SYNTHESIS AND CHARACTERIZATION OF GROUP IV AND V METAL DIBORIDE NANOCRYSTALS VIA BOROTHERMAL REDUCTION OF METAL OXIDE WITH NaBH₄

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Key words: metal diboride, nanocrystals, borothermal, sodium borohydride, metal oxide

Group IV and V metal diborides (MB₂) have a unique combination of properties such as a very high melting point (>3000°C), high hardness, good solid-state phase stability, high thermal and electrical conductivity. Metal diboride-based ceramics are expected to be potential candidate materials for ultra-high-temperature applications in the aerospace industry [1]. Due to the poor sinterability of commercial powders, the availability of nanometric boride particles has indeed the potential to improve several stages of ceramic processing [2], or for instance to facilitate the sintering of bulk ceramics due to enhanced particle reactivity [3]. Several synthesis have been developed to achieve nanoborides: chemical route from inorganic precursors, mechanical alloying and self-propagating high-temperature synthesis [4–6].

In this work we proposed the synthesis of group IV and V metal diboride (MB₂, M= Ti, Zr, Hf, Nb, Ta) nanocrystals by a thermal treatment of the metal oxide and sodium borohydride (NaBH₄) at 700°C under atmospheric pressure [7]. The reaction occurs first via decomposition of NaBH₄, followed by the formation of amorphous boron and crystalline ternary species with general formula NaₓMᵧOz and NaₓBᵧOz. Finally all of the intermediary species yield metal diboride (MB₂) and sodium meta-borate (NaBO₂).

Synthesized TiB₂ nanocrystals have an average size of 11 nm and the powder has a specific surface area (s.s.a) of 33.45 m²/g. ZrB₂ grains have a platelet morphology with an aspect ratio of 10, average size of 22.5 nm and s.s.a of 24.97 m²/g; HfB₂ has a similar morphology with a crystals size of 28 nm, while the s.s.a is even higher, 36.36 m²/g. As far as we know, the latter is the finest powder obtained via borothermal reduction of metal oxides ever reported. Synthesized NbB₂ powder consists of crystallites around 12 nm and has a s.s.a of 21.09 m²/g. TaB₂ powder has a s.s.a of 11.38 m²/g and consists of 200 nm agglomerates of spherical and needle-shaped nanocrystals with average size of 11 nm.

References