World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:16, No:02, 2022

Dual-Phase High Entropy $(Ti_{0.25}V_{0.25}Zr_{0.25}Hf_{0.25})$ BxCy Ceramics Produced by Spark Plasma Sintering

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Abstract : High entropy ceramic (HEC) materials are characterized by their compositional disorder due to different metallic element atoms occupying the cation position and non-metal elements occupying the anion position. Several studies have focused on the processing and characterization of high entropy carbides and high entropy borides, as these HECs present interesting mechanical and chemical properties. A few studies have been published on HECs containing two non-metallic elements in the composition. Dual-phase high entropy $(Ti_{0.25}V_{0.25}Zr_{0.25}Hf_{0.25})$BxCy ceramics with different amounts of x and y, (0.25 HfC + 0.25 ZrC + 0.25 VC + 0.25 TiB_2), (0.25 HfC + 0.25 ZrC + 0.25 VB2 + 0.25 TiB_2) and (0.25 HfC + 0.25 ZrB2 + 0.25 VB2 + 0.25 TiB_2) were sintered from boride and carbide precursor powders using SPS at 2000°C with holding time of 10 min, uniaxial pressure of 50 MPa and under Ar atmosphere. The sintered specimens formed two HEC phases: a Zr-Hf rich FCC phase and a Ti-V HCP phase, and both phases contained all the metallic elements from 5-50 at%. Phase quantification analysis of XRD data revealed that the molar amount of hexagonal phase increased with increased mole fraction of borides in the starting powders, whereas cubic FCC phase increased with increased carbide in the starting powders. SPS consolidated $(Ti_{0.25}V_{0.25}Zr_{0.25}Hf_{0.25})$BC0.5 and $(Ti_{0.25}V_{0.25}Zr_{0.25}Hf_{0.25})$B1.5C0.25 had respectively 94.74% and 88.56% relative density. $(Ti_{0.25}V_{0.25}Zr_{0.25}Hf_{0.25})$B0.5C0.75 presented the highest relative density of 95.99%, with Vickers hardness of 26.58±1.2 GPa for the borides phase and 18.29±0.8 GPa for the carbides phase, which exceeded the reported hardness values reported in the literature for high entropy ceramics. The SPS sintered specimens containing lower boron and higher carbon presented superior properties even though the metallic composition in each phase was similar to other compositions investigated. Dual-phase high entropy $(Ti_{0.25}V_{0.25}Zr_{0.25}H_{0.25})$BxCy ceramics were successfully fabricated in a boride-carbide solid solution and the amount of boron and carbon was shown to influence the phase fraction, hardness of phases, and density of the consolidated HECs. The microstructure and phase formation was highly dependent on the amount of non-metallic elements in the composition and not only the molar ratio between metals when producing high entropy ceramics with more than one anion in the sublattice. These findings show the importance of further studies about the optimization of the ratio between C and B for further improvements in the properties of dual-phase high entropy ceramics.

Keywords : high-entropy ceramics, borides, carbides, dual-phase
Conference Title : ICHEM 2022 : International Conference on High-Entropy Materials
Conference Location : Paris, France
Conference Dates : February 17-18, 2022