

## Oxidation Resistance of $\text{Si}_3\text{N}_4$ 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  $\text{Si}_3\text{N}_4$  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  $\text{Si}_3\text{N}_4$  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  $\text{ZrB}_2/\text{SiC}$  ceramics<sup>1</sup>. 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.%  $\text{Al}_2\text{O}_3$  and 5 wt.%  $\text{Y}_2\text{O}_3$  as sintering aids was additionally modified with transition-metal diborides ( $\text{CrB}_2$ ,  $\text{TaB}_2$ , and  $\text{ZrB}_2$ ), oxides ( $\text{Cr}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ , and  $\text{ZrO}_2$ ), and BN. The mixtures were hot-pressed at 1825°C and 20 MPa in He for 1 hour. The oxidation behavior of the ceramics was characterized after furnace heating at 1200 - 1600°C in air as a function of the composition and structure of oxidized surface layer. The baseline  $\text{Si}_3\text{N}_4$  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  $\text{CrB}_2$  or  $\text{Cr}_2\text{O}_3$  led to an increase in the oxidation resistance of  $\text{Si}_3\text{N}_4$  ceramics in air up to 1550°C. A change in the  $\text{CrB}_2$  content significantly affected the structure the protective layer. The presence of  $\text{Cr}_2\text{O}_3$  in the surface melt (as a result of the oxidation of  $\text{CrB}_2$ ) induced extensive immiscibility and catalyzed in-situ crystallization of  $\text{Y}_2\text{O}_3 \cdot 2\text{SiO}_2$  (Figure 1). The presence of  $\text{Y}_2\text{O}_3 \cdot 2\text{SiO}_2$  crystals which have a melting (decomposition) temperature of 1775°C provided effective oxidation protection. The highest oxidation resistance was shown by the ceramics containing less than 5 vol. %  $\text{CrB}_2$ .

## References:

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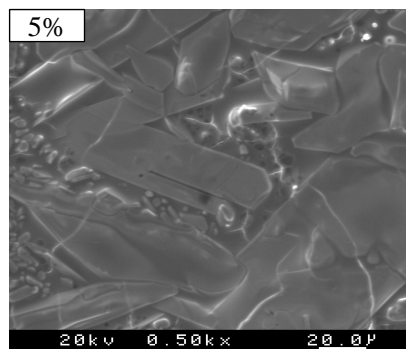


Figure 1: SEM Micrograph of the Surface of  $\text{Si}_3\text{N}_4/\text{Y}_2\text{O}_3+\text{Al}_2\text{O}_3$  Ceramics Containing 5 volume %  $\text{CrB}_2$  After Oxidation at 1400°C for 10 Hours