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Microstructural Investigation of Dual-Phase Boride/Carbide High-Entropy Ceramics

[1]Sara Ines Moussaoui, [2]Annamária Naughton Duszová, [2]Monika Hrubovčáková, [2]Marek Vojtko, [3,4]Mark Windisch, [5]Péter Pinke, [2,5]János Dusza

[1] *Obuda University, Doctoral School on Materials Sciences and Technologies, Budapest, Hungary*
[2] *Institute of Materials Research, Slovak Academy of Sciences, Košice, Slovakia*
[3] *Bay Zoltán Nonprofit Ltd. for Applied Research, Budapest, Hungary*
[4] *Department of Materials Physics, Eötvös Loránd University, Budapest, Hungary*
[5] *Obuda University, Bánki Donát Faculty of Mechanical and Safety Engineering, Budapest, Hungary*

Abstract

Reactive sintered (Ti-Zr-Nb-Ta-Hf)B_2 - (Ti-Zr-Nb-Ta-Hf)C dual-phase, high-entropy ceramics were prepared via a two-step spark plasma sintering (SPS) process at a maximum temperature of 2100°C, with a sintering time of 5 minutes at an applied pressure of 70 MPa. Microstructure analyses revealed no structural defects in the form of large pores, microcracks, or large grain clusters. The composite shows high relative density (~ 99%), and relatively homogeneous microstructure with average grain sizes of the boride and carbide phases 3 µm and 2 µm, respectively, with a negligible oxide content (HfO_2/ZrO_2 < 1wt%). It was found that Ti, Zr, and Nb elements are predominantly enriched in the boride phase, whereas Ta and Hf are concentrated more in the carbide phase.

Keywords: ceramic materials, dual-phase boride/carbide, high-entropy ceramics

1. Introduction

High-entropy ultra-high temperature ceramics (HE-UHTCs) represent a rapidly evolving class of materials designed to withstand extreme environments, offering exceptional mechanical, thermal, and tribological properties. These materials have garnered significant attention for applications in aerospace, hypersonic vehicles, and other high-temperature industrial settings. Recent research efforts have focused on innovative synthesis techniques, microstructural evolution, and the mechanical properties of these ceramics to optimize their performance [1-3].

A very promising group of these advanced ceramics developed as potential systems for ultrahigh temperature applications is the so-called dual-phase high-entropy ultra-high temperature ceramics (DPHE-UHTCs) [4-14].

Different processing routes have been applied for the preparation of DPHE-UHTCs:

• Reactive sintering of a mixture of boride and carbide powders applying spark plasma sintering (SPS) or hot pressing (HP) [4,5];

• Co-synthesis - boro-carbothermal reduction of the powder mixture of commercial oxides, carbon, and boron carbide to produce a mixture of high entropy boride (HEB) and high entropy carbide (HEC) powders, which is further spark plasma sintered [6,7];

• Sequential synthesis - carbothermal reduction of oxides and carbon to produce the high-

entropy carbide powders, which are mixed with boron carbide and zirconium hydride, followed by a reaction to produce a high-entropy boride phase by consuming part of the carbide phase [8].

The method applied for the first time by Qin et al. [4] for the preparation of DPHE-UHTCs is the reactive sintering of individual commercially available carbide and boride powders. In this work, they processed and published DPHE-UHTCs from commercial boride and carbide powders utilizing high-energy ball milling followed by SPS, achieving relative densities higher than 99 %, consisting of a hexagonal HEB and a cubic HEC phase. The hardness of the prepared DPHE-UHTCs was higher than the weighted linear average of the two single-phase high-entropy UHTCs, which are already harder than the RoM averages of the individual binary carbides and borides.

Applying co-synthesis, Luo et al. [6] synthesized single-phase HEB and HEC powders together with dual-phase high-entropy powders via a simple one-step boro/carbothermal reduction at 1650 oC. Based on these powders, a series of high-density, homogeneously distributed dual-phase high-entropy ceramics were produced by SPS at 2000 °C with average grain size ranging from 0.5 to 1.5 μm and high Vickers hardness and fracture toughness with values 24.2 ± 0.3 GPa and 3.19 ± 0.24 MPa·m1/2, respectively.

