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SURFACE ALLOYING OF TUNGSTEN CARBIDE WITH TITANIUM, USING ELECTRON BEAM IRRADIATION

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ABSTRACT

The demand for higher performance products (car parts and elements parts) and special working conditions are the main reason to substitute components in cast iron and steel, with components made of "light alloy", such as aluminum and titanium alloys. These alloys are characterized by reduced hardness and wear behavior especially in abrasive wear, representing a severe barrier to their use in tribological applications.

Surface alloying process of titanium materials with tungsten carbide powder was made possible in a limited domain of energy process, from 300 W/mm to 330 W/mm. Microscopic structure of alloyed area consists of titanium carbide (TiC) distributed in phases of chromium-titanium ($CrTi_4$), titanium-tungsten (TiW) and cobalt-titanium ($CoTi_2$). Alloyed surface hardness with subsequent redoubles has values up to 748 $HV_{0.3}$ and superior wear resistance, assigned to wear hard phase of titanium carbide (TiC). It was also observed that the formation of cobalt-titanium phase ($CoTi_2$) led to a decrease in the coefficient of friction up to 0.365. Alloying process has led to an increase in the corrosion rate for TiWC. Areas of titanium alloyed with tungsten carbide powder (TiWC) possess residual compressive stresses, which may lead to an increased fatigue resistance of the material. The surfaces of titanium alloyed with tungsten carbide powder in the arreas of cobalt-chromium, present the best wear behavior in pin-on-disk tests, proving to be a better solution in applications where wear resistance is needed.

Keywords: constructions, seismic action, displacement, loading

1. INTRODUCTION

Manufacture of thin films using nano-technologies offers possibilities of getting the desired properties the engineers are inetrested in. suprafețele Particularly applications try to combine basic material properties (e.g. low density, mechanical-resistant) with the high hardness, wear-resistant and corrosion resistance of the deposit layer. A great variety of surface engineering techniques have been applied with the aim of improving the tribological properties of titanium alloys. Such techniques include ion-implantation, PVD and CVD coatings as well as brazing operations with at-SER. Common goal of these processes is to use an outer layer with good tribological properties, such as nitrides (TiN, CrN, ZrN) diamond-like, borides and carbides (TiB), etc.

Thermal sprayed coatings are increasingly used due to their high rates of depositing and the possibility of coupling with a very varied range of materials. As a result, among other surface methods the thermal spraying is considered as one of the most effective.

Despite numerous methods of surface engineering, they show some desadvantages, such as porosity, thickness, coating delamination insufficient, high residual voltages and high processing times, plate-like structure of the layers deposited by thermal spray and reduced adhesion of layers can have negative consequences during operation.

In the case of titanium and its alloys, coating process may have a negative effect on corrosion behaviour. Therefore, the monitoring carried out at the anticorrosive properties of titanium, hardness and wear resistance of coatings.

The most efficient and reliable method that provides the interface with the desired metallurgical properties of the mixed base material and coating is the superficial alloying with electron beam, due to the advantages it has over laser technologies in terms of scanning beam, depth of penetration and working conditions.

The paper addressed contributes to the effort to achieve the coating with reduced friction coefficients and high resistance to wear. Emphasis is placed on characterizing the microstructure and surface properties of titanium alloyed with tungsten carbide powder, by electron beam action.

Titanium is a transitional metal in nature, primarily in the form of rutile and ilmenit. It presents two polymorphic states: an alpha (α) with a hexagonal structure and a beta (β) with cubic structure with centred volume. Titanium-based alloys may be divided into three groups: alpha alloys, solders and alpha-beta beta alloys. Alloying elements are determining their capability of stabilizing either alpha phase, or the beta phase, thereby stabilizing elements neutral elements, alpha and beta stabilizers. Titanium and its alloys are characterized by low densities (approx. 60% of the density of steel), a very high resistance to corrosion and a good cryogenic-Daddy characteristic. These properties have led to an increased use of titanium in the aerospace and transport industry in applications such as jets, trains, tanks, landing rotary heads and machine building industry as valves, springs, pistons and other many applications.

But titanium alloys also exhibit disadvantages, such as low resistance to fatigue and abrasive wear, and to take full advantage of the properties of these alloys in applications is logical to increase surface hardness, reducing thus the coefficients of friction. Common engineering processes of titanium alloy surface treatment include: ion implantation, thermochemical treatments, plating, laser treatments and thermal spray coating, with some shortcomings, such as small thicknesses layer, high porosity and high residual stresses.

Anti-corrosion properties of titanium combine with those of anti-wear coatings, reducing friction coefficient, finishing layer structure by elimination of oxide inclusions and porosity and improve adhesion to the substrate layer by surface alloying of titanium powder-based tungsten carbide.

3. MATERIALS AND PROGRAM OF EXPERIMENTAL WORKS

Titanium alloy grade Tikrutan RT 12 from ThyssenKrupp Titanium has been used as a basic material in the experimental program. The chemical composition is presented in Table 1.

