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PROPERTIES OF CARBIDE LAYERS PRODUCED BY MEANS OF THE VACUUM TITANIZING PROCESS COMBINED WITH GALVANIC TREATMENT

Keywords

Vacuum titanizing, carbide layer, tribological properties, corrosion resistance, electrochemical tests.

Abstract

A new technological processes combining a vacuum titanizing with a preliminary electrolytic deposition of Co-W or Ni-Mo alloys on the tool steel surface have been proposed to increase the corrosion resistance of the carbide layers of the TiC type. As a result, composite carbide layers of the TiC+(Co-W) and TiC+(Ni-Mo) type on the steel surfaces have been obtained. It has been proved that the wear resistance by friction of these composite layers produced by means vacuum titanizing of steel covered with electrolytic coatings is as good as the TiC carbides layers produced on the steel surface without electrolytic coatings, but their corrosion resistance is higher.

Introduction

Diffusion titanizing is applied to increase the durability of tools which operate under wear conditions. Titanizing of tool steel results in hard and wear resistant coatings based on titanium carbide. There is considerable

bibliographical data concerning the diffusion titanizing process, in particular, problems connected with hard titanium carbide layers are quite well elaborated [1, 2]. In the Institute of Precision Mechanics, a titanizing method was developed which consists in holding steel at a temperature of over 1000°C in titanium vapour under low pressure conditions [3]. However, the received carbide layers exhibited rather poor corrosion resistance in chloride media [3÷5]. To improve their corrosion resistance, Co-W or Ni-Mo alloys were deposited electrolytically on the steel surface before the titanizing process. This resulted in the formation of TiC+(Co-W) or TiC+(Ni-Mo) type composite carbide layers with modified characteristics. The objective of this paper was to determine the corrosion resistance in chloride solution of such composite layers produced on tool steel surface, as well as their tribological properties.

1. Experimental

The titanizing processes were carried out in a cold-wall vacuum oven at the temperature range of 1050 -1100°C at the pressure ranged from 10 Pa down to 10⁻³ Pa. Experiments were carried out on samples made of X210Cr12 tool steel.

Composite carbide layers of the TiC+(Co-W) type were produced by means of the vacuum titanizing process combined with preliminary electrolytic deposition of Co-W alloy on the steel samples surfaces. First, the steel samples were covered with 5 µm thick electrolytic coatings of 70% Co–30% W alloy. Subsequently vacuum titanizing of these samples was applied [4]. Composite carbide layers of the TiC+(Ni-Mo) type were produced in vacuum titanizing process on the steel samples with 5 µm thick electrolytic coatings of 70% Ni-30% Mo alloy. Carbide titanized layers were obtained on the steel samples without any electrolytic coatings. In the following part of this paper these carbide layers are appointed as TiC layers.

The layers obtained were investigated by performing an X-ray structural analysis and a spectral line analysis with a microanalyser. Metallographic examinations and thickness measurements of the layers were carried out with an optical microscope. The layer microstructure was revealed by initial etching.

Electrochemical corrosion measurements of obtained layers were performed in 0.5 M NaCl solution*. Potentiometric, voltammetric and impedance techniques were employed using Autolab system (GPSTAT 20 + FRA) [4].

Tribological properties of the layers were evaluated by sliding wear tests with concentrated contact. The tests were performed on sets of taper-three rolls test pieces at constant surface pressure in the range 50÷300 MPa [5].

* Electrochemical corrosion measurements were made on Faculty of Chemistry of Warsaw University of Technology.

2. Results

2.1. Layers constitution

A metallographic cross-sections of the TiC+(Co-W) and the TiC+(Ni-Mo) composite layers, as well as the TiC carbide layers have shown that the layers were unetched, as opposed to the steel base.

An X-ray surface structure analysis of titanized surfaces on the tool steel revealed a substantial presence of titanium carbide (TiC) and a trace Fe₂Ti intermetallic phase. Concentration depth profiles of Ti, Cr, C and Fe in the layer diffusion zone were typical of a carbide titanized layer [3]. Concentration of titanium in the TiC carbide layer was about 78 wt. % and of carbon about 19 wt. %. Thickness of the layer was about 10 μm .

The analysis of the X-ray diffraction patterns of the TiC+(Co-W) composite coatings revealed the occurrence of titanium carbide TiC and CoTi intermetallic phase. Concentration depth profiles of Ti, Co, W, Cr and Fe in the layer diffusion zone obtained by means of the X-ray microanalyses are shown in Fig. 1a.

