Investigation of SHS-products in titanium and carbon powder mixtures with excess of titanium content

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Abstract. The products of self-propagating high-temperature synthesis (SHS) in the reaction mixtures of titanium and carbon (carbon black) containing an excess of titanium content with the purpose of obtaining composite “titanium carbide–titanium binder” powders from the synthesis products were studied by X-ray diffraction analysis, optical and scanning electron microscopy. Based on the results of the investigation of the phase and elemental composition of SHS powders synthesized in argon, the formation of non-stoichiometric titanium carbide has been established which led to a decrease in the content of the titanium binder in composite powders in comparison with the target values. The results of the study of the morphology and structure dependencies of the carbide phase in composite powders on the content of titanium in reactive mixtures have been discussed in conjunction with the results of the determination of the thermo-kinetic characteristics of SHS in the wave combustion mode.

1. Introduction
Composite materials and coatings with the structure consisted of disperse solid particles enclosed into a metal matrix (binder) are well-known to have a unique combination of hardness, strength, elasticity and wear resistance under abrasive wear and in tribological conjunctions [1, 2]. A specific example of such materials is tool hard alloys produced by sintering of disperse carbides and metal binder powder mixtures [3]. Moreover, the physical and mechanical properties and durability of composite materials are better-known to be primarily determined by the structure [3-5] (volume fraction, dispersion, and morphology of the strengthening phase).

To increase the wear resistance of parts under intensive wear, coatings deposited on the surfaces by cladding or sputtering are widely used [6-12]. In the majority of implemented technologies, to clad or sputter a coating, commercial iron- and nickel base powders are used. The main dopants in these powders are boron and silicon that reduce the melting temperature of the alloys and enhance the flowability. Under crystallization, these elements form solid silicides and borides inclusions, the presence of which in the coating metal basis ensures increased wear resistance. However, the crystallization origin of these inclusions does not allow to form the optimal morphology and dispersity of the strengthening phases in the composite coating structure.

A specific practical interest is drawn by wear-resistant coatings on titanium alloys that are widely used in aerospace industry. The titanium alloys are known to have low wear resistance due to seizure effect in tribological conjunctions with almost any metallic material [13]. The thickness of coatings
deposited on the surface of titanium and titanium alloys by nitriding, chromium coating, nickel-plating, vacuum arc discharge and magnetron deposition is too small to ensure the necessary lifetime of the coated parts. In addition, for the majority of said methods, there is the problem of adhesion, i.e. reliable bonding of the coating with the substrate.

To produce thick wear resistant coatings, powder cladding is used. The composition of the powder additives is selected to produce a coating with the structure of matrix composite composed of dispersed hard refractory particles (carbides, borides, silicides) imbedded into the titanium matrix. Titanium carbide in the titanium-based metal-matrix composites draws the largest interest as a hard and refractory strengthening phase. To clad TiC-Ti composite coatings, mechanical mixtures of titanium, titanium carbide or graphite powders in different combinations are used [6, 14-17]. Almost in all afore-described methods of laser and electron-beam cladding, the particles of titanium carbide precipitate from liquid titanium-carbon solution in the crystallization process during cool down. In this connection, the morphology, dispersity and volume fraction of carbide inclusions in the structure of metal-matrix composite is very difficult to control. This control problem of the cladded coating structure is easily solved by using “Ti-C–titanium binder” composite powders with predetermined characteristics of the structure. It is necessary to select such technological regimes of cladding that presume no overheating of powder granules resulting dissolution of carbide inclusions in the melt. In addition, these composites can be used as starting materials in the MAX-phase synthesis reaction [18-20], followed by the preparation of MXenes [21-23].

