Synthesis of materials with multiscale porosity from fine powders of boron, titanium, aluminum and coarse granules of VT6 alloy

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Abstract. The material with different-scale porosity was prepared from powder mixtures with significantly different particle sizes of components by the method of self-propagating high-temperature synthesis in the combustion mode. Model mixtures were formed from coarse particles of VT6 alloy previously coated with a layer of aluminum, and fine-fraction powders of titanium and boron. Synthesis in such a system took place in stages — the fine components were the first to enter into chemical interaction in the combustion wave, with the formation of a porous boride framework. A strongly exothermic reaction between titanium and boron provided the entry of coarse particles of the VT6 alloy with aluminum coating into the reaction. The melt of reacting components and formed intermetallic compounds impregnated the porous boride matrix. The stages of the synthesis are reflected in the thermograms of the combustion process. The EDS, SEM, and XRD data of the obtained material are consistent with the observed stages of the process. Up to four different scales in pore size are distinguished in the synthesis product.

1. Introduction
The aim of the study was to obtain a porous material by the method of self-propagating high-temperature synthesis (SHS) in one technological stage in the mixtures consisting of fine powders of titanium and boron with the addition of coarse spherical granules of titanium alloy VT6, previously clad with aluminum. In the model powder mixtures under study, the synthesis was possible without preheating, unlike the mixtures of Ti–Al and Ti–B systems with coarse titanium granules, which required for heating the compacts up to 1000°C [1]. The chemical reaction between the fine powders of titanium and boron, acting as a “chemical oven” [2, 3], allows to heat coarse clad granules of titanium alloy and their subsequent reaction. A wide range of particle dispersion of the metal components of the powder mixture, which melt with the combustion wave propagation, can provide a multiscale porosity of the resulting material: from macropores of several hundred microns to pores of submicron size. Stages in the course of the synthesis make it possible to obtain a product similar in structure to the composite material [3], since the fine pores of the boride matrix resulting from the chemical reaction between the fine components can be filled with a melt of the initial VT6 and aluminum as well as intermetallics resulted from the chemical reaction at the clad granule combustion.
2. Experimental

2.1. Preparation of model mixtures
Model mixtures from (Ti + 2B) and coarse clad granules of Ti(s) + Al alloy were prepared for the experiments. Black amorphous boron (99.8 wt %) with the particle size \(d_b = 0.2–6 \mu \text{m}\) was used as a nonmetal component in the mixtures. The metal components included Ti powder of the type PTS (average particle size \(d_t \approx 120 \mu \text{m}\), chemical impurities content in titanium (wt %): N – 0.08, C – 0.05, H – 0.35, Fe + Ni – 0.4, Si – 0.1, Cl – 0.004) and coarse mono-dispersed spherical granules of Ti(s) alloy clad with aluminum layer. Ti (s) granules obtained by the method of plasma spraying of a “rotating electrode” had the following characteristics: the specific surface area was 0.64 m\(^2\)/g; the average diameter was \(d_t = 290\pm30 \mu \text{m}\). The chemical composition corresponded to VT6 alloy (major elements (wt %): Ti – 86.45–90.9, Al – from 5.3 to 68, V – from 3.5 to 5.3). To obtain clad particles, the powder mixture of Ti(s) + Al (36 wt % aluminum powder ASD–4 and 64 wt % VT6 alloy granules) was pressed into billets (up to a relative density of 0.5), heated to \(\sim 700^\circ\text{C}\) in argon atmosphere, hold for 10 min and cooled. The billets were crushed into separate rounded forms of clad particles (Ti(s) + Al) with the coating thickness of \(\sim 20–30 \mu \text{m}\). The average particle diameter \(d_s = 320\pm30 \mu \text{m}\). The composition, element distribution and structure of particles are shown in figure 1.

A mixture of Ti(\(d_1\)) + 2B (69 wt % titanium and 31 wt % boron) was prepared from titanium Ti(\(d_1\)) and boron powders. Mixtures of \(a(\text{Ti}(s) + \text{Al}) + (1–a)(\text{Ti}(d_1) + 2\text{B})\) were formed from the mixture Ti(\(d_1\)) + 2B and clad particles (\(a\) is the mass fraction of the clad particles in the mixture).

