

## HIGHLY DISPERSED TITANIUM CARBIDE OBTAINED BY MECHANICAL ACTIVATION

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The products of the mechanochemical interaction in the system Ti – C held in the high energy planetary ball mill were studied by the methods of diffraction with synchrotron radiation (quantum energy 33.7 keV) and of the high-resolution scanning electron microscopy. The reasonable assumption was made about the mechanism of mechanochemically induced reactions in this system. The interaction proceeds with the formation of mechano-composites Ti/C at the first stage, followed by melting of titanium, spreading it over the carbon particle surface and practically simultaneous crystallization of titanium carbide. The use of the activator allows to accelerate the process of the TiC formation significantly.

### Introduction

The titanium carbides are widely used in various industries due to their high refractoriness, hardness, heat resistance, conductivity, a low evaporation rate, etc. Tools from alloys based on titanium carbide can withstand changing speeds in a wider range compared with alloys based on WC or ceramics. Hard alloys based on titanium carbide are promising materials for the manufacturing of structural parts (bearings, seals, etc.) of the friction units operating at temperatures up to 1100 °C.

A large group of materials based on titanium carbide are carbide-containing steels, whose properties and appointment are intermediate between fast-cutting steels and hard alloys.

Carbide-containing steels in some cases are superior to hard alloys for wear resistance, thermo stability and plasticity. This class of materials has the lowest friction coefficient in comparison with any wear-resistant materials used in industry.

Carbide-containing steels well proved themselves in various industries, including automotive and aviation. High wear resistance of this material can be used successfully for the manufacture of machine parts [1].

The one of the most promising methods of obtaining highly dispersed powders is the mechanochemical synthesis in high-energy systems [2] or the interaction between solid and liquid metals [3].

The studies of the mechanism of the mechanochemical reactions with a large exothermal effect are difficult because the most part carried out in steel drums in the planetary regime with high rotation speeds of the drums around a common, and around their own axes. For this reason, there used the results of a classic study of SHS processes for understanding the mechanism, for example, in the system titanium – carbon [4-9].

The combustion temperature in the adiabatic conditions is  $\sim 3000$  K, the melting point of titanium and carbon – 1940 and 4300 K, respectively, so that the titanium melts and spreads over the surface of the carbon due to the good wettability.

The appearance of liquid metal sharply reduces the strength characteristics of the solid phase [10]. The contact surface area between them increases by several orders of magnitude, compared with solid-phase interactions [11] due to the dispersion of a solid-phase component and the spreading of liquid metal on its surface [12].

Electron microscopic studies have shown that the chemical interaction between the reagents begins simultaneously with the appearance of the molten metal, which penetrates into the layer of highly dispersed carbon (“capillary spreading”) [6]. It is shown for the system Ti – C that the mechanical action significantly affected on the intensity of dispersion of the solid components in the presence liquid metal [13]. This is due to the fact that the contact surface is increased not only by the solid phase grinding. Because of the friction the reaction product is removed from the contact surface, whereby the liquid metal again contacts with a fresh solid surface and produce a new layer of the reaction product [14].

The combination of factors such as high energy of the systems, melting and mechanical activation of solid and liquid phases allows to provide a high speed of chemical interaction.

The authors [15, 16] performed synthesis of TiC in a quartz reactor of vibration mill with high-speed video recording and two high-speed infrared thermocouples. The thermograms of a mixture of carbon and titanium (50:50 at. %) show that the activation time up to a sharp temperature rise is 600 min under these conditions. Then the reaction occurs spontaneously, and very high temperatures are reached equal to the adiabatic. Direct study of the process showed that it was initiated

locally and started inside the powder particles. Combustion reaction is propagated by a chain mechanism and lasts less than a second. The overall process kinetics is controlled by the molten phase.

It can be assumed that the time during which the mechanocomposite Ti/C is formed, and a time of reaching of the titanium melting temperature essentially depend on the mode of mechanical activation.

The purpose of this work was to study the dynamics, morphological, structural and phase transformations in the system Ti – C (50:50 at. %) in a high-energy planetary ball mill.

### **Experimental**

We used powders of titanium grade PTOM and lamp black PM-15. The Ti/C mechanocomposites and titanium carbide ultra fine powders were obtained in high-energy ball planetary mill AGO-2 with water cooling, in inert atmosphere (argon). Drum volume is 250 cm<sup>3</sup>, the balls diameter is 5 mm, load is 200 g, the weighed of treated sample is 10 g, the rotation speed of the drums around a common axis is ~1000 rpm [18]. Diffraction studies of the structure of the obtained samples were carried out using synchrotron radiation (quantum energy 33.7 Kev). The study of morphological characteristics of the obtained samples was performed using scanning electron microscope (SEM): high resolution Oxford Instruments, (England); scanning electron microscope Hitachi TM-1000, accelerating voltage of 15 kV.

