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THE DEPENDENCE OF THE CHEMICAL COMPOSITION OF Al-Ti-Cr MULTI-COMPONENT COATINGS ON PARAMETERS OF THE ARC-EVAPORATION PROCESS

Key words: transmission coefficient, arc-evaporation method, PVD methods.

Abstract: One of the most perspective directions of the development of surface engineering concerns hard multicomponent coatings prepared using PVD technologies. Reactive arc vacuum sputtering is the best known and most widely used technology for manufacturing multicomponent antiwear coatings. Using this method requires the application of suitably composed targets to obtain coatings with suitable compositions. One of the problems that occur during the design of multicomponent coatings is the selection of the chemical composition of the cathode of the arc source. In the case of the arc vacuum method, the chemical composition of the cathode does not coincide with the chemical composition of the obtained coating. It is connected with the „transfer coefficient." It depends mainly on the intensity of the evaporation of the material from multicomponent targets, and it changes depending on the melting temperature of the element.

The authors present the results of the analysis of the transmission rate of the chemical composition of cathodes composed based on elements with different melting points (Al, Ti, Cr). The article presents the influence of chemical composition of two- and three-component cathodes on the chemical composition of the obtained coating. The study was carried out with the EDS method using a scanning electron microscope with a chemical composition analyser.

Zależność składu chemicznego powłok wieloskładnikowych Al-Ti-Cr od parametrów procesu odparowania źródła łukowego

Słowa kluczowe: współczynnik przenoszenia składu chemicznego, metoda odparowania łukiem elektrycznym, metody PVD.

Streszczenie: Jednym z najbardziej perspektywicznych kierunków rozwoju inżynierii powierzchni są powłoki wieloskładnikowe wytwarzane przy wykorzystaniu technologii plazmowych. Jedną z powszechnie stosowanych technik wytwarzania przeciwzużyciowych powłok wieloskładnikowych jest reaktywne odparowanie łukiem elektrycznym. Technika ta umożliwia wykorzystywanie targetów wieloskładnikowych, które pozwalają na otrzymywanie powłok o zróżnicowanym składzie chemicznym. Jednym z problemów występujących na etapie projektowania powłok wieloskładnikowych jest dobór składu chemicznego katody źródła łukowego. W przypadku metody łukowo-próżniowej skład chemiczny katod nie pokrywa się ze składem chemicznym otrzymanej powłoki. Związane jest to z intensywnością przenoszenia składu chemicznego katody. Zależy on głównie od intensywności parowania danego materiału z targetów wieloskładnikowych i zmienia się w zależności od wielu różnych czynników związanych zarówno z procesem technologicznym, konfiguracją technologiczną, jak również z parametrami katody oraz procesem jej wytwarzania.

W pracy autorzy przedstawili wyniki analizy głównych czynników mających istotny wpływ na intensywność przenoszenia składu chemicznego z katody na skład chemiczny powłoki. Autorzy skupili się w pracy głównie na analizie czynników związanych z parametrami katody źródła łukowego. Zbadano intensywność przenoszenia się składu chemicznego katod dwu- oraz trzyskładnikowych na bazie aluminium tytanu oraz chromu na skład chemiczny otrzymanej powłoki wieloskładnikowej. Badanie zrealizowano metodą EDS przy wykorzystaniu mikroskopu elektronowego wyposażonego w analizator składu chemicznego.

Introduction

Hard multicomponent coatings prepared using PVD technologies are one of the most perspective directions of surface engineering development. They are successfully used to improve the durability of many machines elements and tools used in many different areas, like aviation, and the metal and tool industries [1, 2, 3]. The possibility of forming various basic parameters, such as phase and chemical composition, microstructure and grain size [4, 5], enables the chance of creating their functional properties, including mechanical and tribological properties [6, 7].

The best known and most widely used technology for manufacturing multicomponent antiwear coatings is reactive vacuum arc evaporation [8]. At the stage of designing properties of the coatings obtained by this method, many factors should be considered, such as the configuration and parameters of the technological process. One of aforementioned configuration factors is the type and method of manufacturing cathodes and their arrangement in the reactive chamber. Moreover, droplet phase separation by plasma filters and element rotation during the process are among the key factors during multilayer structure formation [9]. On the other hand, parameters of the technological process that affect the process are the temperature and the bias voltage of the substrate, as well as the discharge power and the pressure of the working atmosphere. What is more, the use of the vacuum arc evaporation method requires the use of proper targets. This is essential for targets that enable the preparation of multicomponent coatings [10]. In the case of the vacuum arc evaporation method, the chemical composition of the cathode does not coincide with the chemical composition of the obtained coating. It is connected with the „transmission coefficient.” It depends mainly on the intensity of particular material evaporation from the multicomponent target, and it changes depending on the melting point of a particular element and the presence of other elements in the chemical composition of the target. Literature studies show that some researchers were able to determine the chemical composition of the coating with the knowledge of the chemical composition of the cathode. Such a formula was created for the arc ion plating method [11]. However, the designed formula is not correct for the vacuum arc evaporation method.