Fine-grained dual-phase high-entropy ceramic was synthesized using a sequential boro/carbothermal process by Smith et al. [8]. Solid solution formation occurred at the densification temperature of 1900 °C, resulting in a relative density higher than 99 %. The Vickers hardness of the system was 26.5 ± 1.4 GPa at a load of 2 N.

The most recent published contributions in this field focus on processing routes, theoretical predictions, and characterization/testing of the systems applying advanced methods as high-resolution transmission electron microscopy (HRTEM), nanoindentation, microcantilever test, tribological methods, etc. [9-14].

The aim of the present investigation was to study the microstructure characteristics of recently developed reactive sintered (Ti-Zr-Nb-Ta-Hf)B2 - (Ti-Zr-Nb-Ta-Hf)C dual-phase, high-entropy ceramics.

2. Experimental procedure

Commercially available powders (Alfa Aesar) were used with molar ratios of 2TaC:2HfC: ZrC: ZrB2: 2NbB2: 2TiB2 in order to achieve the target composition of a 50 mol.% (TaHf-Zr-Nb-Ti)C - 50 mol.% (Ta-Hf-Zr-Nb-Ti)B2 dual-phase high-entropy ceramics.

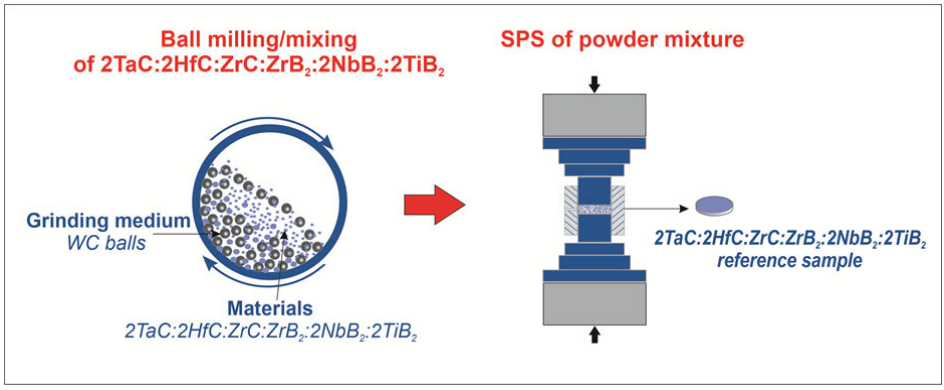

Figure 1. Schematic illustration of the processing route for the preparation of the composite

The raw powders were mixed and milled in a planetary ball mill; the homogenized powder was sintered in a Spark Plasma Sintering (SPS) device (FCT HP D10-SD) at a temperature of 2100°C, pressure of 70 MPa, and sintering time of 5 min (Figure 1).

The density of the sintered samples was determined by Archimedes' method in distilled water as an immersion medium. Specimens for microstructure examination were prepared by routine ceramographic procedure; they were cut, ground, and polished down to a 1 μm size polishing suspension. The crystalline phase composition of the sintered sample was determined by X-ray diffractometry (XRD) using a Philips X'PertPro device (Cu Kα radiation). The microstructure characteristics and elemental composition of the sintered sample were determined by scanning electron microscopy (FIB-SEM ZEISS AURIGA Compact) equipped with an energy dispersive X-ray spectroscopy (EDS) detector. Microstructural characteristics, phase distribution, and porosity were also examined using scanning electron microscopy (SEM) (JEOL JSM-60LV). Electron backscatter diffraction (EBSD) maps provided insights into grain orientation and texture.

The grain size was determined by the line intercept method, counting the number of grain boundaries intercepting the line of a known length drawn on an SEM image of the sample. In total, 100 grains were counted for the analyses.

3. Results and discussion

XRD results of the investigated (Ta-Hf-Zr-Nb-Ti)C-(Ta-Hf-Zr-Nb-Ti)B_2 composite ceramics, confirming the successful formation of a dual-phase high-entropy ceramic with negligible oxide content (HfO_2/ZrO_2 < 1 wt%). The carbide and boride phases, denoted as HEC and HEB, respectively, exhibit lattice parameters of a = 4.5246(7) Å for the cubic carbide (Fm-3m) and a = 3.0974(6) Å, c = 3.3643(8) Å for the hexagonal boride (P6/mmm), as determined by Rietveld refinement.