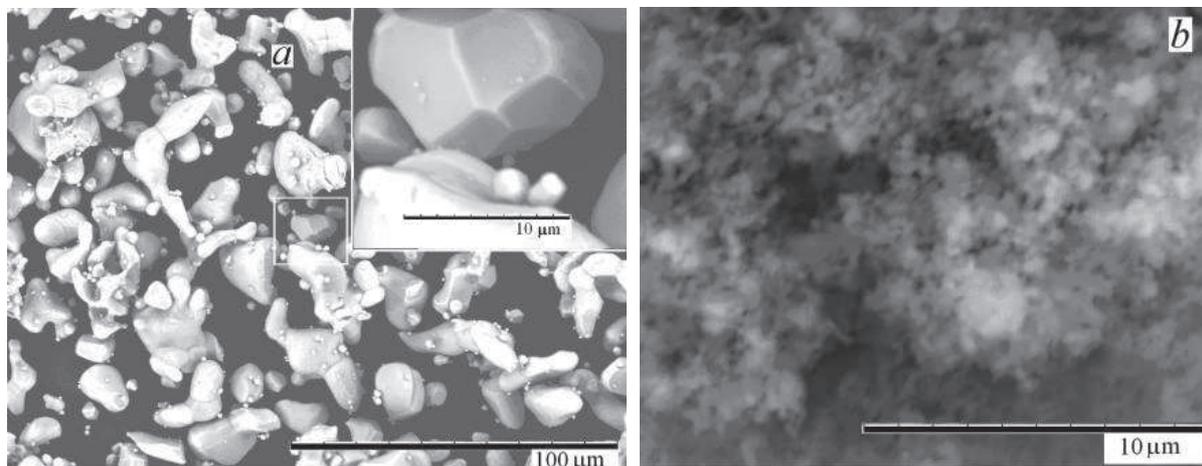
### **Results and discussion**

According to the equilibrium diagram of the system Ti – C [20] the only compound, namely titanium carbide TiC having a very wide region of homogeneity, formed in this system. Non-stoichiometric insertion compounds are formed, if the atomic radii of the metal and nonmetal  $R_{Me}$  and  $R_X$  satisfy the Hagg's condition:  $0.41 < R_X/R_{Me} < 0.59$ , while nonmetal atoms occupy places in the largest interstices of the metal lattice [21]. So, for titanium and carbon  $R_C/R_{Ti} = 0.526$ , therefore, the titanium carbides are typical non-stoichiometric compounds of insertion. The area of homogeneous phase of TiC is from  $TiC_{0.48}$  to  $TiC_{1.0}$ , space group  $Fm\bar{3}m$ , type B1 structure (NaCl). For the composition  $TiC_{0.48}$  on the lower boundary of the homogeneity region of the carbon sublattice contains more than 50% structural vacancies [22].

The system Ti – C is high-energy: enthalpy  $\Delta H_{298 K} (TiC) = -209$  kJ/mol, Gibbs free energy,  $\Delta G_{298 K} (TiC) = -205$  kJ/mol [23].

The SEM images of the initial titanium and carbon powders are shown on Fig. 1. The titanium particles have a “crab” form mainly, with a relatively smooth surface, and a wide range of particle sizes from 0.2 to

