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# TUNGSTEN DOPED $TiB_2$ COATINGS OBTAINED BY MAGNETRON SPUTTERING



**Key words:** magnetron sputtering, $TiB_2$ coatings, functional coatings.

**Abstract:** The aim of the work was to investigate the possibilities of shaping the properties of $TiB_2$ coatings by doping with tungsten, which create hard boron phases (e.g., $WB_2$, $WB_4$, and $W_2B_5$). The coatings were produced by a DC magnetron sputtering processes using two circular magnetrons (M1, M2) equipped respectively with M1 – target $TiB_2$, and M2 – target W. Ti-W-B coatings with different tungsten contents (3%, 6%, 10%) were prepared for which the reference coating was the $TiB_2$ coating. The work studied chemical composition (WDS), mechanical properties (Nano Hardness Tester), and the microstructure of coatings (SEM). It has been shown that doping $TiB_2$ coating with tungsten significantly changes their microstructure and brittle fracture mechanism. According to the authors, the Ti-W-B coatings which were obtained show promising results regarding the prognosis of increasing their resistance to abrasion, erosion, and brittle cracking, if they are paired with the appropriate substrate material.

## Powłoki $TiB_2$ domieszkowane wolframem, wytwarzane metodą rozpylania magnetronowego

**Słowa kluczowe:** rozpylanie magnetronowe, powłoki $TiB_2$, powłoki funkcjonalne.

**Streszczenie:** Celem pracy było zbadanie możliwości kształtowania właściwości powłok $TiB_2$ poprzez domieszkowanie wolframem, który tworzy twarde fazy z borem (np. $WB_2$, $WB_4$, $W_2B_5$). Powłoki wytwarzano w procesie stałoprądowego rozpylania magnetronowego z wykorzystaniem dwóch magnetronów kołowych wyposażonych odpowiednio: M1 – target TiB, M2 – target W. Wytworzono powłoki Ti-W-B o różnej zawartości wolframu (3%, 6%, 10%), dla których powłoką referencyjną była powłoka $TiB_2$. W pracy badano skład chemiczny (WDS), właściwości mechaniczne (Nano Hardness Tester) oraz budowę wewnętrzną powłok (SEM). Wykazano, że domieszkowanie powłok $TiB_2$ wolframem istotnie zmienia ich mikrostrukturę oraz mechanizm kruchego pękania. W ocenie autorów wytworzone powłoki Ti-W-B wykazują obiecujące wyniki dotyczące prognozowania wzrostu ich odporności na zużycie ścierne, erozyjne oraz kruche pękanie, jeśli będą sparowane z odpowiednim materiałem podłoża.

## Introduction

Technical development is closely related to the development of knowledge in the area of designing, manufacturing, and the processing of new functional materials [1–3]. Particularly intensive impact of new materials on the innovation progress is observed in the area of the automotive industry [4] and aviation [5], but primarily in the area of the tool industry [6]. Advanced solutions for the production of thin antiwear coatings are of extreme importance. New anti-wear coatings have made it possible to modify the functional properties of machine parts and tools, thanks to which they could be better adapted to work in increasingly difficult operating conditions, e.g., at high mechanical and thermal loads, intensive wear, or corrosive environmental impact. A very important area of research on thin antiwear coatings is ultra-hard thin coatings [7–10] (e.g., ta-C, nc-TiN / a-$Si_3N_4$, $CrB_2$, $BC_4$, $TiB_2$, c-BN, and (TiZrNbAlYCr) N), of which $TiB_2$ is a very interesting material.

Titanium diboride $TiB_2$ crystallizes in a hexagonal system with a structure of aluminium boride and a space group P6/mmm. Among the boron and titanium atoms, there are mainly covalent bonds, which make it a material with high thermodynamic stability. Titanium diboride $TiB_2$ is characterized by high hardness and Young's modulus (≈400 GPa) [11], high thermal conductivity

(60 W/mK) [12], as well as high chemical resistance [13], and thermal resistance [14]. It was also shown that the $TiB_2$ coating is characterized by a very low affinity to aluminium [15], which indicates that it can be a good anti-wear material for cutting tools for machining aluminium alloys. However, despite the very interesting properties of the coating, $TiB_2$ has not found wide commercial use. The reason for this is the very high brittleness of the $TiB_2$ coatings [16] due to the high state of internal stresses. For this reason, $TiB_2$ coatings are characterized by limited adhesion and low resistance to variable loads.

