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EVOLUTION OF MAGNETRON-SPUTTERED TIB_2

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Abstract: Deposition processes for prepared thin hard flayers are known for several decades, but still new inventions of layer and their combinations are coming. The first TiN coatings were used, later the industry started to use carbide and nitride coatings, diamond coatings, multilayers and nanocomposite. Although it appears, that possibilities of improvement of the properties of coatings have been depleted is not true. The latest research shows on the perspective usage coated materials of the types TiB_2, TiAl-TiB, TiB-Ti, which have the special properties, very interesting for some applications. For successfully applications it is important to study the deposition parameters, properties, behavior of the system „*film – substrate*“ and microstructure of the films. In this paper are study the first basic properties of TiB_2 research, like roughness profile by Augerov Electron Sectroscopy, details study of the texture by X-ray diffraction, microhardness was achieved more than $5000HV_{0,05}$ by Vicker’s method and AFM analyze. TiB_2 coatings were deposited onto Si (001) substrates and mirror polished stainless steel substrates by DC magnetron sputtering method.

Key words: TiB_2, coating, PVD technique, cutting tool

INTRODUCTION

The latest research shows the perspective of using of coated materials types *TiB_2, TiAl-TiB, TiB-Ti,* which have special properties, very important for some applications. Specific resistance (6,4-9,1$\mu\Omega$cm) is low, temperature coefficient of dilatability is ($4,6*10^{-6}$ K^{-1}). This chemical stability, high heat resistance ceramic materials with high hardness and high wear resistance fulfil high demands for modern progressive cutting tools. Prepared diboride coatings show a high potential for tribological applications.

Titanium diboride (TiB_2) is ceramic compound with hexagonal structure in which boron atoms form a covalently bonded network within metallic Ti matrix. TiB_2 is well known for its high hardness, reported hardness values of up to 6700 HV result in their being regarded as so-called ultrahard or superhard and high chemical stability at higher temperature, wear and corrosion resistance and good electric conductivity. This combination of properties makes TiB_2 very interesting as a coating material for various applications, especially for cutting tools. The deposition of TiB_2 based coatings is usually carried out by physical vapor deposition (PVD), plasma assisted chemical vapor deposition (PACVD) or CVD techniques. Magnetron sputtering appears to be the most suitable, because deposition temperature can be reached with relatively high deposition speed. Mentioned process also allows preparing coatings on substrates with complicated shapes. Next advantage is the absence of toxic and explosive gases during deposition. However, application of TiB_2 coatings is complicated as poor coatings adhesion cause high residual stress level. This problem can be solved with substrate heating and bias application [1- 4].

In this paper are study the first basic properties of TiB_2 research, like roughness profile by Augerov Electron Sectroscopy, details study of the texture by X-ray diffraction, microhardness was achieved more than $5000HV_{0,05}$ by Vicker’s method and AFM analyze.

TiB_2 coatings were deposited onto Si (001) substrates and mirror polished stainless steel substrates by DC magnetron sputtering method.

EXPERIMENTAL WORK

As substrate material Si (001) substrates and mirror polished stainless steel substrates were used. Before deposition, the substrates were cleaned in an ultrasonically pured acetone, izopropylalcohol and distilled water bath. The deposition was carried out using DC magnetron configuration. Visual characterization of the sputtering process indicated a concentration of the plasma at the target centre and that lead to higher growth rate for substrates located close to the centre of the substrate holder.

TiB_2 target have diameter 40 mm and thickness 6 mm. The substrates have stationary positioned 5 cm from the TiB_2 target. The used process gas was argon with the purity of 99,994%. Starting vacuum was 2 x 10^{-3} Pa, the substrates were in-situ cleaned by argon-ion etched for 15 min using substrate bias voltage –500 V and an Ar pressure of 2 Pa. Deposition time was 15 min. The pressure was changed from deposition to deposition in range 0.2 – 1 Pa by the 0.2 Pa step. Magnetron current was 1.4 A and corresponding magnetron voltage was changed from 350 V to 390 V. Preferred orientation and phase composition was observed by X – Ray Diffraction (XRD) analysis in Bragg – Brentano geometry, using HZG4 equipment with CuK monochromator (wave length – 0,015418 nm). Auger Electron Spectrometry (AES) was applied for control the coating's stoichiometry. Surface quality and roughness was analysed by Atomic Force Microscope (AFM) – Solver P47. Coatings morphology and thickness were examined by SEM (JEOL) microscopy. Parameters of sputtering process were optimized for Si (001) substrates. Stainless steel substrates were used for microharness measurement (INDENTEC indenter).