Due to the lack of any indication in the literature of how to obtain the transmission coefficient, which is necessary for creating functional properties of the coatings, it is essential to gather knowledge in the field of the analysis of transferring the chemical composition of the multicomponent cathode directly on the chemical composition of the coating, particularly those composed of elements with different melting points.

1. Experimental details

1.1. Preparation of hybrid layers

Samples selected for investigations were made of pure iron (Armco). The investigated multilayers were created by means of the arc-evaporation method.

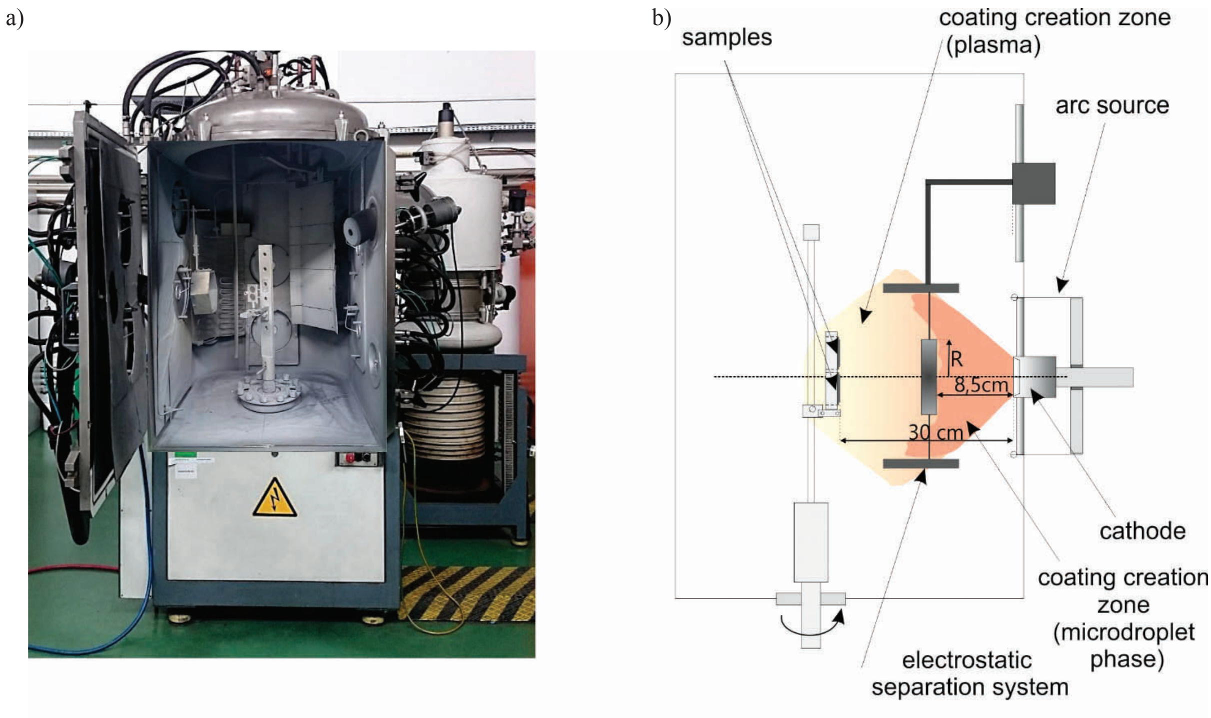

Fig. 1. The technological equipment and scheme of surface treatment technology: a) MZ383 device, and b) the scheme of Arc-PVD technology

Source: Authors.

The PVD coating deposition process was executed with the use of a MZ 383 device (Fig. 1a). The device was equipped with arc sources with the cathode diameter of Ø = 80 mm, modern, reliable power systems, a substrate polarization system, as well as the systems of monitoring and measuring substrate temperature and atmospheric gas pressure. The developed technological configuration of the process is schematically shown in Fig. 1b. It included the implementation of processes using plasma separator, function of which is to reduce droplet phase in the structure of the coating, which can significantly impact the change in the share of individual elements in the chemical composition the coating. The arc source is equipped with an electrostatic separation system (Figure 2a). The operation of electrostatic separation systems consists in using a shield placed between the plasma arc source and the substrate, perpendicularly or at an angle to the plasma and microdroplets' flux (Figure 2b). The shield is isolated from the arc source electrodes or is properly polarized [12].

