Fabrication and characterization of Bulk Ultrarefractory Ceramics by Reactive and Non reactive SPS

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Highlights

- Reactive and non-reactive SPS as alternative routes to produce bulk UHTCs.
- Densities above 95% and homogeneous microstructures are generally obtained.
- The consolidation by SPS of combustion synthesized powders is often preferable.

Materials based on transition metal borides and carbides, often referred to as Ultra High Temperature Ceramics (UHTCs), aroused the interest of scientific community due to their unique combination of physical, thermal and mechanical properties, such as melting temperatures above 3000°C, high hardness, high electrical and thermal conductivity, high refractoriness, chemical inertness, good resistance to thermal shock and to ablation in oxidizing environments [1]. These characteristics make UHTCs suitable for several room- and high-temperature structural applications, like cutting tools, high temperature crucibles, microelectronics thermal protection structures for aerospace vehicles, etc. [1]. UHTCs possess also good spectral selectivity and low emittance at high temperatures, characteristics that make these materials interesting for energy applications [1-2].

The high covalent character of the atomic bonding, the typical presence of oxygen impurities at the particle surfaces hinder the sinterability of UHTC powders. High temperature and pressure and long processing time are generally required, when traditional Hot Pressing (HP) technique is adopted. Nonetheless, materials with coarse microstructure and residual porosity are often produced. One of the possible solution proposed to improve the intrinsically low sintering ability of UHTCs is based on the use of sintering aids like SiC, Si_3N_4 or $MoSi_2$ [3], etc., although the consolidation time remains high. Alternatively, dense UHTCs with uniform and fine microstructure can be fabricated, relatively faster and at lower temperature levels with respect to HP, by taking advantage of the Spark Plasma Sintering (SPS) technology.

Densification could be also facilitated when starting from powders obtained by Self propagating High-temperature Synthesis (SHS), whose higher sinterability is related to higher defect concentration and very fine grain size (few microns) which favor the formation of stronger bonds at the interfaces among the different ceramic phases formed in-situ [4].

Besides the use of efficient production technology, the development of UHTCs is strongly hindered by their low fracture toughness characteristics. Usually, these properties can be further improved through the addition of certain Si-containing compounds, particularly SiC, able to activate toughening mechanisms and also effective in increasing the oxidation resistance at high temperatures of this class of ceramics [5].

A summary of main results achieved for the preparation of bulk monolithic MB_2 and MC (M = Zr, Hf, Ta, Ti) and related composites by means of reactive SPS and SHS followed by SPS (SHS-SPS), is presented in this work. Depending on the system investigated and on the processing route employed, UHTC powders have been consolidated by SPS at 1750-1900°C, to generally produce 95% or denser materials [Table 1 and reference therein]. For the case of the low exothermic compositions (i.e. Ta-based), a preliminary 20 min ball milling treatment of the starting reactants is usually required to activate the corresponding SHS reactions.

It was generally found that SHS-SPS approach allowed for the obtainment of denser materials, and more uniform and finer microstructure, under relatively milder conditions with respect to RSPS method.

Hardness, fracture toughness and oxidation resistance of dense UHTCs are similar to, and in some cases superior than, those related to analogous products synthesized by alternative, less rapid, methods.

Other than for producing highly dense UHTCs with uniform microstructure, the combination of the SHS and SPS techniques was recently exploited for the preparation of porous graded materials (PMGs) [2]. The latter ones are suitable for solar energy applications, as more favorable absorption conditions for the incident radiation are provided when using porous surfaces. On the other hand, mechanical strength can be preserved if porosity is progressively lowered when moving towards the bulk of the material. Specifically, PGM products were obtained after consolidation by SPS of additive-free ZrB_2 SHS powders by taking advantage of an asymmetric die configuration with changing cross section. Due to the temperature gradient established along the longitudinal direction, porosity changes up to about 26 vol.% were generated across the volume. As clearly seen in Fig. 1, where the cross section of one PGM sample is shown, the region located on the top side is highly dense, whereas porosity degree progressively increases when moving downwards across the specimen.

Table 1. Example of UHTCs obtained by SPS with corresponding density.

System	Method	Density %	Ref.
ZrB_2	RSPS	95.6	[6]
	SHS-SPS	98.5	
HfB_2	RSPS	98.8	[5]
TaB_2	RSPS	94.2	[6]
	SHS-SPS	93.9	
ZrC	SHS-SPS	98	[7]
HfC	SHS-SPS	99.9	-
TaC	SHS-SPS	98	[8]
ZrB_2-SiC	RSPS	99.5	[9]
	SHS-SPS	99.5	
HfB_2-SiC	SHS-SPS	99.5	[3]
HfB_2-SiCw	SHS-SPS	96	[5]
HfB_2-HfSi2	SHS-SPS	> 99.9	[10]
TaB_2-SiC	SHS-SPS	96	[11]
ZrB_2-ZrC-SiC	SHS-SPS	99.7	[4]
HfB_2-HfC-SiC	SHS-SPS	98.5	[3]
TaB_2-TaC-SiC	SHS-SPS	96	[11]

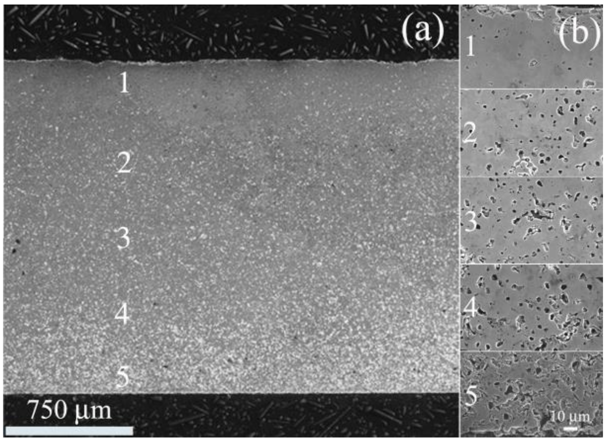

Figure 1. Micrographs of the cross section of porous graded ZrB_2 sample obtained by SPS

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Keywords

Self-propagating High-temperature Synthesis, Spark Plasma Sintering, Ultra High Temperature Ceramics.