The literature describes the results of various research studies made to reduce the brittleness of the $TiB_2$ coating. The most commonly used activities concerned changes in the technological parameters of the $TiB_2$ coating deposition process [16–20]. Despite the improvement of tribological properties, the reduction of brittleness of $TiB_2$ coatings has not been achieved. Another solution was the creation of composite coatings containing hard $TiB_2$ particles in a soft matrix, e.g., $TiB_2$ – Ni composite [21]. Along with increasing the nickel content, the brittleness decreasing of the $TiB_2$ – Ni composite coating was observed. The $TiB_2$ – Ni composite coating with a content of 6.8% Ni was characterized by the highest hardness (44 GPa). A further increase in the nickel content caused a decrease in brittleness, with a decrease in hardness (28 GPa – 12.8% Ni) and Young's modulus (330 GPa – 12.8% Ni). Nickel does not create phases with boron. In this case, the tribological resistance of the $TiB_2$ - Ni composite coating should definitely decrease as the amount of the soft Ni matrix increases.

A very interesting direction of increasing the fracture toughness of $TiB_2$ coatings is their doping with metal forming the boron phase. An example is, among others, composite coatings $(Ti,W,Cr)B_2$ [22] and W-Ti-B [23], in which, apart from the $TiB_2$ phase, it is possible to form compounds $WB_2$ and $CrB_2$, as well as multi-metallic phases of the $Ti_xW_{1-x}B_{2-z}$ type. In both cases, the composite coatings were produced by magnetron sputtering using targets obtained by the sintering reaction of $TiB_2$, $WB_2$, and $CrB_2$ powders.

The aim of this paper was to investigate the effect of doped the titanium diboride coatings with tungsten using two different targets: titanium diboride – $TiB_2$ and pure W, by the DC magnetron sputtering method. The authors analysed the changes in hardness, Young's modulus, and the microstructure of Ti-W-B coatings in the range of 3.0–10% W.

## 1. Experimental procedure

### 1.1. Coating deposition

$TiB_2$ coatings doped with tungsten were obtained by the DC magnetron sputtering method using two circular magnetrons placed at an angle of 120° to each other and equipped, respectively, with $TiB_2$ and pure-W (diameter Ø = 100 mm, thickness g = 7 mm). A diagram and photographs of the magnetron system used are shown in Figures 1a, b, c. The parameters of the Ti-W-B coating process are shown in Table 1.

The tested coatings were applied to samples made of high-speed steels SW7M with a diameter of 25 mm, a thickness of 6 mm, and a surface roughness of Ra ≤ 0.05 μm, and on samples of monocrystalline Si (100). Prior to being placed in the process chamber, the samples were washed in pure alcohol 99.9%. Immediately prior to the coating process, the samples were ion-etched in the Ar + plasma. During the coating process, the sample temperature was stabilized at 300°C using resistance heaters. The deposition time of each coating was 1 h.

### 1.2. Coating characterization

Samples of SW7M steel coated with the produced coatings were subjected to hardness testing and Young's modulus using a nanohardness tester CSM