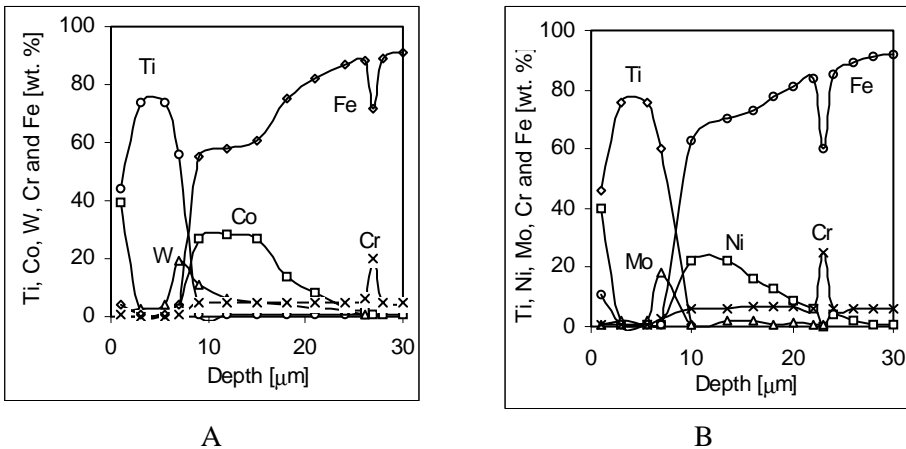


Fig. 1. Depth profiles of elements concentration of titanized layers produced on tool steel surface: a – the TiC+(Co-W) layer produced on the steel surface covered with Co-W alloy, b – the TiC+(Ni-Mo) layer produced on the steel surface covered with Ni-Mo alloy

An X-ray structural analysis of titanized surfaces on the tool steel precoated with an electrolytic Ni-Mo alloy coating revealed the presence of titanium carbide TiC and a NiTi intermetallic phase. Concentration depth profiles of Ti, Ni, Mo, Cr and Fe in the TiC+(Ni-Mo) composite layer diffusion zone obtained by means of the X-ray microanalyses are shown in Fig. 1b.

2.2. Layers corrosion resistance

Corrosion tests were performed for the following samples:

- the tool steel, without layer;
- the TiC carbide layer on the tool steel surface (titanized steel);
- the TiC+(Co-W) composite layer on the tool steel surface (electroplated with Co-W alloy and subsequently titanized steel);
- the TiC+(Ni-Mo) composite layer on the tool steel surface (electroplated with Ni-Mo alloy and subsequently titanized steel).

Electrochemical corrosion measurements of obtained materials were performed in 0.5 M NaCl solution at a temperature 24°C. The solution was open to the air. The exposed area of the sample was 1 cm². Potentiometric tests were employed to determine the time dependencies of the open circuit potential of the samples in the corrosive solution. Electrochemical studies revealed significant differences in the corrosion behavior of the samples under test. Steady state values of the open circuit potential (after 30 minutes exposure) are given in Table 1.

The bare steel samples exhibited very negative potentials below $E_{\text{corr}} = -590$ mV. The potential of the steel with the TiC carbide layers and with the TiC+(Co-W) composite layers was about 160 mV and 210 mV more positive, respectively, than that for the bare steel. The highest values of the open circuit potential $E_{\text{corr}} = -220$ mV were observed for the steel with the TiC+(Ni-Mo) composite layers. This suggests the highest corrosion resistance of this material.

The course of anodic polarization curves confirmed this view. Fig. 2 shows representative anodic curves for the samples under test. The shape of the curves for bare steel (a fast increase in anodic current) indicated an intense active dissolution of the steel samples. The steel samples with the TiC+(Co-W) and the TiC+(Ni-Mo) composite layers, as well as the TiC carbide layers exhibited spontaneous passivation and remained passive in wide ranges of potentials, whereas the steel without layer corroded actively (Fig. 2).

Some parameters extracted from the analysis of polarization data and remarks about the appearance of the sample surface after the test are given in Table 1. Active dissolution (a lack of passivation) of the bare steel samples resulted in a gray-rusty coloration of this material. Steel with the TiC carbide layer exhibited higher passive current than those observed for the samples with the TiC+(Co-W) and the TiC+(Ni-Mo) composite layers. The lower passive currents for steel with composite layers indicate the better protective action of the passive film developed on this material. Indeed, samples with TiC+(Ni-Mo) composite layers showed no changes after test; whereas, rusty spots occurred on samples with the TiC carbide layers, and scarce pits were observed on samples with the TiC+(Co-W) composite layers.

