Oxidation Resistance of Si_3N_4 Ceramics Modified with Boron and Transition Metal Diborides

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Silicon nitride ceramics are one of the most promising materials for high-temperature structural applications in oxidizing environments such as components in the hot-section of gas turbines. However, the use of Si_3N_4 ceramics at very high temperatures is limited by oxidation, scale reactions with combustion atmosphere, and volatility. The goal of the project is to enhance the oxidation resistance of Si_3N_4 ceramics by the modification of their bulk composition to induce phase separation (liquid-liquid immiscibility) in a surface protective glass layer formed as a result of exposure to an oxidizing atmosphere. The immiscibility-based control of oxidation behavior was developed and successfully applied to ZrB_2/SiC ceramics[1]. An increased liquidus temperature and viscosity of immiscible glasses are considered responsible for the improvement in oxidation resistance of the ceramics containing transition-metal diboride additives.

Silicon nitride containing 2 wt.% Al_2O_3 and 5 wt.% Y_2O_3 as sintering aids was additionally modified with transition-metal diborides (CrB_2, TaB_2, and ZrB_2), oxides (Cr_2O_3, Ta_2O_5, and ZrO_2), and BN. The mixtures were hot-pressed at 1825^{o}C and 20 MPa in He for 1 hour. The oxidation behavior of the ceramics was characterized after furnace heating at 1200 - 1600^{o}C in air as a function of the composition and structure of oxidized surface layer. The baseline Si_3N_4 ceramics exhibited glass phase separation with the formation of yttria-rich matrix phase and silica-rich droplets. The presence of Ta and Zr diborides and oxides, as well as BN did not improve high temperature oxidation resistance of the baseline composition. Only the introduction of CrB_2 or Cr_2O_3 led to an increase in the oxidation resistance of Si_3N_4 ceramics in air up to 1550^{o}C. A change in the CrB_2 content significantly affected the structure the protective layer. The presence of Cr_2O_3 in the surface melt (as a result of the oxidation of CrB_2) induced extensive immiscibility and catalyzed in-situ crystallization of $Y_2O_3 \cdot 2SiO_2$ (Figure 1). The presence of $Y_2O_3 \cdot 2SiO_2$ crystals which have a melting (decomposition) temperature of 1775ºC provided effective oxidation protection. The highest oxidation resistance was shown by the ceramics containing less than 5 vol. % CrB_2.

Figure 1: SEM Micrograph of the Surface of $Si_3N_4/Y_2O_3+Al_2O_3$ Ceramics Containing 5 volume % CrB_2 After Oxidation at 1400^oC for 10 Hours

References:

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