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Thermal imaging research of structural features and thermophysical stability of protective oxide layers, applied by the ion-plasma spraying method

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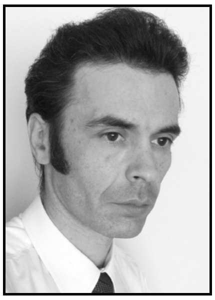

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Abstract

The aim of the work was to investigate structural changes of oxide protective based on MgO, Al_2O_3, and TiO_2 layers. Structural and thermophysical stability of the coatings was investigated by both the scanning electron microscope (SEM) REMMA-102-02 and an infrared camera (SC7600). The oxide layers were applied by the method of ion-plasma spraying. Surface topography was investigated by the atomic-force microscope Solver P47-PRO. The dielectric layers MgO and Al_2O_3 deposited on the substrates made of 40H13 and AMg_2 alloys had lower defectiveness and higher stability of their thermophysical properties.

Keywords: ion-plasma spraying oxide layers, structural and thermophysical properties, SEM, AFM, infrared camera.

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Badania termowizyjne cech strukturalnych oraz stabilności parametrów termofizycznych ochronnych warstw tlenkowych, naniesionych metodą natryskiwania jonowo-plazmowego

Streszczenie

Celem pracy było zbadanie zmian strukturalnych ochronnych warstw tlenkowych wykonanych z MgO, Al_2O_3 i TiO_2. Strukturę oraz stabilność parametrów termofizycznych otrzymanych powłok badano za pomocą SEM (*ang. Scanning Electron Microscope*) oraz kamery termowizyjnej (SC7600). Warstwy tlenku naniesiono metodą natryskiwania jonowo-plazmowego. Strukturę wykonanych i stosowanych warstw powierzchniowych badano za pomocą skaningowego mikroskopu elektronowego REMMA 102-02. W badaniach wykazano możliwość zastosowania kamery termowizyjnej do oceny stabilności strukturalnej warstw dielektrycznych. Topografię powierzchni warstw ochronnych badano z pomocą mikroskopu sił atomowych Solver P47-PRO. Wykazano, że jakość stosowanych pokryć ochronnych oraz jednorodność rozkładu pola temperatury mierzona za pomocą kamery termowizyjnej na powierzchni, zależy od warunków w jakich są stosowane. W szczególności warstwy dielektryczne MgO oraz Al_2O_3 osadzone na podłożach z 40H13 oraz stopów AMg_2 charakteryzują się mniejszą wadliwością i większą stabilnością właściwości termofizycznych. Stopy magnezu, aluminium i tytanu są często stosowane w ochronnych warstwach dielektrycznych na podłożach różnych materiałów

konstrukcyjnych. Właściwości fizyko-mechaniczne powłok ochronnych wykonanych z materiałów tlenkowych muszą być stabilne zarówno przy ogrzewaniu jak i chłodzeniu. Badanie termiczne za pomocą kamery termowizyjnej wykonano stosując metodę fali cieplnej. Do badanej próbki dostarczono energię w postaci impulsu i mierzono w stanie dynamicznym, zmiany wartości temperatury. Na podstawie badań termowizyjnych oceniono jednorodność rozkładu temperatury i właściwości termofizyczne badanych warstw ochronnych.

Słowa kluczowe: ochronne warstwy tlenkowe, napylanie jonowo-plazmowe, właściwości struk-turalne oraz termofizyczne, SEM, AFM, kamera na podczerwień.

1. Introduction

Magnesium, aluminum and titanium alloys are of great interest when preparing the protective dielectric layers on substrates made of different structural materials (Table 1). Magnesium oxide (MgO), in particular, combines in a unique way high heat conductivity (λ), maximal exploitation temperature ($T_{\text{exp-max}}$), width of the bandgap (E), dielectric strength (ε), optimal dielectric constant (χ) (here “optimum” - means sufficient for use of this material as a dielectric) and thermal-expansion coefficient (α). It possesses high chemical and thermal stability and preserves its high electric resistance up to temperature 1000 ºC [1-4]. Aluminum oxide, in its turn, is widely used in radioelectronics and microelectronics. It is in nine crystallographic forms, among which α modification is the most important. This oxide possesses high dielectric characteristics at the operation temperature of 1800-1900 K.

