Adhesion of AlCrN coating deposited on TiB$_2$/Ti composites sintered by SPS dedicated for high temperature tribological applications

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Abstract. The aim of the work was to investigate the adhesion of AlCrN coating deposited by PVD method on TiB$_2$/Ti composites manufactured by Spark Plasma Sintering (SPS). The composites were produced from three kinds of mixtures of powders: (1) Ti and TiB$_2$, (2) Ti6Al4V and TiB$_2$ and (3) Ti and B. Each of the mixtures was prepared at 50/50 wt. % ratio of components. Before the coating deposition the specimens were polished to obtain the surface roughness typically required for machine parts. For each set of specimens an individual surface preparation procedure was developed. The coating adhesion was measured using a scratch tester. The process of scratching was carried out to observe the characteristic moments of adhesive and cohesive failures. The highest critical loads were obtained for the coating deposited on composites produced from the mixture of two powders containing pure Ti and TiB$_2$.

1. Introduction
A vast amount of manufacturing processes takes place at high temperatures and depend on the durability and reliability of components capable to cope with this harsh environment [1]. The overall objective of the work is to extend the lifetime of components operating under relative motion at high temperatures (HT), in the range from 400 to 1000°C, by the development and application of novel lubrication concept based on the double-lubrication approach which relies on the design of innovative high temperature self-lubricating materials and lubricous multifunctional coatings [2]. To optimize the benefits achievable from coatings, it is vital to consider their implementation in the design stage [4, 5, 6]. The aim of this study was to select the input powder materials and methods of preparation for TiB$_2$/Ti ceramic-based bulk composites intended for PVD coatings deposition [7, 8]. One of the main factors enabling the successful application of PVD coating is the ability to remain attached to the substrate under required operating conditions. The adhesion between a coating and a substrate depends on many factors, among others on material structure and surface finishing, so in practice, it can be evaluated only in the experimental manner [9, 10]. So, the paper presents the results of research, aimed at the selection of the most suitable technology of TiB$_2$/Ti composites manufacturing and surface preparation for the deposition of the PVD coating.
2. Materials and Methods

2.1. TiB$_2$/Ti composites

Samples were designed to achieve target Ti-TiB composite with Ti/TiB = 15/85 wt.% in fully reacted state. Ceramic titanium diboride plays the role of the hard phase interconnected by metallic titanium. Target 15/85 weight ratio of Ti/TiB corresponds to Ti:B = 1.2167:1 molar ratio, hence, the raw powders resemble approximately 50/50 weight ratio for Ti/TiB$_2$ and Ti6Al4V/TiB$_2$ compositions (exact numbers are mentioned in Table 1). For powder preparation by self-propagating high-temperature synthesis method (SHS) the elemental titanium and boron powders were used, and the respective Ti/B ratio was calculated as 84.3/15.7 wt.%.

| Table 1. Samples preparation procedure | Powder development | SPS parameters |
|--------------------------------------|--------------------|----------------|
| Name                                 | Raw powders        | Preparation procedure | Pressure | Time | Temp. |
|                                      | Ti [wt.%] | Ti6Al4V | TiB$_2$ | B | t [min] | T [°C] |
| Group I                              | 50.33 | 49.67 | Conventional mixing | 50 | 15 | 1250 |
|                                      |          |        |          |      |      | 1450 |
| Group II                             | 52.3 | 47.7 | Disintegrator mixing | 50 | 15 | 1050 |
|                                      |          |        |          |      |      | 1150 |
|                                      |          |        |          |      |      | 1250 |
| Group III                            | 84.3 | 15.7 | SHS synthesis, disintegrator mixing | 50 | 15 | 1050 |
|                                      |          |        |          |      |      | 1150 |
|                                      |          |        |          |      |      | 1350 |

All samples are arrayed into three groups according to the different manufacturing strategies. Group I contains samples fabricated from the powder mixture prepared by the conventional rotative mixing of the pure titanium (99.98% purity) and titanium diboride (98.5% purity) raw powders. Powder development for samples listed in Group II was performed by the help of laboratory disintegrator milling system DSL-175, while titanium alloy (Ti6Al4V Grade 5) raw powder instead of pure titanium was used because of the spherical shape of particles.

