Synthesis and study of high-entropy ceramics based on the carbides of refractory metals

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Abstract. Production of single-phase carbide high entropy ceramic (Hf$_{0.2}$Ta$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Mo$_{0.2}$ or Zr$_{0.2}$)C by self-propagating high-temperature synthesis (SHS) from a mechanically activated (MA) reaction mixtures and mechanical synthesized (MS) materials is discussed. The influence of mechanical treatment time at ball mill, on the formation of the phase of a high-entropy material is investigated. Spark plasma sintering and their structure, phase composition, obtained bulk samples and mechanical properties were studied. A self-propagating high-temperature synthesis of high-entropic carbide based on refractory elements was also carried out. The microstructure and mechanical properties of high-entropy ceramics obtained by the methods of mechanical synthesis and SHS were compared.

1. Introduction

Conventionally, the majority of alloys are based on one main constituent element. For the increase of properties and performance, they are alloyed by alloying elements which enhance the alloy’s strength, corrosion resistance and other properties. Thus, the families of alloys are made. However, the number of elements is limited; therefore, the number of alloys which could be developed on the base of one or two main constituent elements is finite. However, what if one is to go outside the classical definition and increase the number of constituent elements? This conception was first suggested in 1995 [1], and these materials were later branded as high-entropy alloys [2].

High-entropy materials by definition contain five or more main constituent elements with the concentration between 5% and 35% [3]. The currently available data in the areas of physical metallurgy and binary and ternary diagram suggests that such multicomponent alloys might contain dozens of phases and intermetallics, which are usually brittle and have limited applicability. However, in contrary to these expectations that the increased entropy in these alloys leads to the formation of solid solutions with a relatively simple structure, thus diminishing the content of unwanted phases or eliminating them. These peculiar features, related to high entropy, are of the utmost importance for the development and applications of the high-entropy alloys.

During the last years of investigation of high-entropy materials, more than 300 compositions with wide functionality were developed on the basis on non-ferrous and refractory metals. Currently, the hottest topic is the development of high-entropy alloys (HEA) for high-temperature applications, which require high phase stability upon heating up to 1800°C, oxidation resistance and high-temperature strength.
Due to their unique multi-component compositions, HEAs might possess a complex of outstanding properties, including high strength and hardness, unmatched high-temperature strength, good structural stability, and corrosion resistance. The close interest in the development of these materials is driven by the demand for the materials with increased operating temperature from the aerospace industry.

Equimolar composition HfTaTiZrNbMo was investigated in the article [4] and demonstrated the high mechanical properties at room temperature and 1200 °C. Xueliang Yan et al. in their recent article [5] synthesized a high-entropy with the composition (Hf0.2Zr0.2Ta0.2Nb0.2Ti0.2)C from the monocarbides, which were mixed in a mill and consolidated by spark plasma sintering at 2000 °C. The produced material is characterized by high thermal conductivity, thermal diffusivity, and the coefficient of thermal expansion, which was compared to the initial monocarbides. In various articles dedicated to the investigation of HEAs, the samples are usually produced by arc melting. However, this production route often leads to the formation of a dendritic structure, leading to the degradation of mechanical properties. To retain the fine-grain structure, which is most beneficial for mechanical properties, the powder metallurgy route is most perspective, since it ensures the homogeneity of material. Also, as a new class of high-entropy, Jian Luo et al. [6] described the ultra-high-temperature diboride ceramic based on the Hf–Ta–Ti–Nb–Mo–Zr system. In our work, a high-entropy alloy Hf–Ta–Ti–Nb–Mo–Zr and the related high-entropy carbide were produced by high-energy ball milling and spark plasma sintering.

2. Materials and Methods

The majority of high-entropy materials are produced by vacuum arc melting, which requires high energy expenditures. In this work, high-entropy materials were produced by various routes, which involve the mixing of metal powders and carbon, subsequent synthesis, and sintering.

For the production of high-entropy ceramics (HEC-1 corresponds to the composition (Hf0.2Ta0.2Ti0.2Nb0.2Mo0.2)C; HEC-2 corresponds to the composition (Hf0.2Ta0.2Ti0.2Zr0.2Nb0.2Zr0.2)C), the mixture of powders were treated in the planetary ball mill Aktivator-2S (Russia). High-energy ball milling (HEBM) was organized according to two schemes: 1) milling of the mixture of metals and graphite during 120 min (mechanochemical synthesis); 2) milling of the mixture of metals during 90 min (+ 5 min with hexane to ensure the unloading the powder from the surface of jars and balls), then milling of pre-milled metal powders with graphite for 5 min (mechanical activation of reaction mixtures).

After the treatment according to scheme 2 (mechanical activation), combustion synthesis of the reaction mixtures was conducted in the lab reactor developed in the framework of the U.M.N.I.K. project. Combustion temperature and rate were measured during the synthesis.