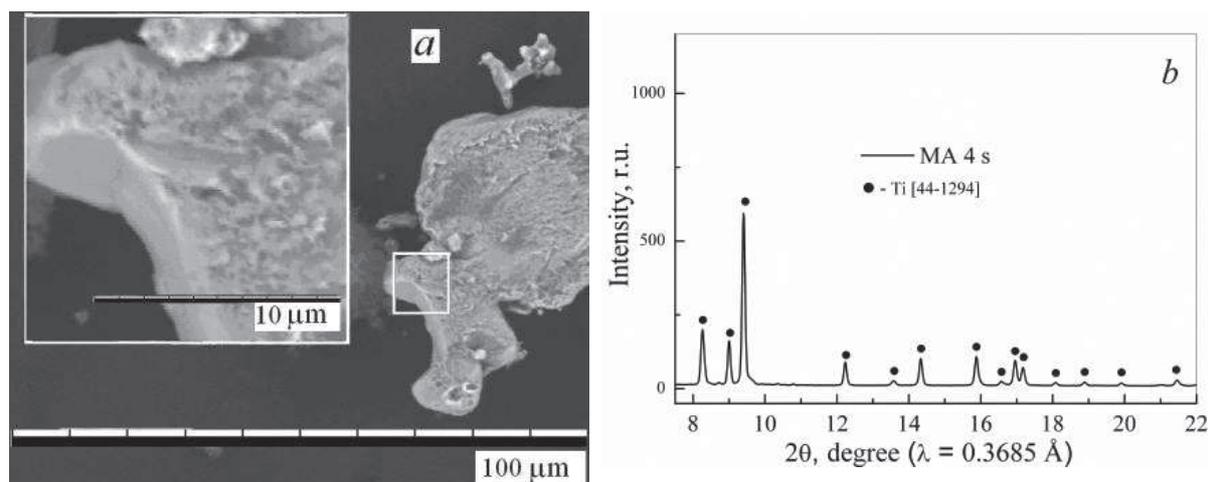
50 microns (Fig. 1a). Some particles are spherical, minor part of particles are crystalline. The agglomerates of carbon particles vary in shape and size, they consist of spherical particles predominantly, with dimensions of  $\leq 0.2 \mu\text{m}$  (Fig. 1b).



**Fig. 1.** SEM images of the initial powders of titanium (*a*) and carbon (*b*)

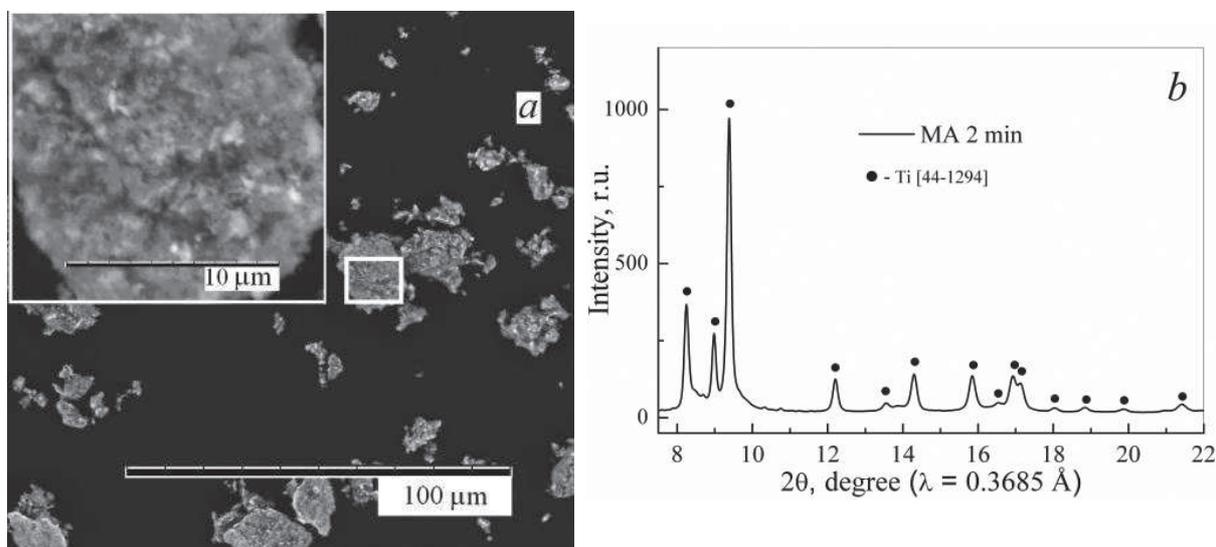
To obtain a mixture of titanium + carbon (50:50) a short-time mechanical activation (in a few seconds) was carried out, which does not significant change in the shape and size of titanium and carbon particles.

The surface of titanium particles becomes pitted and rough (Fig. 2a). The proportion of small particles increases. Apparent changes in the size and shape of carbon particles do not occur. The diffraction pattern of mixture activated for a few seconds shows the reflections of titanium only (Fig. 2b).