Table 1. The chemical composition (wt%) of the base material, Tikrutan RT 1

Element	(C)	H	Fe	N	A	TI
wt%	0.06	0.013	0.15	0.05	0.12	99.60

Tungsten carbide powder was used as grade TOILET-86104 Caplain from Thermico GmbH & Ko., characterized by very high melting temperatures, high hardness and high temperature stability. An analysis of x-ray diffraction identified tungsten carbide, chromium carbide-tungsten and cobalt.

The depositing process uses a mixture of gaseous or liquid fuel, fed continuously into a combustion chamber. Coating material in powder form is injected into the gas stream, where partial melting occurs and very high speeds for covering.

Tungsten carbide powder in cobalt-chrome matrix was deposited by thermal spray, high velocity oxy-fuel coating spraying (HVOF).

For powder-based deposit with tungsten carbide, a rate of 21 l/h kerosene and 20 l/min nitrogen was used. The process has been conducted in 13 passages, for obtaining a coating of 350 μm.

In the case of tungsten carbide, it may be seen that it presents inclusion oxides and high porosity.

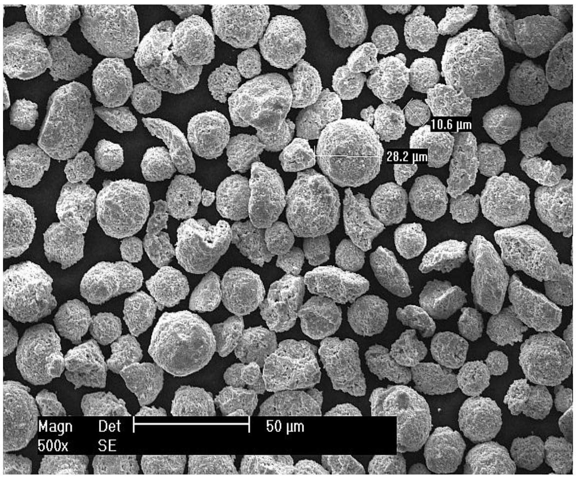


Fig. 1. Image of WC powder MEB-86104 Caplain

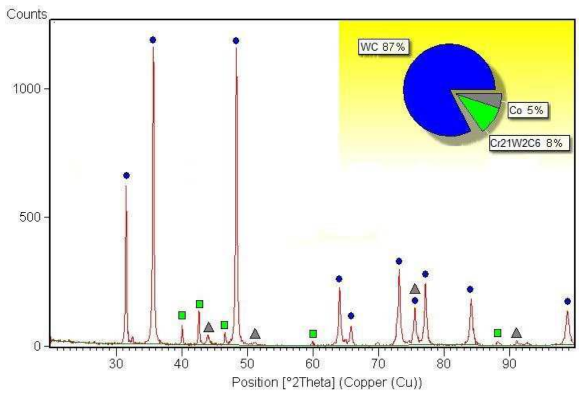


Fig. 2. The spectrum of x-ray diffraction of powder toilet Caplain 84106 [13]

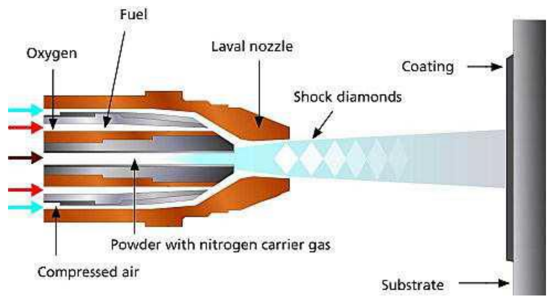


Fig. 3. The principle of flame thermal spraying with high velocity oxy-fuel coating spraying (HVOF) [13]

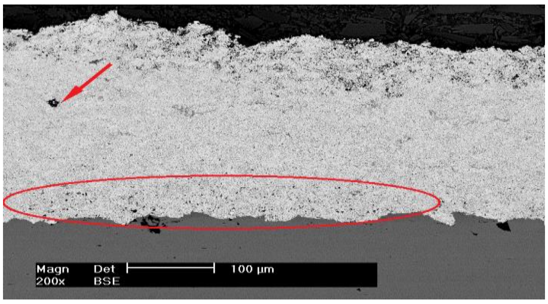


Fig. 4. The quality of the deposited layers: layer of WC-86104 Caplain

3. THE PROCESS WITH BEAM REMELTING TAKEMOTO DEPOSITED LAYERS

The previously mentioned disadvantages of deposited layers can be reduced by a process of electron beam remelting. Remelting process is done with the help of an electron beam. The surface very quickly reaches the melting temperature and the liquid-solid interface begins to move forward in the substrate layer. Liquid-solid interface is advancing up the phenomenon of interdiffusion between layer and substrate. The resolidification process takes place with very high speeds and advancing to the surface, resulting in an alloyed area between the base material and the deposited layer.