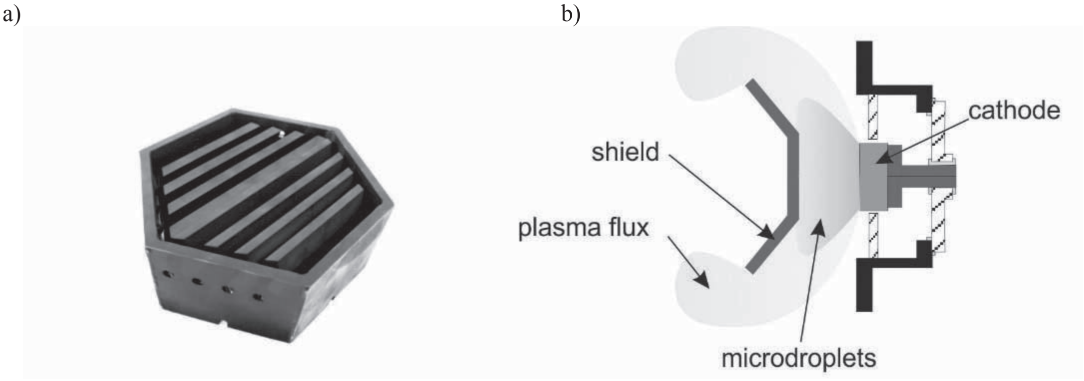

Fig. 2. Electrostatic separation system: a) electrostatic separator produced by ITeE-PIB in Radom (Poland), b) the scheme of construction of electrostatic separation system

Source: Authors.

Five different multicomponent coatings were deposited with the use of five targets with different chemical compositions based on elements of aluminium, titanium, and chromium, which differ in melting point, respectively: Al 660°C, Ti 1668°C, Cr 1860°C [13]. Parameters of the PVD surface treatment technology are presented in Table 1.

Table 1. Parameters of the Arc-Evaporation method

Cathode	Pressure [mbar]	Temperature [°C]	U_{bias} [V]	Separator current [A]	Arc current [A]	Time [min]
Al70Cr30	<1 x 10^{-5}	250–350	-100	50	50	120
Al70Cr15Ti15	<1 x 10^{-5}	250–350	-100	50	50	120
Al70Cr20Ti10	<1 x 10^{-5}	250–350	-100	50	50	120
Al70Cr25Ti5	<1 x 10^{-5}	250–350	-100	50	50	120
Al70Ti30	<1 x 10^{-5}	250–350	-100	50	50	120

1.2. Characterization of hybrid layers

The microstructure and surface morphology of the multicomponent coatings were characterised with the use of a SU-70 Hitachi scanning microscope equipped with the Energy Dispersive Spectrometer (EDS). The microstructure observations were carried out on the properly prepared sample in the form of metallographic specimens. The metallographic samples were mechanically polished using Struers equipment and technique.

The Chemical composition of the investigated PVD coatings was determined with the EDS method with an X-ray microanalyzer type EDS produced by Thermo Scientific company enabling the detection of elements from beryllium to uranium.

2. Research results

The results of analysis of the microstructure and surface morphology of the coatings prepared using the binary cathodes (Al70Ti30 Al70Cr30) and ternary cathodes (Al70Cr25Ti5, Al70Cr15Ti15, Al70Cr20Ti10) are shown in Figures 3 and 4. All obtained coatings are characterized by a lack of a droplet phase.

The analysis of the microstructure of coatings prepared using the binary cathodes showed significant differences in their structural construction (Fig. 3). The AlCr coating is characterized by very irregular, porous structure with a grain size not exceeding 50 nm; whereas, the AlTi coating is characterized by a much larger grain size and a densely packed porous structure.

A similar phenomenon was observed during the analysis of the microstructure of the coatings prepared with the use of a ternary AlCrTi cathode (Fig. 4). Reducing the amount of chromium and increasing the amount of titanium in the chemical composition of the cathode will homogenise the structure of obtained coatings. The coating obtained using Al70Cr15Ti15 cathode (Fig. 4c) is characterized by densely packed, non-porous, homogeneous structure in contrast to coatings produced with the use of Al70C25Ti5 and Al70Cr20Ti10 cathodes. In the case of other ternary coatings, heterogeneous and porous structure was observed. Increasing the chromium content in the composition of the cathode also caused grain refinement (Figs. 4a, b).