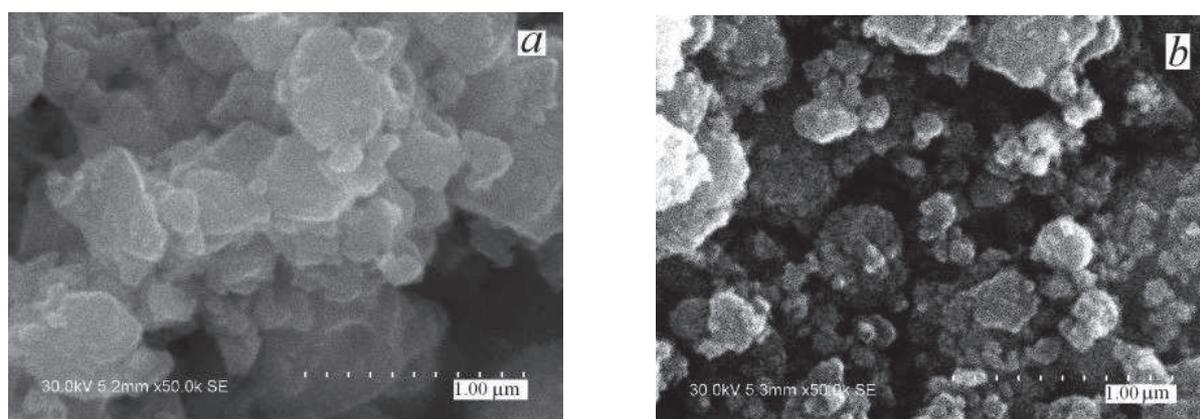
**Fig. 2.** SEM image (*a*) and diffraction pattern (*b*) of titanium and carbon mixture (50:50) after MA for 4 s

Further increase of activation time up to 2 min leads to decreasing in the size of agglomerates consisting of particles predominantly oval shape with dimensions of  $\sim 0.5 \mu\text{m}$  (Fig. 3a). On diffraction pattern the broadened reflections of titanium are recorded (Fig. 3b).

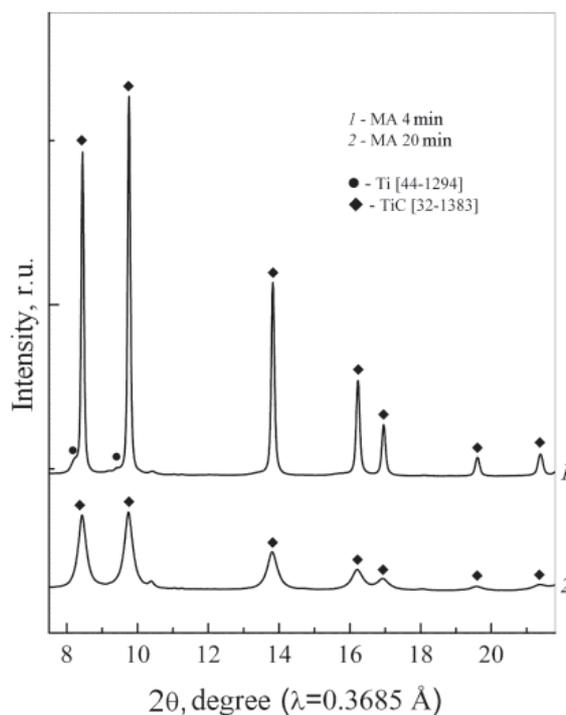


**Fig. 3.** SEM image (a) and diffraction pattern (b) of titanium and carbon mixture (50:50) after MA for 2 min

During mechanical activation for 4 min the aggregates consisting of crystalline particles with jagged edges and plate-like shape are formed (Fig. 4a). On the diffraction pattern of this mixture (Fig. 5, I) the intensive reflexes of titanium carbide and very weak intensive reflexes of residual minor amounts of titanium are registered.



**Fig. 4.** SEM images of a titanium and carbon mixture (50:50) after MA for 4 (a) and 20 min (b)



**Fig. 5.** The diffraction patterns of a titanium and carbon mixture (50:50) after MA for 4 (1) and 20 min (2)

The diffraction pattern of this type, with narrow and intense reflections, usually indicate a pre-melting of one of the phases and crystallization of the product from the melt [3], in this case, of the titanium carbide from the titanium melt. The increase of activation time up to 20 min leads to a significant increase in the proportion of titanium carbide particles with dimensions  $\leq 0.1 \text{ \mu m}$  (Fig. 4b). The only titanium carbide reflexes are shown at the diffraction pattern, the intensities are reduced significantly and the widths are increased, which is consistent with the decrease of particle size of titanium carbide (Fig. 5, 2).

Thus, the studies of mechanochemical interactions in the system titanium–carbon (50:50) in the proposed MA conditions showed that the melting of titanium started after the formation of mechanocomposite titanium/carbon. The titanium melt was spread on the carbon particle surface with simultaneous crystallization of TiC from titanium melt. The formation of TiC was completed for 4 min MA. Further mechanochemical activation led only to the size reduction of formed crystallites of titanium carbide.

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