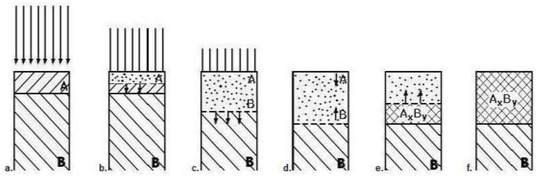
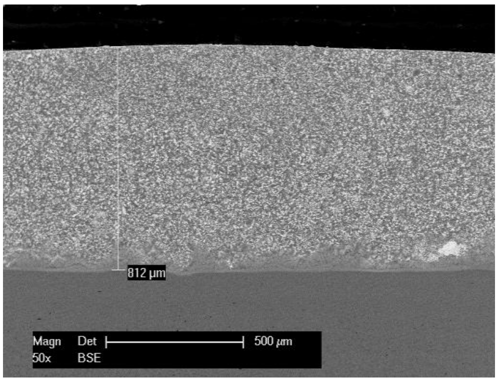


Fig. 5. Stages of electron beam remelting [13]

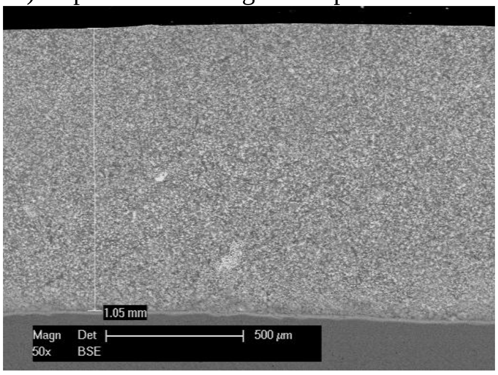
Table 2. Parameters of remelting coating made of WC-86104 Caplain (U=60 kV)

Scan modus	I [mA]	v [mm/s]	Sample
line	20	5	TIWC1.1
	20	2.5	TIWC1.2
	25	5	TIWC1.3
	30	5	TIWC1.4
	30	10	TIWC1.5
	30	15	TIWC1.6
	35	15	TIWC1.7
	40	15	TIWC1.8
	40	20	TIWC1.9
	50	20	TIWC1.10
	40	10	TIWC1.11
	35	10	TIWC1.12
	35	8	TIWC1.13
	45	10	TIWC2.1
	40	10	TIWC2.2
	50	10	TIWC2.3
	55	10	TIWC2.4
field	50	10	TIWC2.5
	55	10	TIWC2.6

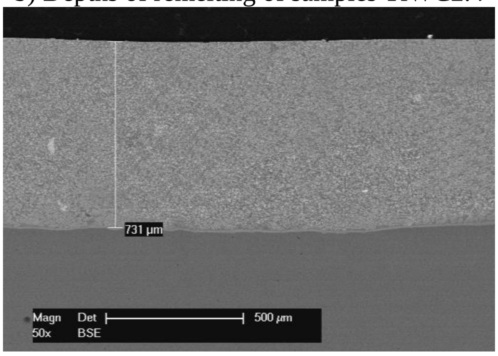
Process parameters, used in remelting coating with tungsten carbides, are presented in Table 2. The process was carried out at a constant voltage of 60 kV, varying intensity between 20 mA and 55 mA and a remelting speed between 2.5...20 mm/s has also been used for two modes of energy distribution, namely, in the form of line and field. Figure 6 illustrates the depths of surface remelting of titanium alloyed with tungsten carbide powder.



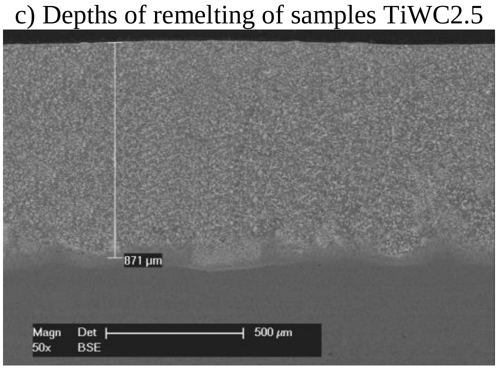
a) Depths of remelting of samples TiWC2.3



b) Depths of remelting of samples TiWC2.4



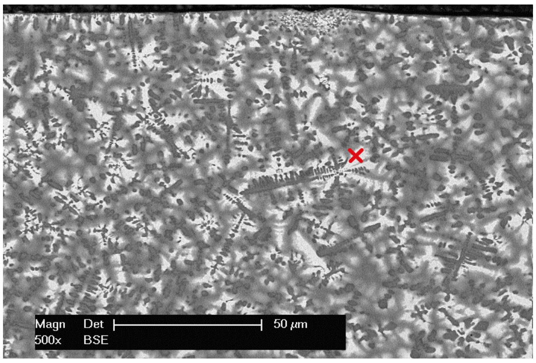
c) Depths of remelting of samples TiWC2.5



