Prospective SHS composites for high-temperature applications

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Abstract In this article, a succinct review of the SHS ceramics prospective for the high-temperature applications is provided. Macrokinetic features and mechanisms of combustion and structure formation were studied for the systems Ta–Zr–C, Ta–Hf–C, Zr–Ta–B, Hf–Ta–B, Zr–B–Si–C, Ta–Si–C, Mo–Hf–Si–B, and Zr–Ta–B–Si. Materials were produced by the combination of SHS with hot pressing (HP) and spark plasma sintering (SPS), and their structure and properties were investigated.

1. Introduction
The development of advanced materials resistant against the oxidation and ablation in the flow of high-enthalpy gas containing abrasive particles is a crucial area of modern materials science. Such materials are employed for the high-speed aircraft as sharp wing edges and nose tips [1] as well as for the spacecraft as the nozzles for solid-fuel thrusters. Prospective materials and coatings for these applications include the composites based on HfB$_2$ ($T_m = 3653$ K), ZrB$_2$ ($3473$ K), TaB$_2$ ($3473$ K), NbB$_2$ ($3323$ K) which are characterized by the melting point above $3000$ K [2], high strength, fracture toughness, wear resistance and thermal shock resistance. An essential advantage of the boride-based composites is their high thermal conductivity, which ensures the enhanced heat sink from the surfaces which are in contact with the high-temperature oxidative gas flow.

Development of the efficient production technologies for ultra-high temperature ceramics (UHTCs) based on carbides HfC ($T_m = 3900$°C), TaC ($3800$°C), borides and their solid solutions is a significant problem. Solid solutions possess higher melting points as compared to simple compounds. For example, the single-phase carbide (Ta,Hf)C with 20 % HfC has the melting point of approx. $4223$ K. Moreover, the dependences of hardness, the coefficient of thermal expansion (CTE) and thermal conductivity on the composition of solid solutions are non-linear and have maxima at optimal compositions. Combination of high thermal conductivity and low CTE defines the resistance of material towards the thermal shocks.

The synthesis of single-phase compounds (Ta,Zr)C, (Ta,Hf)C, (Ta,Zr)B$_2$, (Ta,Hf)B$_2$ is another important problem. Various methods of production of complex carbides and borides are known, including the heating of the mixture of powders, co-reduction of the mixture of oxides by carbon, precipitation from solutions, microwave synthesis, sol-gel synthesis, hot pressing, etc. SHS provides unique possibilities for the production of UHTCs. Hybrid technologies SHS + HP, SHS + SPS, reactive HP and SPS demonstrated their perspectivity for the production of the dense high-temperature materials and cathodes-targets with unique structure and properties [3, 4].
2. Results and discussion

Kinetics and mechanisms of combustion and structure formation were investigated for the systems Ta–Zr–C, Ta–Hf–C, Zr–Ta–B, Hf–Ta–B, Hf–Ta–B, Zr–B–Si–C, Ta–Si–C, Mo–Hf–Si–B, Zr–Ta–B–Si [3–15, 18–21]. Mechanical activation (MA) of the reaction mixtures and optimization of the synthesis parameters play a crucial role in the production of the solid solutions (Ta,Hf)C, (Ta,Zr)C. MA SHS allows the formation of single-phase (Ta,Hf)C with the lattice parameter \( a = 0.4487 \) nm, which corresponds to the 18 at % dissolved HfC, while the HfO impurities do not exceed 1 %. Solid solution powders are outstanding raw material for the subsequent sintering of dense ceramics by HP and SPS. For example, (Ta,Hf)C ceramics has the relative density of 98%, hardness of 27 GPa, Young modulus of 484 GPa, elastic recovery of 46%.