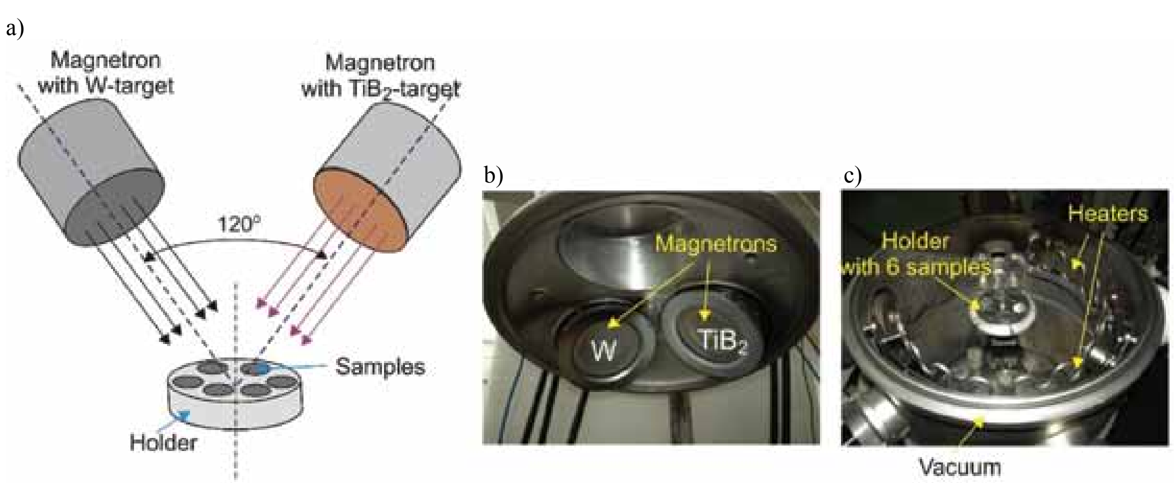


**Fig. 1. Dual DC magnetron system used to apply $TiB_2$ coatings doped by tungsten: a) scheme, b-c) process chamber view**

**Table 1. Deposition parameters of $TiB_2$ reference coating and $TiB_2$ coating doped by tungsten**

| Coating | Atmosphere | Pressure p [Pa] | $U_{Bias}$ [V] | Power of magnetron | | Temperature T [°C] |
|---|---|---|---|---|---|---|
| | | | | $P_{TiB2}$ [W] | $P_W$ [W] | |
| $TiB_2$ | Ar 100% | 0.5 | −50 | 1000 | – | 300 |
| Ti-W-B (25) | | | | 1000 | 25 | |
| Ti-W-B (50) | | | | 1000 | 50 | |
| Ti-W-B (75) | | | | 1000 | 75 | |

with a Berkovich diamond intender. The measurement results made it possible to determine the H/E or H3/E2 indices as parameters by which wear resistance can be predicted. The quotient H/E is called the plasticity index or load factor and is responsible for the maximum elastic deflection at which the coating is not destroyed. The quotient H3/E2 is an indicator of resistance to plastic deformation, and the increase of this quotient leads to an improvement in the load capacity of the coating.

Samples of monocrystalline Si (100) were used for chemical composition analysis by Wavelength-Dispersive X-Ray Spectroscopy – WDS (Nova NanoSEM 450 with WDS-IbeX), as well as surface topography analysis and fracture microstructure analysis using Scanning Electron Microscopy – SEM (Hitechi TM3000).

## 2. Results and discussion

The prepared coatings were subjected to chemical composition analysis using the WDS method. The obtained results (Table 2) showed that the tungsten content introduced into the $TiB_2$ coating increased with increasing tungsten atomisation power and ranged from 3–10%. The B/Ti ratio was determined in the $TiB_2$ and B/Ti + W coatings and in Ti-W-B coatings. Table 3 shows the results of hardness and Young's modulus measurements and the values of determined H/E or $H^3/E^2$ indices.

The investigations of the chemical composition of the $TiB_2$ coating showed its good stoichiometry (B/Ti = 2.2) and high hardness (35 GPa) comparable to the literature results [11]. As a result of doping the $TiB_2$ coating with tungsten, the ratio changes of the boron atomic content to the metals included in the coating. For Ti-W-B coating containing W 3%, the ratio (B/Ti + W) = 3 at content W3%, which may suggest the formation of free boron or non-stoichiometric multi-metallic phases with boron type, e.g., $Ti_xW_{1-x}B_{2-z}$ [24]. However, the demonstrated slight increase in the hardness of the Ti-W-B coating (W3%) allows one to conclude that, even with a small amount of boron, it must at least partially participate in the formation of hard phases with tungsten richer in boron (e.g., $W_2B_5$, WB4). According to the authors, this also confirms the increase in the Young's modulus ($E_{Ti\text{-}W\text{-}B(W3\%)}$ = 415GPa), which indicates a higher elasticity of the coating. Increasing the tungsten content to 6% and 10% causes a further increase in hardness and Young's modulus (Table 2). At the same time, the ratio of the boron atomic content to the metals included in the coating is clearly reduced, assuming (B/Ti + W) = 2.5 at content W6% and (B/Ti + W) = 2.1

**Table 2. The results of the chemical composition investigations of $TiB_2$ and Ti-W-B coatings were made using the WDS method**

| Coating | Chemical composition [at. %] | | | B/Ti+W |
|---|---|---|---|---|
| | Ti | W | B | |
| $TiB_2$ | 31 | – | 69 | 2.2 |
| Ti-W-B (25) | 22 | 3 | 75 | 3.0 |
| Ti-W-B (50) | 22 | 6 | 72 | 2.5 |
| Ti-W-B (75) | 22 | 10 | 68 | 2.1 |