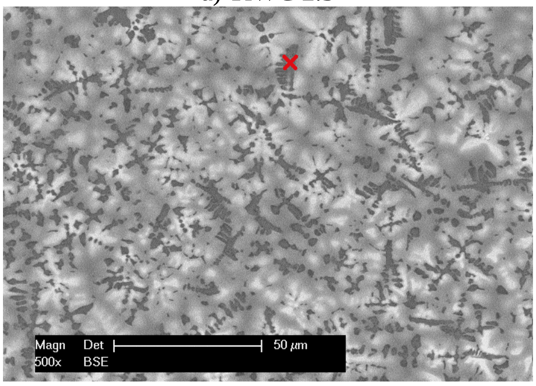
d) Depths of remelting of samples TiWC2.6

Fig. 6. Depths of remelting of samples

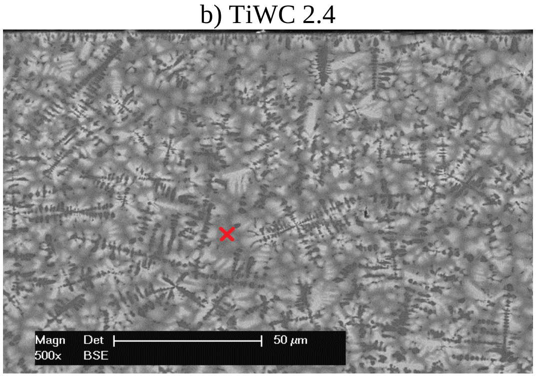
They have about 800-1000 µm, respectively, by using a linear distributions of energy process. Using a sub distributions for the field energy of the process, a moderate reduction of the depth can be observed into the range of 730...870 µm, respectively.



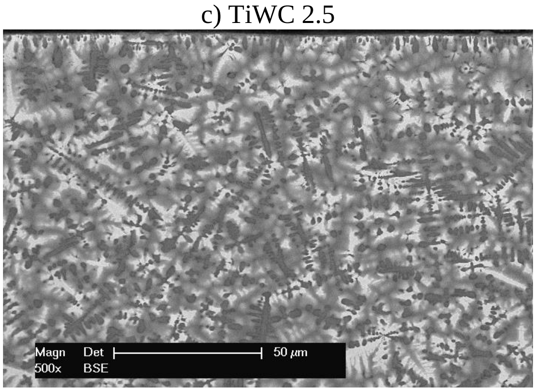
a) TiWC 2.3



b) TiWC 2.4



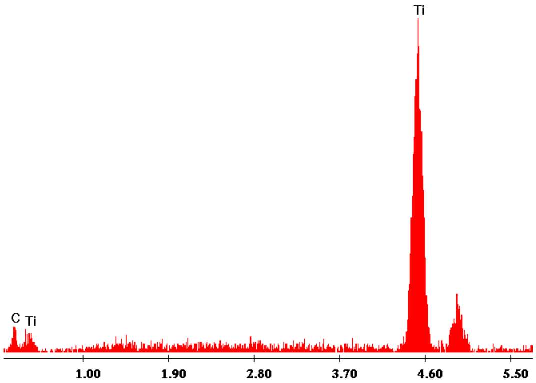
c) TiWC 2.5



d) TiWC 2.6

Fig. 7. Microstructure alloyedd zones

Microscopy images in Figure 7 show a dendritical structure of the alloyed areas. The EDX analysis (Fig. 8) shows that the lightest phase is composed of titanium and tungsten, dendritical phase consists of titanium and carbon, and the analysis on grey phase shows that it contains titanium, cobalt and chromium. EDX analyses correlated with the spectra of X-ray diffraction can be asserted that the alloyed zone structure consists of spherical carbide and dendritical titanium, chromium-tungsten-titanium, chromium and cobalt-titanium (Fig. 9).



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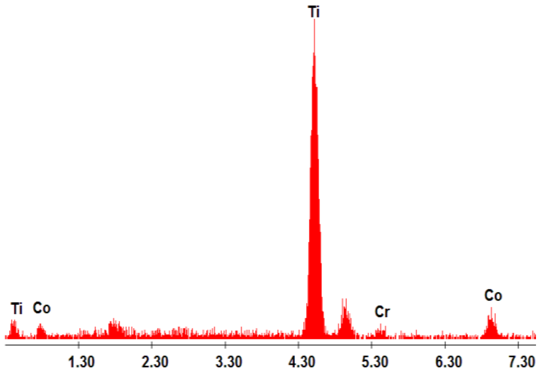