Studies the structure and phase composition of composite powders produced by self-propagating high-temperature synthesis (SHS) [24, 25] in powder mixtures of titanium and black carbon was carried out in the present work. The thermodynamics and macrokinetics of SHS in powder mixtures of titanium and carbon are investigated in details elsewhere [26]. Synthesis products in powder mixtures of titanium and carbon in a wide range of the components concentrations are studied in [27]. The work has established the non-stoichiometry of the titanium carbide composition (according to the equilibrium diagram of titanium and carbon [28]) and has studied the dependence of the reaction rate on the C/Ti ratio of the components in reaction mixtures. It was also established that the ultimate value of C/Ti strongly depends on the specimen diameter in the range from 12 to 20 mm. In this connection, along with the study of synthesis products, a goal of our work was to determine the concentration limits of steady wave mode combustion (ultimate content of titanium in reaction mixtures) in large-diameter compacts that were used to produce powders for coating deposition. Another goal was to determine a real content of the titanium binder in composite powders produced by the synthesis.

### 2. Experimental

A composite powders with target binder content from 30 to 60 vol.% were synthesized in the wave combustion mode. The synthesis was carried out in cylindrical compacts of 34 and 57 mm diameter and 200 and 400 grams respectively. Starting powders are titanium (<160 μm) and carbon black (1 μm). The reaction mixtures were prepared by dry mixing of powder charges in a drum tumbler for 4 hours. To accelerate the mixing, steel strips were added into the tumbler. After mixing, powder charges were pressed in cylindrical press form. The pressure was chosen to get 40-45% initial porosity of the compacts. Table 1 shows four powder compositions used for SHS without preliminary mechanical activation of the reaction mixtures.

The combustion was initiated by heating of an igniting pellet by molybdenum wire coil. On the periphery of the compact, which had the diameter bigger than that of the igniting pellet, the igniting powder mixture was put above the compact to increase the initiating heat impulse and to make the shape of the reaction front plainer. Two different modes of the synthesis had been applied: synthesis in argon under 0.5 atm. excess pressure with a consequent slow cool down in the reactor, and air synthesis with following fast cool down in water. The goal was to investigate the effect of cooldown rate on the SHS product structure and elemental composition. It was presumed that during the synthesis in the air, there is no appreciable interaction of hot product with atmospheric gases over the several seconds from the reaction initiation until the cooldown in water. This assumption was made on the basis of the well-known effect of gas emission in the vicinity of the reaction front [30]. A pressure
growth due to the gas emission might prevent atmospheric gases penetration from outer surface to inside of the porous SHS product body.

| Elemental composition of the reaction mixtures [mass. %] | Target phase composition of SHS products | Actual phase composition [%] | $a$ [nm] | $X$ [29] |
|---------------------------------------------------------|------------------------------------------|-----------------------------|---------|---------|
| Ti 85.66 14.34                                         | TiC+30 vol.%Ti                           | 100                         | -*      | 0.4320  | 0.69   |
| 87.58 12.42                                           | TiC+40 vol.%Ti                           | 9.5                         | 4.5     | 0.4310  | 0.58   |
| 89.56 10.44                                           | TiC+50 vol.%Ti                           | 93.5                        | 6.5     | 0.4302  | 0.50   |
| 91.58 8.42                                            | TiC+60 vol.%Ti                           | 75.4                        | 24.6    | 0.4299  | < 0.50 |

* Calculated under the assumption of the equiatomic carbide formation

Finally, SHS-products were ground and size of particles was graded. The synthesis products were studied at Nanotech Common Use Center of ISPMS SB RAS by XRD analysis (DRON-7 Burevestnik diffractometer, Russia), optical metallography (AXIOVERT-200MAT, Zeiss, Germany) and scanning electron microscopy (EVO 50, Zeiss, Germany).

3. Results

Figure 1 illustrates morphology of composite powders with $<50 \mu m$ dispersity produced by a screening of the crashed SHS products synthesized in argon from reaction mixtures with different titanium content.

![Figure 1](image1)

**Figure 1.** Morphology of SHS products synthesized in argon with different target (actual) titanium binder content (vol.%): a) – 30 (0); b) – 40 (4.5); c) – 50 (6.5); d) – 60 (24.6).
According to the XRD data the real content of titanium binder calculated using the sum of X-ray reflections intensities in all SHS products is significantly less than that estimated under the assumption of the equiatomic titanium carbide formation (tables 1 and 2). Tables 1 and 2 include also the stoichiometric coefficient $X$ values in $\text{TiC}_X$ formula calculated from the lattice parameter and known dependencies [29] of the lattice parameter on carbon content in the carbide. Titanium reflections are absent at all on the X-ray patterns of the argon synthesized product with 20 vol.% target binder content (table 1).