The characteristic microstructure of the sintered dual-phase material at different magnifications is illustrated in Figure 2. According to the results of the microstructure analyses, both the carbide (light grey) and boride grains (dark grey) are relatively homogenously distributed with only a small amount of porosity, resulting in a relative density of 99%. The grain size varies between 1 μm and 8 μm, with a slightly lower average size for carbides (~2 μm) than for borides (~3 μm), forming small clusters of grains. Very small pores were detected at the grain boundaries with a size of approximately 100 nm.

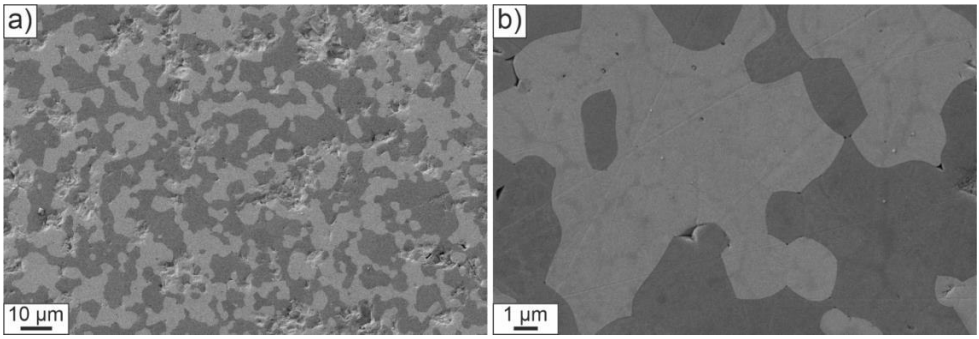

Figure 2. Characteristic microstructures of the investigated dual-phase boride/carbide composite at low (a) and high (b) magnifications

The EBSD analysis further proved the presence of separate hexagonal HEB and cubic HEC phases (Figure 3a) with an inverse pole figure (IPF) map (Figure 3b) revealing equiaxed grains with random crystallographic orientations, indicating a randomized texture. The EBSD analysis is very useful when the influence of the crystallographic orientation on the local mechanical properties is studied.

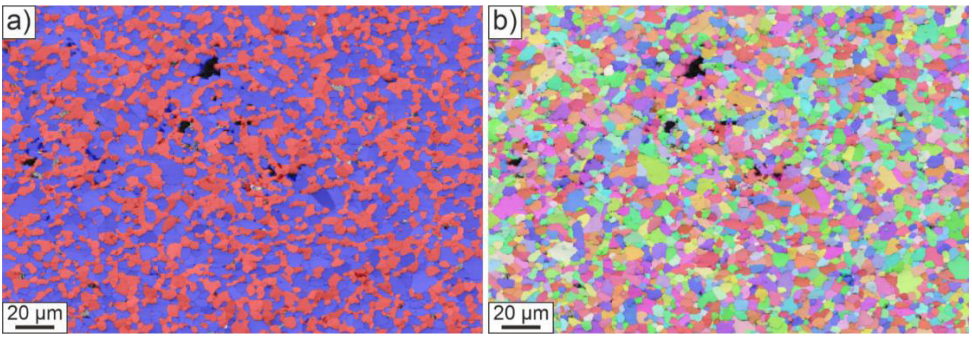

Figure 3. (a) EBSD phase map of the distribution of HEC (blue) and HEB (red) phases (b) Inverse Pole Figure (IPF) map of random crystallographic orientations and equiaxed grains

The grain sizes in the developed system (Figure 4) are similar to the grain sizes for the system published by Qin et al. [4] who reported a definite correlation between the grain sizes of the carbide and boride phases with the phase fraction and the lowest grain sizes approximately 7 µm with similar mol% of carbide/boride. In the systems, Luo et al. [6] reported significantly lower average grain sizes of 0.64 ± 0.2 µm for the boride and 1.5 ± 0.4 µm for the carbide in their dual-phase ceramic, processed using different processing routes.