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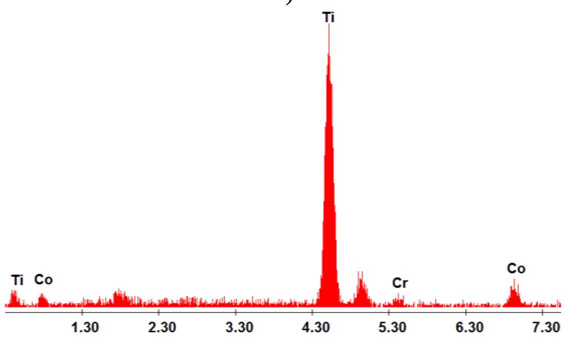


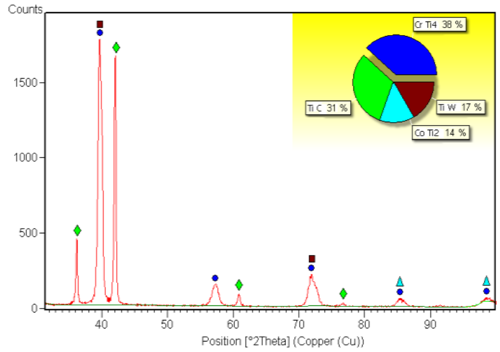
c)

Fig. 8. Analysis of dispersiva energy spectroscopy of phase samples TiWC

Table 3. TiWC Composition of phasic structure (%)

Sample	$CrTi_4$	TiC	TiW	$CoTi_2$
TiWC2.3	38.0%	31.0%	17.0%	14.0%
TiWC2.4	50.0%	28.0%	12.0%	10.0%
TiWC2.5	37.0%	28.0%	17.0%	18.0%
TiWC2.6	40.0%	24. 0%	14.0%	22.0%
	cubic	*cubic*	*cubic*	*cubic*

In Table 3, it can be seen that the ratio between the phases is heavily influenced by process parameters. High energy, involving a more pronounced contribution of subtreatment, encourages the formation of much larger amounts of chromium-titanium. Also, the use of a form of field distributions of energy process leads to the formation of larger percentages of cobalt-titanium in the alloyed zone.



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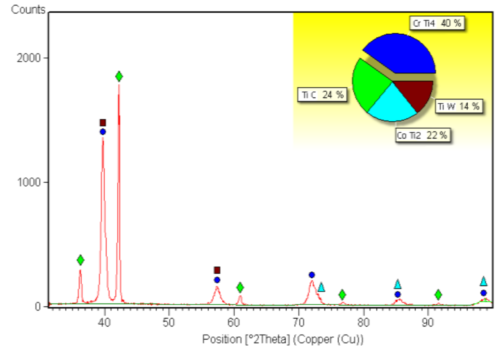

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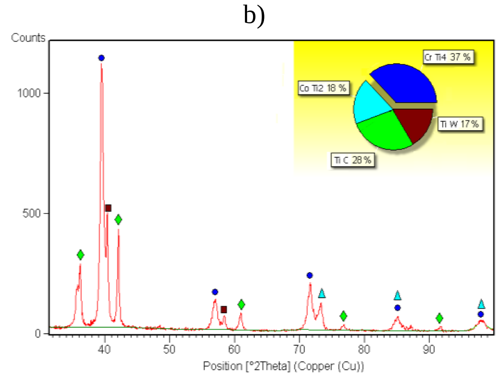

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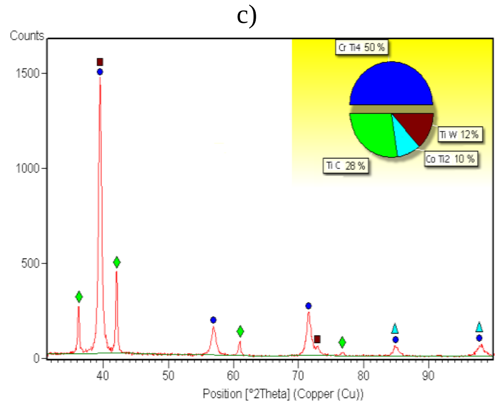


d)

Fig. 9. The spectra of x-ray diffraction of areas alloyed TiWC

4. MICROHARDNESS OF TITANIUM ALLOYED WITH TUNGSTEN CARBIDE POWDER (TIWC)

Gradients of hardness of titanium surfaces alloyed with powder-based carbide tungsten are presented in Fig 10.