Sintering of the powders produced by mechanochemical synthesis (120 min of co-milling of metals and graphite) and by combustion synthesis (90 min milling of metals, 5 min milling of mixture of metals and graphite and subsequent combustion synthesis in lab reactor) was conducted on the hot pressing installation Dr. Fritsch DSP 515 (Germany) and spark plasma sintering installation SPS Labox 650 (Japan) in a graphite matrix in vacuum at temperatures 1500, 1800 and 1900°C, pressure 30 and 50 MPa, dwelling time 5 min. Heating and cooling rates were equal to 100 and 50°C min⁻¹, correspondingly. The structure of powders and sintered materials were analyzed by means of scanning electron microscopy (SEM) on the Vega 3 (TESCAN, Czech Republic) and Nanolab Helios 600 (FEI, United States) systems. The last one, exhibiting the ion and electron beams, allows for the acquisition of a cross section of the particle in any direction, while the electron beam enables one to analyze its microstructure. The X-ray diffraction analysis was conducted on a DRON-3 diffractometer (Burevestnik, Russia). Material’s hardness was measured on the Struers Durascan 70 tester with a load of 3 kN.
3. Results and Discussion

Long HEBM treatment (120 min) allowed the homogeneous distribution of graphite in the mixture and eliminated agglomerates. SEM of the cross-cut polished powders is presented in figure 1, featuring the uniform structure and absence of phase segregation in the powders and suggesting the completion of mechanochemical synthesis during the HEBM.

As the SEM of Hf$_{0.2}$Ta$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Mo$_{0.2}$C ceramic demonstrates (figure 2a) the material has relatively high residual porosity due to insufficient pressure and dwelling time. At higher resolution, bright inclusions with the size ≤ 1 µm can be seen. EDS analysis suggests that these inclusions are comprised of hafnia (figures 2b, 2c). Unlike the Hf$_{0.2}$Ta$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Mo$_{0.2}$C, the microstructural investigation of HEC with the composition Hf$_{0.2}$Ta$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Zr$_{0.2}$C (figures 2d–2f) demonstrated the absence of oxides or secondary phases. The material is porous as well, but its structure is uniform. Usually, the uniform structure provides higher mechanical properties, including hardness and high-temperature strength.

![Figure 1](image1)

**Figure 1.** SEM of the cross-cut powders with the composition Hf$_{0.2}$Ta$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Mo$_{0.2}$C (a, b) and Hf$_{0.2}$Ta$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Zr$_{0.2}$C (c, d) after 120 min HEBM.

Sintering at 1800°C of the powders produced by SHS yielded more densified material, but SEM (figure 4) reveals the presence of minor phase decomposition and oxide contamination. Grain structure is somewhat coarser as compared to the materials sintered at 1500°C.
Figure 2. SEM of ceramic Hf_{0.2}Ta_{0.2}Ti_{0.2}Nb_{0.2}Mo_{0.2}C (a) and Hf_{0.2}Ta_{0.2}Ti_{0.2}Nb_{0.2}Zr_{0.2}C (d–f); EDS results (b, c).

Figure 3. XRD patterns of ceramics Hf_{0.2}Ta_{0.2}Ti_{0.2}Nb_{0.2}Mo_{0.2}C (a) and Hf_{0.2}Ta_{0.2}Ti_{0.2}Nb_{0.2}Zr_{0.2}C (b) produced by hot pressing of powders after 120 min HEBM.
Figure 4. SEM and EDS maps of ceramics: HEC-1, hot-pressed at 1800°C (a, b); HEC-1 SPsed at 1800°C (c, d); HEC-2 hot-pressed at 1800°C (e, f); HEC-2 SPsed at 1800°C (g, h).
The material produced by SHS and SPS demonstrated higher hardness as compared to the specimens produced by mechanochemical synthesis and hot pressing (table 1).

XRD data (figure 3) demonstrates the formation of single-phase solid solution with FCC lattice during the HEBM and sintering. Sintering at higher temperature leads to the formation of impurities, probably due to oxygen contamination during the unloading of jars.

The second approach includes preparation of metallic HEA, mixing it with carbon and combustion synthesis. First-stage HEBM produced amorphous powders, which did not react with the carbon during the second stage of HEBM. Then the carbide was synthesized in the lab reactor in an argon atmosphere. Combustion temperature and rate were measured during the synthesis. Combustion rate was 4.17 mm/s and 7.69 mm/s for HEC-1 and HEC-2 respectively. XRD data (figure 5) reveals the formation of single-phase with FCC lattice and absence of oxides or monocarbides in the combustion products.

Table 1. Hardness test result

| Material | Method of synthesis | Method of sintering | Hardness, GPa |
|----------|---------------------|---------------------|---------------|
| HEC-1    | MA 120 min          | Hot pressing 1500°C | 14.33         |
| HEC-1    | MA 120 min          | Hot pressing 1800°C | 15.95         |
| HEC-1    | SHS                 | SPS 1900°C          | 22.62         |
| HEC-2    | MA 120 min          | Hot pressing 1500°C | 16.75         |
| HEC-2    | MA 120 min          | Hot pressing 1800°C | 18.58         |
| HEC-2    | SHS                 | SPS 1900°C          | 20.53         |

Figure 5. XRD patterns for powders after HEBM and combustion synthesis.

4. Conclusions
The following conclusions could be made:
1. High-entropy ceramics can be produced by the mechanochemical synthesis and combustion synthesis
2. Increase if the sintering temperature allows the production of more dense material with high hardness and fracture toughness.
3. These methods were applied for the first time for the production of high-entropy carbide ceramics by SHS.
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