RESULTS AND DISCUSSION

A focused electron beam irradiates a sample surface producing Auger electrons. The energies are characteristic for the element from which they are generated. Compositional depth profiling was accomplished. Auger Electron Spectrometry analysis indicated Ti/B ratio approximately 1/2. Presence of carbon and oxygen was also observed (Fig.1.).

AES determined this composition of the surface layers of a sample- 56,2% Boron, 33,1% Titanium, 4,9% Carbon and 5,7% Oxygen. It is an assumption that coatings contamination by oxygen and carbon resulted into too high initial pressure and in attendance of particles from oil rotation and diffusion pumps.

Dependence of the surface roughness on the deposition pressure was observed on Si – samples by AFM method. Surfaces roughness increased with working pressure. Mean roughness values R_a were in range 0,2 nm, 0.3 nm, 1.2 nm by the Ar pressure 0.2 Pa, 0.6 Pa, 1 Pa and maximal roughness values R_{max} are 1.2 nm, 4 nm, 12nm by the Ar pressure 0.2 Pa, 0.6 Pa, 1 Pa on silicon samples. Mean roughness (R_a) and maximum roughness (R_{max}) values as a function of Ar pressure, measured by AFM on silicon substrates, are in Tab. 1.

Tab.1.

Pressure [Pa]	0.2	0.6	1
R_a[nm]	0,2	0,3	1,2
R_{max}[nm]	1,2	4	12

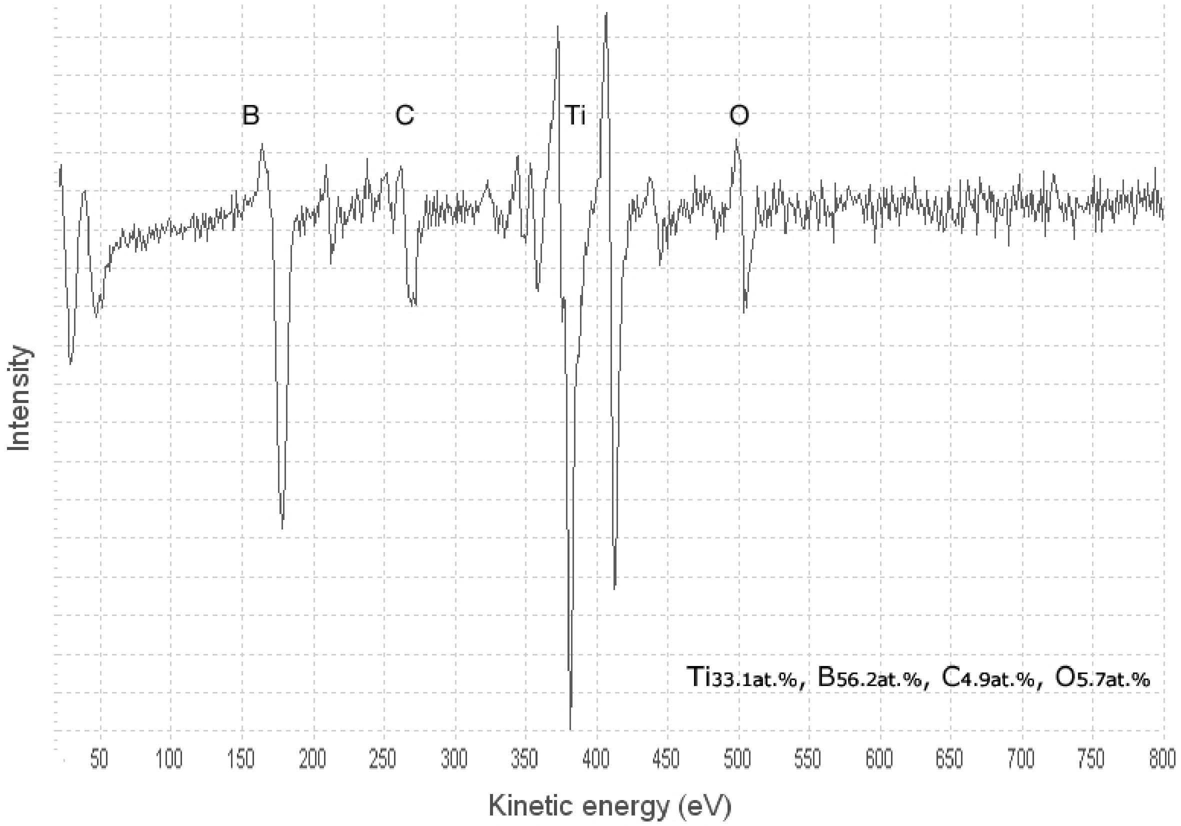

Fig.1. AES spectrum of TiB_2 coating deposited at 0.2 Pa.

