Abstract

A comparative study has been carried out on densification behavior, microstructural evolution, mechanical and thermal properties, as well as oxidation and ablation resistance of the ZrB_2-SiC composites with varying amounts of LaB_6, ZSBCL-7 (7 vol.% LaB_6), ZSBCL-10 (10 vol.% LaB_6) and ZSBCL-14 (14 vol.% LaB_6). The aforementioned composites with B_4C and C as additives were processed by spark plasma sintering at 1600°C and 1800°C under applied ram pressures of 50 MPa and 70 MPa, respectively. The densification kinetics for both the sintering conditions has been analyzed with emphasis on the role of additives and LaB_6 in both reduction of impurity oxides during heating, as well as deformation by creep. The relative density is found to increase with increase in the volume fraction of LaB_6 at both the sintering temperatures, whereas higher densities (98-99.5%) have been achieved by sintering at 1600°C. The densification mechanism during sintering at 1600°C being analyzed using the Bernard-Granger model has exhibited stress exponent (n) ~5-6 suggesting dislocation-climb as the operating mechanism. However, observation of n~2 for the ZSBCL-7 and ZSBCL-10 composites sintered at 1800°C suggests grain boundary sliding aided by diffusion through interfacial glassy phase, whereas n~3 for ZSBCL-14 is considered as signature of dislocation glide-controlled creep. The hardness is found to increase with decreasing grain size for the composites sintered at 1600°C with density ≥98%, but it is influenced by relative density in the incompletely densified composites processed at 1800°C. Further, the indentation fracture toughness of the composites sintered at 1600°C is found to scale with the LaB_6 content.

The oxidation behavior of the composites involving heating under non-isothermal condition till 1400°C, as well as isothermal and cyclic exposure at 1300°C-1500°C has been examined. The mass gain of the ZSBCL-14 is found as the highest during non-isothermal oxidation, whereas it appears to be the least among the composites isothermally exposed for 24 h at all the test temperatures. The kinetics and oxide scale evolution during isothermal exposure at 1300°C for 1, 8, or 24 h have been also examined. Random mass change observed during the first hour at 1300°C stems from a non-protective scale. The variation of mass gain with time at 1300°C has followed a near-parabolic rate law during 0-8 h time period, and significantly more sluggish kinetics during 8-24 h, with the parabolic rate constants (k_p) decreasing sharply. The borosilicate glass (BSG) layer growth rate scales linearly with the LaB_6 content during 0-8 h, but shows an opposite trend on further exposure. During both time periods (0-8 and 8-24 h), the k_p is found to decrease following a linear relationship with increasing BSG layer thickness, indicating its key role as diffusion barrier for oxygen. The oxide scale evolved at 1500°C was examined by scanning and transmission electron microscopy with energy dispersive spectroscopy. It has been found that a BSG layer with a thin film of $La_2Si_2O_7$ is formed on the outermost surface of the protective oxide scale, followed by layers containing BSG along with coarse and fine ZrO_2, and a SiC-depleted ZrB_2 layer. The detailed investigation of the cross-section of the oxide scale has revealed the formation of a layered microstructure formed by growth involving partial crystallization of BSG forming $ZrSiO_4$ along with re-precipitation of $La_2Si_2O_7$ and ZrO_2 after prior dissolution of La_2O_3 and ZrO_2 in the glassy matrix. The mass gain after 24 cycles of 1 h exposure at 1300°C-1500°C is found to be lower than that recorded under isothermal condition for all the composites, with the difference decreasing with LaB_6 content. The oxidation kinetics is found to approach a typically parabolic rate law with increase in cyclic exposure temperature. Further, the value of k_p is found to decrease with increase in LaB_6 content after a few cycles of exposure at each temperature. The outer compact layer comprising BSG, $La_2Si_2O_7$, and $ZrSiO_4$ appears to have a critical role in protection against oxidation, with the k_p decreasing with increase in its thickness.

Compressive creep tests have been carried out at constant load in air at 1300°C-1400°C under 47-78 MPa stress. The steady-state creep rate of ZSBCL-10 composite is found to be higher by one order of magnitude than that of ZSBCL-14 at 1300°C. The value of stress exponents, $n = \sim 2$, as well as the formation of microcracks at both ZrB_2 grain boundaries and ZrB_2-SiC interfaces is suggestive of grain boundary sliding being the operative creep mechanism in ZSBCL-10 composites. On the other hand, the values of stress exponent ~1 obtained for the ZSBCL-14 composites suggest diffusional creep being operative at 1300-1400°C. The value of apparent activation energy as ~ 700 kJ/mol for ZSBCL-14 in temperature range of 1300°C-1400°C suggests that the ZrB_2-ZrB_2 grain boundary diffusion is the rate-limiting mechanism of deformation. The ZSBCL-10 has shown the lowest electrical resistivity due to larger grain size, whereas degradation due to thermal shock is found to scale with LaB_6 content, as brittle $LaBO_3$ content and interfacial area increases. The ZSBCL-14 has shown higher thermal conductivity and resistance to ablation at ~ 1900°C due to closure of pores in ZrO_2 by the $La_2Si_2O_7$, whose formation arrests mass loss by formation and escape of SiO (g).

Keywords: Ultra-high temperature ceramics; ZrB_2-SiC-LaB_6 composites; Spark plasma sintering; Microstructure; Mechanical properties; Densification mechanism; Non-isothermal oxidation; Isothermal oxidation; Cyclic oxidation; Oxidation kinetics; Oxide scale evolution; Creep; Electrical conductivity; Thermal properties; Ablation resistance