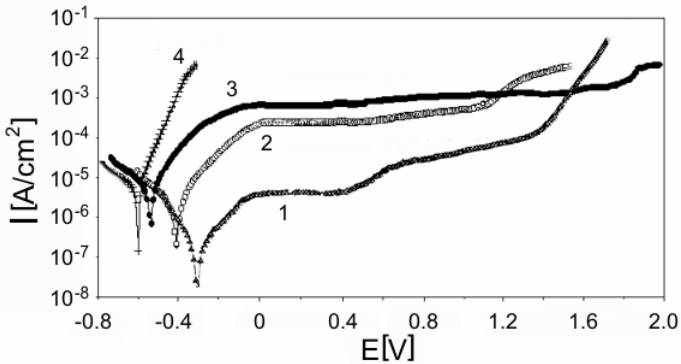


Fig. 2. Anodic polarisation curves of steel samples with the TiC+(Ni-Mo) composite layer (curve 1), the TiC+(Co-W) composite layer (curve 2), the TiC titanzed carbide layer (curve 3) and of bare steel (curve 4)

Table 1. Selected parameters taken from polarization curves

Sample	E_{corr}	I_{pas} ($E=750$ mV)	E_{tp}	Surface appearance
	mV	$\mu\text{A}/\text{cm}^2$	mV	
The steel, without layer	-590	No passivation		Gray-rusty
The TiC carbide layer	-430	60	1640	Rusty spots
The TiC+(Co-W) layer	-379	52	1245	Scarce pits
The TiC+(Ni-Mo) layer	-220	14	1465	No changes

The higher corrosion resistance of steel with the composite layers was confirmed upon the results of impedance measurements. Representative impedance plots for the tested samples are shown in Fig. 3. All the samples under test exhibited a similar pattern of impedance spectra. One capacitive loop was registered. However, there were evident differences in the size of this loop. The smallest loop was observed for the bare steel. The bigger loop was recorded for titanized steel with the TiC carbide layer and a slightly bigger one was observed for titanized steel with the TiC+(Co-W) composite layer (Fig. 3 a). Small impedance values indicated a low corrosion resistance.

Only a part of capacitive loop was registered for the steel with the TiC+(Ni-Mo) composite layer (Fig. 3 b). However, the size of this loop and corresponding impedance values were much higher than for other samples.

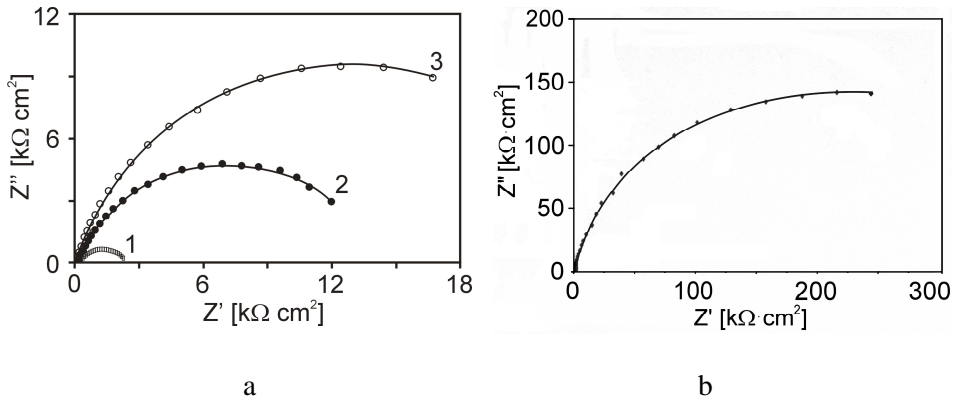


Fig. 3. Impedance spectra for steel samples with: a – bare tool steel (curve 1), the TiC titanzed carbide layer (curve 2), the TiC+(Co-W) composite layer (curve 3), b – the TiC+(Ni-Mo) composite layer

Parameters of the corrosion process, such as charge transfer resistance R_{ct} , were determined upon the analysis of obtained impedance spectra. Obtained values of the charge transfer resistance were confronted in Table 2. Titanized steel showed higher charge transfer resistance than bare steel. Steel with the TiC+(Co-W) composite layers exhibited about 2 times higher charge transfer resistance than titanized steel with the TiC layers. Steel with the TiC+(Ni-Mo) composite layers exhibited about 8 times higher charge transfer resistance than steel with the TiC+(Co-W) layers. This finding indicates superior corrosion resistance of this material.

Table 2. Values of the charge transfer resistance R_{ct} derived from impedance data

Sample	R_{ct} [$k^{\circ}\Omega \cdot cm^2$]	$R_{ct (layer)} / R_{ct (steel)}$
The steel, without layer	2.1	-
The TiC carbide layer	16	8
The TiC+(Co-W) layer	28	13
The TiC+(Ni-Mo) layer	213	101

A comparison between the corrosion resistance ($R_{ct (layer)} / R_{ct (steel)}$) of steel samples with the investigated layers is shown in Fig. 4.

