Studying the properties of carbides in the system ZrC–HfC, TaC–ZrC and TaC–HfC

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Abstract. Considers the chemistry of carbides of zirconium, hafnium and tantalum and their high temperature properties. By hot pressing the obtained dense materials in the systems ZrC–HfC, TaC–ZrC, and TaC–HfC analysed their microstructure, physical and mechanical properties.

1. Introduction

As is known in the systems ZrC–HfC, TaC–ZrC, and TaC–HfC can form complex carbides having a melting temperature of ~4000 °C, which exceeds the melting temperature of the individual carbides (T = 3532 °C (ZrC); T = 3900 °C (HfC); T = 3880 °C (TaC) [1]). To obtain dense bulk materials based on ZrC, HfC and TaC is possible only by hot pressing (HP) [2], hot isostatic pressing (HIP), spark plasma sintering, or pulse (SPS) [3, 4]. The study of patterns of synthesis and properties of single-phase complex carbides allows to obtain heat-resistant materials that can be used as main components for producing products used in missile and space technology.

In works [1, 5], the presence of anomalous physical properties of the carbide composition Ta₄HfC and materials in the systems ZrC–HfC and TaC–ZrC, but the most promising in the system TaC–HfC is a complex tantalum carbide-hafnium (Ta₄HfC₃), which has a record of a melting point over 4000 °C [6, 7].

Materials based on carbides and their compounds can be promising due to the unique properties themselves ZrC, HfC and TaC such as high hardness (~28.5 GPa (ZrC); ~20.0 GPa (HfC); ~19.0 GPa (TaC)) and the modulus of elasticity (412 GPa (ZrC); 425 GPa (HfC); 537 GPa (TaC)), heat resistance in a protective gas atmosphere to a temperature 2500 °C, high electrical conductivity etc., which allows the use of the materials and products on their basis when working in extreme conditions, as lining rocket engines, or the front edges of hypersonic aircraft and missiles and so on [8].

The aim of this work is to study the properties of synthesized single-phase connections of the complex carbides in the systems ZrC–HfC, TaC–ZrC and TaC–HfC by hot pressing, and the microstructure and physical-mechanical properties of obtained materials.

Features of the structure ZrC, HfC and TaC and high temperature properties of materials based on them.

Carbides ZrC, HfC and TaC have a face-centered cubic lattice [9]. Hafnium carbide has exceptional resistance to high temperature oxidation, on its surface forms a stable oxide of hafnium (HfO₂), which serves as a barrier to oxygen diffusion into the bulk material, protecting it from further oxidation [10, 11].
The melting temperature of non-stoichiometric HfC increases with a deficit of carbon, until a maximum at the point of the congruent melting point – HfC0.82 (~ 45 at. % C) [12].

On the surface TaC formed oxide film, which protects the ceramics from oxidation at high temperatures (up to 1800 °C). Removal of oxygen impurity from the surface of the powder TaC is a thermochemical treatment at a temperature of 1000–1500 °C that leads to significant growth of the grains.

Tantalum carbide has relatively poor oxidation resistance and is completely oxidized at a temperature of ~ 850 °C after 5 h in an atmosphere of pure oxygen, forming the pentoxide of tantalum. However, when TaC is used with minimal exposure to oxygen, for example, solid rocket motors with aluminum fuel, it is considered the most effective material for the ceramic veneer.

One of the possible ways of increasing the heat resistance of materials can serve as a synthesis of complex carbides and the introduction of more heat-resistant compounds, for example, adding MoSi2 [14].

2. Materials and Method
The materials were prepared by standard ceramic technique [15–20]. For the synthesis used the commercially available powders of carbides with original size: ZrC (d0.5 = 30.2 µm); HfC (d0.5 = 28.6 µm); TaC (d0.5 = 44.1 kHz µm), which are separately milled in a planetary mill to a size d0.5 = 0.5 to 1.0 µm and, in appropriate ratio, mixed in a drum mixer in the environment of isopropyl alcohol for 20 h. Charge powders were dried and pelletized. Materials of size 225×5 mm were obtained from charge mixtures of powders by hot pressing (T = 1900 °C, P = 30 MPa, t = 1 h), which were then further annealed at a temperature of 2000 °C in a vacuum oven for 1 h in the atmosphere Ar. To determine the mechanical characteristics of sintered materials in the form of discs cut on samples with size 5×5×20 mm.

