

I.L. Shabalin¹, M.V. Luchka², L.I. Shabalin³

Vacuum SHS in systems with group IV transition metals for production of ceramic compositions

¹*Institute for Materials Research, The University of Salford, Greater Manchester, M5 4WT, UK
E-mail: I.Shabalin@salford.ac.uk*

²*Francevich Institute for Problem of Materials Science NAS Ukraine, Kyiv, 03142, Ukraine*

³*Russian State Professional & Pedagogical University, Yekaterinburg, 620012, Russia*

The products of vacuum version of self-propagating high-temperature synthesis (SHS) in the systems of group 4 transition metals (titanium, zirconium, hafnium) with non-metals (carbon, boron, silicon) were explored by means of chemical, densitometric, microscopic and XRD analyses. The consideration of results for SHS with more active carbon component confirmed that the metal carbidization reaction controls the SHS processing in a whole. The appearance of molten quasi-eutectic alloy induces reactions described in details by the series of equations, which proposed in the similar studies firstly. The detail analysis of SHS processing in the ternary Me-X₁-X₂ (Me = Ti, Zr; X₁, X₂ = C, B, Si) systems allows to spread the Korchagin-Aleksandrov-Gusenko mechanism for the combustion synthesis in those systems. Being more effective and accessible than other versions the vacuum SHS can provide the fabrication of the ceramic-ceramic composite precursors based on the oxygen-free refractory compounds of group 4 transition metals in the wide range of component contents.

Keywords: SHS; Milling; Borides; Carbides; Silicides.

Стаття постуила до редакції 21.06.2006; прийнята до друку 10.10.2006.

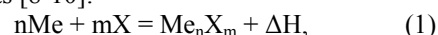
Introduction

Due to their superior physical and chemical properties ceramic composites based on the systems of group 4 transition metals with carbon [1-2], boron [3] and silicon [4-5] are the promising materials for high-temperature applications, e.g. as thermally stressed parts of rocket engines, elements of thermal protection for re-entry flying apparatus, diaphragms for casting and wear-resistant parts of metallurgical devices, highly loaded brake-shoes in automotive engineering, performance cutting tools, abrasives and others.

One of many significant achievements of Russian military applied science in the field of high temperatures is the discovery of so-called self-propagating high-temperature synthesis (SHS) [6-8] by researchers of the scientific institution, which was headed by Nobel Laureate Semenov, while they were exploring solid rocket propellants with some metal additives. This event seems to be in the general tradition of Russian classical school of Chemistry, though most specialists cannot imagine that really the discovery of thermite reaction was made by the Russian chemist Beketov more than 30 years before Goldschmidt got his patent for this processing in 1895.

SHS has proved to be an efficient and energy saving method for obtaining matters in some high melting points

systems of transition metals with non-metals. It is based on the great exothermic heat effect (ΔH) of the reactions between elements [8-10]:



where Me = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and etc.,

X = C, B, Si, S and etc.

which is connected with great values of the enthalpies of formations for the products of these reactions: carbides, borides, silicides and etc. (Table 1).

The similar reactions relate to those of solid flame phenomenon or gasless combustion [10-12], as they are passing in the narrow layer called the combustion zone, which due to heat transfer of reagents, travels through the initial mixture by a wave spreading mechanism converting it to the combustion products after a local initiation (ignition) of reaction in non-heated mixtures. During SHS processing extremely high temperatures of heating can be reached, so the necessary condition for the realisation of SHS is the certain thermal stability of products. Some calculated characteristics of SHS processing are also submitted in Table 1. Theoretical foundations of SHS are considered in numerous works by Merzhanov and his co-workers from the 60s up to date, the most important of them are reviewed in some recent papers [6-8]. The valuable contribution to the development of SHS was given also by Munir [9] and Pampuch [14] with their co-operators. However, for eventual industrial implementation of SHS processing

Table 1

Thermodynamic properties and characteristics of SHS processing for refractory compounds of group 4 transition metals [6,10-13]

| Class | Com- pound | Thermodynamic properties | | Calculated characteristics of SHS-processing | | |
|----------|---------------------------------|--------------------------|---|---|---|--|
| | | Melting point (K) | Enthalpy of formation, - $\Delta H_{298}(\text{kJ mol}^{-1})$ | Adiabatic combustion temperature (K) | Contents of liquid in combustion products (wt %) | Specific enthalpy of reaction(kJ g^{-1}) |
| Carbide | TiC | 3210 | 185 | 3210 | 33 | 3.08 |
| | ZrC | 3690 | 201 | 3400 | – | 1.95 |
| | HfC | 3900 | 230 | 3900 | 26 | 1.21 |
| Boride | TiB | 2500 | 159 | 2500 | – | 2.71 |
| | TiB ₂ | 3190 | 280 | 3190 | 27 | 4.03 |
| | ZrB ₂ | 3310 | 306 | 3310 | 20 | 2.71 |
| Silicide | Ti ₃ Si ₃ | 2390 | 581 | 2400 | – | 1.80 |
| | TiSi | 2190 | 133 | 1920 | – | 1.75 |
| | TiSi ₂ | 1770 | 135 | 1800* | – | 1.31 |
| | Zr ₂ Si | 2490 | 209 | 1940 | – | 1.00 |
| | Zr ₃ Si ₃ | 2520 | 578 | 2800* | – | 1.13 |
| | ZrSi | 2420 | 155 | 2700* | – | 1.24 |
| | ZrSi ₂ | 1950 | 159 | 2100* | – | 1.03 |

Note: *Without taking into account the latent heat of melting.

Table 2

Characteristics of starting materials for SHS processing of ceramic compositions based on the refractory compounds of group IV transition metals

| Material | Manufacturer | Powder type | Contents of general component (wt %) | Contents of essential impurities, (wt %) | Particle size (μm) |
|------------------|-----------------------------------|---------------------------|---|--|---------------------------------------|
| Titanium | BTMK, Berezniki, Russia | TU.48.05.30.71 | ≥ 97 | $\text{O} \leq 3.0$ | ≤ 80 |
| Zirconium | UMZ, Glazov, Russia | Electrolytic TU.95.295.74 | ≥ 99 | $\text{O} \leq 0.2$ $\text{N} \leq 0.03$ $\text{C} \leq 0.02$ $\text{Fe} \leq 0.02$ | ≤ 100 |
| Hafnium | SGMK, Severodonetsk, Ukraine | GFM-1TsMTU.05.179.69 | ≥ 98.5 | $\text{Zr} \leq 1.0$ $\text{Fe} \leq 0.2$ $\text{Ca} \leq 0.15$ $\text{Si} \leq 0.05$ | ≤ 20 |
| Carbon black* | ZGS, Omsk, Russia | TG-10 | ≥ 99 | $\text{O} \leq 0.08$ $\text{H} \leq 0.05$ m.r.* ² ≤ 0.05 | $0.5 \div 5.0$ |
| Boron | UNIKhIM, Yekaterinburg, Russia | Fine-crystal | ≥ 97.5 | $\text{C} \leq 0.25$ $\text{Mg} \leq 0.15$ $\text{Si} \leq 0.1$ $\text{Fe} \leq 0.1$ $\text{Al} \leq 0.05$ | ≤ 60 |
| Silicon | Ukraine | KR-1GOST.2169.79 | ≥ 98 | $\text{Fe} \leq 0.7$ $\text{Al} \leq 0.7$ $\text{Ca} \leq 0.7$ | ≤ 40 |

Notes: *Specific surface – $10 \text{ m}^2 \text{ g}^{-1}$.

*²Mineral remains.

and SHS materials in production of ceramics several necessary experimental data are absent or not available.

The aim of this work is to explore SHS potential with common commercial reagents widely varying ratio of them and using the simplest facilities with vacuum method as one of the most effective and accessible version of SHS [15-16], to analyse the quality of SHS products in the case of maximally efficient application of combustion synthesis⁶ as a production method in ceramic processing. It seems also to be very important to determine areas of reagents contents [16], where SHS could be realized, for the mixtures of titanium, zirconium and hafnium commercial powders without application of any additional special treatments of them.

I. Experimental procedure

1.1. Starting materials and sample preparation.

The following starting materials in this work have been used: more accessible pure metal common commercial powders, the readily graphitizing carbon black with the highest activity recommended in previous studies [17], fine-crystal boron and preliminary milled pure silicon, whose characters are submitted in Table 2. The initial mixtures were prepared with content accounting of general components in starting materials. The reagents were thoroughly mixed in a rolling ball mill and axially pressed in a 35 mm diameter stainless steel die without any binder. A pressure of 60-90 MPa was applied to obtain 15-25 mm height cylindrical pellets with an apparent density corresponding to 50-60 % of the theoretical value. The SHS reaction was carried out in a 5-dm³ volume hermetic steel combustion chamber (reactor) cooled by flowing water. The complete scheme of the technological device, including the reactor is shown in Figure 1. Before reaction processing the chamber was evacuated down to 1-5 Pa. The local

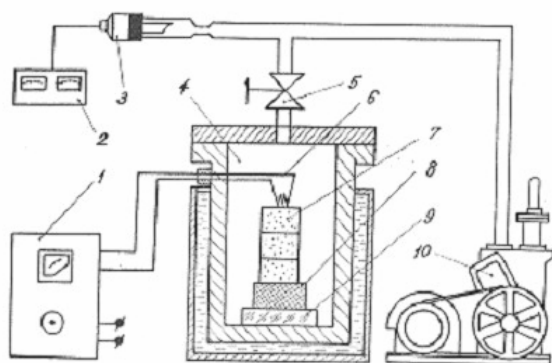


Fig. 1. Schematic diagram of technological device for vacuum SHS processing: 1 – compensator; 2 – vacuum manometer; 3 – thermocouple detector of pressure; 4 – hermetic steel reactor (combustion chamber) cooled by flowing water; 5 – vacuum valve; 6 – tungsten (or molybdenum) wire micro-heater; 7 – testing pressed pellets of reaction mixture; 8 – graphite support; 9 – ceramic separator; 10 – vacuum mechanical pump.

initiation (ignition) of SHS reaction in testing samples was accomplished by a 0.5 mm diameter tungsten or molybdenum wire micro-heater with an 50 Hz alternate current from 5 to 30 A, which was directly increased by a compensator up to the moment of ignition. High temperatures of SHS cause the intensive desorption of gases from the surface of starting materials, so pressure inside the chamber was increasing to 0.1 MPa and sometimes higher. This process allowed using a thermocouple vacuum detector as an indicator of the ignition of the initial mixture. After the combustion burned samples were cooled down inside the chamber to room temperature. The complete technological cycle of SHS processing, including operations of loading, evacuation of reactor, initiation of reaction, cooling down and recovering, lasted 30-40 min. and the most continual procedure of the cycle had to be cooling, which usually took about 70-80 % of all time.

