

ABSTRACT

Due to attractive combination of mechanical properties and oxidation resistance, SiC-reinforced ZrB₂ composites have emerged as a prospective candidate for high-temperature structural applications. However, the consolidation of these composites necessitates simultaneous application of very high temperature and pressure, and hence proves difficult. This study demonstrates that use of appropriate sinter-additive like Al-Si-Mg and/or TiC can allow satisfactory consolidation of ZrB₂-SiC composites by spark plasma sintering (SPS) at a relatively lower temperature and pressure to yield the desired range of mechanical and functional properties.

Three types of additives, namely, 5 vol.% of Al-10Si-0.2Mg pre-alloyed powder, 5-10 vol.% TiC and 5 vol.% (TiC + WC) were explored to study their influence on density, microstructure and mechanical properties of ZrB₂ + 20 vol.% SiC consolidated by SPS. The sintered ZrB₂-SiC-AlSiMg composite achieved a relative density of 99.83%, even though it was processed at a relatively lower temperature of 1700°C in argon atmosphere. Addition of AlSiMg did not cause any shape change or distortion in the ZrB₂-20SiC composite, despite the low liquidus temperature (592°C) of this additive. In case of ZrB₂-SiC-AlSiMg, the enhanced densification (~99.83%) was attributed to early formation of transient liquid phase along boundaries and subsequent reduction of ZrO₂ by Al and Mg. Addition of TiC also reduced the sintering temperature (1700°C) and resulted in a nearly fully dense composite with a relative density of ~99.6%. Incorporation of TiC led to formation of (Zr,Ti)B₂, a diboride compound of Zr and Ti whose, *c/a* ratio varied inversely with the amount of TiC added. While TiC fully dissolved in ZrB₂ in ZrB₂-20SiC-5TiC composite, undissolved TiC was detected in ZrB₂-20SiC-10TiC composite. In contrast, addition of WC (2.5 or 5 vol.%) required a higher sintering temperature of 1800°C for >98% densification. Here too, (Zr,Ti)B₂ and (Zr,W)B₂ solid solutions formed, which was confirmed diffraction and spectroscopic study.

Extensive phase and microstructure analyses showed that no unreacted AlSiMg was present in the sintered composite. Thermodynamic analysis indicated that AlSiMg acted as a reducing agent for ZrO₂ oxide scale and formed high-melting oxide phases. Raman analysis showed that incorporating 5 vol.% of AlSiMg increased the residual compressive stress of SiC. Analytical models pertaining to ZrB₂-20SiC-(5-10)TiC composites indicated that the residual stress of the matrix phase was tensile in nature that decreased with increase in TiC addition, while that of SiC phase was always compressive. Compared to the conventional ZrB₂-20SiC composite, the TiC-added composites exhibited superior bulk and nano-mechanical properties at ambient temperature. The ZrB₂-20SiC-2.5TiC-2.5WC composite recorded the highest Vickers hardness, while the ZrB₂-20SiC-5WC composite developed an excellent combination of fracture toughness and elastic modulus. In linear reciprocating wear test, the ZrB₂-20SiC-5WC composite suffered the minimum wear volume and wear rate.

The effect of AlSiMg, TiC and WC addition on the oxidation kinetics of ZrB₂-SiC composites was also examined. After isothermal oxidation for up to 240 minutes at 1600°C in air, the TiC/WC-containing composites exhibited relatively low mass gain and a thinner oxide layer. All composites formed a protective oxide scale after oxidation, but the thickness of the SiC-depleted region was significantly lower in the ZrB₂-SiC-TiC, ZrB₂-SiC-TiC-WC and ZrB₂-SiC-WC composites compared to that of the ZrB₂-SiC binary system. On the whole, introduction of TiC and WC was found to be beneficial for restricting mass gain and inhibiting the oxide scale growth upon long-term exposure at 1600°C in air.

Keywords:

ZrB₂-SiC; Sinter-additive; Densification; Microstructure; Mechanical Properties; Wear; Oxidation kinetics; Phase stability