

ABSTRACT

The rapid progress in space exploration and hypersonic aviation has intensified the demand for materials capable of withstanding extreme temperatures ($>2000\text{ }^{\circ}\text{C}$) to protect underlying metallic structures. The materials used in these critical regions must possess low density, high modulus, oxidation & ablation resistance, high thermal conductivity, and wear resistance to maintain their structural integrity in extreme, high-temperature, and corrosive environments. Ultra-high-temperature ceramics (UHTCs) are carbides, borides, and nitrides of group IV elements that are promising due to their very high melting points, typically $> 3000\text{ }^{\circ}\text{C}$. Among the family of UHTCs, ZrB_2 possesses an excellent combination of properties such as melting point $> 3000\text{ }^{\circ}\text{C}$, low density, high thermal and electrical conductivities, excellent thermal shock resistance, high hardness, stiffness, and wear resistance, outstanding chemical inertness and oxidation resistance, etc. This makes ZrB_2 ideally suitable for high-temperature aerospace applications. However, the limited sinterability and low fracture toughness of monolithic ZrB_2 restrict its broader applications. To overcome these drawbacks, sintering additives are commonly introduced to enhance both densification and toughness simultaneously. While ZrB_2 -based UHTC composites have shown tremendous potential, in conventional monolithic composites, with uniform distribution of constituents, it is impossible to combine all necessary attributes. A functionally graded material (FGM) may overcome this limitation, as it enables the design of materials with a gradient in structure, composition, and properties along at least one direction, thereby yielding property profiles that are impossible to achieve in any non-graded material.

With this background, in the present work, the development and characterization of novel three-layer functionally graded $\text{ZrB}_2\text{-B}_4\text{C-SiC-LaB}_6$ ceramic matrix composites using spark plasma sintering (SPS) and hot press sintering techniques have been carried out. The top layer of the FGM is most critical for high-temperature applications, as it is exposed to a highly oxidizing atmosphere at these temperatures. In the top layer, high ZrB_2 content is necessary due to its high melting point and high thermal conductivity. Further, the addition of B_4C , SiC , and LaB_6 is essential to improve densification and oxidation resistance. As the inner layers of the FGM are not exposed to a high-temperature oxidizing atmosphere, the composition of these layers is selected primarily to reduce density and thermal conductivity along the thickness of the FGM. As the density and thermal conductivity of B_4C are almost 60% and 75% less than those ZrB_2 , respectively, the bottom layer of the FGM is rich in B_4C . Finally, the primary function of the

middle layer is to serve as an intermediate between the top and the bottom layers. Hence, the composition of the middle layer lies between those of the top and bottom layers. The density of the proposed FGM is ~60% that of monolithic ZrB_2 . Given that weight reduction is a critical requirement for space applications, the composition of each layer has been designed to reduce overall density while maintaining the material's essential functional and structural properties.

Initially, ZrB_2 - B_4C FGMs were developed by SPS and Hot pressing. The FGMs were free from interlayer defects and displayed a smooth transition between the individual layers. A detailed structural characterization of the FGMs was carried out to evaluate the elemental distribution in the graded composite, as well as determine the spatial distribution of the crystalline phases. Vickers hardness was measured within each layer and in the interlayer regions to further evaluate the gradient structure and interlayer transitions. Elastic constants of the FGMs along the thickness and across the layers, measured using ultrasound phase spectroscopy, showed that despite the gradient structure, the FGM can be treated as a quasi-isotropic solid. Further, ZrB_2 - B_4C - SiC - LaB_6 composites of two different configurations, 3-layered FGM and equivalent nongraded composite (NGC), were fabricated using hot pressing. The interlayer regions of the FGM remained intact even after the 3-point bending test and thermal shock from $\Delta T = 800^\circ\text{C}$. The highest average bending strength ($\sim 376\text{ MPa}$) was achieved in the FGM when the ZrB_2 -rich layer was under tensile stress, which was $\sim 20\%$ higher than the NGC samples. While the critical thermal shock temperature was similar for both material types ($\sim 350^\circ\text{C}$), the overall thermal shock resistance of the NGC material was marginally better owing to the favorable thermal residual stress distribution in the as-fabricated materials. In all the compositions discussed above, the presence of 3-6 vol.% porosity was found in the B_4C -rich bottom layer. During application, failure may initiate from the pores present in the B_4C -rich layer, leading to premature fracture. Therefore, the B_4C particle size was further reduced, and spark plasma sintering was employed to fabricate a three-layered ZrB_2 - B_4C - SiC - LaB_6 FGM. The reduction in particle size and the use of SPS fabrication resulted in approximately 99% densification across all compositions. A systematic evaluation of the thermal conductivity of the FGMs and their corresponding individual layers revealed that the FGM comprising ZrB_2 -30 vol.% SiC -10 vol.% B_4C -10 vol.% LaB_6 in the top (outer) layer, ZrB_2 -70 vol.% B_4C in the middle layer, and ZrB_2 -90 vol.% B_4C in the bottom (inner) layer exhibited the highest thermal conductivity at the surface and a significantly lower thermal conductivity along the thickness direction. Hence, it was considered optimum for thermal protection tile application, and its structural, mechanical, thermal shock, and ablation properties were studied. The highest 3-point

bending strength of 659 MPa was achieved for the FGM when the B₄C-rich bottom layer was loaded in tension. Thermal shock tests were performed for three different thermal shock temperature differences, up to 1000 °C, by heating the top surface of the FGM with an LPG-oxygen flame. The thermal shock damage induced over different thermal shock cycles was studied using non-destructive ultrasound phase spectroscopy. The overall thermal shock resistance of the FGM was better than that of NGC. The survival ability of developed FGM in sudden heating conditions was tested by heating it to 1550 °C. Even after 10 minutes holding at 1550 °C, no presence of any crack or delamination could be observed either on the surface of the periphery of the sample, representing its adequate structural integrity and potential for thermal protection tile application at the leading edges and nose cones of hypersonic spacecraft.

Keywords: ultrahigh-temperature ceramics; functionally graded composites; ZrB₂–B₄C composites; spark plasma sintering; mechanical properties; ZrB₂–B₄C–SiC–LaB₆ composites; hot pressing; thermal shock; thermal conductivity; ablation study