1.2. Materials characterisation and testing. A general view of the SHS products obtained by the method, which was described above, after recovering from the combustion chamber is submitted in the photos (Figure 2). The products were explored by the means of

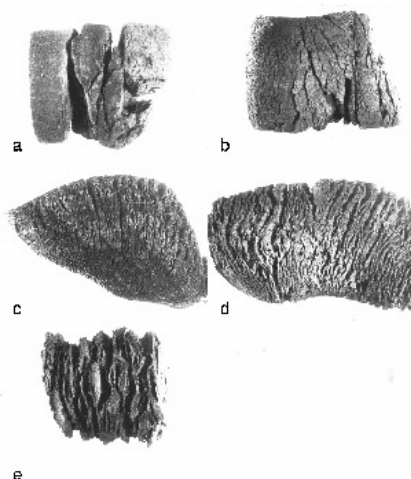


Fig. 2. General view of the SHS products with different molar ratios in initial mixtures: a – Ti + 0.9C; b – Ti + 1.1C; c – Zr + 0.7C; d – Zr + 0.9C; e – 0.8Zr + 0.2Ti + C.

chemical, densitometric, microscopic and XRD analyses. Chemical determination of carbon contents was carried out by coulombmetric method using CuO-Pb flux on the special analyzer, and boron contents was determined by direct volumetric method with alkali. Composition densities were measured by pycnometric method with methylbenzene (toluene) as a working liquid. The contents of chemical phases in SHS products, their structures and lattice parameters were qualified by an X-ray diffractometer DRON with Fe, Cu and Mo filtered radiation. Lattice parameters were calculated with application of extrapolation function $\cos^2\theta$ and special data processing. For testing the suitability of obtained compositions to conventional ceramic processing they were treated in lined by plates of WC-Co alloy rolling

mill with the same material milling balls in ethanol (40-50 % of mill volume). The weight ratios of "composition: balls" were 1:10 for titanium and 1:8 for zirconium and hafnium containing compositions. Sedimentation analyses were carried out by microscopic methods with immersion liquid ($n = 1.78$). Chromatographic method of thermal desorption of argon in dynamic conditions was used for determination of the specific surface of powders. Contamination of powders by tungsten and iron during the treatment was analyzed by colorimetric methods of chemical analysis.

II. Results and discussion

2.1. SHS in the Me-X systems. The phase analysis of SHS products obtained in the Ti-C, Zr-C, Hf-C, Ti-B, Zr-B and Hf-B systems (Table 3) confirms the practical possibility of manufacturing for group 4 transition metal refractory compounds in pure form. The X-ray spectra of the SHS products allow to reveal the presence of well-crystallized phases of Ti, Zr and Hf monocarbides and diborides. The insignificant presence of zirconium dodecaboride ZrB_{12} traces in the mass of zirconium diboride ZrB_2 is not an essential exception, because ZrB_{12} disappears completely after 0.5 h soaking at 1850 K in vacuum. It serves as a witness of the fact that the synthesis in this system is processing in the wide range of temperatures, including 1980-2520 K, which is the area of ZrB_{12} existence. The group 4 transition metal carbides have extremely wide ranges of homogeneity (stoichiometry) [1,13], so it was of great interest to relate the carbon content in initial mixtures to the properties of the SHS products and estimate the completeness of carbide phases and the manufacturing potential of those phases with different grade of stoichiometry. The wave spreading character and high temperatures of SHS reactions cause the partial sublimation and ejection of some reagents. Due to the gas transport reactions with residual oxygen in a combustion chamber certain amounts of carbon and boron could be removed from the reaction amplitude. The Elyutin-Kostikov effect [18] of intense carbon vaporization from high-temperature molten alloys in the temperature range close to their eutectic temperatures also contributes to the process of mass transfer during SHS, because the similar conditions are realised in reaction mixtures. Moreover, due to gases desorption from the surface of powder, separated particles of it are ejected from overheated layer. These particles represent themselves predominantly as fractions of carbon and/or boron, which are smaller in size and lower in density compared with particles of powdered metals. The same phenomena were also observed by Barzykin and Stovbun [12] for systems with carbon and Radev and Marinov [19] while manufacturing TiB_2 and ZrB_2 by SHS. Carbon loss during SHS processing holds a very complicated character, because of both physico-chemical and physico-mechanical nature. The dependencies of carbon loss on its content in initial mixtures (Figure 3) are described by curves with a maximum, which is likely corresponding to the maximal heat effect per a unit of mixture volume, but some

another factors, e.g. mechanical strength characters of initial mixture pellets, seemed to be also very important, could displace the position of maximum or decrease the size of it.

SHS reactions develop very high rate, which can reach to 20 cm s^{-1} , so the reactions last for a short period of time [8]. Contreras et al. [20] showed by the means of time-resolved X-ray diffraction (TRXRD) analysis that titanium content in reaction mixture $2Ti + C + 2B$ was reducing from the initial level to 0 during the period less than 0.3 s. Such transience of synthesis in some cases cannot entirely provide the accomplishment of chemical reactions. This attribute of SHS certainly influences the contents of its products. The smallest amounts of free (not combined into carbide) carbon were revealed in the SHS products with initial ratio of C/Me equalled just to 0.8. While the total carbon content in initial mixtures increases, the amount of free carbon in products accumulates more rapidly than rise of carbon amount reacted with metal (Figure 3). Only due to carbon excess

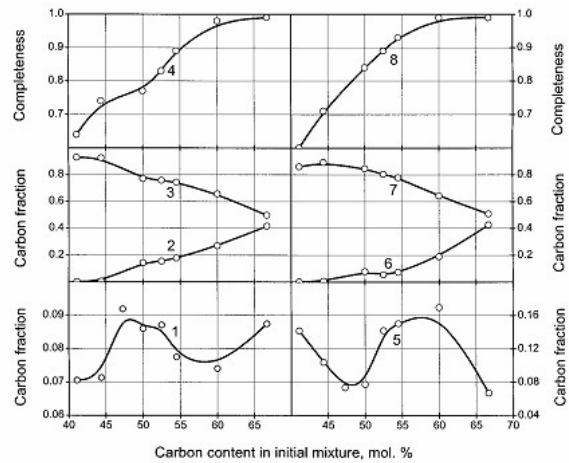


Fig. 3. Behaviour of carbon during vacuum SHS processing in Ti – C (1-4) and Zr – C (5-8) systems: loss of carbon (1, 5); fraction of free carbon (2, 6); fraction of reacted carbon (3, 7); completeness of metal carbidization reaction (4, 8).

reached at 100 % it has become possible to obtain stoichiometric monocarbides with carbon content corresponding to the upper limit of the range of homogeneity [13]. Experimental data of the present work confirm the possibility of manufacturing by SHS for Ti and Zr monocarbides with different C/Me ratio along the whole range of their homogeneity. It is necessary to note that the preparation of off-stoichiometric carbide phases with lowest ratios of C/Me by other methods is rather difficult. The carbothermic reduction of group 4 transition metal oxides (furnace synthesis) bring in this case [21] only to the formation of oxycarbide phases MeC_xO_y with lower values for x , so SHS is practically the only one which can provide the preparation of carbides with $C/Me = 0.5$ or less [22]. The higher values of lattice parameters for obtained Ti, Zr and Hf monocarbides also testify the high rate of purification, which is observed during SHS processing [23] and especially, when the vacuum version is used. The

Table 3

Physico-chemical characteristics of SHS products in Me-X systems

| System | Initial mixture in molar ratio | Non-metal content (wt %) | | | Composition of SHS-products* | Characteristics of synthesized phases | | |
|--------|--------------------------------|--------------------------|-----------------|----------|---|---------------------------------------|-------------------------|-----------------------------------|
| | | in initial mixture | in SHS-products | | | X / Me | Lattice parameters (nm) | XRD density (g cm ⁻³) |
| | | | total | combined | | | | |
| Ti-C | Ti + 0.7C | 14.9 | 14.0 | 14.0 | TiC _{1-x} | 0.64 | 0.4320 | - |
| | Ti + 0.8C | 16.7 | 15.7 | 15.65 | « | 0.74 | 0.4324 | 4.66 |
| | Ti + 0.9C | 18.4 | 17.0 | - | « | - | 0.4327 | - |
| | Ti + C | 20.0 | 18.6 | 15.7 | « | 0.77 | 0.4328 | 4.68 |
| | Ti + 1.1C | 21.6 | 20.1 | 16.7 | « | 0.83 | 0.4328 | 4.74 |
| | Ti + 1.2C | 23.1 | 21.7 | 17.5 | « | 0.89 | 0.4328 | 4.80 |
| | Ti + 1.5C | 27.3 | 25.8 | 18.3 | TiC _{1-x} , C | 0.98 | 0.4327 | 4.89 |
| | Ti + 2.0C | 33.4 | 31.4 | 17.1 | TiC _{1-x} , C | 0.99 | 0.4326 | 4.90 |
| Zr-C | Zr + 0.7C | 8.4 | 7.3 | 7.3 | ZrC _{1-x} | 0.60 | 0.4690 | - |
| | Zr + 0.8C | 9.5 | 8.6 | 8.55 | « | 0.71 | 0.4693 | 6.46 |
| | Zr + 0.9C | 10.6 | 9.9 | - | « | - | 0.4695 | - |
| | Zr + C | 11.6 | 10.8 | 9.9 | « | 0.84 | 0.4695 | 6.50 |
| | Zr + 1.1C | 12.7 | 11.1 | 10.4 | « | 0.89 | 0.4695 | 6.56 |
| | Zr + 1.2C | 13.6 | 11.8 | 10.8 | « | 0.93 | 0.4695 | 6.57 |
| | Zr + 1.5C | 16.5 | 14.1 | 10.9 | ZrC _{1-x} , C | 0.99 | 0.4695 | 6.62 |
| | Zr + 2.0C | 20.4 | 19.3 | 10.5 | ZrC _{1-x} , C | 0.99 | 0.4694 | 6.62 |
| Hf-C | Hf + C | 6.3 | 6.0 | 5.7 | HfC _{1-x} | 0.90 | 0.4642 | 12.52 |
| Ti-B | Ti + 2.1B | 32.1 | - | 31.7 | TiB _{2+x} | 2.06 | a = 0.3026b = 0.3223 | 4.52 |
| Zr-B | Zr + 2.2B | 20.7 | - | 18.7 | ZrB _{2-x} , traces ZrB ₁₂ | 1.94 | a = 0.3172b = 0.3525 | 6.10 |
| Hf-B | Hf + 2.2B | 11.7 | - | 10.8 | HfB ₂ | 2.00 | a = 0.3144b = 0.3470 | 11.19 |

Note: *Results of XRD analysis.