The possibility of SHS of single-phase solid solution on the base of diborides of tantalum and zirconium (Zr,Ta)B₂ as well as diborides of hafnium and tantalum (Hf,Ta)B₂ was demonstrated [14, 18, 19]. By thermodynamic calculations and analysis of the composition and structure of the characteristic areas of the quenched combustion fronts by SEM and EDS, it was established that in the preheating zone the volatile suboxide B₂O₃ forms, chemosorbs on the metallic particles and produces needle-like borides of Ta and Zr. At temperatures above the melting point of zirconium and boron, a melt forms and wets the tantalum particles and borides formed in the preheating zone. Main reactions take place, and ZrB₂ phase precipitates from the oversaturated melt. Borides formed in the preheating zone interact with the melt, and solid solutions are formed (figure 1). On the last stage in the zones of post-combustion and structure formation, a homogenization of the solid solutions takes place. Depending on the composition of the reactive mixture, either single-phase solid solution (Zr,Ta)B₂ or two-phase composite (Zr,Ta)B₂ + TaB₂ are formed [14].

In the Hf–Ta–B system, the phase formation occurs differently. In the Hf–B binary system, at temperature 2153 K and boron content B ≤ 0.8%, contact melting due to the eutectic reaction \( \beta\text{-Hf} + HfB \rightarrow Liq \) takes place and forms a melt containing solid particles HfB + \( \beta\text{-Hf} \). At 2365 K, boron melts, and almost simultaneously the first crystallites of HfB₃ and TaB₂ precipitate. Then, melting of Hf occurs (2505 K), and the active interaction of the melt with the formation of the solid solutions based on the diborides of Ta and Hf takes place [18]. Due to the high combustion temperature and considerable thermal losses, the post-combustion zone is relatively narrow. Concentration homogenization takes place in the post-combustion zone. However, the high porosity of the synthesis products and low diffusion rates do not allow the formation of equilibrium phases to complete. A significant difference in grain composition and size is retained in the synthesis products. However, the produced powders are successfully used for the subsequent consolidation by HP and SPS. A chemical homogeneity on the grain level is achieved [19].

For the Ta–Si–C system, the sequence of chemical and structural transformations in the combustion wave was studied [12]. Thermodynamic analysis, investigation of the quenched combustion fronts and time-resolved XRD revealed the sequence of phase formation during the combustion synthesis of TaSi₂ + SiC ceramics for application in magnetron sputtering of high-temperature tribological coatings. In the post-combustion zone, a significant refinement of the microstructure takes place due to the formation of SiC crystallites (20–40 nm) within the TaC, Ta₃Si₃ and TaSi₂ grains. Since one part of the SiC and TaSi₂ grains crystallizes from the Si melt and another part forms due to the solid–state reactions.

Submicron-sized composite TaSi₂–xSiC powders (x = 10, 30, 50, and 70%) consisting of TaSi₂ and SiC grains 50–100 nm in size were fabricated by SHS. The optimal compositions and hot pressing regimes for SHS powders were determined, ensuring the production of the TaSi₂–SiC ceramics with a hierarchical structure, the relative density of 96–97%, hardness of ~19 GPa, and fracture toughness of 6.5–6.7 MPa m¹/₂. Double-layered composite targets 120 mm in diameter, with the TaSi₂–xSiC working layer (x = 10 and 30%) and molybdenum sublayer, were produced by hot pressing and used for coatings deposition. Si–Ta–C–(N) nanocomposite coatings were deposited using the magnetron sputtering. Structure of as-deposited coatings consisted of fcc Ta(Si,C,N) (the TaSi₂–30%SiC target) or TaSi₂ (the TaSi₂–10%SiC target) nanocrystallites less than 3 nm in size embedded in an amorphous matrix. The coatings were characterized by high thermal stability and oxidation resistance at temperatures below
800°C. A detailed SEM analysis of the coating wear tracks showed that the tribolayer formed at room temperature is dense, although the wear mode remains abrasive. At 600°C, the tribolayer on the wear track bottom is not continuous; furthermore, individual microfibers are appeared. The wear track profile indicates that the abrasive wear still remains the main wear mode. More microfibers, including small ones, are formed at 800°C. These microfibers cover the wear track surface more densely. This leads to a combination of low coefficient of friction and high wear resistance. The fine structure of the microfibers was additionally studied by TEM. The microfibers with 1 µm thick have a smooth surface that is non-uniformly covered with particles of wear products 30–100 nm in size. EDX analysis showed that fibers contain a large amount of oxygen, as well as tantalum and silicon. This indicates that they originate from a thin oxide layer, which was formed on the surface during high-temperature tribological tests. A detailed analysis of fiber microstructure by HRTEM demonstrated that the amorphous matrix (most likely SiOx) contains nanoparticles 2–4 nm in size. The interplanar distances (2.2 and 2.5 Å) and the interplanar angle (~ 55°) indicate that those are nanoparticles of tantalum oxide TaO with fcc structure. Hence, it is fair to assume that the coating surface undergoes oxidation due to the transformation of Ta(C,N) nanocrystallites, with their size remaining unchanged.