**Table 3. The results of the hardness and Young modulus measurements of $TiB_2$ and Ti-W-B coatings were made using nanohardness technique**

| Coating | Hardness H [GPa] | Young modulus E [GP] | H/E | $H^3/E^2$ |
|---|---|---|---|---|
| $TiB_2$ | 34.0 ± 2 | 405 ± 5 | 0.075 | 0.239 |
| Ti-W-B (25) | 35.5 ± 2 | 415 ± 10 | 0.085 | 0.259 |
| Ti-W-B (50) | 37.0 ± 2 | 425 ± 7 | 0.087 | 0.280 |
| Ti-W-B (75) | 38.0 ± 3 | 435 ± 5 | 0.087 | 0.289 |

at content W10%, respectively. This indicates a greater possibility of the formation of a hard $WB_2$ phase, and similar crystallographic parameters to the $TiB_2$ phase.

The results of surface topography and fracture microstructure analysis of the $TiB_2$ and Ti-W-B coatings obtained at various tungsten sputtering powers are shown in Figure 2. All coatings were characterized by very high smoothness (Ra < 0.1 μm). The analysis of breakthroughs showed that the thickness of the coatings was similar and amounted to ≈1.2 mm, which indicates that the applied process parameters for the production of $TiB_2$ and Ti-W-B coatings, shown in Table 1, provided the deposition rate of Vd = 20 nm/min. Based on the observations made at the breakthroughs of $TiB_2$ and Ti-W-B coatings for various tungsten contents, microstructure schemes of coatings were proposed and the directions of the cracking propagation were analysed.

Observations of the microstructure of brittle breakthroughs have shown that the $TiB_2$ coating has a column structure in which the grain diameter is ≈100 nm (Fig. 2a). The breakthrough in the $TiB_2$ coating has a clear internal grain nature. The direction of cracking is parallel to the direction of growth of the columnar grains (perpendicular to the surface of the shell).