Table 4

Physico-chemical characteristics of SHS products in Ti-Zr-X systems

| System | Initial mixture in molar ratio | Total non-metal content (wt %) | | Composition of SHS-products* | Characteristics of synthesized phases | | |
|---------|--------------------------------|--------------------------------|-----------------|---|---------------------------------------|--------|---|
| | | in initial mixture | in SHS-products | | Lattice parameters | | Density (g cm ⁻³)* ² |
| | | | | | a (nm) | b (nm) | |
| Ti-Zr-C | 0.95Ti + 0.05Zr + C | 19.3 | 18.0 | (Ti, Zr)C _{1-x} | 0.4331 | - | 4.90 |
| | 0.6Ti + 0.4Zr + C | 15.5 | 14.4 | « | 0.4497 | - | 5.61 |
| | 0.5Ti + 0.5Zr + C | 14.7 | 13.6 | « | 0.4605 | - | 5.73 |
| | 0.2Ti + 0.8Zr + C | 12.7 | 11.7 | « | 0.4682 | - | 6.33 |
| Ti-Zr-B | 0.6Ti + 0.4Zr + 2B | 24.9 | 24.7 | (Ti, Zr)B _{2+x} | - | - | 5.21 |
| | 0.3Ti + 0.7Zr + 2B | 21.6 | 21.4 | « | - | - | 5.62 |
| | 0.1Ti + 0.9Zr + 2B | 19.9 | 19.8 | « | 0.3168 | 0.3529 | 5.98 |
| | 0.6Ti + 0.4Zr + 2B | 19.5 | 19.5 | (Ti, Zr)B _{2+x} , traces ZrB ₁₂ | 0.3170 | 0.3529 | 6.00 |

Notes: *Results of XRD analysis.

 *²Results obtained by pycnometric method.

contamination of carbides by nitrogen and oxygen with the formation of complicated oxycarbonitride phases $\text{MeC}_x\text{O}_y\text{N}_z$ causes the decrease of lattice parameters [13], e.g. Vecchio et al. [24] give for SHS dynamically compacted $\text{TiC}_{0.9}$ value of $a = 0.4310$ nm and for hot-pressed stoichiometric TiC $a = 0.4320$ nm, that is essentially lower than $0.4326\text{--}0.4328$ nm for $\text{TiC}_{0.89}\text{--TiC}_{0.99}$ prepared in the present work.

The attempts to initiate any SHS reactions in the mixtures of group 4 transition metals and powdered silicon were carrying out with the same metal powders and by the same method that was used in the Me-C and Me-B systems. But all of those attempts failed, mostly due to the lower values of specific enthalpy of reactions with silicon, thus it has been found out to manufacture silicides of Ti, Zr and Hf without preliminary heating in those conditions is impossible. The similar results for the Ti-Si blends were obtained in the study by Pampuch et al. [25], though it is well-known that silicides could be prepared by SHS, but applying different technological finesses [26-27].

2.2. SHS in the Ti-Zr-X systems. One of the main advantages of SHS processing is the certain potential to obtain complicated compositions, including mixed phases, which are forming due to unlimited or upper mutual dissolubility of isostructural refractory compounds¹. In technological practice this advantage can be realized by carrying out a combustion process for mixtures of several chemical elements or compounds. Submitted in Table 4 the results of phase analysis for the SHS products and properties of synthesized phases in the Ti-Zr-C and Ti-Zr-B systems completely prove the potential of SHS processing to prepare mixed monocarbides and diborides in those systems. The character of gasless combustion in mixtures with two or more different metals differs from others, so even external appearance of SHS products in this case is dissimilar compared with those for the binary systems. However, the diffusion difficulties during SHS connected with high rate of chemical conversion do not allow obtaining mixed carbides or borides with the highest grade of uniformity. XRD study of synthesized mixed refractory compounds showed that their XRD patterns are characterized by the completed confluence of diffraction peaks of initial single phases, including (111), (200), (220) – for monocarbides and (001), (100), (101) – for diborides. At the same time these peaks have got the reduced intensities and observable widening at half-height compared with the same peaks, which were explored in the materials soaking at high temperatures for a long period of time. Nevertheless, the SHS manufactured mixed carbides and borides possess well-crystallized structures that are confirmed by calculated lattice parameters for the obtained phases, which agree quite well with the accredited data of earlier research [28-29]. In continuous series of the $\text{TiC}_{1-x}\text{--ZrC}_{1-x}$ solid solutions obtained in present work, it was confirmed small positive deviation of the values of lattice parameters from Vegard's law that was earlier determined for the samples of mixed carbides, which were homogenized by hot-pressing at high temperatures

[30]. The quenching temperature, which is realised during SHS processing in the Ti-Zr-C system, exceed 2300 K, as this value corresponds to the existence of the monophasic $\text{TiC}_{1-x}\text{--ZrC}_{1-x}$ solid solution [28]. XRD study also has shown that homogenisation of borides solid solutions obtained by SHS realize deeper than the same processes in carbides, obviously because of higher specific enthalpy of reactions in boron containing mixtures. These particularities of the Me-B systems provide higher temperatures of heating in metal-boron powdered mixtures while SHS processing and, furthermore, this effect is amplifying due to lower melting points and higher diffusion mobility of atoms, which are inherent to metal borides.

2.3. SHS in the Me- X_1 - X_2 systems. The application of SHS in complicated, such as Me- X_1 - X_2 , systems for ceramic production is very attractive for several reasons. First of all it is an effective method to modify ceramic matrix by necessary additives and inclusions, so SHS products can be excellent precursors in ceramic-metal or ceramic-ceramic composite materials technology processing. Also, during the SHS in those systems it becomes possible to synthesize some different compounds, which could not be produced by the direct SHS method, because of the lower heat effects. So such compounds are forming through additional heat transfer from the most exothermic reaction in the mixture, the so called chemical oven⁸. The accompanying syntheses of modifying phases allow realising the development of advanced ceramic compositions with required microstructure. The exploration of SHS in the Me- X_1 - X_2 systems gives also the possibility to estimate the influence non-metals contamination have on the properties of SHS produced compositions.

2.3.1. SHS in the Ti-C-B system. The contents area of SHS realisation in the Ti-C-B system discovered in the present work is shown in Figure 4a. This area combines the complex of component ratios, where SHS could be

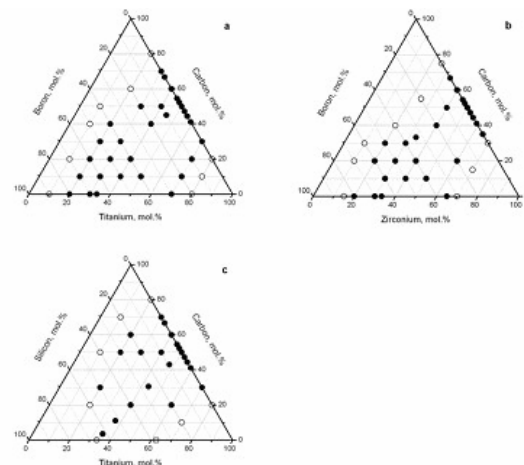
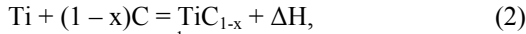


Fig. 4. Contents areas of vacuum SHS realization in Me- X_1 - X_2 systems: a – Ti-C-B; b – Zr-C-B; c – Ti-C-Si (● – combustion; ○ – no combustion; □ – unstable combustion).

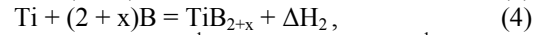
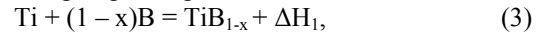
realised without additional heating of initial mixtures and

other technological finesses. Monocarbide, monoboride, diboride of titanium and boron carbide are present in SHS products dependent on the ratio of components (Table 5). Basically, all SHS prepared compositions are characterized by a high rate of interaction between components, though the traces of titanium metal were revealed in some of them. It is difficult sometimes to estimate the grade of equilibrium for obtained SHS products, because of the approximate character of phase areas in the published equilibrium state diagram of the Ti-C-B system [31] as well as values for the quenching temperatures during SHS processing. The conclusion about reactions, which can control the mechanism of SHS in the Ti-C-B system, derived by Shcherbakov and Pityulin [32] and directly confirmed later by Contreras et al. [20] also relates to the present work. Everywhere application of more active and fine-grained carbon with higher value of specific surface relatively to that of boron bring while SHS processing with the Ti-C-B mixtures to the situation, in which the carbidization reaction of titanium:

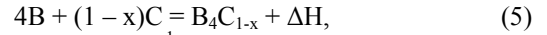


where $\Delta\text{H} = 185 \text{ kJ mol}^{-1}$ for $x \sim 0$ at standard conditions becomes the prioritized process. It happens in spite of lower enthalpy of formation for Ti monocarbide compared with those of Ti diboride, because of more developed Me-C contact surface area in comparison with the same for Me-B, which is inherent for the Ti-C-B mixtures with more active carbon, such as, e.g. carbon black TG-10 (99.5 %) with specific surface $S_s \geq 10 \text{ m}^2 \text{ g}^{-1}$ used in this work or graphite powder Sofacel (99.6 %, $S_s = 27 \text{ m}^2 \text{ g}^{-1}$) used by Contreras et al. [20]. That is why Ti monocarbide phase is present practically in all compositions prepared by SHS in the Ti-C-B system, include actually those, where TiC_{1-x} is not a stable component of the SHS products, but only intermediate phase that remained there due to the insufficiency of treating time, i.e. low heat effect or high thermal loss that

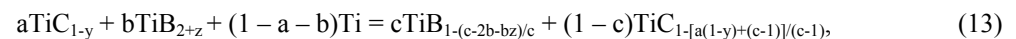
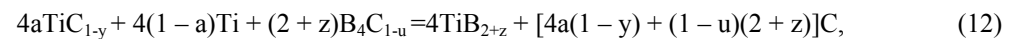
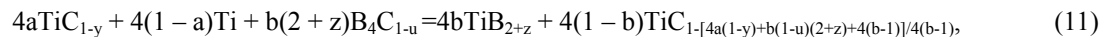
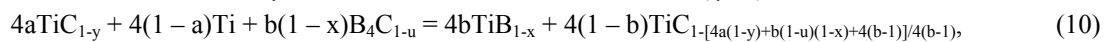
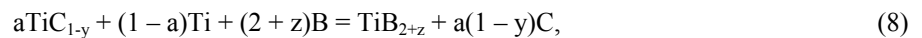
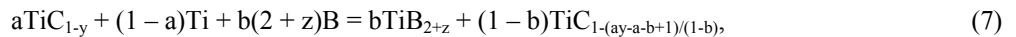
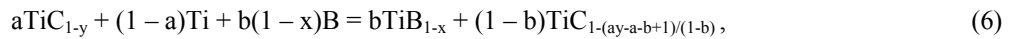
cannot provide necessary conditions for afterburning processes [6] during cooling down of the products. The transient intermediate phase of semicarbide $\text{Ti}_2\text{C}_{1+x}$ discovered by Quinn and Kohlstedt [33] in orthorhombic modification and confirmed later by Banerji et al. [34], was not revealed in the SHS products in this work, though it is likely that namely the Ti_2C (421) peak with $d = 0.2310\text{-}0.233 \text{ nm}$ could not be identified in the earliest stage of $2\text{Ti} + \text{C} + 2\text{B}$ SHS reaction while Contreras et al. [20] were studying the process by the TRXRD. The contact interaction between Ti and generated TiC_{1-x} jointly with essential overheating of reactants bring to the formation of molten matter with the temperature much more than the eutectic temperature in Ti - TiC_{1-x} quasi-binary system (1920 K), so the absence of $\text{Ti}_2\text{C}_{1+x}$ is quite explainable in connection with the fact that the semicarbide phase, in opinion of some researchers, e.g. Wanjara et al. [35], appears to remain stable only up to temperatures of about 1773 K. After the appearance of molten Ti alloy all consequent transformations of the mixture are controlled by the migration and interaction of this matter within the reaction layer, which is moving along the mixture. Although the processes of formation for Ti borides and B carbide are very different, and titanium boridization reactions are going with great heat release:



where $\Delta\text{H}_1 = 159 \text{ kJ mol}^{-1}$, $\Delta\text{H}_2 = 280 \text{ kJ mol}^{-1}$ (both for $x \sim 0$ at standard conditions) at the same time, when the formation of boron carbide:



where $\Delta\text{H} = 72 \text{ kJ mol}^{-1}$ for $x \sim 0$ at standard conditions needs to get additional heat from more exothermic SHS reactions coupled with it, both of these processes are passing in molten medium while afterburning mainly by means of following reactions:



as parallel and consequent stages of dissolution-precipitation (recrystallization) mechanism.