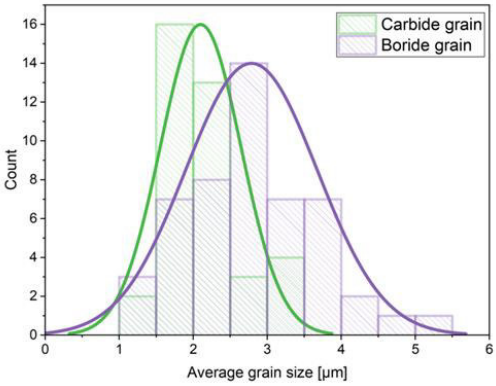

Figure 4. Grain size distributions in the investigated composite

EDS analyses of the polished surface revealed (Figure 5) that the elemental distribution of the component, metallic elements, is not perfectly homogeneous. The carbide phase abounds in Hf and Ta, while Nb, Zr, and Ti segregate predominantly in the boride phase. In addition to the principal element W and O impurity elements are also detected, which is in agreement with the presence of a negligible amount of oxides confirmed by XRD. Tungsten was found mainly in the carbide phase rather than in boride grains, which were introduced most probably during ball milling using WC

balls. Oxygen was detected to form an oxide phase at the grain boundaries, mainly at triple junctions. As it is visible in Figure 5, the SEM+EDAX analyses for such a study are not ideal, detecting boride content in HEC and carbide content in HEB as the result of the large testing volume.

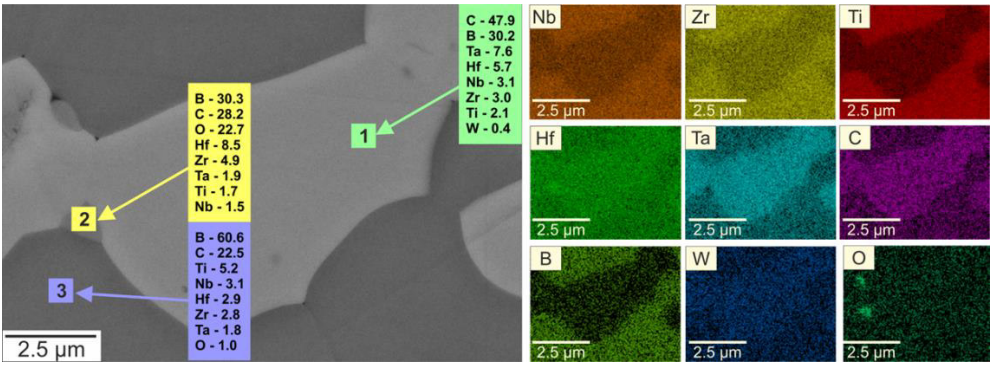

Figure 5. EDX maps for individual elements in the HEC and HEB phases of the investigated system

The applied methods for microstructure study of the investigated system are very useful; however, for the study of the microstructure characteristics at the nano/atomic level, HRTEM is necessary, which will be used in the future.

4. Conclusions

The aim of the present investigation was to study the microstructure characteristics of recently developed reactive sintered (Ti-Zr-Nb-Ta-Hf)B_2 - (Ti-Zr-Nb-Ta-Hf)C dual-phase, high-entropy ceramics. The main results are the following:

- Reactive sintered (Ti-Zr-Nb-Ta-Hf)B2 - (Ti-Zr-Nb-Ta-Hf)C dual-phase, high-entropy ceramics were prepared via a two-step spark plasma sintering (SPS) process at a maximum temperature of 2100°C, with a sintering time of 5 minutes at an applied pressure of 70 MPa;
- Microstructure analyses revealed no structural defects in the form of large pores, microcracks, or large grain clusters. The composite shows high relative density (~ 99%), and relatively homogeneous microstructure with average grain sizes of the boride and carbide phases 3 µm and 2 µm, respectively, with a negligible oxide content (HfO_2/ZrO_2 < 1 wt%).
- It was found that Ti, Zr, and Nb elements are predominantly enriched in the boride phase, whereas Ta and Hf are concentrated more in the carbide phase.