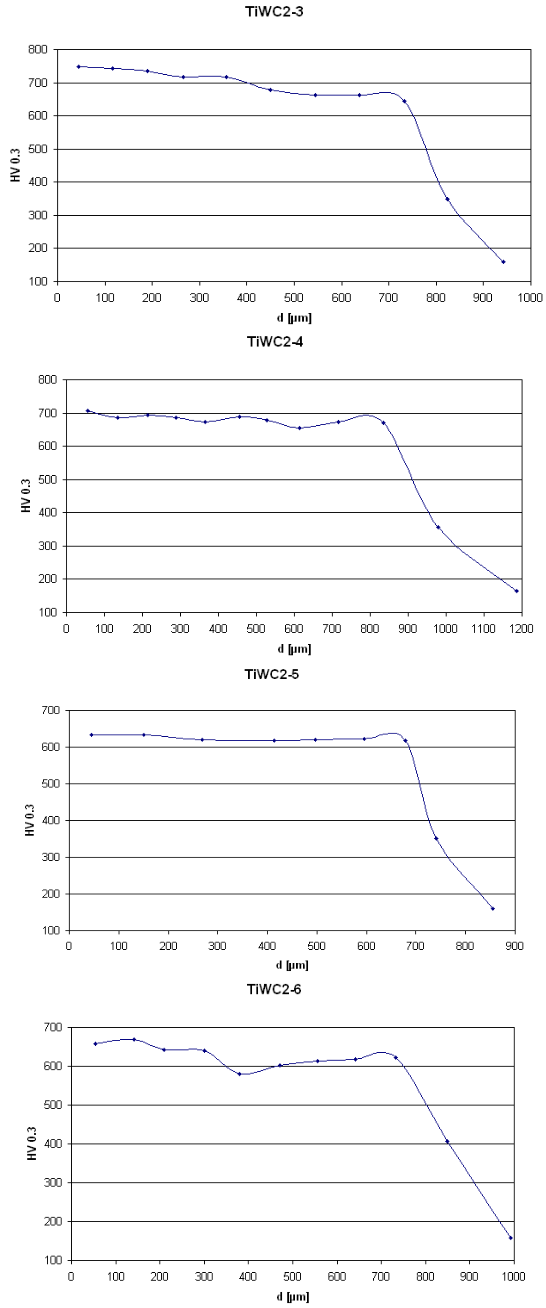


Fig. 10. Gradients of toughness you samples TiWC

The surfaces of titanium alloyed with tungsten carbides have hardness values ranging between 634 and 748 $HV_{0.3}$ on the surface and it decreases to about 350 $HV_{0.3}$ to the interface. High values of hardness (Fig. 11) are attributed to the presence of tough phase of titanium carbide in the alloyed zones.

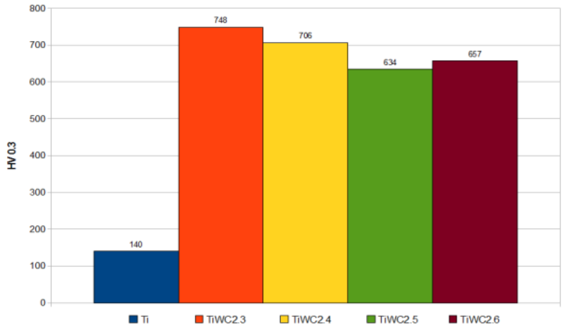


Fig. 11. Hardness test samples TiWC

3.3. RESULTS ON TRIBOLOGICAL BEHAVIOR

The coefficients of friction of alloyed coatings were determined using the device ball-on-disc [??]. Figure 12 illustrated the friction coefficient of base material. The coefficient of friction for titanium surfaces with tungsten carbide powder are presented in Fig. 13.

The measurements in Fig. 13 show that the areas of titanium alloyed powder-based tungsten carbide show lower values for the coefficient of friction than that of the base material; samples TiWC TiWC 2.3 and 2.6 gave values of the friction coefficient with approximately 50% lower. Minimum, medium and maximum values of the friction coefficient are shown in given in Table 4.

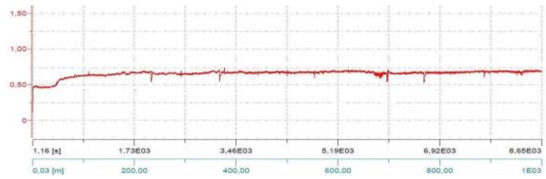


Fig. 12. The friction coefficient of core material

Table 4. The coefficients of friction for samples TiWC

Sample	μ_{min}	μ_{max}	μ_{med}
Ti alloy	0.482	0.751	0.680
TiWC 2-3	0.280	0.520	0.365
TiWC 2-4	0.200	0.557	0.500
TiWC 2-5	0.140	0.588	0.500
TiWC 2-6	0.115	0.388	0.365

Wear rates of samples were determined using the device ball-on-disc by testing the samples over a distance of 1000 m, with a speed of 200 mm/min, under a load of 5 N, against a ball made of WC-Co. For calculating the wear rate, the following dimensions of wear traces are necessary.

$$K = \frac{V}{L \cdot d} \tag{1}$$

$$V = 2\pi r \cdot A \tag{2}$$

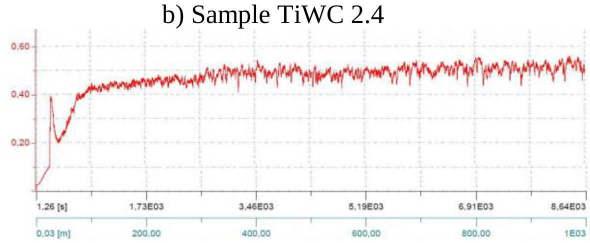
$$A = \frac{h}{6 \cdot s}\left(3h^2 + 4s^2\right) \tag{3}$$

$$(2),(3) \Rightarrow K = \frac{2\pi r \cdot h\left(3h^2 + 4s^2\right)}{6 \cdot L \cdot d \cdot s} \tag{4}$$

where K is the wear rate, V - volume of worn material, L - applied load, d - sliding distance, A - the area of ball wear; h - the height of the used track, s - width of the track.