The equations of chemical reactions (6)-(13) could be used for subsequent computing simulation of processing in the Ti-C-B molten alloy during SHS with taking into account reasonable values of the coefficients accordingly the ranges of homogeneity for the phases of variable composition. Thus, contents of SHS products depend on the amount of liquid phase, which is

controlling the synthesis in the mixture as a whole, so the decrease of total amount of titanium and carbon in the initial mixture certainly brings to the reduction of the amount of liquid phase that is slowing the synthesis of final products. In this case the initial reagents and intermediate phases contents in SHS products increase essentially. On the basis of this conclusion it has become possible to explain the presence of a small amount of not reacted metal titanium in the SHS products, which were

Table 5

Compositions of SHS products in Ti-C-B system

| Initial mixture in molar ratio* | Heat effect* ² , $\Delta H(\text{kJ mol}^{-1})$ | Composition* ³ | J[TiC _{1-x} (200)]: :J[TiB _{2+x} (101)] | J[B ₄ C _{1-x} (021)]: :J[TiB _{2+x} (101)] | J[r-TiB(201)]: :J[TiB _{2+x} (101)] |
|--|---|---|--|---|--|
| 2Ti + C + 7B (2TiB ₂ + 0.75B ₄ C + 0.25C) | 205 | TiB _{2+x} , B ₄ C _{1-x} , traces α -Ti* ⁴ | - | 1 : 11 | - |
| 2Ti + 2C + 6B (2TiB ₂ + 0.5B ₄ C + 1.5C) | 119 | TiB _{2+x} , TiC _{1-x} , B ₄ C _{1-x} , traces α -Ti | 1 : 4.5 | 1 : 5.5 | - |
| 2Ti + 3C + 5B (2TiB ₂ + 0.25B ₄ C + 2.75C) | 116 | TiB _{2+x} , TiC _{1-x} , B ₄ C _{1-x} , traces α -Ti | 1 : 3.1 | 1 : 11 | - |
| 2Ti + 4C + 4B (TiB ₂ + 2C) | 93 | TiC _{1-x} , TiB _{2+x} , B ₄ C _{1-x} | 1.5 : 1 | (1 : 7)* ⁵ | - |
| 3Ti + C + 6B (3TiB ₂ + C) | 210 | TiB _{2+x} , TiC _{1-x} , traces α -Ti | 1 : 9.5 | - | - |
| 3Ti + 2C + 5B (2.5TiB ₂ + 0.5TiC + 1.5C) | 176 | TiB _{2+x} , TiC _{1-x} , traces α -Ti | 1 : 4.3 | - | - |
| 3Ti + 3C + 4B (2TiB ₂ + TiC + 2C) | 149 | TiB _{2+x} , TiC _{1-x} , B ₄ C _{1-x} , traces α -Ti | 1 : 2.2 | 1 : 5 | - |
| 3Ti + 5C + 2B (2TiC + TiB ₂ + 3C) | 108 | TiC _{1-x} , TiB _{2+x} , traces B ₄ C _{1-x} | 10 : 1 | - | - |
| 4Ti + C + 5B (2TiB ₂ + TiB + TiC) | 226 | TiB _{2+x} , TiC _{1-x} , traces r-TiB _{1-x} * ⁶ | 1 : 1.7 | - | ~0 |
| 4Ti + 2C + 4B (TiB ₂ + TiC) | 233 | TiB _{2+x} , TiC _{1-x} , r-TiB _{1-x} | 1 : 1.5 | - | 1 : 6 |
| 4Ti + 4C + 2B (3TiC + TiB ₂ + C) | 167 | TiC _{1-x} , TiB _{2+x} | 14 : 1 | - | - |
| 4Ti + 5C + B (3.5TiC + 0.5TiB ₂ + 1.5C) | 146 | TiC _{1-x} , TiB _{2+x} , traces B ₄ C _{1-x} | 7 : 1 | - | - |
| 4.5Ti + 4.5C + B (4TiC + 0.5TiB ₂ + 0.5C) | 176 | TiC _{1-x} , TiB _{2+x} | 8 : 1 | - | - |
| 5Ti + C + 4B (4TiB + TiC) | 164 | r-TiB _{1-x} , B ₄ C _{1-x} , TiC _{1-x} , TiB _{2+x} | (6.5 : 1)* ⁷ | 6 : 1 | 3 : 1 |

Notes: *Phase ratios in brackets are according the common accredited equilibrium state diagram Ti-C-B system.

*²Calculated for supposed thermodynamically stable products according equilibrium state diagram Ti-C-B system.

*³ By results of XRD analysis, in order to decrease of phase contents in composition.

*⁴ α -Ti – lower temperature modification of titanium metal.

*⁵J[B₄C_{1-x}(110)]:J[TiB_{2+x}(101)]

*⁶ r-TiB_{1-x} – orthorhombic modification of titanium monoboride.

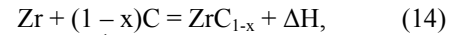
*⁷{J[TiC_{1-x}(200)] + J[r-TiB(210)]} : J[TiB_{2+x}(101)].

obtained in the mixtures with a lack of Ti. Although, at first it seemed to be contradicted to elementary meanings, especially when traces of metal titanium were revealed together with boron carbide phase formed by the reaction (9). But the consideration of the reactions (10)-(12), which sometimes cannot be completed due to the insufficient thermal load, allows to understand the presence of B_4C_{1-x} in some SHS prepared compositions, where its existence is apparently unstable. Titanium monoboride phase TiB_{1-x} found out in SHS products in this work is presented by orthorhombic modification with the lattice parameters well agreed with those in the literature [36], but the stabilization of cubic modification of TiB_{1-x} by actually essential amounts of carbon has not taken place there. Undoubtedly TiB_{1-x} is a necessary intermediate phase of boridization process of titanium, but only when the process is passing under 2460 K, the upper limit of the stable existence of TiB_{1-x} . Otherwise, the reactions (7)-(9) and (11)-(12) dominate, so monoboride phase can appear in the mixtures with higher heat effects only during afterburning. The evidence of presence for other possible phases of Ti-B system, e.g. Ti_3B_4 or TiB_5 , was not found out in the work.

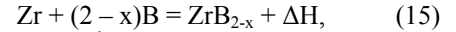
2.3.2. SHS in the Zr-C-B system. The contents area of SHS realisation in the Zr-C-B system discovered in the present work is a few smaller than those in the similar system with titanium (Figure 4b). Depended on the ratio of components (Table 6) monocarbide, diboride of zirconium with traces of dodecaboride and boron carbide were revealed in SHS products after combustion of the

Zr-C-B mixtures. SHS prepared compositions in this system are characterized by high rate of interaction between components, though analogically to the Ti-C-B system it is observed presence of insignificant amounts of pure metal not entered into chemical reactions. The gained experimental data on SHS products in the Zr-C-B system confirmed the mechanism that was proposed above to explain the character of interaction in the Me-C-B mixtures during synthesis processing. This mechanism is realised in the case, when the more active carbon in comparison with boron is used, and it is well agreed with the conclusions made by Tsushida and Yamamoto [37], who had discovered a decisively important role of carbon activation while studying mechanically activated SHS of the Zr-B-C powdered mixtures in air.

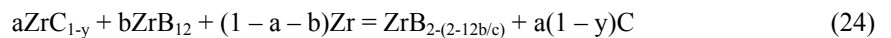
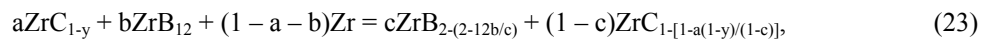
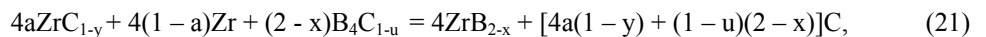
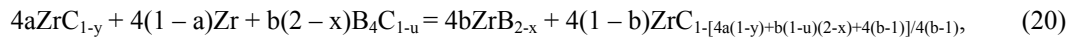
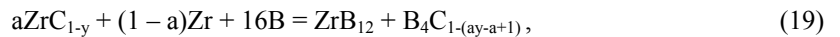
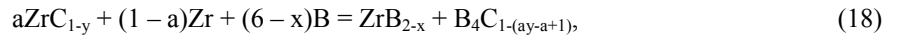
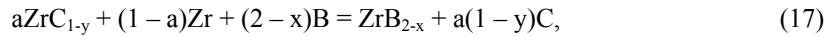
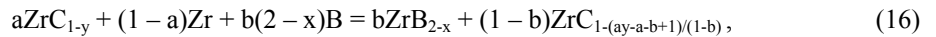
Thus, the carbidization reaction of zirconium:



where $\Delta H = 201 \text{ kJ mol}^{-1}$ for $x \rightarrow 0$ at standard conditions as well as it was shown earlier for the system with titanium, becomes the prioritized process, so it controls the zirconium boridization reaction:



where $\Delta H = 306 \text{ kJ mol}^{-1}$ for $x \rightarrow 0$ at standard conditions and the formation of boron carbide, accordingly to reaction (5). Both of these processes are passing in essentially overheated above 1890 K, the ternary eutectic point $\beta\text{-Zr-ZrB}_2\text{-ZrC}$, molten zirconium alloy while afterburning by means of following reactions:



in the mode of dissolution-precipitation (recrystallization).