The density and porosity of the samples was determined by hydrostatic weighing. Phase composition and lattice parameters using the diffractometric Rigaku Smartlab 3. Ultimate strength in three-point bending was determined on a tensile testing machine ShimadzuAG 130. Examination of the microstructure was performed by scanning electron microscopy, determination of the elemental composition by the method of Microspectral analysis on the microscope Tescan Vega 3 SBH with the console EDX. The microstructure was analyzed using optical microscope Meiji Techno IM 7200. The equipment is provided by the Engineering center St. Petersburg State Technological Institute (Technical University).

3. Results and discussion
In work the method of X-ray analysis to determine the composition of hot-pressed ceramic carbides (Table 1), shows the change in the content of fixed carbon and the lattice parameter of the material before and after additional high temperature annealing. As can be seen from the results of the analysis, the content of bound carbon is markedly reduced, which affects the change in the composition of the sintered material. Thus, carbides of zirconium, hafnium and tantalum have changed the composition of ZrC0.88, HfC0.97 and TaC0.98 at the ZrC0.78, HfC0.94 and TaC0.93. It also indicates the change of lattice parameter (Table 1). Accordingly, we can assume that was a change in the stoichiometry of the complex carbides, for example, (Zr0.6Hf0.4)C0.92 to (Zr0.6Hf0.4)C0.84 and (Ta0.8Hf0.2)C0.97 to (Ta0.8Hf0.2)C0.93 [21].

It is known that the maximum melting temperature is characteristic of nonstoichiometric carbides: ZrC0.8–0.9 (T = 3410–3435 °C [22]); HfC0.9(T = 3820 °C [23]); TaC0.8 (T = 4000 °C [24]). Appreciable decarburization, which occur after the annealing of alloys ZrC–HfC, TaC–ZrC, and TaC–HfC gives reason to assume that the complex carbides are characterized by high melting temperature.
Table 1. Chemical composition and unit cell parameters carbide materials.

| Alloy composition | Chemical composition, wt. % | Option cell a, Å |
|-------------------|-----------------------------|-----------------|
|                   | Bonded carbon Before annealing | After annealing | Zr | Hf | Ta | N | O | Before annealing | After annealing |
| ZrC<sub>0.88</sub> | 11.2 | 0.05 | 11.20 | 9.10 | 88.6 | – | – | 0.02 | 0.18 | 4.689 | 4.695 |
| HfC<sub>0.97</sub> | 6.1 | 0.05 | 6.00 | 5.80 | – | 93.8 | – | 0.01 | 0.09 | 4.640 | 4.639 |
| TaC<sub>0.98</sub> | 6.1 | 0.05 | 6.10 | 5.70 | – | – | 93.8 | 0.01 | 0.09 | 4.454 | 4.444 |
| ZrHfC | 10.5 | 1.80 | 8.70 | 7.50 | 43.2 | 46.0 | – | 0.23 | 0.07 | 4.663 | 4.664 |
| Zr<sub>3</sub>Hf<sub>2</sub>C | 9.9 | 0.24 | 9.66 | 7.70 | 52.0 | 37.6 | – | 0.17 | 0.33 | 4.670 | 4.669 |
| Zr<sub>4</sub>HfC | 10.0 | 0.18 | 9.82 | 9.10 | 70.6 | 19.2 | – | 0.05 | 0.15 | 4.683 | 4.684 |
| Ta<sub>2</sub>ZrC | 5.9 | 0.12 | 5.80 | 5.30 | 16.7 | – | 77.3 | 0.04 | 0.06 | 4.522 | 4.524 |
| Ta<sub>4</sub>ZrC | 6.7 | 0.05 | 6.65 | 5.30 | 8.8 | – | 84.4 | 0.03 | 0.07 | 4.495 | 4.492 |
| Ta<sub>6</sub>ZrC | 6.7 | 0.05 | 6.35 | 5.90 | 5.0 | – | 88.0 | 0.20 | 0.01 | 4.470 | 4.466 |
| Ta<sub>5</sub>HfC | 5.3 | 0.13 | 5.17 | 5.05 | – | 22.0 | 72.1 | 0.43 | 0.17 | 4.486 | 4.483 |
| Ta<sub>4</sub>HfC | 6.4 | 0.14 | 6.45 | 3.54 | – | 12.8 | 80.2 | 0.50 | 0.10 | 4.473 | 4.468 |
| Ta<sub>4</sub>HfC<sub>3</sub> | 15.4 | 0.09 | 15.3 | 10.8 | – | 11.4 | 72.7 | 0.40 | 0.10 | 4.453 | 4.458 |
| Ta<sub>4</sub>HfC | 5.6 | 0.15 | 5.45 | 5.05 | – | 11.6 | 82.2 | 0.37 | 0.23 | 4.473 | 4.472 |

