# ULTRA-HIGH TEMPERATURE CERAMICS FOR HYPERSONIC ENTRY OF SLENDER-SHAPED ADVANCED SPACE VEHICLES

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## ABSTRACT

Transition metal diborides such as $ZrB_2$ and $HfB_2$ are commonly referred to as Ultra High-Temperature Ceramics (UHTC) for their melting temperatures greater than 3300 K. Their physical characteristics enable applications at temperatures above 2000 K, a typical temperature limit of most structural ceramics. In particular, aerospace research in the past decades has been focused on UHTC as candidate materials to increase the heat tolerance resistance of structural thermal protection systems (TPS) such as leading edges and nose-cones for sharp-shaped hypersonic re-entry vehicles. The expected temperatures are above the operational single-use temperature limit of current TPS materials such as SiC-coated C-C composites. Progress has been made in the production of $ZrB_2$-based dense bodies with acceptable thermo-physical and mechanical properties and also in their machining into complex-shaped components. Among the open points of research on UHTC materials is the characterization of surface properties like catalycity in the high temperature range.

The objective of this paper is to present and discuss the results of catalytic properties of two UHTC materials based upon the $ZrB_2$-SiC composition; more specifically, samples machined by diamond-loaded tools (DLT) and samples machined by electrical discharge machining (EDM) were tested to assess the effect of the surface finish (different surface roughness, partial oxidation during machining) upon those properties. The catalycity of these materials is then compared to the one measured on different sintered zirconia, stabilized by yttria, calcia or magnesia.

Micro-structural analyses by SEM, EDS and XPS have shown oxidation-induced surface modifications with oxide layers composed of silica with trace amounts of boron oxide and zirconia if the maximum reached temperature is lower than about 1800 K and only zirconia for higher temperature values. The differences in the oxide layer composition may account for the different catalytic behavior. The higher recombination coefficients measured in the case of $ZrB_2$-$HfB_2$-SiC materials can be correlated with the presence of hafnia, probably characterized by higher catalytic activity compared to zirconia. In any case the investigated materials show on the inspected temperature range a low catalytic activity with maximum values of recombination coefficients close to 0.1.

This study highlighted the extreme complexity of UHTC oxidation behavior, as well as the need of an exhaustive knowledge of the phenomena regulating surface oxidation in order to explain the surface properties of this class of materials.