![Figure 1.](image)

Figure 1. Structure and composition (wt %) (polished particles in Wood alloy): (a) distribution of elements (Ti and Al) near the transition zone; (b) composition in the layer (S1, S6, S7), transition zone (S2, S3), and particles (S4, S5).

2.2. Compaction of powder mixture
Cylindrical quartz glasses were filled with the green mixture by sequential portion packing of "thin" layers of the mixture [5]. The length of glasses were 43 mm, an inner diameter \(D = 4–4.4 \text{ mm}\) and an outer diameter \(D_o = 7.8 \text{ mm}\) (\(D/d_s > H, D/d_2 > H, D/d_2 > 1, D/d_2 \sim 13\), where \(H\) is the thin layer height). Each layer of the mixture was packed due to the momentum received from the impactor with
m = 684 g falling from the height h = 43 mm. The sample contained 19–23 layers. The height of each layer was 1200–1400 μm. The size of the portions contributed to the formation of fragments with ordered arrangement of clad granules in the layers [5]. Packing within the "thin" layers was achieved due to the movements and stacking of clad particles into denser and more ordered fragments without particle destruction. Boron (D \( d_b \sim 1000 \), \( d_2/d_b \sim 100 \)) and titanium particles Ti (\( d_{1} \)) (\( d_1/d_{d1} \sim 2.5 \), \( d_2/d_{d1} \sim 3 \)) served as an intermediate medium and "solid lubricant" for coarse-dispersed clad particles (Ti(s) + Al) and provided their arrangement.

2.3. Synthesis and measurements
The synthesis proceeded in argon atmosphere (at 1 atm) [3]. The quartz glass and the plugs at its ends prevented the change in the dimensions of the sample. The temperature in the synthesis wave was determined using tungsten–rhenium thermocouples (type A, the diameter of the junction with the protective layer of 0.25–0.35 mm), a QMBox 4050–8–1 temperature recorder and a PC ASUS–A52J. The combustion wave propagation was recorded using Sony HDR–CX130E. Electron microscopy was carried out using a field-emission SEM LEO 1450 VP Carl Zeiss.

3. Results and discussion

3.1. Combustion of pressed samples and stage-character of the synthesis
The synthesis in the samples from mixtures of \( a(Ti(s) + Al) + (1–a)(Ti(d1) + 2B) \) proceeded in the combustion mode at \( a \leq 0.6 \) with the initial temperature \( T_0 = 20°C \). At \( a \geq 0.6 \) the samples did not burn. The average combustion rate (\( u \)) decreased by 3 times from 5 cm/s at \( a = 0 \) to 1.5 cm/s at \( a = 0.5 \). With an increase in \( a \), the maximum temperature \( T_b \) in the combustion wave decreased from 2260°C at \( a = 0 \) to 1515°C at \( a = 0.5 \) (figure 2).

![Figure 2. Dependence of maximum temperature in the combustion wave on \( a \).](image)

Peculiar jumps were observed on the thermograms \( T_b = f (t) \), which are related to the stage-character of the synthesis process [3]. The thickness of interlayers of Ti(\( d1 \)) + 2B mixture between the titanium clad particles are 100–200 μm. In the heating zone, the titanium particles of the dendritic structure and, in particular, the finest particles (the particle fraction smaller than 40 μm in the Ti (\( d1 \)) composition is \( \sim 30 \) mass %) undergo the fastest heating. In thin (up to \( \sim 150 \) μm) samples, in the form of a Ti + 2B mixture placed between the flat walls, the propagation of the combustion wave is possible, moreover, with high combustion rates [6]. This circumstance explains the observed combustion of Ti (\( d1 \)) + 2B) mixture in the interlayers between the clad particles in a single transverse monolayer. The burning mixture of Ti(\( d1 \)) + 2B acts as a "chemical oven" and leads to heating of clad particles, melting of aluminum coating and Ti (s) granules and their mutual reaction. The resulting melt penetrates into the surrounding boride layer.
3.2. Macro, micro and porous structure of the product

The synthesis product has a developed porous structure (depending on \( a \)) and the total porosity of \( \sim 45\text{–}60\% \); the closed porosity being 1–5\% (figure 3). With an increase in \( a \), the total porosity decreases and the closed porosity increases.