Manufacturing routine for samples combined in Group III consists of two steps. Firstly titanium-boron mixture was used for combustion synthesis conducted in CPR3.5L constant pressure SHS reactor. Secondly, SHS product was broken into pieces by rolling mill and crushed to powder by disintegrator. The manufactured samples (discs) are presented in Figure 1. SEM images of developed powders are represented in Figure 2 (first row).

![Figure 1](image-url)

Figure 1. The sample (disc) made of TiB$_2$/Ti composite: a) a scheme, b) the state after sintering.
The developed powders were consolidated by spark plasma sintering (SPS) device (FCT Systeme GmbH, Germany) at 50 MPa pressure with the dwell time of 15 min, heating rate 100 Celsius per minute, applying different sintering temperatures, as mentioned in Table 1. Images of typical SPS produced samples of each group are shown in Figure 2 (second row).

**Figure 2.** SEM images of the developed powders (first row), and the prepared samples (second row).

### 2.2. Surface preparation

The samples preparation was divided into the following steps. The first step was to remove the post-sintering scale from the surfaces of the specimens and the preliminary examination of samples surface. The second step was to put the number on the side of each sample using laser engraving.

The third step was to adjust the thickness of the samples to the test requirements using a grinder equipped with a grinding wheel (1A1 200x20x5x51 D151 K75 MBm). As the selected grinding wheel is intended for sinters and carbides, it contains diamond particles with a grain size of 126-150 µm, at K75 concentration and a soft resin binder. During the process a cooling-cutting fluid was used.

All of the grinding processes were done at the linear speed of 35 m/s. The grinding time (approx. 1h needed for thickness reduction of 0.5 mm per side), was adjusted according to the samples surface quality and hardness.

After obtaining the required thickness, the samples were polished by means of ATM Saphir 550 automatic polisher using the procedure presented in the Table 2.

**Table 2.** Samples polishing procedure.

| Parameter                  | Stage 1 | Stage 2 | Stage 3 | Stage 4 |
|----------------------------|---------|---------|---------|---------|
| Polishing plate            | Blue disc | Silver disc | White cloth | Red cloth |
| Lubricant                  | Water | Bio Diamant | Bio Diamant | Bio Diamant |
| Diamond particle size [µm] | -     | 9       | 3       | 1       |
| Plate speed [rpm]          | 150** | 150**   | 150**   | 150**   |
| Head speed [rpm]           | 125*   | 125**   | 125**   | 125**   |
| Load per sample [N]        | 30     | 25      | 20      | 15      |
| Time [min]                 | 60     | 30      | 60      | 60      |

* * clock wise rotation direction, ** counterclockwise rotation direction
The given time is understood as a maximal required for the samples from the first group having the highest hardness, to reach the average roughness $Ra < 0.1 \, \mu m$.

2.3. Coating deposition

Nowadays, there is a wide range of either single layer coatings (e.g. TiN, CrN, ZrN, TiB$_2$), or multilayer coatings, with combined properties of several materials, pioneered by TiC/Al$_2$O$_3$/TiN, or multi-element coatings such as TiAIN, BCN, TiBCN, SiNC, AlCrN and TiAlYN-systems [11]. The modification of a coating composition leads to increase its area of application. The addition of Al to the TiN and CrN coatings results in increase in the wear resistance and thermal stability at temperatures up to 1000°C. For this study, from numerous coatings of interest, the widely available one was selected. The commercial coating AlCrN-based (BALINIT® ALCRONA PRO made by Oerlikon Balzers) was deposited on discs made of various types of TiB$_2$/Ti. The detailed deposition process parameters are not provided by the coating supplier. The selected coating exhibits excellent tribological characteristics at extremely high temperatures [12]. The chemical composition of the coating, measured by X-ray microprobe EDS, is summarized in Table 3, while the other properties can be found in Table 4.