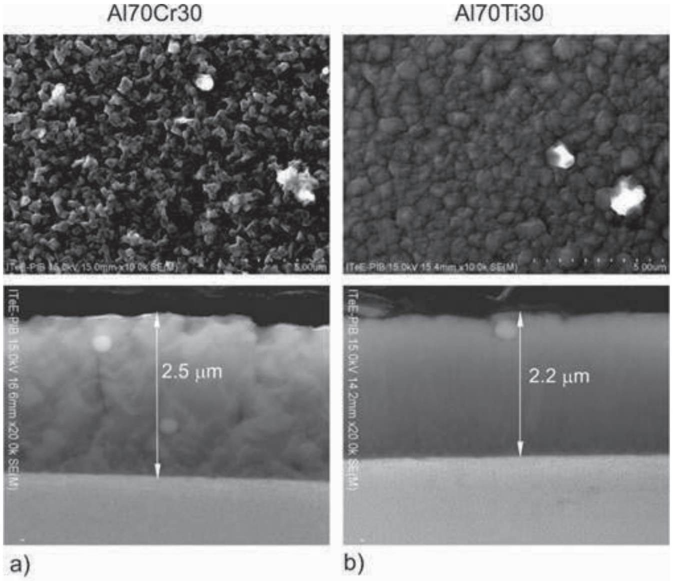

Fig. 3. SEM images of microstructure and morphology of the coatings: a) Al70Cr30, b) Al70Ti30

Source: Authors.

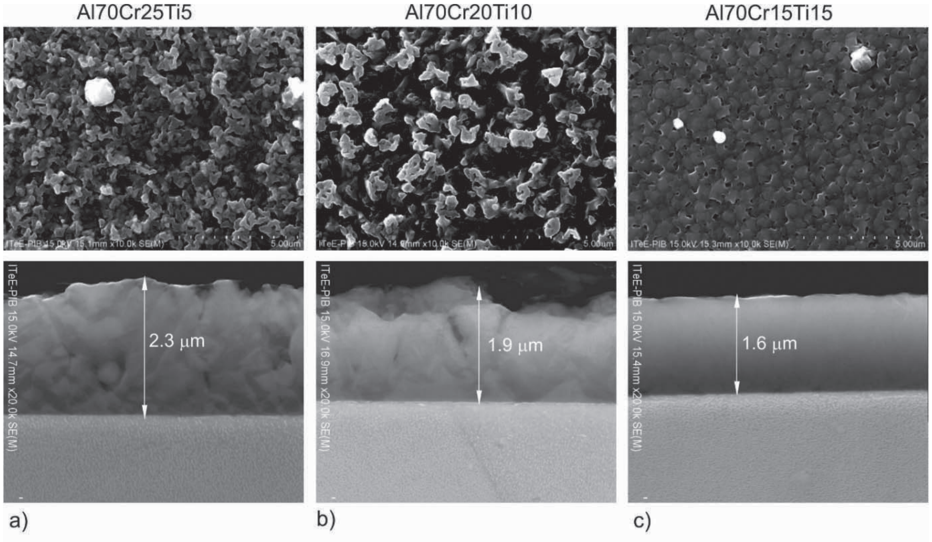

Fig. 4. SEM images of microstructure and morphology of the coatings: a) Al70Cr25Ti5, b) Al70Cr20Ti10, c) Al70Cr15Ti15

Source: Authors.

The observed changes in the microstructure of the coatings are related, among others, to the intensity of the surface diffusion process.

The study of the chemical composition of all tested coatings was carried out on their surface, and the data was collected from the area of 0.5 µm x 0.2 µm. The results represent the average content of elements from three measurements. The results of the chemical composition are shown in Table 2.

Table 2. Chemical composition of the coating

Cathode	Al [% atm]	Cr [% atm]	Ti [% atm]
Al70Cr30	85±0.5	15±0.5	-
Al70Cr25Ti5	84±0.2	14±0.2	2±0.2
Al70Cr20Ti10	83±0.4	12±0.3	5±0.3
Al70Cr15Ti15	89±0.3	6±0.3	5±0.1
Al70Ti30	85±0.1	-	19±0.1

The obtained results confirmed the existing differences in the chemical compositions of coatings in relation to the chemical composition of the cathode. The significantly higher aluminium content in the chemical composition of the coating in relation to the chemical composition of the cathode confirms the increased intensity of the evaporation of this element in comparison to other elements with higher melting points.

Conclusion

The obtained results show an important influence of the chemical composition of the cathode on the microstructure of prepared coatings. The melting point of the elements constituting the coating has a decisive impact on its growth mechanism. According to the Thorton growth model [14], the type of the structure of the coating depends, inter alia, on the ratio of the substrate temperature to the melting point of the deposited element.

In the case of using a cathode composed of aluminium (melting point of 660°C) and chromium (melting point of 1860°C), we received a porous and heterogeneous structure, which was built of columnar crystallites and voids between them. Limited surface diffusion of atoms of deposited material contributed to the formation of such a microstructure. A simultaneous gradual increase of titanium, which is characterized by a low melting point (1668°C) and a reduction of chromium, resulted in the increase of the density and homogeneity of the structure as well as loss of porosity.

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