Tab. 1. Properties of oxides [1-6]
Tab. 1. Właściwości tlenków [1-6]

	λ, W/ (m·K)	$T_{\text{exp-max}}$ K	E eV	ε kV/mm	χ	α, $10^{-6}\cdot K^{-1}$
MgO	28	2273	7,8	10-35	8-10	11,7-14,2
Al_2O_3	24	1800	6	10-35	12	5-6,7
TiO_2	11.7	1700	3.2-3.8	4	31-173	9,8-10,8

Titanium dioxide (TiO_2) represents the crystalline base of technological ceramics. It has high dielectric permeability to compare with other ceramic materials. The oxide titanium films thanks to their physicochemical properties are widely used as protective and optical coatings in the gas sensors and in the photocatalysis. They are also employed in microelectronics (dynamic memory, field transistors, ferromagnetic) [5]. Besides, TiO_2 is used in electronic engineering, particularly for condensers production. Titanium dioxide in a pure form does not exist in nature. It is produced by chemical processing of titanium ores: $FeTiO_3$, $CaTiSiO_5$, $CaTiO_3$ and other. Titanium dioxide exists in three forms: anatase, brookite, rutile. A high-temperature form of rutile is the most stable into which two other pass irreversibly. Titanium dioxide in the anatase modification is used as a catalyst and a component of solar cell batteries [6]. The high reflection coefficient of titanium dioxide (in a wide almost used optical and infra-red frequency range) allows using it for protection of space shuttles against solar irradiation. A special type of TiO_2 called “capacitor” is produced for ceramic industry.

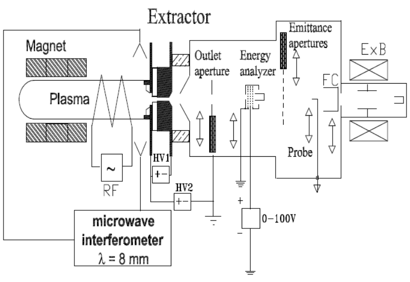

Fig. 1. High-plasma-density helicon source for ion beam application [8]
Rys. 1. Źródło helikonowe wysokiej gęstości plazmy do napylania jonowego [8]

The mentioned ceramic materials are conventionally obtained by the oxide powders sintering at different temperatures. However, with the development of high-energy engineering methods it is possible to change the chemical composition, structure and phase state of the surface in order to give it the improved operation properties. Such technologies include: vapor-phase epitaxy, molecular-beam epitaxy, ion-plasma spraying, magnetron high-frequency spraying and constant-current spraying, ion implantation and laser treatment [6].

New possibilities of preparation and use of oxide coatings in food, building, agriculture industries, microelectronics etc have been introduced lately. As a result, a new generation of electric heaters has been developed with application of high-energy methods of surface engineering. They are characterized by a sequential location of the dielectric and resistive layer on the metal substrate and are called Film Heating Elements (FHE). The main function of the dielectric layer in the film heating element is to ensure a reliable insulation between the substrate and the resistive layer. That is why the dielectric layer must possess high resistivity and its Coefficient of Thermal Expansion (CTE) should be close to CTE of the substrate. Besides, it must have a good-quality surface and low porosity. Its physical and mechanical properties must be stable under heating and cooling [7]. An inadequate level of at least one of the properties of the insulation layer can cause failure of all FHE construction. In particular, if the dielectric layer resistance is low, the flow current increases, thus causing a short circuit between the substrate and the resistor. A significant deviation of CTE will lead to cracking of the functional layers, while high porosity – to a larger higroscopicity and a significant decrease of dielectric characteristics. Regarding the above mentioned remarks, the preparation of good-quality dielectric layers and detailed study of their properties are very important.