All deposited coatings showed a metallic grey and brilliant mirror surface. It can be seen that surfaces roughness of TiB_2 layers of samples prepared by the various deposition pressure had increased with working pressure on the Fig.2.

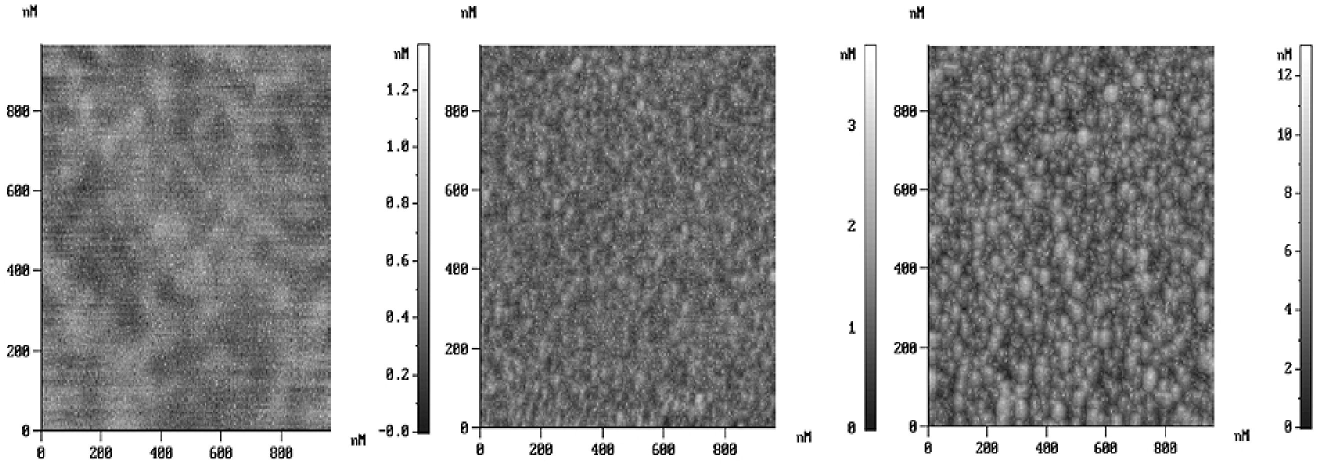

Fig.2. AFM images of TiB_2 surface deposited at Ar pressure a) 0, 2 Pa b) 0, 6 Pa and c) 1 Pa

No significant texture of TiB_2 coatings was observed, as XRD patterns shows on Fig. 3. The only sharp diffraction peak besides the Si (004) substrate peak is $2\theta = 44.5°$ and it can be attributed to (101) diffraction of TiB_2 phase. Typical SEM image of fractured coating format deposited on silicon substrates is shown in Fig.4. The coatings thickness was 2, 5 µm. The micro hardness of TiB_2 was higher than 5000 $HV_{0, 05}$ for all applied deposition parameters.