5. References

[1] R.Z. Zhang, M.J. Reece, Review of high entropy ceramics: design, synthesis, structure and properties, J. Mater. Chem. A. 7 (2019) 22148–22162. https://doi.org/10.1039/c9ta05698j

[2] Oses, C., Toher, C. & Curtarolo, S. High-entropy ceramics. Nat Rev Mater 5, 295–309 (2020). https://doi.org/10.1038/s41578-019-0170-8

[3] S. Akrami, P. Edalati, M. Fuji, K. Edalati, High-entropy ceramics: Review of principles, production, and applications, Mater. Sci. Eng. R Reports. 146 (2021) 100644. https://doi.org/10.1016/j.mser.2021.100644

[4] M. Qin, J. Gild, C. Hu, H. Wang, M.S. Bin Hoque, J.L. Braun, T.J. Harrington, P.E. Hopkins, K.S. Vecchio, J. Luo, Dual-phase high-entropy ultra-high temperature ceramics, J. Eur. Ceram. Soc. 40 (2020) 5037–5050. https://doi.org/10.1016/J.JEURCERAMSOC.2020.05.040

[5] S. Huo, L. Chen, X. Liu, Q. Kong, Y. Wang, H. Gu, Y. Zhou, Reactive sintering of dual-phase high-entropy ceramics with superior mechanical properties, J. Mater. Sci. Technol. 129 (2022) 223–227. https://doi.org/10.1016/J.JMST.2022.03.035

[6] S.C. Luo, W.M. Guo, K. Plucknett, H.T. Lin, Fine-grained dual-phase high-entropy ceramics derived from boro/carbothermal reduction, J. Eur. Ceram. Soc. (2020). https://doi.org/10.21203/rs.3.rs-58173/v1

[7] L. Feng, W.G. Fahrenholtz, G.E. Hilmas, S. Curtarolo, Boro/carbothermal reduction co-synthesis of dual-phase high-entropy boride-carbide ceramics, J. Eur. Ceram. Soc. 43 (2023) 2708–2712. https://doi.org/10.1016/j.jeurceramsoc.2022.12.056

[8] S.M. Smith, L. Feng, W.G. Fahrenholtz, G.E. Hilmas, T. Huang, High-entropy boride–carbide ceramics by sequential boro/carbothermal synthesis, J. Am. Ceram. Soc. (2022). https://doi.org/10.1111/jace.18517

[9] S.M. Smith II, W.G. Fahrenholtz, G.E. Hilmas, S. Curtarolo, Thermodynamic analysis of metal segregation in dual phase high entropy ceramics, Journal of Materiomics, available online 14 January (2024). https://doi.org/10.1016/j.jmat.2023.12.007

[10] A. Naughton-Duszová, P. Švec, A. Kovalčíková, R. Sedlák, P. Tatarko, P. Hvizdoš, P. Šajgalík, J. Dusza, On the phase and grain boundaries in dual phase carbide/boride ceramics from micro to atomic level, J. Eur. Ceram. Soc. 43 (2023) 6765–6773. https://doi.org/10.1016/j.jeurceramsoc.2023.07.034

[11] A. Naughton-Duszová, M. Hrubovčáková, M. Vojtko, D. Albov, D. Medveď, L. Ďaková, Ľ. Medvecký, P. Hvizdoš, T. Csanádi, Fracture strength of grains and grain boundaries in a dual-phase high-entropy ultra-high temperature ceramics, J. Eur. Ceram. Soc. 44 (2024) 5422–5431.https://doi.org/10.1016/j.jeurceramsoc.2024.01.034

[12] S.M. Smith II, N. Gilli, W.G. Fahrenholtz, G.E. Hilmas, S. García-González, E. Jiménez-Piqué, S. Curtarolo, L. Silvestroni, Dual-phase ceramics based on multication boride and carbide: Investigations at the nanoscale, Journal of Materiomics, https://doi.org/10.1016/j.jmat.2024.06.002

[13] S. Filipovic, S.M. Smith II, G. Hilmas, W. Fahrenholtz, N. Obradovi, S. Curtarolo, Synthesis and properties of (Hf,Mo,Ti,W,Zr)B2–(Hf,Mo,Ti,W,Zr)C dual phase ceramics, J. Eur. Ceram. Soc. 44 (2024) 116670. https://doi.org/10.1016/j.jeurceramsoc.2024.116670

[14] A. Naughton Duszová, L. Ďaková, T. Csanádi, A. Kovalčíková, V. Kombamuthu, H. Ünsal, P. Tatarko, M. Tatarková, P. Hvizdoš, P. Šajgalík, Nanohardness and indentation fracture resistance of dual-phase high-entropy ceramic, Ceram. Int. 49 (2023) 24239-24245. https://doi.org/10.1016/j.ceramint.2022.12.027