The comparative analysis of contents for SHS products in the Me-C-B systems shows that the completeness of the SHS reactions in the mixtures with Zr is lower than the same character in Ti containing matters. Therefore the mixtures with equal molar ratio Me:C: B, e.g. 3:1:6, 3:2:5, 4:4:2 and some others, have essentially higher content of intermediate phase, such as B_4C_{1-x} , in the Zr-C-B system than in the similar system with Ti. In the $3Zr + 3C + 4B$ mixture on account of the slowdown of reactions (20)-(21) B_4C_{1-x} , although it is an intermediate phase, becomes the main component of the SHS products, but at the same time in analogous, the $3Ti + 3C + 4B$ mixture, the contents of titanium carbide

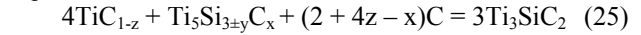
and boride phases considerably exceed the boron carbide content. The cause of these differences between Ti and Zr containing mixtures is in higher thermal load while SHS processing that is inherent for the system with Ti. The specific enthalpies of reactions (2) and (4) exceed those for reactions (14) and (15) up to 50-60 %, but the increase of densities for Zr compounds compared with those of Ti amounts only about 35 %. Hence, the heat released in the unit of volume in the Ti-C-B mixtures can exceed the same character for the Zr-C-B mixtures more than 35-45 %. Furthermore, this effect is amplified, because at the same temperatures the diffusivity of atoms in Zr compounds is lower compared to those for Ti, so the lower grade of balance for the SHS products obtained in the Zr-C-B system is quite understandable. Another

particularity of the products obtained in the Zr-C-B system is the observable redistribution of XRD peaks intensities in spectra of Zr monocarbide phase that is probably because of the dissolution of boron into cubic ZrC_{1-x} and the formation of the mixed phase of borocarbide $Zr(C,B)$.

2.3.3. SHS in the Ti-C-Si system. For the lower heat effects, which are proper to the interaction between titanium and silicon, the contents area of SHS realisation in the Ti-C-Si system is essentially smaller than those in the systems considered in the present work above (Figure 4c). Inadequate thermal load observed in the Ti-Si powdered mixtures while SHS processing extremely decrease the rate of chemical reactions. For instance, determined by Kachelmyer et al. [38] employing the TRXRD method, rate of interaction in $5Ti + 3Si$ mixture is about 60 times lower than that for the $2Ti + C + 2B$ mixture defined by Contreras et al. [20] applying the same method. In different mixtures that were represented the Ti-C-Si ternary system and tested for combustion synthesis three Si containing phases were found out in the SHS products by the means of XRD analysis: non-stoichiometric titanium silicon carbide $Ti_5Si_{3\pm y}C_x$ (Nowotny phase), titanium disilicide $TiSi_2$ and silicon carbide SiC (Table 7). In spite of insufficiently high values of specific enthalpies of the formation reactions for Si containing phases neither metal titanium nor elemental silicon were revealed in the SHS products in this system. Though it was reported about the partiality of the Ti-C-Si alloys to form amorphous phases [39], all SHS prepared compositions, including one obtained from the $2Ti + 6C + 2Si$ mixture with the lowest heat effect, are characterized by well crystallized structure of phases. Practically the same SHS products were obtained by Tomoshige et al. [40] for the initial mixtures with Ti:C:Si ratios from 5:1:1 to 1:1:1, the only one exception is Ti_5Si_4 , which was revealed in the sample with equimolar ratio of components.

There is really no doubt about the prioritized process in the Ti-C-Si system, because the interaction between Ti and C dominates both in heat release and in contact surface area on those of the Ti-Si couple. Thus it

becomes possible to use the conclusions gained above for the SHS in the ternary systems with boron, but due to major amount of works devoted to the SHS in the Ti-C-Si mixtures, it is more interesting to discuss the obtained results. The great amount of papers, published recently in this direction, could have been explained by the attractiveness of Ti_3SiC_2 as a unique phase [25,41-43]. The SHS processing conditions realized in the present work did not allow to synthesize Ti_3SiC_2 and confirmed the necessity of some finesses to manufacture it, which should provide the passing of the eventual stage of Ti_3SiC_2 formation [44-45] according to following equation:



properly. For the essential difficulties this stage required large energy, so just the application of 150-second post-combustion heating time appeared to increase the Ti_3SiC_2 yield more than twice [46]. Anselmi-Tamburini et al.[47] also emphasize the importance of afterburning processes in the interaction between Ti and Si while carrying out the SHS by different technological methods. It is understandable that the economizing version of SHS processing, designed for broad application in different ceramic productions, which was employed in the present work, cannot afford to provide all conditions for successful fabrication of Ti_3SiC_2 . Therefore, only the precursors of Ti_3SiC_2 synthesis could have been obtained under the deficiency of heat released by the internal sources. But it needs also to note that the quasi-isomorphic crystal structures for $Ti_5Si_{3\pm y}C_x$ (hexagonal Mn_5Si_3 -type, $D_{6h}^3 - P6_3/mcm$) [48] and Ti_3SiC_2 (hexagonal $MgZn_2$ -type, $D_{6h}^4 - P6_3/mmc$) [42] allow to assume the existence of extensive mutual dissolubility. Hence, the exact determination of Ti_3SiC_2 in similar compositions becomes of great trouble or impossible.

The consideration of SHS processing in the Ti-C-Si system together with others (see 3.3.1 and 3.3.2) helps to understand the mechanism of interaction between group 4 transition metals and non-metals while SHS processing. As it was shown above, the appearance of molten metal alloy induces SHS reactions, which for the Ti-C-Si mixtures are expressed by following equations:

$$5aTiC_{1-z} + 5(1 - a)Ti + b(3 \pm y)Si = bTi_5Si_{3\pm y}C_x + 5(1 - b)TiC_{1-[5(1-b)-5a(1-z)+bx]/5(1-b)}, \quad (26)$$

$$aTiC_{1-z} + (1 - a)Ti + 2bSi = bTiSi_2 + (1 - b)TiC_{1-[1-a(1-z)]/(1-b)}, \quad (27)$$

$$aTiC_{1-z} + (1 - a)Ti + [2 + a(1 - z)]Si = TiSi_2 + a(1 - z)SiC, \quad (28)$$

$$5aTiC_{1-z} + 5(1 - a)Ti + b(3 \pm y)SiC = bTi_5Si_{3\pm y}C_x + 5(1 - b)TiC_{1-[5(1-b)-5a(1-z)-b(3\pm y)+bx]/5(1-b)}, \quad (29)$$

$$aTiC_{1-z} + (1 - a)Ti + 2bSiC = bTiSi_2 + (1 - b)TiC_{1-[1-3b-a(1-z)]/(1-b)}, \quad (30)$$

$$10aTiC_{1-z} + [10 - 10a - c(3 \pm y)]Ti + c(3 \pm y)TiSi_2 = 2cTi_5Si_{3\pm y}C_x + 10(1 - c)TiC_{1-[5(1-c)-5a(1-z)+cx]/5(1-c)}. \quad (31)$$

The most detailed consideration of reactions in the Ti-C-Si system during SHS processing presented by Pampuch and Stobierski [14] became further development of the Korchagin-Aleksandrov-Gusenko mechanism previously proposed for the SHS in the binary systems with titanium [49-50]. The quintessence of “metal – non-metal” interaction, in accordance with it, consists in growth of the reaction layer at the “carbon (solid) – reaction layer (solid)” interface and the concomitant dissolution of this layer at the opposite “reaction layer (solid) – molten metal alloy (liquid)” interface. Titanium (zirconium) carbide formed by the reactions (2) and (14) on the “solid – solid” interface under the consideration after this mechanism could be

called as “primary carbide” unlike from the metal carbide phases of the different degree of stoichiometry, which appear by precipitation from molten alloy during SHS, include afterburning processes, by the reactions (6)-(7), (10)-(11), (13), (16), (20), (23), (26)-(27) and (29)-(31) and should be called in this case as “secondary carbides”.

A great deal of achievements and publications in SHS technology [14,25,44-47] as well as nanostructural in situ observations of group 4 transition metal alloys, for instance the recent research by Iwamoto et al. [51], confirm the proposed mechanism, which describes the formation of silicides in the Ti-C-Si mixtures during SHS processing by following stages. The appearance of quasi-eutectic liquid caused the dissolution of solid powder

Table 6

Compositions of SHS products in Zr-C-B system

| Initial mixture in molar ratio* | Heat effect* ² , – $\Delta H(\text{kJ mol}^{-1})$ | Composition* ³ | J[ZrC _x (200)]: : J[ZrB _{2-x} (101)] | J[B ₄ C _{1-x} (021)]: : J[ZrB _{2-x} (101)] | J[ZrB ₁₂ (200)]: : J[ZrB _{2-x} (101)] |
|---|---|---|---|--|--|
| 2Zr + C + 7B (2ZrB ₂ + 0.75B ₄ C + 0.25C) | 222 | ZrB _{2-x} , B ₄ C _{1-x} , traces ZrC _{1-x} and ZrB ₁₂ | ~0 | 1 : 8 | ~0 |
| 2Zr + 2C + 6B (2ZrB ₂ + 0.5B ₄ C + 1.5C) | 162 | ZrB _{2-x} , B ₄ C _{1-x} , ZrC _{1-x} , ZrB ₁₂ | 1 : 7.5 | (1 : 4)* ⁴ | 1 : 9 |
| 2Zr + 3C + 5B (2ZrB ₂ + 0.25B ₄ C + 2.75C) | 126 | ZrB _{2-x} , B ₄ C _{1-x} , ZrC _{1-x} , traces ZrB ₁₂ | 1 : 2.3 | (1 : 3.6)* ⁴ | ~0 |
| 3Zr + C + 6B (3ZrB ₂ + C) | 230 | ZrB _{2-x} , B ₄ C _{1-x} , ZrC _{1-x} , traces ZrB ₁₂ | 1 : 11 | 1 : 1.3 | ~0 |
| 3Zr + 2C + 5B (2.5ZrB ₂ + 1.5ZrC + 0.5C) | 237 | ZrB _{2-x} , ZrC _{1-x} , B ₄ C _{1-x} , traces ZrB ₁₂ | 1 : 6 | 1 : 15 | ~0 |
| 3Zr + 3C + 4B (2ZrB ₂ + ZrC + 2C) | 203 | B ₄ C _{1-x} , ZrC _{1-x} , ZrB _{2-x} , traces ZrB ₁₂ | 1 : 1 | 6 : 1 | ~0 |
| 3.33Zr + 3.33C + 3.33B (ZrB ₂ + ZrC + C) | 169 | ZrC _{1-x} , ZrB _{2-x} | 13 : 1 | - | - |
| 4Zr + C + 5B (2.5ZrB ₂ + ZrC + 0.5Zr) | 242 | ZrB _{2-x} , ZrC _{1-x} , traces B ₄ C _{1-x} | 1 : 2 | ~0 | - |
| 4Zr + 2C + 4B (ZrB ₂ + ZrC) | 254 | ZrB _{2-x} , ZrC _{1-x} , B ₄ C _{1-x} , traces ZrB ₁₂ | 1 : 1.6 | 1 : 2.6 | ~0 |
| 4Zr + 4C + 2B (3ZrC + ZrB ₂ + C) | 182 | ZrC _{1-x} , ZrB _{2-x} , traces B ₄ C _{1-x} and α -Zr* ⁵ | 8 : 1 | - | - |
| 4Zr + 5C + B (3.5ZrC + 0.5ZrB ₂ + 1.5C) | 156 | ZrC _{1-x} , ZrB _{2-x} , traces B ₄ C _{1-x} and α -Zr | 20 : 1 | - | - |
| 5Zr + C + 4B (2ZrB ₂ + ZrC + 2Zr) | 163 | ZrC _{1-x} , ZrB _{2-x} , B ₄ C _{1-x} , traces α - Zr | 1 : 1.3 | 1 : 5.5 | - |

Notes: *Phase ratios in brackets are according the common accredited equilibrium state diagram Zr-C-B system.

