Scripta Materialia 158 (2019) 100–104

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Novel processing route for the fabrication of bulk high-entropy metal diborides

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ARTICLE INFO

Article history:
Received 9 July 2018
Received in revised form 22 August 2018
Accepted 22 August 2018
Available online xxxx

Keywords:
High-entropy ceramics
Borides
Spark Plasma Sintering
Self-propagating High-temperature Synthesis
X-ray diffraction (XRD)

ABSTRACT

A single high-entropy phase material with hexagonal structure is produced by a two-steps processing method. Elemental reactants are first remarkably converted by Self-propagating High-temperature Synthesis (SHS). The completion of the chemical transformation to the desired $(Hf_{0.2}Mo_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2$ phase and its concurrent consolidation up to 92.5% relative density is achieved by processing the SHS powders at 1950 °C via Spark Plasma Sintering. It is clearly evidenced that the use of the SHS technique is extremely beneficial to promote the formation of high-entropy ceramics, as compared to the time consuming ball milling treatment alternatively adopted.

The growing interest in Ultra-High Temperature Ceramics (UHTCs) based on transition metal diborides is readily justified by their unusual combination of attractive physico-chemical properties, such as melting temperature exceeding 3000 K, high hardness, chemical inertness, good electrical and thermal conductivity, intrinsic solar selectivity, low neutron absorption, etc. [1]. Aerospace (wing leading edges, nosetips, etc.), solar energy (receivers for concentrating solar power plants), nuclear reactors, metallurgy (molten metal crucibles), cutting tools, microelectronics, etc., are only few examples of application fields where UHTCs are extremely desirable. In spite of this, a suitable diffusion of such material family is not reached yet, due to their relatively low fracture toughness and not adequate high temperature oxidation properties, other than because of the difficulties encountered for the obtainment of highly dense bodies.

In this context, a new emerging class of UHTCs, the so called High-Entropy Borides (HEBs) was recently developed at the University of California, San Diego (USA) [2]. HEBs belong to the more general family of high-entropy alloys, where metallic elements are properly combined in near equimolar ratios to generate new crystalline solid-solutions characterized by a maximum configurational entropy $\Delta S_{mix} = R \cdot \ln N$, where R and N are the gas constant and the total number of the equimolar components, respectively [3]. The strong interest in these materials stems from the improved thermal stability and strengthening they usually exhibit with respect to conventional alloys [3–5].

So far, the research activity in this field has been mostly focused on metallic phases, whereas only few and recent studies are available on high-entropy ceramics, either oxides [6–10] or non-oxides [2,11–15].

As for non-oxides high entropy ceramics, six types of five-components HEBs have been prepared by Gild et al. [2]. The adopted process basically consisted of a co-milling treatment of their individual MeB_2 constituents (Me = Zr, Hf, Ta, Ti, Mo, Nb, Cr) combined in equimolar proportions and the resulting powders were densified for 5 min by SPS at 2000 °C and 30 MPa. The obtained products were single-phase materials, up to 92.4% dense, which display higher hardness and oxidation resistance as compared to the average properties of individual components fabricated and tested under the same conditions. Improved performances (hardness and thermal stability) were also reported when considering of HEB thin films prepared by non-reactive physical vapor deposition [13]. Similar findings were also obtained when characterizing the 99% dense equiatomic high-entropy carbides, namely (Hf-Ta-Zr-Nb)C, produced very recently via SPS (2300 °C) from ball milled powders [11].

The major concern related to the previously mentioned fabrication methods is represented by the intense mechanical pre-treatment of the powder mixture requested to induce the formation of a single phase product during the subsequent densification stage. For instance, Gild et al. [2] processed the diborides mixture for 6 h by high energy ball milling before SPS. Moreover, the duration of the mechanical

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https://doi.org/10.1016/j.scriptamat.2018.08.039
1359-6462/

treatment was even longer (24 h) for the fabrication of high-entropy carbides [11].

As a consequence, the corresponding whole processing time becomes very long. Furthermore, the extremely abrasive character of transition metal diborides and carbides makes the related powders prone to be contaminated from milling media, which certainly represents a crucial issue.

In this work, an alternative, more efficient, two-step processing method, consisting of the Self-propagating High-temperature Synthesis (SHS) of the high entropy product followed by the SPS of the resulting powders, is proposed. While the latter approach was already successfully exploited for the obtainment of various standard monophasic and composite UHTCs [16], it is the first time that crystalline high entropy ceramics are produced following such route.

SHS experiments were performed starting from Hf (Alfa Aesar, cod. 00337, particle size <44 μm, 99.6% purity), Mo (Aldrich, cod 26.689-2, particle size <149 μm, ≥99% purity), Ta (Alfa Aesar, cod 00337, particle size <44 μm, 99.9% purity), Nb (Alfa Aesar, cod 010275, particle size <44 μm, 99.8% purity), Ti (Aldrich, cod 26.849-6, particle size <149 μm, 99.7% purity), and B (Aldrich, cod 15580, amorphous, ≥99% purity) powders. Mixing of reactants was carried out according to the following reactions stoichiometry:

$$0.2\,Hf + 0.2Mo + 0.2Ta + 0.2Nb + 0.2Ti + (2+x)B \rightarrow (Hf_{0.2}Mo_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2 \quad (1)$$

The use of a slight excess of B ($x = 0.2$) with respect to the stoichiometric value allows for, in agreement to previous studies related to the obtainment of individual metal diborides [17–18], the removal of oxide impurities initially present in the raw powders. SHS experiments were conducted inside a closed stainless steel vessel under Argon atmosphere using cylindrical pellets (10 mm diameter and 30 mm high) obtained after cold-pressing about 10 g of the reactants mixture. The reaction was activated at one pellet end using an electrically heated tungsten coil.