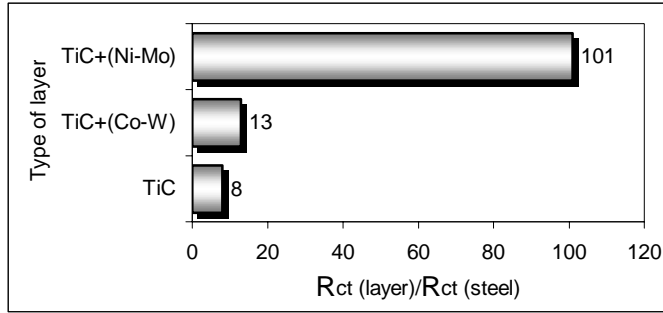


Fig. 4. A comparison between the corrosion resistance ($R_{ct}(\text{layer})/R_{ct}(\text{steel})$) of titanized steel samples with the TiC+(Ni-Mo) and the TiC+(Ni-Mo) composite layers, and the TiC carbide layer

2.3. Layers wear resistance

Sliding wear resistance tests were performed at pressures of 50, 100 and 300 MPa and a rotational speed of the tapered counter sample of 576 rev/min. The wear time was 100 min. Results of wear resistance of the titanized layers subjected to the tribological damage are presented on Fig. 5 which shows a linear wear in function of units pressure for 100 min friction time.

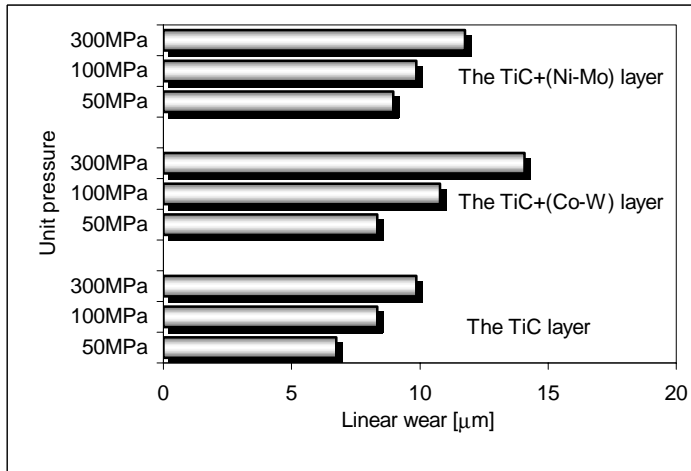


Fig. 5. The linear wear of tool steel samples with the TiC+(Ni-Mo) and the TiC+(Co-W) composite layers, and the TiC carbide layer, vs. friction time and units pressure

Conclusions

The results of performed investigations revealed that the corrosion resistance of titanized tool steel samples with the TiC+(Co-W) and the TiC+(Ni-Mo) composite layers as well as with the TiC carbide layers is higher than that for the steel without any layers. Electrochemical corrosion tests revealed that the TiC+(Co-W) and the TiC+(Ni-Mo) composite layers applied on tool steel surface could offer an effective protection against corrosion in 0.5 M NaCl. The steel samples with titanized layers exhibited spontaneous passivation and remained passive in a wide range of potentials, whereas the steel without layer corroded actively. The TiC+(Ni-Mo) and the TiC+(Co-W) composite layers assure lower passive current and higher corrosion resistance in chloride solution than the TiC carbide layers. The highest corrosion resistance was observed for samples with the TiC+(Ni-Mo) composite layers, which showed the least passive current density and the highest charge transfer resistance. It has been proved that the wear resistance by friction of the TiC+(Ni-Mo) and the TiC+(Co-W) composite layers, produced by means vacuum titanizing of tool steel covered with electrolytic coatings (with Ni-Mo or Co-W alloys), is as good as of the TiC carbides layers produced on the steel surface without any electrolytic coating, but their corrosion resistance is several times higher. The composite titanizing layers can be useful for applications where high resistance against wear and corrosion is needed.

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Reviewer:

Tadeusz PISARKIEWICZ

Właściwości warstw węglkowych wytwarzanych za pomocą procesu tytanowania próżniowego połączonego z obróbką galwaniczną

Słowa kluczowe

Tytanowanie próżniowe, warstwa węglkowa, właściwości tribologiczne, odporność korozyjna, testy elektrochemiczne.

Streszczenie

W pracy przedstawiono wyniki badań dotyczących właściwości użytkowych warstw kompozytowych typu $TiC+(Co-W)$ oraz $TiC+(Ni-Mo)$ wytwarzanych w procesie tytanowania próżniowego na powierzchni stali X210Cr12 pokrytej elektrolitycznie stopami Co-W lub Ni-Mo. Określono właściwości tribologiczne oraz odporność korozyjną warstw. Stwierdzono, że odporność na zużycie przez tarcie warstw kompozytowych typu $TiC+(Co-W)$ oraz $TiC+(Ni-Mo)$ wytwarzanych w procesie chromowania próżniowego na stali pokrytej powłokami Co-W lub Ni-Mo, jest równie dobra, jak warstw węglkowych typu TiC, wytwarzanych bez wstępnego osadzania powłoki elektrolitycznej, natomiast ich odporność korozyjna jest kilkakrotnie większa.

