Investigation of Ti/TiB₂ Composite Wear Resistance and Corrosion Resistance Coatings in Aggressive Medium and at Variable Temperatures

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Abstract. The present work investigates the influence of conditions like the climate of the Arctic shelf, such as aggressive medium, hydroabrasive wear and variable temperatures on Ti/TiB₂ composite coatings. The applicable composite powders were investigated with the use of thermogravimetric analysis. The values of corrosion resistance and wear resistance of the coatings were also investigated.

1. Introduction
Currently, the strategy of the Arctic zone development in various industries is actively implemented. One of the promising important issues is the development of materials applicable for the Arctic climate operation. The specifics of the Arctic climate is a prolonged effect of low temperatures on materials; a significant temperature difference during the whole year, especially in the continental zone (from -60°C to +40°C); strong winds; marine high humidity; icing and snow adhering; ice coverage of sea water; high solar radiation during polar days, etc. The combination of marked factors (e.g. moisture and low temperatures, zero transitions as a process of defrosting / freezing) [1].

At the moment, chemically homogeneous materials, including anthropogenic, practically exhausted their operational potential, and material science efforts are focused on creation of composite materials with advanced and synergistic properties with at least two different substances in the form of isolated phases [2-4].

Composites are manufactured from different chemical composition materials (polymers, metals, glass, ceramics, carbon and natural materials) with different morphology of components (powders, fibers, plates and more complex structures), and a wide range of their relations with mixed serviceability in created samples. Composites synergy enables not only to preserve characteristics of individual components, but also to form brand new additional properties.

Composite materials being used in the Arctic climate allow to develop such industries as: ice class sea-, or river-going ships, ice fleet; terrestrial and ice transport; mining and transportation of hydrocarbons and mineral raw materials, materials for mining engineering, and wind power plants.

In the presented work titanium powders and titanium diboride are used as starting materials for development of composite coatings to be operated in the Arctic zone. The usage of these components is determined by the ability of sprayed coatings to resist temperature differential from -60°C to +40°C, and retain hardness and wear resistance.
The objective of this study is to identify the serviceability of microplasma Ti/TiB₂ coatings [5-7] (with different titanium diboride content of 10%, 20% and 30%) for the Arctic climate. In order to study the corrosion resistance, the samples were exposed to variable temperatures from -60°C to +40°C with their coatings tested by synthesized sea water in alternating wetting [8]. Wear resistance shall be determined by the interaction of samples with composite coatings and with a pure steel sample [9, 10]. To study temperature dependence on formation of new phases a thermogravimetric analysis (TGA) will be carried out in homogenized and synthesized Ti/TiB₂ system powders.

2. Materials and experimental methods
For thermogravimetric analysis, homogenized compounds were used, in which the PTOM-1 titanium powders with a fraction of 2.5 to 40 μm were used and the A TiB₂ with a fraction of 0.5 to 4 μm. The synthesized composite powders obtained from homogenized titanium compounds and titaniumdiboride with a reinforcing component of 10%, 20% and 30% were also studied. The synthesis of powders was carried out by the volumetric reinforcement on the eraser with vibration-band bowl.

Thermogravimetric analysis was carried out using the thermal analytical system TGA/DSC-1/1600HF. TGA is a method for analyzing materials and substances based on the continuous registration of the dependence of the mass change on time and temperature. DSC (differential-thermal analysis) allows to identify and explore the phase transformations and chemical reactions occurring in a substance when heated and cooling, in thermal effects accompanying this change [11]. The study of powders was carried out in the temperature range from 25°C to 500°C at the heating rate of 20 K/min, in the air.

Experiments on the study of the corrosion resistance of the manufactured Ti/TiB₂ composite coatings were performed in the ESPEC SU-261 heat-cold climatic chamber. This chamber works in accordance with the system of balanced temperature control. The system balances the temperature so that the necessary conditions have been achieved in the testing zone. The limit range of exploited temperatures is in the zone from -60 °C to +150 °C.

Determination of wear resistance was carried out on special samples on the kinematic circuit diagram ring-ring (Figure 4) on friction testing machine 2168UFT. This refers to universal machines and allows you to experience various friction pairs with various characteristics of the movement in a wide range of speeds and loads, with the possibility of feeding into the zone of friction of lubricants.

3. Experimental results and discussion
During the TGA/DSC the studies of homogenized compounds and the synthesized Ti/TiB₂ powders, the nature of the mass change and phase transformations was studied depending on the temperature exposure, given in Figures 1 and 2.

Figure 1 shows that the most intense oxidation is observed in the synthesized powders with the content of the reinforcing component 20% and 30%.