Table 2. Phase content of air synthesized SHS products, lattice parameter and stoichiometric coefficients of titanium carbide and oxycarbide.

| Target phase composition | Actual phase content, % | $a$ [nm] | Stoichiometric coefficient $X$ [29] |
|-------------------------|-------------------------|----------|----------------------------------|
| TiC+30 vol %Ti          | 91.3                    | 8.7      | 0.4308                           | 0.56 |
| TiC+40 vol %Ti          | 91.3                    | 8.7      | 0.4301                           | < 0.50 |
| TiC+50 vol %Ti          | 95.3                    | 4.7      | 0.4292                           | < 0.50 |
| TiC+60 vol %Ti          | 74.4 23.2               | 2.4      | 0.4311                           | 0.58 |

Figure 2. Structure of TiC-Ti SHS composite powders: Ar synthesized (a, c) and air synthesized with following quenching in water (b, d). Target (actual) content of titanium binder [vol. %]: (a, b) – 50 (6.5); (c, d) – 60 (24.6).

Titanium reflections are present only at the X-ray patterns of synthesized powders with the target content of titanium binder of 60 vol.%. In addition, it was established that in all cases, the titanium carbide lattice parameter is appreciably less than the known value of 0.4329 nm for the equiatomic
carbide [31]. The obtained dependence of the lattice parameter on the composition of reaction mixtures corresponds with results presented in [32, 33]. To clarify the issue of a possible dependence of the dispersity and morphology of the carbide phase on the cool down rate of synthesis products (quenching in water and slow cooldown in the reactor), an optical metallography was used to study the structure of the powders embedded into epoxy resin (figure 2).

The metallographic specimens of satisfactory quality were obtained only for the powders containing titanium binder. In terms of the structures presented in, we can conclude that the cooldown rate after the synthesis do not effect on the structure of synthesis products. The powder not containing titanium binder (figure 1a) represents crystalline aggregates of carbide grains or separate large particles. The structure of SHS products containing titanium binder (figures 1b, 1c and 1d) is more dispersed one.

For air synthesized SHS products, along with nonstoichiometry, there is one more implausible reason for decreased carbide lattice parameter: the introduction of atoms of atmosphere gases (oxygen and nitrogen) into the carbide lattice with the formation of oxycarbide or carbonitride. The cubic lattice parameter of these complex compounds is considerably smaller than the lattice parameter of equiatomic titanium carbide [32-36].

According to the XRD analysis results, the air synthesized SHS products contain titanium dioxide (table 2). The presence of titanium dioxide in the air synthesized products is the additional confirmation of possible titanium oxycarbide formation. However, the assumption on the substitution of vacancies in titanium carbide lattice by oxygen and nitrogen atoms cannot be confirmed or denied only on the basis of diffraction studies due to the coincidence of lattice parameters of nonstoichiometric titanium carbide and oxycarbides.

4. Conclusion

In the powder mixtures of titanium and carbon - containing titanium excess (as compared to the amount necessary to produce titanium carbide of equiatomic composition), nonstoichiometric TiCx titanium carbide forms during SHS. The value of stoichiometric coefficient X decreases with the increase in titanium content in reaction mixtures up to X=0.5 at the limit of concentration interval of stable wave mode combustion. Changing the titanium content in reaction mixtures allows to control the average particle size of the carbide phase in the SHS products. At a large content of titanium powder in the reactive mixtures, the SHS product structure consist of dispersed carbide particles imbedded into titanium matrix. During the air synthesis, a partial oxidation of synthesis products occurs with the formation of titanium dioxide in the form of dispersed particles and oxygen dissolution in the surface layer of the titanium carbide crystals. No oxygen dissolution in an α-Ti binder of the synthesis products has been detected.

Acknowledgements

The research was supported by Russian Scientific Foundation (project No. 17-19-01425).

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