a) Sample TiWC 2.3

b) Sample TiWC 2.4



c) Sample TiWC 2.5

d) Sample TiWC 2.6

Fig. 13. The coefficients of friction you samples TiWC

An example of determing the measurements of wear surfaces of titanium alloyed with tungsten carbide powder, as well as measuring the wear of the ball shield illustrated in Fig. 14, for sample TiWC 2.3.

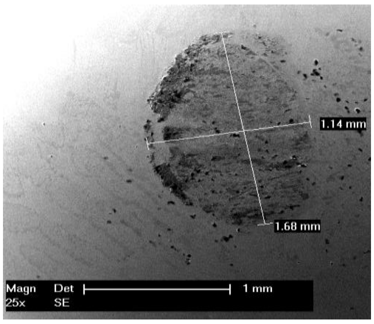


Fig. 14. Measurement of wear of the ball for the sample TiWC 2.3

Table 5. Measurements of wear rates [x10^{-5} mm^3/(n.m)] of samples TiWC

Sample	h [µm]	s [µm]	A [µm2]	Ball wear diagonales [µm]	Wear rate
Ti alloy	148.8	1879.5	187141		126.8
TiWC2-3	15.4	1112	14764	1140 x 1680	6.7
TiWC2-4	9.38	1705	13722	1230 x 1960	6.84
TiWC2-5	12.6	1262.2	18417	1830 x 933	9.32
TiWC2-6	16.8	1262.8	19580	1680 x 837	9.9

Improved wear behavior of tungsten carbide with the histogram in Figure 15 is due to the cubic phase formation of chromium-cobalt-titanium, titanium, titanium and tungsten and titanium carbides, in particular, in the alloyed area, sample TiWC 2.3 possessing the highest hardness values and the highest content of

Tungsten carbides behave better in tests, while wear of samples TiWC, TiWC 2.5 and TiWC 2.5 2.6 was characterized by a high content of cobalt-titanium, exhibiting higher wear rates.

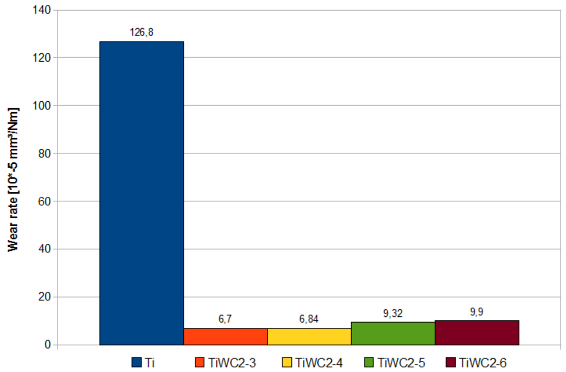


Fig. 15. Wear rates of samples TiWC

The results of the measurements of wear rates are given in Table 5 showing that the friction coefficient is reduced. TiWC samples have led to less wear in the alloyed zone. In the case of sample TiWC 2.4, the recorded wear depths was 9 µm. This, however, caused the loss of material on the surface of the sample and the surface-based interface between the sample and the test ball.

5. CORROSION BEHAVIOR

Corrosion behavior of surfaces were investigated through electro-corrosion test in 1 m H_2SO_4 solution. A calomel electrode was used as reference electrode, a Platinum electrode as auxiliary electrode and the sample represented the working electrode. The samples were polarized over a period between -1500 +1500 mV, applied between the working electrode and calomel and the corrosion rate, **i**, was measured expressed in current density.

Test results of electrocorrosion for surfaces made of titanium alloyed powder tungsten Hamid-r show a shifting of the corrosion potential from -576 to 120 mV and an increased current density up to 0.99 µA/cm^2.

