Ultra-high temperature ceramics (UHTCs) for severe environment

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Borides and carbides of hafnium, zirconium, tantalum and related composites are materials of great interest. These groups of ceramics, combining outstanding levels of robustness and refractoriness, are currently widely recognized as the unique materials for harsh service environments, especially for aerospace, rocket propulsion and energy applications. For instance, the strong need of thermal protection structures for the next generation of aerospace vehicles flying at hypersonic speeds is calling an impressive interest on this focus. Additional applications that take significant advantages from the high-temperature characteristics of UHTC include refractory linings and furnace heating elements, high temperature electrodes, substrates for microelectronics and cutting tools to name a few. Hafnium carbide is also an excellent candidate as an high-temperature solar absorber and conductor because of its melting point above 3300°C and has an intrinsic spectral selectivity. HfC and ZrC can be considered for thermionic/thermoelectric converters at high temperatures, exploiting proper tuning of the grain boundary or secondary phases, or modifying carrier concentration and mobility.

The open literature in the field of processing and materials science of UHTCs is nearly scarce up to the eighties of the past century. In recent years, at ISTEC-CNR, different routes were attempted to improve fabrication and performances of Zr- and Hf-based borides and carbides:

i) the incorporation of sintering aids associated to a conventional densification technique like hot pressing (HP) or gas-pressure sintering [1-6];
ii) innovative densification methods like spark plasma sintering (SPS), successfully used to densify several non oxide ceramics, and UHTC compounds[7-11];
iii) a careful “materials design” to increase strength, toughness, oxidation resistance, thermal shock resistance through the addition of reinforcing phases, including short fibers or whiskers [12-14].

The durability in oxidizing environment and the thermal and mechanical properties under severe conditions have been widely studied. Moreover, the behaviour in a simulated re-entry environment is a key issue for all the space applications [15,16].

ISTEC is the only Italian and, as far as we know, European research Institute, that has developed expertises on UHTCs that cover the basic science or the fabrication of articles and prototypes with complex shapes, up to the understanding of the material stability at very high temperatures in an aeroheating environment. Thanks to the developed know-how, dense monolithic and composite ceramics can be obtained with addition of SiC (Fig. 1a-d), MoSi2 particles, or SiC elongated reinforcements (Fig. 1c,d) and fabricated through different procedures:

- pressureless sintering, provided that MoSi2 is added, at least in amount of 5 vol%;
- hot pressing using sintering aids, specifically Si3N4, AlN, HfN, MoSi2, SiC, TaSi2;
- spark plasma sintering, with and without additives;

The composition of the starting powder mixtures and the fabrication route influence microstructure, physical and mechanical properties. A proper selection of sintering aids and the incorporation of second reinforcing phases allow to obtain near fully dense compacts and high strength values. The best values of room temperature strength approach 900 MPa (for hot pressed ZrB2+TaSi2), the strength at 1500°C in air is about 500 MPa for ZrB2-MoSi2 composites, while it reaches about 800 MPa for SPS HfB2-MoSi2-composites. Improvements in the oxidation resistance can be made with addition of Si-containing species or cations which induce immiscibility in the external glassy layer.

Improvements in the fracture toughness can obtained through addition of SiC whisker and SiC fibers, reaching values as high as 5.7 MPa-m$^{1/2}$. The Know-how developed at ISTEC includes set-up and fabrication of near-net-shape articles through slip casting, multilayered structures (tape casting) and porous materials, fabrication of dense massive UHTC test articles: billets (15 cm wide and 5 cm thick), nose-cones (10 cm high, Fig. 1e), set of screw-bolt-ring, other mock-up (Fig. 1f).
Fig. 1a. Polished surface of a hot pressed ZrB$_2$-12wt%SiC composite.

Fig. 1b. Polished surface of a hot pressed HfB$_2$-6.5wt%SiC composite.

Fig. 1c. Polished surface of a hot pressed ZrB$_2$-SiC whisker reinforced composite.

Fig. 1d. Polished surface of a hot pressed ZrB$_2$-SiC fiber reinforced composite.

Fig. 1e. ISTEC prototype of a nosecone.

Fig. 1f. ISTEC prototype of a leading edge.

References