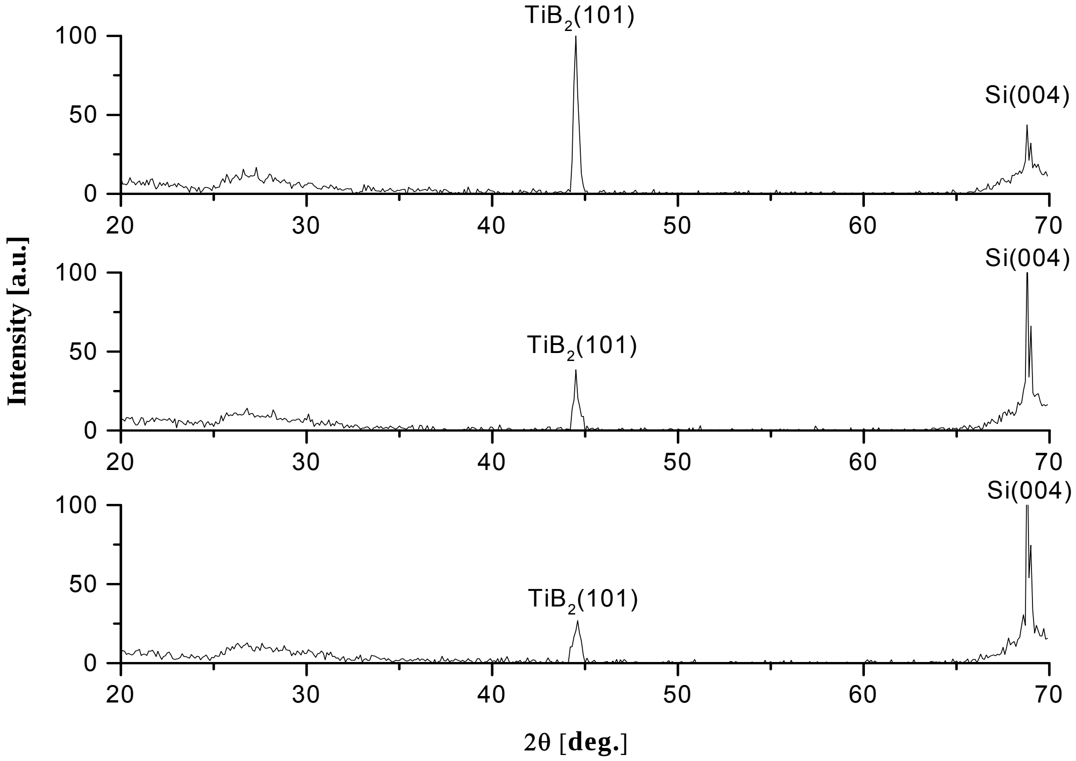

Fig.3. Typical XRD patterns of TiB_2 coatings deposited on Si (001) substrates at a) 0.2 Pa, b) 0.6 Pa and c) 1 Pa.

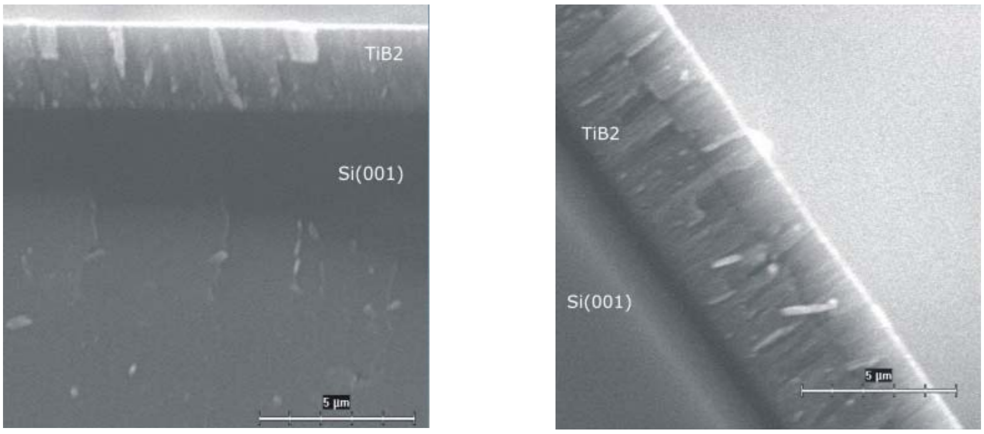

Fig.4. Typical SEM micrograph of fractured TiB_2 coating

It follows from Tab. 1 and Fig. 2 that the roughness increased with increasing Ar pressure. X - ray analysis shows (101) the diffraction peak of TiB_2 phase, which is the most intense diffraction peak of ideal TiB_2 polycrystalline. Coatings growth rate was 2, 8 $nm.s^{-1}$. Despite the absence of significant (001) TiB_2 peak (often observed for values of micro hardness over 5000 $HV_{0, 05}$, the coatings had very high micro hardness. Such micro hardness values can be explained by nanocomposite character of the coatings. This is also in agreement with observed X – ray diffraction patterns. In order to determine the nanocomposite character of these coatings, it would be necessary to analyze them with electron diffraction. The presented study is still in progress.

CONCLUSION

This interesting new-coated material on the TiB_2 base is object of our research project with the title "Research of the properties of new super-hard coatings on base TiB on the cutting tools". Within this work, the possibility of DC magnetron sputtering deposition of the TiB_2 coatings has been shown. TiB_2 coatings micro hardness was reproducibly higher than 5000 $HV_{0,\ 05}$. The roughness (R_a) changed with deposition pressure. No significant texture was observed. In respect with the micro hardness and the surface roughness, the best TiB_2 coatings were reached at working pressure of 0.2 Pa. We conclude that TiB_2 coatings prepared by DC magnetron sputtering exhibit the high micro hardness and small roughness thus they are very promising for fabrication of superconducting MgB_2 oriented thin films with hexagonal structure, as well as for practical applications in tool engineering.

Present results indicate special properties of these coatings, still examined in basic research, and it can be predicted that they will form new base coated materials with expanded recourses for usage for cutting tools.

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