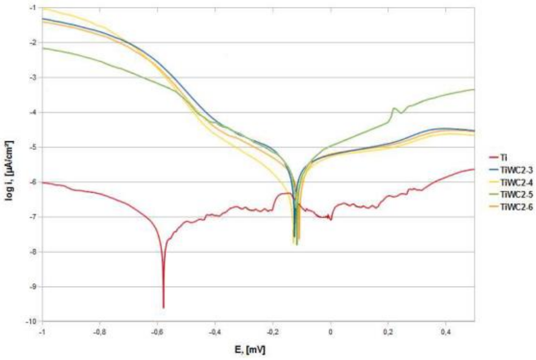


Fig. 16. Polarization curves of samples TiWC

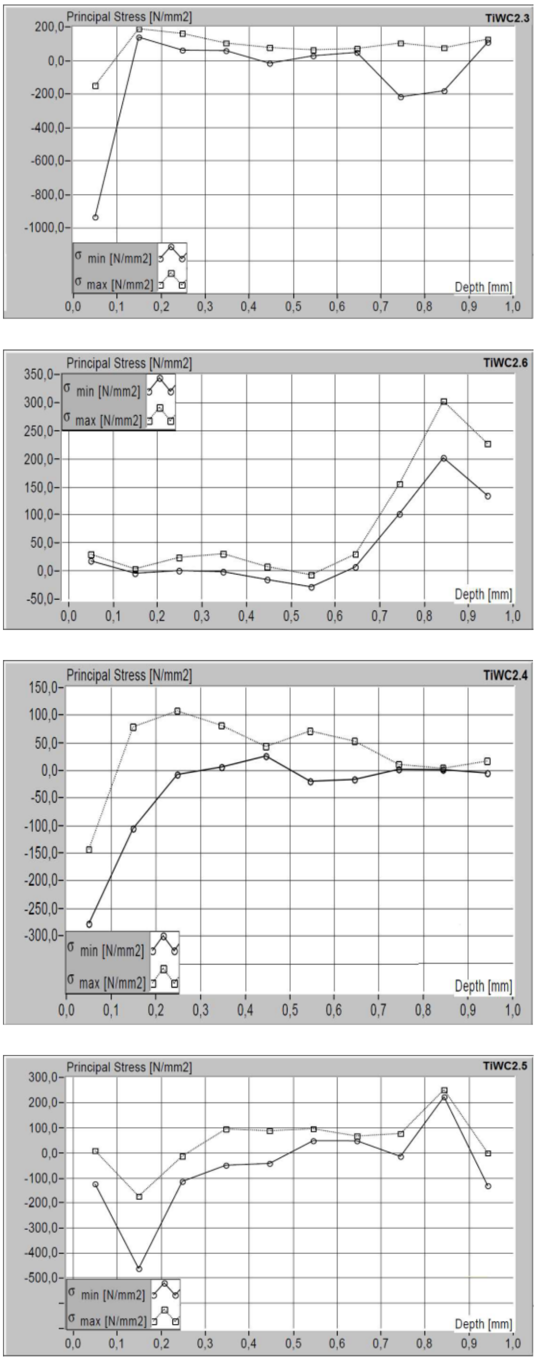


Fig. 17. Residual stress analysis of samples TiWC

Table 6. Electrochemical data of samples TiWC

	Ti	TiWC 2-3	TiWC 2-4	TiWC 2-5	TiWC 2-6
E_{corr} [mV]	-576.3	-122.1	-125.7	-116.4	-106.0
icorr [μA/cm²]	0.0061	0.9929	0.9763	0.5286	0.4875

Although the evidence does not show any major differences in the corrosion behaviour, lower rates of corrosion analysis of samples TiWC TiWC 2.5 and 2.6 can be attributed to the higher content of titanium in cobalt-alloyed area.

Surface stresses of alloyed waste were determined with the help of tensometric gauges The investigations were carried out on depths between 0.5-1.0 mm, depending on the depth of the alloyed zones, and stresses were calculated by integral method.

In the case of samples with tungsten carbide, TiWC 2.3 presents a voltage-pressure of 950 N/mm² during the first 0.2 mm, where tensions changes sign. The magnitude of the residual streses of compression in the samples TiWC, TiWC 2.4 and 2.5 touches 300 N/mm^2, 500 N/mm^2, respectively, up to a depth of 0.3 mm, and TiWC sample possess residual voltages 2.6 times greater, growing toward the interface.

Residual stresses analysis of samples TiWC are illustrated in Fig. 17.

4. CONCLUSIONS

Surface alloying process of titanium materials with tungsten carbide powder was made possible in a limited domain of energy process, from 300 W/mm to 330 W/mm.

- microscopic structure of alloyed area consists of titanium carbide (TiC) distributed in phases of chromium-titanium ($CrTi_4$), titanium-tungsten (TiW) and cobalt-titanium ($CoTi_2$);

- alloyed surface hardness with subsequent redoubles has values up to 748 $HV_{0.3}$ and superior wear resistance, assigned to wear hard phase of titanium carbide (TiC). It was also observed that the formation of cobalt-titanium phase ($CoTi_2$) led to a decrease in the coefficient of friction up to 0.365;

- alloying process has led to an increase in the corrosion rate for TiWC;

- measurements for determining residual stresses showed that areas of titanium alloyed with tungsten carbide powder (TiWC) possess residual compressive stresses, which may lead to an increased fatigue resistance of the material;

- the surfaces of titanium alloyed with tungsten carbide powder in the arreas of cobalt-chromium, using an electron beam line, present the best wear behavior in pin-on-disk tests, proving to be the best solution in applications where wear resistance is needed.

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