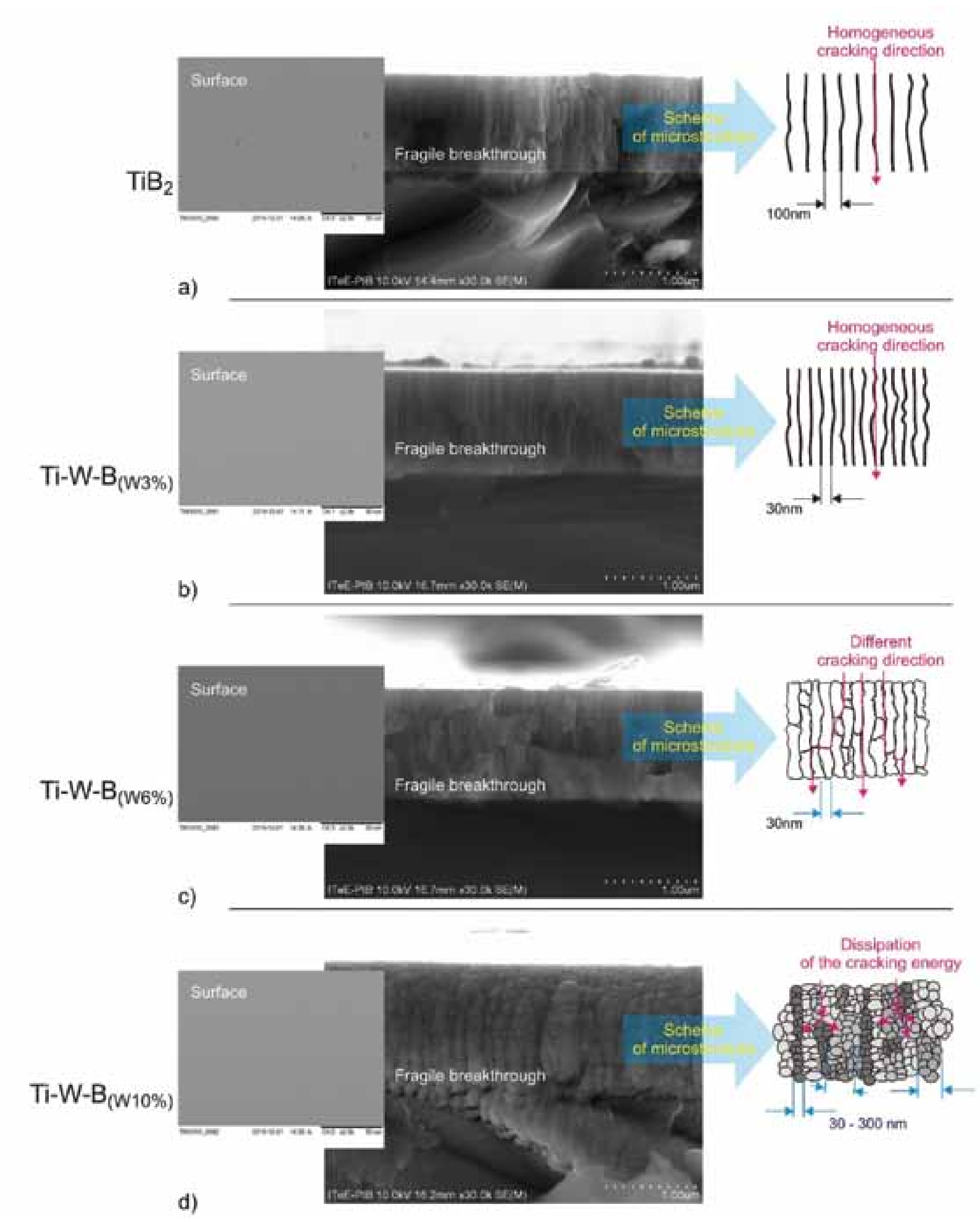


**Fig. 2. The results of scanning electron microscopy analysis of $TiB_2$ and Ti-W-B coatings: a) $TiB_2$, b) Ti-W-B$_{(W3\%)}$, c) Ti-W-B$_{(W6\%)}$, d) Ti-W-B$_{(W10\%)}$**

The doping of the $TiB_2$ coating with 3% tungsten results in the fragmentation of the columnar grains, whose diameter is ≈30 nm (Fig. 2b). The grain refinement does not change the cracking mechanism, which continues to run mainly in the direction perpendicular to the surface. In Ti-W-B coatings containing W6%, the column structure with grains with a diameter of 30 nm also dominates (Fig. 2c). The cracking mechanism is noticeably changed, in which the directions of parallel and perpendicular cracking to the surface of the coating are equivalent. At the transverse breakthrough, we observe the occurrence of small structural forms that may indicate the occurrence of a composite structure or equi-axial grains, which would justify the occurrence of different coating cracking directions and increase in hardness ($H_{Ti\text{-}W\text{-}B(W6\%)}$ = 37 GPa).

The introduction of $TiB_2$ coating 10% of tungsten caused a clear change in Ti-W-B coating microstructure. Observations of the brittle breakthrough of the Ti-W-B coating (W10%) revealed the presence of a compact column structure in which the individual columns are conglomerates of equi-axial grains with a diameter of ≈100 nm (Fig. 2d). This allows one to conclude the possible occurrence of composite microstructure in Ti-W-B coatings (W10%), which would be confirmed by the results of studies presented by O.V. Sobol [25]. The cracking process is not directed, which indicates the possibility of dissipating energy during cracking. This allows concluding that Ti-W-B coatings (W10%) should have the highest resistance to brittle fracture.

Verification of the proposed microstructure schemes and properties of Ti-W-B coatings (abrasion resistance, erosion resistance, resistance to brittle fracture) requires a broader study using advanced material testing techniques (STEM, XRD, tribology and erosion tests).

## Conclusions

The article describes the use of a magnetron sputtering process for producing $TiB_2$ coatings doped with tungsten. The chemical composition of Ti-W-B coatings, their microstructure, and mechanical properties (H, E) were investigated. The main results are summarized in the following conclusions:

- Magnetron sputtering is an effective method of producing multi-component coatings, including $TiB_2$ ceramic coatings doped with metals. The use of several magnetrons equipped with targets made of different materials and the control of magnetron sputtering power allows precise control of the chemical composition of the coatings.
- Doping of $TiB_2$ coating with tungsten causes fragmentation of the microstructure and a change from the column microstructure (for $TiB_2$) to the nanocomposite (for Ti-W-B W10%). The changes of the microstructure allow the generation of new directions of cracking, which results in the dissipation of the crack energy. As a result, according to the authors, it is possible to increase fracture toughness. $TiB_2$ coatings doped with tungsten should be considered a very promising material solution for anti-wear coatings.
- The obtained results of material tests and the proposed changes in the microstructure, as well as the predicted increase in fracture toughness of $TiB_2$ coatings doped with tungsten requires further advanced material and test investigations that the authors will continue.

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