2. Experimental investigations

The dielectric layers were prepared from oxides of magnesium, aluminum and titanium by the ion-plasma discharge system – Figure 1 [7, 8].

It is a multi-functional equipment that includes a high-frequency source of helicon-discharge plasma and plasma-arc accelerators for the CVD process realization. Application of a helicon source ensures constant action of argon ions on the substrate during the whole technological process. In such a way the foreign impurity atoms absorbed by the substrate surface are effectively removed from it. This increases the adhesion of the applied layers. Process of generating micro droplets is related to the macroscopic chaotic displacement of cathode spots at the cathode working surface. The main role in this movement plays a plasma, which arises at the micro-explosion at that cathode spot position. A plasma arc, that spreading along the cathode surface, results in the redistribution of the electric-field near heterogeneities ledge on a cathode surface. Therefore, if you change the plasma parameters, it is possible to expect considerable changes in case of occurring and development of spots. Such a change, for example, is additional ion cathode bombardment by the gas phase, generated from its surface. It is thus possible to attain diminishing of the cathode overheat at the point of existent cathode spot localization, that will result in diminishing the part of the micro-drop phase. A high degree of plasma flow ionization (>80%) allows us to control the layer thickness during application by the charge value which is integrally passed to the substrate.

The ion-plasma spraying was carried out under regimes that differ by the process duration (τ), some solar source customisation parameter — potential of displacement to the substrate (E_{disp}), pressure (p) and some ion source customisation parameter — plasma arc current (I) (Table 2). Oxide layers were deposited on steel and magnesium-alumina rectangle substrates of size 16×2×60 mm by spraying magnesium, aluminum and titanium cathodes in the oxygen atmosphere. Cathode elements were produced in the form of rods with a diameter of 40 mm by machining factory casting ingots. As materials there were used: magnesium Mg-98 (for MgO), aluminum A1 99,7 (for Al_2O_3) and titanium BT1-00 (TiO_2). To improve the adhesion characteristics of oxide coatings, the substrate surface was preliminary grinded and polished to get the twelfth grade of roughness (R_a=0.20 µm). The substrates were placed in a special holder at a distance of 40-50 cm from the cathode. This distance ensures the maximum density of ions in the plasma flow. The substrate was heated in the furnace installed directly in the reaction camera of the ion-plasma system as a result the coating better cohesion was better. Finish cleaning of the substrates in the argon plasma flow at pressure of 0,933 Pa with the potential on the substrate E=-100 V and current on the specimen 0.15 A was carried out for 30 min by a helicon source in the "column" regime. This allowed the additional cleaning of the surface from deterioration and removing of internal pressures which arose during production and preliminary treatment.

Tab. 2. Conditions of oxide layers preparation [9-10]
Tab. 2. Warunki napylania warstw tlenkowych [9-10]

Coating	*Substrate*	τ, min	*p*, mm Hg	E_{disp}, V	*I*, A
MgO	40H13	25	$3 \cdot 10^{-2} \div 8 \cdot 10^{-3}$	-14	40
Al_2O_3	AMg_2	10	$(1,5 \div 2) \cdot 10^{-2}$	-60	32
TiO_2	40H13	19	$2 \cdot 10^{-2}$	-14	30

The structure of the applied surface layers was investigated by the scanning electron microscope REMMA-102-02 while their thermal properties – by the infrared camera SC7600 (Figure 2). This camera is a device that records the infrared irradiation and transforms it into an electron signal which is processed and represented on the screen as a thermal imager.

