Study of phase formation and properties of high-entropy carbide HfTaTiNbZrC₅ obtained by selfpropagating high-temperature synthesis

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Abstract. This work is devoted to the study of the combustion synthesis mechanism in complex multi-component systems using the quenching of the combustion front in a copper block. Bulk specimens were produced by reactive spark plasma sintering (R-SPS) of mechanically activated mixtures as well as by SPS of high-entropy ceramics obtained by combustion synthesis. The resistance of high-entropy carbides towards oxidation was studied in relation to the number of metallic constituents.

1. Introduction
In the last decades there is a surge of interest towards materials with enhanced structural and functional properties. To achieve this goal, the complexity of the composition of materials is increased. Complex-alloyed high-end steels and heat resistant alloys are prime examples of this trend. An increase in the number of alloying elements usually is associated with an increase in the number of phases in the alloy, which complicates the design of the material. This is the case for alloys based on a single main constituent. Recently, a new direction in materials science has emerged – the design of high-entropy materials with near-equimolar ratio of constituents [1-4]. The diversification of this field gave rise to high-entropy carbide and boride ceramics [5-6]. Due to the high refractoriness, high-entropy ceramics are proposed as candidates for ultra-high-temperature applications. This work focused on the production of high-entropy ceramics HfTaTiNbZrC₅ and HfTaTiNbMoC₅ via combustion synthesis (also known as SHS), which allows for a single-stage low-cost synthesis [7,8] The goal of this work was to investigate the mechanism of phase formation within the combustion front of the related systems and to compare the properties of ceramics produced by SHS and reactive spark plasma sintering.

2. Materials and Methods
The methodology for the synthesis of high-entropy ceramic powders by combustion is described in [7]. Sintering was carried out on an SPS Labox 650 (Sinterland, Japan) spark plasma sintering unit at temperatures of 1800 °C and 2000 °C, the pressure applied to the punches was 50 MPa. The density of samples was measured by hydrostatic weighing. The structure of HEC powders and bulk materials was analyzed using SEM on a JSM 7600F (JEOL, Japan) with a microanalysis system EDX (Oxford Instruments). X-ray phase analysis was carried out on a DRON-4-07 (Burevestnik, Russia).
3. Results and Discussion

The mechanisms of phase and structure formation in the Hf-Ta-Ti-Nb-Zr-C system during SHS were studied by quenching the combustion fronts in a copper block, which was carried out in 3 stages: 1) preparation of reactive mixture; 2) pressing the reactive mixture into green triangles (relative density ~ 60%); 3) ignition of combustion with subsequent quenching. The quenched combustion front was then polished along the axis of the combustion front propagation and studied by SEM and EDS (Figure 1). Figure 1a provides a general view of the quenched combustion front; one can see both the initial component and the combustion products. As the wave propagates through the reactive mixture, the components melt and then the main product phase begin to crystallize (Figure 1b). The after-combustion zone features ring structures (Figure 1c), within which crystals of high-entropy carbide lie. In the secondary structure formation zone, the ring structures experience recrystallization (Figure 1d) into submicron (150-400 nm) grains of high-entropy carbide (Figure 1e).

High-entropy carbide with the composition Hf0.2Ta0.2Ti0.2Nb0.2Zr0.2C (HEC2z), produced by SHS, was then consolidated by spark plasma sintering (SPS). The sintering of HEC specimens was carried out at a pressure of 50 MPa and at temperatures of 1500 - 2200 °C to ascertain the influence of the sintering temperature on the relative density and mechanical properties of materials. The relative density increased from 90.5 to 94.8%.

In addition, the reactive SPS method was used, which allows one to combine the combustion reaction and consolidation of the ceramics (Figure 2). Due to the higher vacuum in the SPS apparatus as compared to SHS reactor, the method is expected to yield higher purity products with lower residual oxide content, refined microstructure and higher mechanical properties. The structural refinement is related to the suppression of the recrystallization processes characteristic for SHS.

The XRD analysis of the combustion products (Figure 3a) demonstrated the formation of single-phase high-entropy carbide with an FCC lattice. The consolidation of combustion products at 1800 and 2000 °C (Figure 3 b, c) did not alter the single-phase FCC solid solution, suggesting that the phase is stable at high temperatures. The R-SPS method yielded an identical solid solution phase (Figure 3d)
Figure 2. Sintering monitoring curves: voltage-current-pressing force-shrinkage versus time

Figure 3. XRD analysis of combustion products and sintered materials of high-entropy ceramics

The combustion kinetics did not show any pronounced dependencies on the relative density of green pellets. Figure 4 provides the morphology of the SHS products $\text{HEC}_Zr$, with the 0.1-5 $\mu$m crystals form 20-50 $\mu$m agglomerates.

Figure 4. Morphology of $\text{HEC}_Zr$ powder particles after SHS compressed at different pressures (a - 8 kg·f, b - 80 kg·f, c - d - 160 kg·f)
The structure of the consolidated SHS ceramics is shown in Figure 5. They feature rounded grains, which become increasingly more coarse at higher temperature (0.5-4 µm at 1800 °C and 1-10 µm at 2000 °C). The density of specimens sintered at 1800 and 2000 °C was 7.75 g/cm³ and 8.12 g/cm³. However, the hardness of HECZr, sintered at 1800 °C (21.5 GPa) was higher than at 2000 °C (19.1 GPa), presumably due to the grain coarsening. The R–SPS method yielded fine grains with a narrow size distribution (1-3 °C) due to the application of pressure and higher cooling rate realized in the R-SPS method; the specimens demonstrated a density of 8.34 g/cm³ and a hardness of 26 GPa.

![Figure 5. Microstructures of sintered HECZr at 1800 °C (a), 2000 °C (b) and reaction sintering at 2000 °C (c)](image)

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