X-ray phase and microstructural analyses confirmed the formation in all materials, single-phase connection (Figure 1). The porosity of samples of complex carbides does not exceed 7.0–10.0 % (Table 2). Strength of materials maximum obtained for compositions located close to equimolar ratio, however, the strength values are greatly influenced by porosity. The modulus of elasticity of materials is a function of strength and also depends on porosity (Table 2) as the concentration of carbon carbide in the complex increases its porosity and, consequently, reduced the level of mechanical characteristics (Table 2). By analogy with the nonstoichiometric compounds (ZrC<sub>0.8</sub>-0.9HfC<sub>0.9</sub>TaC<sub>0.8</sub>) having a high heat resistance, it can be assumed that the decrease of the concentration of carbon in the compounds, for example, from Ta<sub>3</sub>HfC to Ta<sub>5</sub>HfC also will increase the heat resistance of the material.
Figure 1. Microstructure of the materials Ta₄HfC₅ (a) and Ta₄HfC (b).

Table 2. Physical and mechanical properties of hot-pressed materials in systems ZrC–HfC, TaC–ZrC and TaC–HfC.

| Composition carbides | Density, g/cm³ | Porosity, % | The modulus of elasticity, GPa | Bending strength, MPa |
|----------------------|----------------|-------------|-------------------------------|----------------------|
| ZrHfC                | 8,82           | 6,8         | 358±5                         | 418±8                |
| Zr₃Hf₂C              | 8,19           | 8,1         | 410±8                         | 384±12               |
| Zr₄HfC               | 7,09           | 9,4         | 407±11                        | 346±4                |
| Ta₂ZrC               | 10,92          | 7,3         | 433±4                         | 357±17               |
| Ta₃ZrC               | 11,63          | 9,0         | 474±9                         | 346±11               |
| Ta₅ZrC               | 12,10          | 10,1        | 496±13                        | 309±6                |
| Ta₃HfC               | 12,56          | 8,8         | 418±5                         | 394±13               |
| Ta₄HfC               | 12,55          | 9,6         | 443±8                         | 381±26               |
| Ta₄HfC₅              | 12,77          | 6,6         | 459±6                         | 384±11               |
| Ta₅HfC               | 12,50          | 10,4        | 463±9                         | 342±10               |

The most promising from the point of view of heat resistance, are system NbC–HfC, TaC–NbC, in which the synthesis and analysis of physical-mechanical and high temperature properties can be used to detect the formation of single-phase complex carbides, characterized by record melting temperature (over 4000 °C).

4. Conclusion
In the work by hot pressing of the synthesized single-phase complex carbides in the systems ZrC–HfC, TaC–ZrC and TaC–HfC, studied their chemical composition and determined the lattice parameters and physico-mechanical properties. Specificity of oxidation and explained the nature of high-temperature materials, the maximum temperature of the material melting in the system Zr–C corresponds to the composition ZrC₀,8-₀,9 (T = 3410–3435 °C) in the system Hf–C the composition of HfC₀,9 (T = 3820 °C) and for the system Ta–C the maximum melting temperature is close to the composition of the material TaC₀,8 (T = 4000 °C). The most promising system TaC–HfC are complex carbides of tantalum-hafnium composition Ta₄HfC₅ and Ta₄HfC having a melting point over 4000 °C.

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