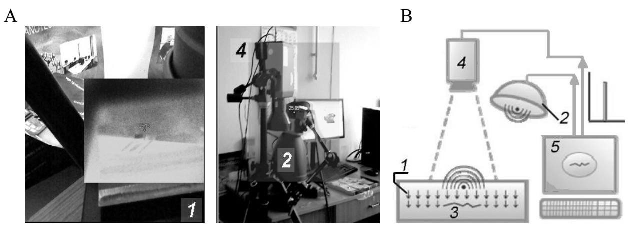

Fig. 2. A view of the investigated surface (A) and experiment setup using pulse thermography method (B)
Rys. 2. Widok badanej powierzchni (A) oraz stanowisko do badań termowizyjną metodą impulsową (B)

The distribution of temperature on the imager display is in the form of a field in which a certain color corresponds to a certain temperature and this is indicated on the given temperature range. The technical characteristics of the infrared camera SC7600 are as follows: sensor – InSb; the wave length range (1.5-5.1) µm; resolution (640×512) pixel; aperture F/3; frame frequency, 100 Hz; integration time 0.50 ms; excitation duration – 2.00 s; excitation source - Flash with Hensel generator 6 kJ, delay 1 ms.

The pulse method was used for investigations which consisted in the creation (using heat source 2) of heat waves *l,* partly absorbed by the investigated specimens surfaces. When propagation of the heat wave reached the region of object 3 within which the change of thermophysical properties (cracks, disbonding, additives) was recorded, it was partly blocked. The wave reflected from this region encountered the wave formed on the surface and as a result there was a possibility of recording the change of temperature characteristics. This effect was recorded by a thermal imager 4 and on the bases of mathematical analysis (software IR-NDT) the information about structural temperature-determined characteristics of the surface was obtained. It should be noted that the state of the surface (recorded) distribution of heat flow was affected, giving a deformation indent, not only a part of the heat flow arising from the heterogeneities of the investigated coatings internal structure but also by some additional parameters of structure, in particular adhesion and porosity.

Surface topography was investigated by the atomic-force microscope Solver P47-PRO. The analysis of the obtained images was identified by "Image Analysis-2" software.

3. Results and discussion

Figure 3 shows the infrared image of the original surface of magnesium-alumina alloy and steel. The original surface is rough, though homogeneous in structure, with no cracks and visible defects. Microrelief indentations formed during surface cleaning from imputity atoms (prepared before oxide powders sintering) are identified by more dark tone colors of the infrared image.

Figure 4 illustrates the morphology of structure and surface of oxide layers in infrared irradiation. The MgO layer structure (Figure 4a) consists of the round shape grains of different dispersion degree. The grain size is within 20 µm to 70 nm. The grain growth occurs, probably, by the island mechanism where grain nuclei are the base for the formation of new centers of crystallization and their future growth. New formed grains are grouped into clusters of different size. Owing to a specific microrelief, it is characterized by a great specific interface that increases because of the lobes formed in the direction perpendicular to the grain. The thickness of the identified lobes is 10-20 nm. Such a mechanism of layer construction and a significant difference between sizes of grain clusters lead to a pronounced porosity of the dielectric layer and thus to its larger hygroscopicity.

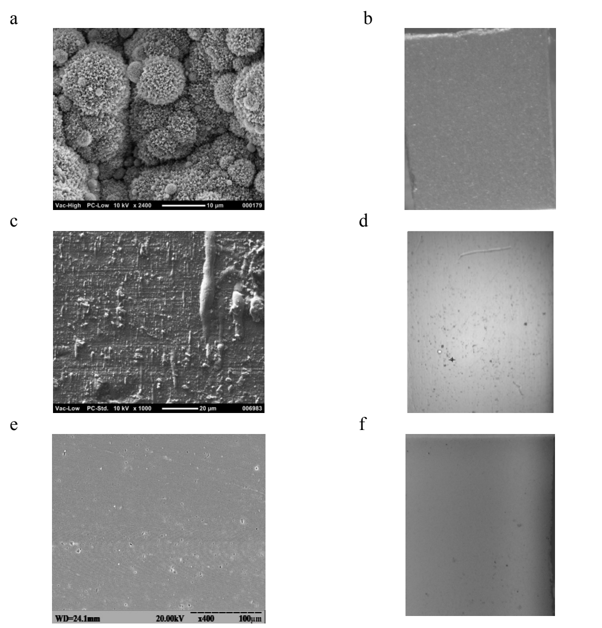

Fig. 4. Morphology (1) and infrared image of surface (2) of oxide layers: (a, b) – MgO; (c, d) – Al_2O_3; (e, f) – TiO_2
Rys. 4. Morfologia (1), obraz w podczerwieni powierzchni (2) warstwy tlenku: (a, b) – MgO; (c, d) – Al_2O_3; (e, f) – TiO_2