*²Calculated for supposed thermodynamically stable products in standard conditions according equilibrium state diagram Zr-C-B system.

*³By results of XRD analysis, in order to decrease of phase contents in composition.

*⁴J[B₄C_{1-x}(110)] : J[ZrB_{2-x}(101)]

*⁵ α -Zr – lower temperature modification of zirconium metal.

Compositions of SHS products in Ti-C-Si system

| Initial mixture in molar ratio* | Heat effect* ² , $\Delta H(\text{kJ mol}^{-1})$ | Composition* ³ | $J[\alpha\text{-SiC}(101)]$: : $J[\text{TiC}_{1-x}(200)]$ | $J[\text{Ti}_5\text{Si}_{3\pm y}\text{C}_x(102)]$: : $J[\text{TiC}_{1-x}(200)]$ | $J[\text{TiSi}_2(311)]$: : $J[\text{TiC}_{1-x}(200)]$ |
|---|---|---|---|---|---|
| 2Ti + 6C + 2Si (TiC + SiC + C) | 84 | TiC _{1-x} , α -SiC | 1 : 2 | - | - |
| 2Ti + 5C + 3Si (2TiC + 3SiC) | 114 | Ti ₅ Si _{3\pmy} C _x , α -SiC, TiC _{1-x} , TiSi ₂ | 1 : 2 | 3 : 1 | 1 : 1.3 |
| 3Ti + 5C + 2Si (3TiC + 2SiC) | 138 | TiC _{1-x} , α -SiC, TiSi ₂ , Ti ₅ Si _{3\pmy} C _x | 1 : 13 | 1 : 20 | 1 : 3 |
| 4Ti + 5C + Si (4TiC + SiC) | 161 | TiC _{1-x} , Ti ₅ Si _{3\pmy} C _x , TiSi ₂ , α -SiC | 1 : 7.5 | 1 : 1 | 1 : 1.7 |
| 3.45Ti + 0.35C + 6.2Si (TiC + 9TiSi ₂) | 140 | TiSi ₂ , Ti ₅ Si _{3\pmy} C _x , TiC _{1-x} | - | (3 : 1)* ⁴ | (20 : 1)* ⁵ |
| 3.7Ti + 1.1C + 5.2Si (3TiC + 7TiSi ₂) | 150 | TiSi ₂ , Ti ₅ Si _{3\pmy} C _x , TiC _{1-x} | - | (1.3 : 1)* ⁴ | (5 : 1)* ⁵ |
| 4Ti + 2C + 4Si (TiC + TiSi ₂) | 160 | TiSi ₂ , Ti ₅ Si _{3\pmy} C _x , TiC _{1-x} , α -SiC | 1 : 2 | 1 : 1.4 | 2.5 : 1 |
| 4.35Ti + 3.05C + 2.6Si (7TiC + 3TiSi ₂) | 170 | TiC _{1-x} , TiSi ₂ , Ti ₅ Si _{3\pmy} C _x , α - SiC | 1 : 1.3 | 1.2 : 1 | 1.5 : 1 |
| 4.75Ti + 4.3C + 0.95Si (9TiC + TiSi ₂) | 180 | TiC _{1-x} , Ti ₅ Si _{3\pmy} C _x , TiSi ₂ | - | 1 : 3.5 | 1 : 5 |

Notes: *Phase ratios in brackets are according to the common accredited equilibrium state diagram Ti-C-Si system without taking into account the existence of Ti₃SiC₂ ternary phase.

*²Calculated for supposed thermodynamically stable products in standard conditions according to equilibrium state diagram Ti-C-Si system without taking into account the existence of Ti₃SiC₂ ternary phase.

*³By results of XRD analysis, in order to decrease of phase contents in composition.

*⁴ $J[\text{Ti}_5\text{Si}_{3\pm y}\text{C}_x(102)] : J[\text{TiC}_{1-x}(220)]$

*⁵ $J[\text{TiSi}_2(311)] : J[\text{TiC}_{1-x}(220)]$.

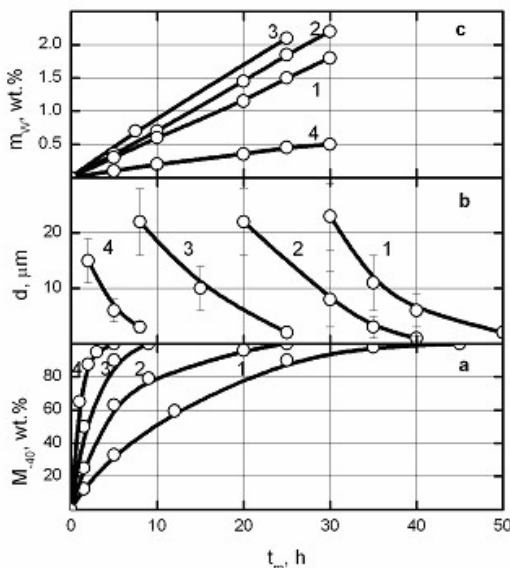


Fig. 5. Evolution of the fraction of $-40 \mu\text{m}$ powder particles M_{-40} (a), the average size of powder particles d (b) and tungsten contamination of powders m_w (c) as a function of milling time t_m for: 1 – SHS titanium carbide (initial molar ratio Ti + 1.1C); 2 – SHS zirconium carbide (Zr + 1.1C); 3 – SHS hafnium carbide (Hf + 1.1C); 4 – furnace synthesised from oxide, carbothermic titanium carbide.

oversaturated with Ti and Si in the course of continuous dissolution, the precipitation of silicides made up pro rata of the phase diagram, but the presence of intermediate phases in the eventual products could be mostly due to the lack of sufficient reaction time to complete the phase transformation of SHS products. The results obtained in the present study allow to spread of the considered mechanism to all discovered systems with group 4 transition metals. The mechanism helps to explain some particularities of contents for SHS products, which could be prepared in the Me-X₁-X₂ systems. Thus, the presence of Ti or Zr monocarbide phase in all specimens tested for the combustion synthesis in this study irrespectively to their compositions (see Tables 5-7) became absolutely clear after the consideration of “primary carbide” formation and its role in SHS processing. The only one exception to this phenomenon was found among the Ti-C-B burnt mixtures, when initial boron content exceeds that of carbon 7 times.

2.4. Testing SHS products for production of ceramics. The aptitude of SHS products to ceramics production became of great interest for technologists since SHS has been invented in the 60 s. Furthermore, the behaviour of SHS powdered materials has some particularities compared to conventional ceramic powders. Figure 5 shows variations in the fraction of -

40 μm , the average size and contamination as a function (carbides, borides) group 4 transition metals (titanium,

Table 8

Physico-chemical characteristics of SHS powdered ceramic compositions

| Base | Modifying additions (0 ÷ 40 vol %) | Milling time (h) | Particle size (μm) | Specific surface ($\text{m}^2 \text{g}^{-1}$) | Density (g cm^{-3}) | Contamination (wt %) | |
|--------------------|---|---------------------|------------------------------------|--|-----------------------------------|----------------------|----------|
| | | | | | | W | Fe |
| TiC_{1-x} | TiB_{2+x} , $\text{Ti}_5\text{Si}_{3\pm y}\text{C}_x$, TiSi_2 , B_4C_{1-x} , α - SiC , carbon | 40-60 | 1-8 | 1.0-1.5 | 4.4-4.8 | 1.5-2.5 | 0.3-0.5 |
| ZrC_{1-x} | ZrB_{2-x} , B_4C_{1-x} , α - SiC , carbon | 30-40 | 1-6 | 1.3-1.8 | 6.0-6.4 | 1.0-2.0 | 0.1-0.2 |
| HfC_{1-x} | HfB_2 , B_4C_{1-x} , α - SiC , carbon | 20-30 | 0.5-4 | 2.2-2.6 | 11.6-12.2 | 0.8-1.8 | 0.05-0.1 |

of milling time for SHS manufactured specimens with initial mixture molar ratio $\text{Me}(\text{Ti, Zr, Hf})\text{:C} = 1\text{:}1.1$ and titanium carbide, furnace synthesised by carbothermic reduction from oxide as a usual object for the comparative analysis of milling character [52]. The gained experimental data demonstrate that the suitability for fine milling raises in the series of manufactured by the SHS vacuum version carbide materials TiC_{1-x} - ZrC_{1-x} - HfC_{1-x} . In this series the melting points of materials increase, but the specific enthalpies of carbidization decrease, so it brings about the reduction of reaction sintering effect and, respectively, relative density and strength of "carbide sponge". That is why the milling procedure for SHS manufactured titanium carbide materials is more difficult in comparison with other group 4 transition metal carbides. Theoretical strengths of all carbides of this series [53] differ insignificantly, so micro-milling of fine carbide powders is passing with approximately equal rate. Evidently, the contamination while milling linearly depends on the specific surface of milled materials, so it is great disadvantage of conventional means for milling in ceramic production of pure refractory compounds. However, SHS powdered materials possess a higher level of abrasiveness than the same contents materials, for instance, synthesised by carbothermic reduction, therefore the procedure of milling for the SHS materials is much more resource-intensive and difficult. The application of the similar to the milled materials in the process of milling as lining plates and milling balls becomes possible after the enlargement of production scale. Such steps allow essentially to decrease the contamination of milled SHS materials while processing. The experience in SHS ceramic compositions fabrication is summarised in Table 8, where generalized physico-chemical characters for different kinds of ceramic-ceramic composite precursors are presented.