### Table 3. The chemical composition of the coating (measured by EDS).

| Coating name | Chemical composition [at. %] |
|--------------|-------------------------------|
|              | Al   | Cr   | N    |
| AlCrN        | 36.9±0.2 | 39.1±0.2 | 21.2±0.3 |

### Table 4. The properties of the selected coating (manufacturer data).

| Parameter                              | Value |
|----------------------------------------|-------|
| Maximum work temp. [°C]                | 1100  |
| Hardness Hv (0.05)                     | 3200  |
| Residual compressive stress [GPa]      | -3    |
| Thickness (calo-test) [µm]             | 1.2–1.3 |

The coating was deposited on a flat surface of the discs (samples) manufactured according to technology described in section 2.1 and finished following procedure presented in section 2.2.

2.4. Adhesion measurement

Adhesion of AlCrN coating was measured by means of the scratch-test method using REVETEST Scratch-Tester, manufactured by Anton Paar. A Rockwell C type indenter with the angle of 120° and tip radius of 0.2 mm was used. The following test parameters were applied: maximum force of 100 N, progressive load from 0 to 100 N, incremental load rate of 10 N/mm, 10 mm/min scratch speed, and 10 mm scratch length. The values of the critical load $L_c$, causing characteristic damage of the coating, were determined through the analysis of the tangential force (Ft) and changes in the level of acoustic signal emission (AE), as well as optical observation of the scratch.

3. Results and discussion

3.1. Surface characteristics

The aim of the polishing process was to obtain a sample surface without extreme irregularities. For composite materials the surface preparation is much more complex than it is for steel alloys because of the presence of at least two phases of different mechanical properties and high porosity. There is no exact values of roughness parameters required by PVD technology, but it is obvious that the surface character has a strong influence on the performance of the coating-substrate systems. The finishing process was performed using the procedure described in section 2.2. The values of $R_a$ parameter for each group of the samples are summarized in Figure 3.
Figure 3. The average roughness of the polished samples (without coating).

The roughest surfaces, with the Ra values, even 10-fold higher than in other cases were obtained for the composite material of group II. The high roughness of samples from group II resulted from a numerous pores present in the surface, which are visible in 2D profiles measured using stylus profilometry – Figure 4. It was observed that sintering temperature affected the structure of the composite and in consequence the surface roughness. In most cases (group I and II) the increase in temperature caused the decrease in final surface roughness. The maximum depth of pores for the samples of group I is c.a. 2.5 µm, of group III is c.a. 1.5 µm, while for group II it reaches more than 30 µm.

Figure 4. 2D profiles of the composite surfaces after polishing process.

The distribution of phases present in the surface is shown in Figure 5. The composite surface is not homogeneous, thus it can be expected that the adhesion between the coating and the substrate may vary depending on the particular phase present on the surface.
Because of the porosity and the difference in particular phases mechanical properties it is very difficult to receive a surface which would be smoother than the obtained one. The continuation of the polishing process leads not only to flattening the existing asperities, but also opens the new holes, which is well visible in 3D images presented in Figure 6, especially for the composites from group I and II.

3.2. Coating adhesion

The scratch test was used to assess the thin coating adhesion to the substrates. Some of the types of failures depend on adhesion i.e. failure at the coating-substrate interface. Others depend on plastic deformation and fracture within the coating. There is no unique critical load defining the adhesion of a coating. So, for each coating three critical loads were determined: Lc1, Lc2 and Lc3. The typical failure for Lc1 was brittle tensile cracking. It is assumed that Lc1 critical load is considered to be a resistance to crack initiation. Lc2 represents the load at which first signs of chipping and delamination is visible on the scratch. When a gross spallation or a substrate exposure takes place the Lc3 critical load is reached. The critical loads measured for each coating-substrate system are presented in Figure 7.