![Figure 3. Structure consisting of (a) macropores \((a = 0.4,\) polished section) and (b) macropore \((a = 0.2,\) cleavage); cleavage structure near (c) medium size pores and (d) macropores.](image)

Four types of the pore size are distinguished (figure 3). Coarse spherical macropores \((\sim 300\text{–}350\ \mu m\) in diameter, figure 3a) connected with each other by capillaries; they appeared in place of clad particles as a result of capillary spreading of the melt from the granules to the pores of boride matrix; the spatial location of the macropores inherits the elements of order in the structure of the granules arrangement. Pores of irregular shape of medium size \((\sim 10\text{–}120\ \mu m)\) appeared in place of Ti\((d1)\) particles after melting and spreading of the melt into the surrounding boron at combustion of Ti\((d1)+2B\) interlayers [7, 8]. Small round pores \((\sim 1\text{–}5\ \mu m\) in diameter) appeared in the interaction stage of the finest titanium particles Ti\((s) + Al\) into the boride matrix, the fine pores are partially filled with aluminum and titanium aluminides, VT6 alloy [9]. Pores of submicron size \((< 1\ \mu m)\) appeared during phase formation and located between the grains or were captured by the growing faces of crystalline boride grains.

The microstructure of the material around the macropores changes with an increase in the parameter \( a \) from fine-grained with \( a = 0.2 \) to coarse-grained with \( a > 0.4 \). At low values of \( a \), the melt after melting of the clad particles completely flowed by the capillaries of the matrix, as a result, the granular structures of the matrix are clearly visible on the surface of the macropores and pores of the medium size (figures 3c and 3d). When \( a = 0.5 \), the specific fraction of the melt from the clad granules increases and, after capillary spreading, its excess remains inside the macropores. In this case, the structure of the matrix on the surface of the macropores becomes poorly distinguished under a thin
layer of intermetallics. At $a = 0.5$, elongated crystallites are seen in the near-surface ($\sim 10 \, \mu\text{m}$) layer in the structure of the boride matrix, while micron and submicron size crystallites ($\sim 200–1000 \, \text{nm}$) are observed far from the macropores.

The phase composition of the synthesis product and the distribution of elements in different sections of the sample correspond to the staged nature of the process occurring in the synthesis wave (figures 4 and 5). Dark gray fragments correspond to an increased content of boron and titanium (points $S_2$ and $S_3$ in figure 4b and points $S_1–S_3$ in figure 5), TiB$_2$ and TiB phase (according to XRD analysis). In light gray interlayers (0.3–0.6 $\mu$m) around the grains of the dark gray phase (0.5–1.5 $\mu$m) and in larger light gray fragments (1–15 $\mu$m), an increased content of aluminum, titanium and vanadium is determined, (points $S_1$ and $S_4$, figure 4b). These fragments appeared as a result of the reaction in the clad granules and the penetration of the melt into the pores of the boride matrix. The composition in them is close to that of the original alloy VT6 and titanium aluminides (Ti$_3$Al and TiAl – according to XRD). The presence of aluminum in the absence of vanadium in the dark gray fragments (points $S_2$ and $S_3$, figure 4b) is associated with filling part of the fine pores of the matrix only with aluminum melt from the cladding layer. The distribution of elements between macropores (figure 4a) indicates the spreading of the melt into the matrix at a distance of more than 70 $\mu$m.

The synthesis product contains TiB$_2$, TiAl, Ti$_3$Al phases and a relatively small amount of TiB.

**Figure 4.** (a) Microstructure of product and element distribution along the line, and (b) composition in points (wt %), $a = 0.5$.

**Figure 5.** Microstructure and composition in points, $a = 0.2$ (wt %).
4. Conclusion
The purposeful selection of the components of the powder mixture according to the quality and dispersion composition, and sequential portion packing make it possible:
- to carry out the synthesis in the system with large components without preheating due to the stage nature of the process – one part of the mixture (of fine powders of boron and titanium) reacts in the combustion mode with a high temperature and high thermal effect, forms a porous refractory product – a boride matrix; at the same time, this mixture acts as a “chemical oven” for the inert and slightly exothermic part of the mixture – aluminum – clad granules of VT6 alloy, which react to form intermetallic compounds, filling the matrix pores with the melt;
- to obtain a porous product with developed multiscale porosity and characteristic fragmentarily ordered structure with coarse spherical pores.

The structure of the synthesized refractory product is a porous diboride matrix partially filled with titanium aluminides.

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