The coating matrix is saturated with oxygen and retains its amorphous structure. The friction coefficient of the coatings decreases with temperature from 0.38 (25°C) to 0.28 (600°C) and 0.23 (800°C), while their wear resistance increased. A thin (~ 100 nm) oxide layer and TaSi, O microfibers played a key role in enhanced tribological behavior, reducing the coefficient of friction and wear due to rolling friction. Disilicides MoSi2, ZrSi2, and TaSi2 are widely used as the alloying addition to the boride
and carbide ceramics to increase the ceramic’s oxidation resistance. For example, MoSi$_2$ has an outstanding oxidation resistance and retains its properties for 2000 h at 1923 K. During the oxidation of ZrSi$_2$, glassy ZrSiO$_4$/SiO$_2$ forms, increasing the high-temperature oxidation resistance and providing the ability to self-heal the forming defects. Ceramics with the 1–2 µm boride grains and 2–4 µm silicide grains were produced by elemental SHS. Within the MoSi$_2$ grains, 50–300-nm eutectic colonies Me$^{IV}$Si$_2$–MoSi$_2$ are present.

Powders produced by the milling of combustion products were used for the fabrication of the dense samples. Physical-mechanical properties of the samples are presented in Table 1. Boride compositions possess high hardness and elastic modulus, significantly surpassing the known analogous [16, 17] and reaching the level of super-hard materials. Such high values were explained by the low content of the oxides (below 1%) and high internal stresses.

| Composition | Sintering conditions | Relative density, % | Hardness, GPa | Elastic modulus, GPa |
|-------------|----------------------|---------------------|---------------|---------------------|
| (Ta,Zr)C    | SHS + HP             | 96                  | 32            | 520                 |
| (Ta,Zr)C    | SHS + SPS            | 98                  | 36            | 536                 |
| (Ta,Hf)C    | SHS + HP             | 96                  | 28            | 423                 |
| (Ta,Hf)C    | SHS + SPS            | 99                  | 32            | 484                 |
| 70%TaSi$_2$+30%SiC | SHS + HP | 97                  | 19            | 340–370             |
| (Zr,Ta)B$_2$ | SHS + HP             | 97                  | 70            | 594–619             |
| 80%(Zr,Ta)B$_2$+20%TaB$_2$ | SHS + HP | 96                  | 74            | 647–672             |
| (Hf,Ta)B$_2$ | SHS+SPS              | 98                  | 62            | 570–597             |
| 80%(Hf,Ta)B$_2$+20%TaB$_2$ | SHS+SPS | 98                  | 70            | 587–628             |

Consolidated UHTCs underwent the plasma jet tests and demonstrated the 15–20% reduction of the linear erosion rate in comparison with the commercial SiC-coated carbon-carbon composites. UHTCs on the base of (Ta,Zr)B$_2$, (Ta,Hf)B$_2$ were characterized by the enthalpy of decomposition 390 kJ/g, which is an order of magnitude higher as compared to the analogous carbides and boride-silicide composites. Solid solutions (Ta,Hf)C, (Ta,Zr),C, (Hf,Ta)B$_2$ as well as ceramics (Zr,Ta)B$_2$ + 35% TaSi$_2$ and ZrB$_2$ + ZrSi$_2$ were characterized by the best high-temperature oxidation resistance.

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