Chapter 4
Processing of Ultra–High Temperature Ceramics for Hostile Environments

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ABSTRACT

A detailed review of the processing of zirconium, hafnium, and tantalum based boride-carbide-nitride composites is presented. The processing methodology and important steps involved in producing a pore-free microstructure are reported. The effect of addition of secondary and ternary compounds on densification is highlighted as is the reactive processing of ultra-high temperature ceramics (UHTCs) based on zirconium carbide through the formation of a transient non-stoichiometric carbide and transient liquid phase, which enable densification at much lower temperatures. The reactive processing method is promising in that it readily leads to variation in the composition of secondary/ternary non-oxide phases in the composites as well as the incorporation of fibres which may otherwise degrade. Since the processing temperatures are lower, the grain size obtained after densification is finer and may lead to better mechanical properties (hardness, fracture toughness, and strength). Processing of fibre based composites with boride particulates and silicon carbide through the ceramic precursor route are also discussed.
INTRODUCTION

Zirconium, hafnium, tantalum based diborides (ZrB₂, HfB₂ and TaB₂), carbides (ZrC, HfC and TaC) and nitrides (ZrN, HfN and TaN) with silicon carbide (SiC) up to 30vol% are promising refractory non-oxide ceramics for future generation re-entry vehicles in nose cones, thermal protection and propulsion systems. These composites have to perform under the hostile environments of high temperatures and thermal cycling. These materials, generally referred as ultra-high temperature ceramics (UHTCs), have high melting temperatures (>3000°C) and moderate erosion-oxidation-thermal shock resistance, are good electrical and thermal conductors. In addition, refractory carbides exhibit a brittle-to ductile transition at high temperature depending on stoichiometry. In reusable space vehicles (under hostile environments), the external thermal protection systems in the form of rigid surfaces are required to withstand temperatures beyond 1800°C and, in addition to being refractory, must be able to tolerate the high-heat-flux and mechanical stress associated with vibrations at launch and re-entry into the atmosphere. Therefore, it is necessary that thermal protection materials provide good oxidation resistance, thermal-shock resistance, ablation resistance as well as dimensional stability. Carbon fiber reinforced carbon matrix composites (Cf/C) have received much attention due to their excellent high temperature strength, high thermal conductivity, low coefficient of thermal expansion (CTE) and good thermal-shock resistance. However, the poor oxidation resistance of Cf/C composites beyond ~500°C restricts for high temperature applications. Making a thin oxidation resistant layer such as boride/silicide on the Cf/C composite has been proved with high performance but cracking tends to occur during thermal cycling due to the CTE mismatch of Cf/C composite and the coating material. Once the coating is destroyed, the oxidation protection cannot be sustained. Regarding this aspect, several groups made large attempts in producing the bulk composites to work effectively under severe environments. The refractory borides like ZrB₂ and HfB₂ have been candidates for such applications, not only because of strength retention at high temperature but also because their oxides are capable of withstanding temperatures in the range ~1900-2500°C (Upadhya et al., 1997; Fahrenholtz et al., 2007; Rangaraj et al., 2009; Guo, 2009). However, the rapid oxidation of borides at ~600°C results in the formation of B₂O₃, which evaporates at ~1100°C. The addition of silica formers, notably SiC, can reduce the oxidation rate through the formation of a more stable borosilicate glass up to ~1600°C, and further degradation of material takes place through active/passive oxidation. The oxidation resistance and performance of the UHTCs are beyond the scope of the present review.
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