Conclusions

Being more effective and accessible than other versions of SHS, the vacuum method provides the production of precursors for ceramic-ceramic composite materials based on the oxygen-free refractory compounds

zirconium, hafnium) in wide ranges of the molar ratios for the common commercial reagents: metal powders and elemental powders of non-metals (carbon, boron, silicon). Applying vacuum SHS technique there could be successfully synthesised: cubic monocarbide phases MeC_{1-x} ($\text{Me} = \text{Ti, Zr, Hf}$) in the Ti-C, Zr-C, Hf-C, Ti-Zr-C, Ti-C-B, Zr-C-B and Ti-C-Si systems; orthorhombic monoboride TiB_{1-x} in the Ti-C-B system; hexagonal diboride phases $\text{MeB}_{2\pm x}$ ($\text{Me} = \text{Ti, Zr, Hf}$) in the Ti-B, Zr-B, Hf-B, Ti-Zr-B, Ti-C-B and Zr-C-B systems; hexagonal titanium silicon carbide $\text{Ti}_5\text{Si}_{3\pm y}\text{C}_x$ and titanium disilicide TiSi_2 in the Ti-C-Si system; boron carbide B_4C_{1-x} in the Ti-C-B and Zr-C-B systems and silicon carbide as an α -SiC phase in the Ti-C-Si system. All these obtained phases were characterized by well-crystallized structures in spite of the evident transience of synthesis, though traces of initial reagents, for instance metal Ti or Zr, were observed in some manufactured compositions in the Ti-C-B and Zr-C-B systems. The values of lattice parameters and densities for synthesized phases are in good agreement with those in literature. The insignificant presence of zirconium dodecaboride ZrB_{12} could be expelled completely after 0.5 h soaking at 1850 K in vacuum.

Titanium and zirconium monocarbide phases MeC_{1-x} could be prepared by vacuum SHS with different C/Me ratio along the whole range of their homogeneity, but the fabrication of stoichiometric carbides is connected with some diffusion difficulties, so MeC_{1-x} with x values less than 0.05 could be formed in SHS products prepared from the initial mixtures with molar ratio $\text{Me} + 1.5 \text{C}$ or richer in carbon content. Taking into account the loss of carbon while SHS processing, the mixtures $\text{Me} + 1.1 \text{C}$ are recommended to manufacture pure monocarbide phases with maximal value of C/Me ratio, although the amount of free (not combined with metal) carbon in such SHS products is about 7.5-15 % of total carbon content. Prepared by vacuum SHS titanium-zirconium mixed monocarbide phases $(\text{Ti,Zr})\text{C}_{1-x}$ in the Ti-Zr-C system as well as mixed diborides $(\text{Ti,Zr})\text{B}_{2\pm x}$ in the Ti-Zr-B system also possess well-crystallized structures, but not so perfect as it was explored in the materials soaking at high temperatures for a long period of time. Nevertheless, it was possible to confirm the positive deviation of the values of lattice parameters from

Wegard's law in the continuous series of $TiC_{1-x}-ZrC_{1-x}$ solid solutions, which was determined for the samples homogenized by high-temperature hot-pressing. The comparative analysis of SHS processing in the Me- X_1-X_2 systems shows that the contents area of SHS realization for the investigated systems is maximal for the Ti-C-B system and minimal for the Ti-C-Si system. This conclusion is quite evident, because due to the lower values of specific enthalpy for reactions with silicon all attempts to initiate SHS in the Ti-Si mixtures were failed.

The analysis of results obtained in the present study for SHS, which was realized with more active carbon component, confirmed that the metal carbidization reaction controls the SHS processing as a whole. The appearance of molten quasi-eutectic alloy induces SHS reactions that are described in details by the series of equations proposed in the similar studies first. The further consideration of SHS processing in the Me- X_1-X_2 systems carried out in the present study allows to spread the Korchagin – Aleksandrov – Gusenko mechanism, developed successively by Pampuch with co-workers, for the combustion synthesis in these systems. In accordance with this mechanism metal – non-metal interaction during SHS consists in the growth of the reaction layer at the “carbon (solid) – reaction layer (solid)” interface and the concomitant dissolution of this layer at the opposite “reaction layer (solid) – molten metal alloy (liquid)” interface. So metal carbide formed by the main reaction on the “solid – solid” interface could be called as “primary carbide” unlike from metal carbide phases or other phases of the different degree of stoichiometry, which appear by precipitation from molten alloy during SHS, include afterburning processes, and should be called in this case as “secondary carbides” or “secondary compounds”. The present study jointly with recent achievements and publications in SHS technology as well as nanostructural in situ observations of group 4 transition metal alloys confirm this mechanism, which describes the formation of borides, silicides and non-metal carbides in the Me- X_1-X_2 mixtures during SHS processing by following stages. The appearance of quasi-eutectic liquid caused the dissolution of solid powder particles into the molten phase. When the liquid is oversaturated with any elements in the course of continuous dissolution, the precipitation of corresponding compounds made up accordingly to the phase diagram, meanwhile the presence of intermediate phases in the eventual products could be mostly due to the lack of sufficient reaction time to complete the phase transformation of SHS products.

The suitability of obtained SHS products for fine milling raises in the series of compositions based on carbides $TiC_{1-x}-ZrC_{1-x}-HfC_{1-x}$. In this series melting points of materials increase, but specific enthalpies of carbidization decrease, so it brings about the reduction of reaction sintering effect and, respectively, relative density and strength of “carbide sponge”. Therefore procedure for SHS manufactured titanium carbide materials is more difficult in comparison with other carbides. Theoretical strengths of all carbides of this series differ insignificantly, so micro-milling of fine carbide powders is passing with approximately equal rate and the contamination while milling linearly depends on the specific surface of milled materials. SHS powdered materials possess a higher level of abrasiveness than the same contents materials, for instance, synthesised by carbothermic reduction, therefore the procedure of milling for SHS materials is much more resource-intensive and difficult. The application of the similar to the milled materials in the process of milling as lining plates and milling balls allows essentially to decrease the contamination of milled SHS materials.

Thus, tested in the present work vacuum SHS technique provides the fabrication of the ceramic-ceramic composite precursors based on the oxygen-free refractory compounds of group 4 transition metals in the wide range of component contents, which could be treated subsequently by the conventional methods of ceramic production.

Acknowledgements

The authors wish to thank Prof. A.R. Beketov, Ural State Technical University, Russia and Prof. G.M. Romantsev, Russian State Professional & Pedagogical University for providing the necessary technological and research facilities. One of the authors, I.L. Shabalin, would like to express his gratitude to Prof. Keith Ross and Dr. Dan Bull for support and help in the preparation this work for publishing.

Шабалін І.Л. – професор Салфордського університету;
Лучка М.В. – кандидат технічних наук, старший науковий співробітник;
Шабалін Л.І. – аспірант.

- [1] R.A. Andrievskii, I.I. Spivak. *Strength of Refractory Compounds and Materials Based on Them*, Metallurghiya, Chelyabinsk. pp. 5-62 (1989).
- [2] I.L. Shabalin, A.R. Beketov, S.G. Gorinskii, M.I. Podkovyrkin, O.V. Fedorenko. A study of strength characteristics of titanium carbide-silicon carbide-carbon hot-pressed materials. *In Alloys of Refractory and Rare Metals for High-Temperature Application. Proceedings of the All-USSR Conference on Physico-Chemical Principles of Development for Heat-Resisting Metal Materials*, ed. E.M. Savitskii. Nauka, Moscow. pp. 186-189 (1984).
- [3] A.F. Kokorin, S.G. Gorinskii, A.R. Beketov, I.L. Shabalin, M.V. Pokrovskii, I.G. Gulyaev. Monochromatic radiating ability of TiC-TiB₂-C materials // *High Temperatures*, **17**(1), pp. 63-65 (1979).

- [4] S.G. Gorinskii, A.R. Beketov, M.I. Podkovyrkin, I.L. Shabalin, A.F. Kokorin. Electrical resistivity of hot-pressed TiC-SiC-C composite materials // *Sov. Powder Metall. Met. Ceram.*, **21**(11), pp. 867-871 (1982).
- [5] S.G. Gorinskii, I.L. Shabalin, A.R. Beketov, M.I. Podkovyrkin, A.F. Kokorin, V.V. Pakholkov. Electrical resistivity of sintered TiC-SiC materials // *Sov. Powder Metall. Met. Ceram.*, **19**(11), pp. 780-783 (1980).
- [6] A.G. Merzhanov, Combustion processes that synthesize materials // *J. Mater. Process. Technol.*, **56**, pp. 222-241 (1996).
- [7] A.G. Merzhanov, History and recent developments in SHS // *Ceram. Int.*, **21**, pp. 371-379 (1995).
- [8] A.G. Merzhanov, The chemistry of self-propagating high-temperature synthesis // *J. Mater. Chem.*, **14**, pp. 1779-1786 (2004).
- [9] Z.A. Munir, U. Anselmi-Tamburini. Self-propagating exothermic reactions: the synthesis of high-temperature materials by combustion // *Mater. Sci. Rep.*, **3**(7-8), pp. 277-365 (1989).
- [10] N.P. Novikov, I.P. Borovinskaya, A.G. Merzhanov. Thermodynamic analysis of reactions of self-propagating high-temperature synthesis. In *Combustion Processes in Chemical Technology and Metallurgy*, ed. A.G. Merzhanov. Division of the USSR Academy of Science Institute of Chemical Physics, Chernogolovka, Moscow Region. pp. 174-188 (1975).
- [11] V.K. Prokudina, V.I. Ratnikov, V.M. Maslov, I.P. Borovinskaya, A.G. Merzhanov. Technology of titanium carbide // *Ibidem*, pp. 136-141.
- [12] V.V. Barzykin, V.P. Stovbun. A study of relationships for ignition of heterogeneous systems with refractory reaction products // *Ibidem*, pp. 274-283.
- [13] E.K. Storms. *The Refractory Carbides*, Academic Press, New York & London, pp. 1-46, pp. 225-247 (1967).
- [14] R. Pampuch, L. Stobierski. Solid combustion synthesis of refractory carbides: (A review) // *Ceram. Int.*, **17**, pp. 69-77 (1991).
- [15] D.C. Halverson, Combustion synthesis of nonoxide ceramic and composite performs for liquid-metal infiltration // *Tech. Rep. UCRL – CR – 105155*, Lawrence Livermore National Laboratory, CA, Oct. (1990).
- [16] I.L. Shabalin, M.I. Podkovyrkin, A.R. Beketov, E.V. Levashov. Manufacturing of composites based on the refractory compounds in a mode of combustion. In *Technological Research of Metal Powders and Sintered Materials*, ed. V.Ya. Bulanov. USSR Academy of Science Ural Scientific Centre, Sverdlovsk, pp. 105-110 (1980).
- [17] V.M. Shkuro, I.P. Borovinskaya, A.G. Merzhanov. Reactive properties exhibited by various types of carbon during the preparation of titanium carbide by self-propagating high-temperature synthesis // *Sov. Powder Metall. Met. Ceram.*, **18**(10), pp. 684-687 (1979).
- [18] V.P. Elyutin, V.I. Kostikov, M.A. Maurakh, I.A. Berezin, I.A. Dmitriev. About the mechanism of effect for intensive vaporization of carbon. In *Structural Materials Based on Carbon*, ed. V.I. Kostikov. Metallurghiya, Moscow. **9**, pp. 190-200 (1974).
- [19] D.D. Radev, M. Marinov. Properties of titanium and zirconium diborides obtained by self-propagated high-temperature synthesis // *J. Alloys Comp.*, **244**, pp. 48-51 (1996).
- [20] L. Contreras, X. Turrillas, G.B.M. Vaughan, A. Kvik, M.A. Rodrigues. Time-resolved XRD study of TiC-TiB₂ composites obtained by SHS // *Acta Mater.*, **52**, pp. 4783-4790 (2004).
- [21] Yu.G. Zainulin, S.I. Alyamovskii, I.E. Pavlov, G.P. Shveikin. Lattice completeness and period of titanium-rich oxycarbides TiC_xO_y [(x + y) < 0.8] // *Izv. Akad. Nauk SSSR Neorg. Mater.*, **13**(2), pp. 381-382 (1977).
- [22] Yu.A. Gordoplov, N.G. Zaripov. Formation of graded and fine-grained structures upon hot deformation of SHS products // *Mater. Sci. Forum*, **423-425**, 219-222 (2003).
- [23] N.A. Martirosyan, S.K. Dolukhanyan, G.M. Mkrtchyan, I.P. Borovinskaya, A.G. Merzhanov. Refinement processes occurring the preparation of refractory compounds by self-propagating high-temperature synthesis // *Sov. Powder Metall. Met. Ceram.*, **16**(7), 522-525 (1977).
- [24] K.S. Vecchio, J.C. LaSalvio, M.A. Meyers, G.T. Gray. III, Microstructural characterization of self-propagating high-temperature synthesis/dynamically compacted and hot-pressed titanium carbides // *Metall. Mat. Trans. A, Phys. Metall. Mat. Sci.*, **23A**(1), pp. 87-97 (1992).
- [25] R. Pampuch, J. Lis, L. Stobierski, M. Tymkiewicz. Solid combustion synthesis of Ti₃SiC₂ // *J. Eur. Ceram. Soc.*, **5**, pp. 283-287 (1989).
- [26] T.S. Azatyan, V.M. Maltsev, A.G. Merzhanov, V.A. Selesnev. Some principles of combustion of titanium-silicon mixtures // *Combust. Explos. Shock Waves*, **15**(1), pp. 35-40 (1979).
- [27] F. Maglia, U. Anselmi-Tamburini, G. Cocco, M. Monagheddu, N. Bertolino, Z.A. Munir. Combustion synthesis of mechanically activated powders in the Ti-Si system // *J. Mater. Res.*, **16**(4), pp. 1074-1082 (2001).
- [28] V.V. Ogorodnikov, A.A. Ogorodnikova. Theoretical phase diagrams of pseudobinary systems formed by the carbides of Ti, Zr, and Hf // *Izv. Akad. Nauk SSSR Neorg. Mater.*, **13**(4), pp. 658-662 (1977).
- [29] M. Moriyama, H. Aori, Y. Kobayashi. Fabrication and mechanical properties of hot-pressed TiB₂-ZrB₂ ceramic system // *J. Ceram. Soc. Jpn.*, **106**(12), pp. 1196-1200 (1998).
- [30] R. Kieffer, F. Benesovsky. *Hartstoffe*, Springer – Verlag, Wien – New York. pp. 185-187 (1963).
- [31] E. Rudy. Compendium of phase data, ternary phase equilibria in transition metal-boron-carbon-silicon systems. *Tech. Rep. AFML-TR-65-2*, Air Force Materials Laboratory, Wright-Patterson Air Force Base, OH, Pt. 5, pp. 1-689 (1969).