On the shown curves in Figures 1 and 2 it can be selected in two sections. The left plot of graphics can be considered gentle. In Figure 1 in the right part of the schedule there is a sharp jump in a curve, which indicates the intensive increase in the mass. The weight gain for homogenized powders is in the range of 1.4 % to 2.6 %, and in 1.6 % synthesized to 3.9 %. The presented reaction begins to proceed when the temperature reaches the 490°C. An increase in the mass of the samples is due to oxidation.

On DSC-curves, Figure 2, there is an endothermic peak in the range of 320-360°C, which is formed as a result of the reaction of the solid-phase transformation of TiB₂ into TiB, i.e. TiB₂ is saturated with titanium. Upon reaching 490°C the heat flux increases. In samples of synthesized powders with a contents of titanium diboride 20% and 30%, an exothermic peak is observed in the right section of the DSC-curve.
As a result of the thermogravimetric analysis, it can be concluded that the appearance of titanium dioxide phase, which was determined in early work [12], was formed in the process of homogenized Ti/TiB$_2$ powders synthesizing by the volumetric reinforcement, when using a vibration-band bowl. The synthesis takes place in the bowls with internal working bodies in which the source material and air are present. The local / mechanical heating of the powder occurs, which causes the flow of the
reaction between titanium and oxygen. As a result of this interaction, the TiO$_2$ phase is formed, which positively affects the hardness of the sprayed coating.

To study coatings on corrosion resistance, 12 samples were prepared: 3 of them with coatings of Ti, 3 with TiB$_2$ (10%), 3 with TiB$_2$ (20%), and 3 with TiB$_2$ (30%). Accelerated laboratory tests that imitate the climatic effects of moisture and low temperatures, zero transition is the process of defrosting / freezing, consisted in the cyclic effects of temperatures from -60°C to +40°C and impregnating with synthetic sea water for 504 hours with a change of 21 cycles. The experiment results are presented in Table 1 and Figure 3.

### Table 1. Parameters of corrosion resistance researches.

| №  | Type of coating                  | Time of the experiment, h | Loss of mass, g |
|----|---------------------------------|---------------------------|-----------------|
| 1  | Ti                              | 168                       | 0.06            |
| 2  | Ti                              | 336                       | 0.13            |
| 3  | Ti                              | 504                       | 0.18            |
| 4  | Ti/TiB$_2$ (10%)                | 168                       | 0.06            |
| 5  | Ti/TiB$_2$ (10%)                | 336                       | 0.11            |
| 6  | Ti/TiB$_2$ (10%)                | 504                       | 0.15            |
| 7  | Ti/TiB$_2$ (20%)                | 168                       | 0.03            |
| 8  | Ti/TiB$_2$ (20%)                | 336                       | 0.08            |
| 9  | Ti/TiB$_2$ (20%)                | 504                       | 0.12            |
| 10 | Ti/TiB$_2$ (30%)                | 168                       | 0.02            |
| 11 | Ti/TiB$_2$ (30%)                | 336                       | 0.05            |
| 12 | Ti/TiB$_2$ (30%)                | 504                       | 0.09            |

According to the data presented, it can be argued that the coatings sprayed by the microplasma from the Ti/TiB$_2$ composite powder are not inferior to titanium by corrosive resistance.

It can be seen in Figure 3 that reddish shades are formed on the coatings. This suggests that during experiment as a result of slit corrosion, the substrate material was dissolved and the oxidation products were sedated on the coatings. The red color of corrosion products is peculiar to affect iron, as well as titanium corrosion products correspond to white color. The corrosion resistance of composite coatings can be assigned to completely persistent, since the corrosion rate was less than 0.001 mm per year.

For trimming tests according to the kinematic circuit diagram ring-ring (Figure 4), the following parameters were used: loading 0.5 MPa; rotation speed 100 rpm; time 5 hours. The sample without
coating was static, i.e. it was fixed during the experiment, and samples with coatings were in motion. During the whole experiment, the samples were wetted with water to prevent overheating. Tests results are presented in table 2.

| №  | Type               | Wear, g / km | Wear rate, g / h |
|----|--------------------|--------------|------------------|
| 1  | Pure steel         | 0.024538     | 0.011095         |
|    | Ti/TiB₂ (10%)     | 0.008397     | 0.003797         |
| 2  | Pure steel         | 0.011790     | 0.005331         |
|    | Ti/TiB₂ (20%)     | 0.004481     | 0.002026         |
| 3  | Pure steel         | 0.005438     | 0.002459         |
|    | Ti/TiB₂ (30%)     | 0.003176     | 0.001436         |

4. Conclusions
From the conducted research it follows that all the studied samples with the Ti/TiB₂ composite coating are less susceptible to wear compared to steel samples. With the titanium diboride content increase in the coating, the friction wear resistance increases.

According to the results of tests for wear resistance, it can be argued that composite coatings with a content of 30% titanium diboride are most effective under friction conditions.

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