The SHS product was pulverized after a short (20 min) ball milling treatment using a SPEX 8000 (SPEX CertiPrep, USA) shaker device with a ball-to-powder weight ratio of 2. Particle size of the resulting powders was evaluated by laser light scattering analysis (CILAS 1180, France). Their consolidation was carried out by SPS (515S model, Fuji Electronic Industrial Co., Ltd., Kanagawa, Japan) at 1950 °C for 20 min under a mechanical pressure of 20 MPa and vacuum conditions. Disks of about 14.7 mm diameter and 3 mm thickness were obtained. Details on the SPS apparatus and procedure can be found elsewhere [17–18].

Compositional and structural characterization of the SHS and SPS products was performed by X-ray diffraction analysis (Philips PW 1830, Netherlands) using Cu K_α radiation, over a range of scattering angles 2θ from 20 to 130, in steps of 0.05° with 15 s acquisition time per angle. The XRD patterns were analyzed by the Rietveld method using the MAUD program to determine and quantify the phases content and the corresponding microstructural parameters [19]. In addition, the compositional uniformity in sintered samples was assessed by examining their cross section by high resolution scanning electron microscopy (HRSEM) (mod. S4000, Hitachi, Tokyo, Japan) equipped with a UltraDry EDS Detector (Thermo Fisher Scientific, Waltham, MA, USA).

As schematically represented in Fig. 1, the first processing stage consists in the preparation of $(Hf_{0.2}Mo_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2$ by SHS according to reaction (1). The initial mixture, containing the starting reagents, has been analyzed by XRD. The pattern integrated with the Rietveld analysis is reported in Fig. 2a, and it confirms the presence of the all metals with the expected concentration (see Table 1). Bragg reflections of Boron cannot be detected in this pattern because its amorphous nature and the low scattering, if compared with the other heavy metals. Upon ignition, the reaction front displayed a self-sustaining character with a measured maximum temperature of about 2000 °C and average velocity of 4.75 ± 0.25 mm/s. Such behavior was similar to that observed when the individual diborides were synthesized by SHS, for instance HfB_2 [17], TaB_2 [18] and TiB_2 [20], and is consistent with their high enthalpies of formation ($-\Delta H_f^0$), i.e. 335.975, 209.200 and 323.800 kJ/mol, respectively [21].

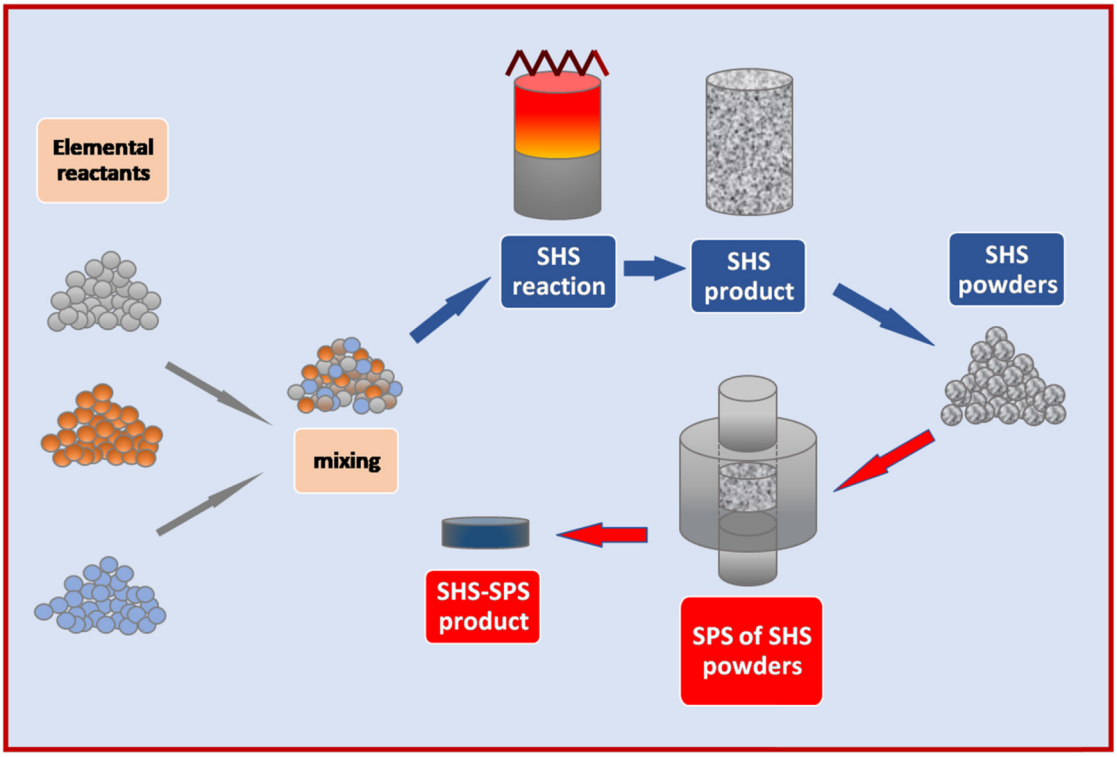

Fig. 1. Schematic representation of the processing route adopted for the fabrication of high entropy ceramics.