The highest values of critical loads were obtained for the samples with the coating deposited on materials of group I - samples fabricated from the powder mixture prepared by the conventional rotative mixing of the pure titanium and titanium diboride raw powders. The first brittle cracks were found at loads a bit above 30 N, the partial delamination in the range of 36-40 N, and exposure of the substrate (total removal of the coatings) at loads slightly above 75 N.

For the samples of group II it turned out to be impossible in most cases to measure the critical loads. Extremally rough surface caused that the first symptoms of coating failure were hidden in the background of numerous surface defects and pores of the composite. The total exposure of the substrate took place for loads of about 20 N. Because of the difficulty of precise determination of the critical loads and their low values, Lc1 and Lc2 for samples of group II were not presented in Figure 7.
Figure 7. Scratch test results of AlCrN coating: Lc1 (brittle cracking), Lc2 (chipping, delamination), Lc3 (gross spallation, exposure of substrate).

For the coating deposited on substrate of group III, - samples produced from the powder mixture of pure titanium and boride powders the first brittle cracking was determined at the loads much lower than in the case of the group I samples. In case of the coated samples of group III, the first brittle cracking was observed at approx. 15 N, partial delamination below 40 N, and exposure of the substrate (total removal of the coatings) at the loads between 60 and 75 N.

The micrographs of the scratches on the coated samples from group I, at the Lc1, Lc2 and Lc3, are presented in Figure 8.

Figure 8. Evolution of the coating failure during the scratch test – Group I substrate, sintering temperature a) 1250°C, b) 1450°C.

The increase of sintering temperature from 1250 to 1450°C lead to increase of the adhesion of the AlCrN coating. Lc1 and Lc2 critical loads were higher for higher temperature, but the point the coating
total removal was not changed. So, there can be clearly observed a dependence between sintering temperature and coating resistance to brittle cracking.

Evolution of the coating failure during the scratch test on the coating deposited on samples from group II is presented in Figure 9. Because of high roughness and porosity of the substrate it was not possible to perform precise estimation of the Lc1 and Lc2 critical loads. The group II composites requires further optimization, in the direction of obtaining a less porous bulk material, which would make it possible to investigate the aspect of coating-substrate adhesion.

![Figure 9](image_url)

**Figure 9.** Evolution of the coating failure during the scratch test – Group II substrate (sintering temperature 1050°C).

The critical loads obtained for the coating deposited on the surface of composites from group III depend on sintering temperature. Evolution of the coating failure during the scratch test is presented in Figure 10.

![Figure 10](image_url)

**Figure 10.** Evolution of the coating failure during the scratch test – Group III substrate, sintering temperature a) 1050°C, b) 1150°C, c) 1350°C.
The highest Lc3 (exposure of substrate) was observed for the substrate sintered at the temperature of 1150°C, however the first symptoms of coating failure was visible at relatively low Lc1 critical load (14.3 N).

4. Conclusions
On the basis of obtained results, the selection of input powder materials and methods of preparation for ceramic-based bulk TiB$_2$/Ti composites, intended for high temperature PVD coatings was done. The most suitable are the composites of group I, i.e. produced from a mixture of two powders: pure Ti and TiB$_2$, with 50/50 wt.% ratio. For this composite it is possible to obtain satisfactory quality of the surface and high adhesion of PVD coating. It could be assumed, that the selected substrate material and preparation method will be also suitable for other coatings. This is an important step forward to elaborate materials and technology towards a novel lubrication concept relying on the double-lubrication approach i.e. lubricious substrates and lubricious coatings.

5. Acknowledgments
Project HOTselflub is supported by the National Science Centre, Poland, under the M-ERA.NET 2, which has received funding from the European Union's Horizon 2020 research and innovation programme, under grant agreement no 685451.

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