- [32] V.A. Shcherbakov, A.N. Pityulin. Unique features of combustion of the system Ti-C-B // *Combust. Explos. Shock Waves*, **19**(5), pp. 631-633 (1983).
- [33] C.J. Quinn, D.L. Kohlstedt. Solid-state reaction between titanium carbide and titanium metal // *J. Am. Ceram. Soc.*, **67**(5), pp. 305-310 (1984).
- [34] A. Banerji, Q. Feng, W. Reif. Structural elucidation of crystallisation centers in aluminium inoculated with titanium // *Acta Metall. Mater.*, **41**(8), pp. 2461-2472 (1993).
- [35] P. Wanjara, R.A.L. Drew, J. Root, S. Yue. Evidence for stable stoichiometric Ti₂C at the interface in TiC particulate reinforced Ti alloy composites // *Acta Mater.*, **48**(7), pp. 1443-1450 (2000).
- [36] M. De Graef, J.P.A. Lofvander, C. McCullough, C.G. Levi. The evolution of metastable B_f borides in a Ti-Al-B alloy // *Acta Metall. Mater.*, **40**(12), pp. 3395-3406 (1992).
- [37] T. Tsuchida, S. Yamamoto. Mechanical activation assisted self-propagating high-temperature synthesis of ZrC and ZrB₂ in air from Zr/B/C powder mixtures // *J. Eur. Ceram. Soc.*, **24**(1), pp. 45-51 (2004).
- [38] C.R. Kachelmyer, I.O. Khomeiko, A.S. Rogachev, A. Varma. A time-resolved X-ray diffraction study of Ti₅Si₃ product formation during combustion synthesis // *J. Mater. Res.*, **12**(12), pp. 3230-3240 (1997).
- [39] M. Naka, H. Sakai, M. Maeda, H. Mori. Formation and thermal stability of amorphous Ti-Si-C alloys // *Mater. Sci. Eng.*, **A226-228**, pp.774-778 (1997).
- [40] R. Tomoshige, T. Goto, T. Matsushita, K. Imamura, A. Chiba, M. Fujita. High-temperature-shock compaction of ceramics/silicide composites produced by combustion synthesis // *J. Mater. Process. Technol.*, **85**(1-3), pp. 100-104 (1999).
- [41] Y. Khoptiar, I. Gotman. Synthesis of dense Ti₃SiC₂-based ceramics by thermal explosion under pressure // *J. Eur. Ceram. Soc.*, **23**(1), pp. 47-53 (2003).
- [42] L. Yong-Ming, P. Wei, L. Shuqin, C. Jian. Synthesis and mechanical properties of in-situ hot-pressed Ti₃SiC₂ polycrystals // *Ceram. Int.*, **28**(2), pp. 227-230 (2002).
- [43] S.B. Li, J.X. Xie, L.T. Zhang, L.F. Cheng. Synthesis and some properties of Ti₃SiC₂ by hot pressing of titanium, silicon and carbon powders. Part I – Effect of starting composition on formation of Ti₃SiC₂ and observation of Ti₃SiC₂ crystal morphology // *Mater. Sci. Technol.*, **19**(10), pp. 1442-1446 (2003).
- [44] T. El-Raghy, M.W. Barsoum, Processing and mechanical properties of Ti₃/SiC₂. I. Reaction path and microstructure evolution // *J. Am. Ceram. Soc.*, **82**(10), pp. 2849-2854 (1999).
- [45] E. Wu, D.P. Riley, E.H. Kisi, R.I. Smith. Reaction kinetics in Ti₃SiC₂ synthesis studied by time-resolved neutron diffraction // *J. Eur. Ceram. Soc.*, **25**(15), pp. 3503-3508 (2005).
- [46] T.Y. Huang, C.C. Chen. Ternary ceramics Ti₃SiC₂: Combustion synthesis and the reaction mechanism // *Mater. Sci. Forum*, **475-479**(11), pp. 1609-1614 (2005).
- [47] U. Anselmi-Tamburini, F. Maglia, G. Spinolo, S. Doppiu, M. Monagheddu, G. Cocco. Self-propagating reactions in the Ti-Si system: a SHS-MASHS comparative study // *J. Mater. Synth. Process.*, **8**(5-6), pp. 377-383 (2000).
- [48] J.J. Williams, Y.Y. Ye, M.J. Kramer, K.M. Ho, L. Hong, C.L. Fu, S.K. Malik. Theoretical calculations and experimental measurements of the structure of Ti₅Si₃ with interstitial additions // *Intermetallics*, **8**(8), pp. 937-943 (2000).
- [49] V.A. Neronov, M.A. Korchagin, V.V. Aleksandrov, S.N. Gusenko. Investigation of the interaction between boron and titanium // *J. Less Common Met.*, **82**(1-2), pp. 125-129 (1981).
- [50] V.V. Aleksandrov, M.A. Korchagin. Mechanism and macrokinetics of reactions accompanying the combustion of SHS systems // *Combust. Explos. Shock Waves*, **23**(5), pp. 557-564 (1987).
- [51] C. Iwamoto, K. Matsunga, T. Yamamoto, Y. Ikuhara. In situ HRTEM observations of the formation of reaction phases from liquid Ag-Cu-Ti alloy and SiC, Si and C substrates // *Nanotechnology*, **15**(6), pp. S398-S401 (2004).
- [52] R.A. Andrievskii, A.Zh. Dzneladze, L.N. Petrov, S.V. Yudin. Attritor milling of titanium carbide and titanium nitride produced by self-propagating high-temperature synthesis // *Sov. Powder Metall. Met. Ceram.*, **22**(11), pp. 867-869 (1983).
- [53] V.V. Ogorodnikov, Yu.I. Rogovoi. Calculation of the surface energies, energies of rupture and theoretical strength of cubic monocarbides // *Sov. Powder Metall. Met. Ceram.*, **15**(1), pp. 56-59 (1976).

І.Л. Шабалін¹, М.В. Лучка², Л.І. Шабалін³

Вакуум СВС в системі ІV групи перехідних металів для створення металокерамічних композицій

¹Салфордський університет, Інститут дослідження матеріалів, Великий Манчестер, Великобританія,
E-mail: I.Shabalin@salford.ac.uk

²Інститут проблем матеріалознавства НАН України ім. І.М. Францевича
вул. Кржижанівського, 3, м. Київ, 03142, Україна

³Російський державний професійно-педагогічний університет, Єкатеринбург, 620012, Росія

Розробка вакуумної версії високотемпературного синтезу, що сам поширюється (СВС), у сполуках 4 групи перехідних металів (тітан, цирконій, гафній) з неметалами (вуглець, бор, кремній), були досліджені за допомогою хімічного, денсиметричного, мікроскопічного і фазового рентгенівського XRD аналізу. Результати розгляду СВС із великою кількістю активованого вугілля підтверджують, що реакція карбідізації металу в цілому керує СВС. Зовнішній вигляд розплавленого квазі-евтектичного сплаву стимулює реакції, детально описані низкою рівнянь, які запропоновані в подібних дослідженнях уперше. Детальний аналіз СВС, що робить у потрібних Me-X₁-X₂ (Me = Ti, Zr-X₁, X₂ = C, B, Si) системах допускає можливість поширити механізм Корчагіна -Александрова - Гузенко на синтез горінням у таких системах. Будучи більш ефективною і доступною, чим інші версії вакуум СВС, може забезпечувати в широких межах концентрацій конфабуляцію керам-керамічних складних прекурсорів, заснованих на бескисневих вогнетривких сполуках перехідних металів 4 групи.

Ключові слова: самопоширюючийся високотемпературний синтез, дроблення, бориди, карбіди, силіциди.