\) and B\(_2\)O\(_3\), and the intensity of diffraction peak of Al\(_4\)B\(_2\)O\(_9\) increased as increasing Zr\(_x\)Al\(_y\)C\(_z\) content. The experimental results show that when the composite ceramic contains Zr\(_x\)Al\(_y\)C\(_z\) compound, the Al-B-O glass phase formed after oxidation, reducing the volatilization of B\(_2\)O\(_3\) and hindering the diffusion of oxygen atoms into the interior. However, when the content is high, the crystal phases Al\(_4\)B\(_2\)O\(_9\) and Al\(_2\)O\(_3\) are formed to lose the liquid phase film and the oxidation is intensified.

Figure 9. XRD patterns of ZrB\(_2\)/30vol%Zr\(_2\)Al\(_4\)C\(_5\) multiphase ceramics at different oxidation temperature (a) 800°C, (b) 1000°C, (c) 1200°C, (d) 1400°C, (e) 1500°C.

Figure 9 shows the XRD pattern of the surface of ZrB\(_2\)/30vol%Zr\(_2\)Al\(_4\)C\(_5\) multiphase ceramics after oxidation at different oxidation temperatures for 30 min. It can be seen from the figure that the phase of the ceramic surface is different for different oxidation temperatures. When the oxidation temperature is 800°C, unoxidized Zr\(_2\)Al\(_4\)C\(_5\) and ZrB\(_2\) are the major phase and a small amount of ZrO\(_2\) and Al\(_4\)B\(_2\)O\(_9\) are found. When the temperature is raised to 1000°C, the major phase is ZrO\(_2\) on the surface after oxidation and Al\(_2\)O\(_3\) and Al\(_4\)B\(_2\)O\(_9\) appear, while the ZrB\(_2\) phase has not been detected. When the oxidation temperature is 1200°C, in addition to the ZrO\(_2\), Al\(_2\)O\(_3\) and Al\(_4\)B\(_2\)O\(_9\) diffraction peaks, the diffraction peaks of B\(_2\)O\(_3\) and Al\(_9\)B\(_2\)O\(_{11}\) appear. The resulting liquid phase glass phase covers the ceramic oxide surface layer, thereby preventing oxygen atoms from diffusing into the matrix.

Figure 10 shows the surface morphologies of the ZrB\(_2\)/30vol%Zr\(_2\)Al\(_4\)C\(_5\) multiphase ceramics after oxidation at different temperatures. When the oxidation temperature is 800°C, a fine needle-like structure is formed, and it can be identified as B\(_2\)O\(_3\) and Al\(_2\)O\(_3\) compounds through EDS analysis. As increasing the oxidation temperature, the fine needle-like structure reduced significantly and the surface became uneven, which is probably due to volatilization of formed gases of CO\(_2\) and CO resulted from the oxidation of Zr-Al-C compound, leaving a large number of holes on the surface.
4. Summary
ZrB₂/ZrₓAlₓCₓ composite ceramics with different volume contents of ZrₓAlₓCₓ were fabricated by the spark plasma sintering. The sintering behavior, microstructure, mechanical properties and oxidation resistance were studied. It was generalized that the growth of ZrB₂ grain appeared to be inhibited or pinned by adding ZrₓAlₓCₓ grains, and the restriction in grain growth could further improve the densification and the material’s stability at elevated temperature during sintering. The mechanical properties of the sintered materials were also investigated, the composites with 20 vol% ZrₓAlₓCₓ show a maximum value of hardness of 16.4 GPa, and a maximum value of Young’s modulus of 406 GPa, and the fracture toughness of the ZrB₂-40vol% ZrₓAlₓCₓ composite was 3.56 MPa-m⁰. The ceramic oxidation weight gain increases as increasing oxidation temperature. As increasing the content of ZrₓAlₓCₓ, the oxidation resistance of composite ceramics was obviously enhanced. When the content of ZrₓAlₓCₓ is 20vol%, the weight gain after oxidation is smaller and ceramic’s oxidation resistance is the best. The high-temperature oxidation resulted in dense and stable Al-B-O glass due to adding ZrₓAlₓCₓ into the composite ceramics, those resulting products effectively blocked the oxygen atoms entering into the ceramic matrix.

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