This is proved by an insignificant relief of the MgO oxide layer in the infrared spectrum (Figure 4b), what is explained by the peculiarities of technological process of ion-plasma spraying. In particular, a small mass of magnesium atoms makes a dense packing of the fragments of layer structure more complicated and increases its roughness. The thermal image of MgO layer testifies to its homogeneous structure, while dark regions, sometimes seen on the surface, may indicate the presence of dielectric phases or impurity atoms.

The Al_2O_3 surface layer is characterized by a smooth, solid, visually pore-free structure of the surface (Figure 4c). Sometimes there are small recesses of a size to 1 µm that appeared as a result of the surface fusion by the brought microdrop fraction of aluminum irradiated from the cathode. The prevailing orientation of the surface structural elements of an elongated form is caused by the concentrated action of ion-plasma arc. Their volume fraction is about 50%. The layer quality is verified by the infrared images. The elongated ledges have possibly a little bit higher conductivity to compare with the main fraction of the layer.

The TiO_2 layer surface is characterized by an insignificant porosity (20-30% volume). Pores sizes are within the values of 0.08 to 1 µm. This agrees with the thermal image of the TiO_2 surface on which they are seen as the change of temperature properties of the layer, thus causing their more dark color representation.

Interesting information was obtained from the study of microrelief surface layers by atomic force microscopy. Particularly, Figure 5 shows a three-dimensional image of the surface formed as a result of processing of ion-plasma spraying method (Figure 5a) and the distribution of the roughness (Figure 5b). MgO layer has a structured surface, with clearly defined boundaries between ledges that are characterized by directivity of their growth (Figure 5a). The maximum height of ledges on the surface layer is 335 nm. Thus the bulk of the surface layer of MgO ledges takes up 100-200 nm (Figure 5b).

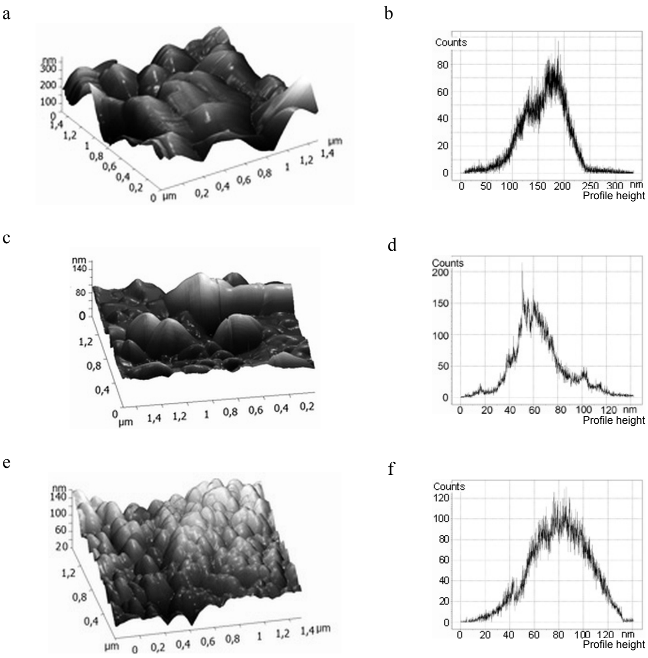

Fig. 5. Three-dimensional image of the surface formed as a result of processing of ion-plasma spraying method

Rys. 5. Trójwymiarowy obraz powierzchni utworzonej w wyniku plazmowo-jonowego natryskiwania

During research of Al_2O_3 layer surface - microrelief of dimples-structure, focused normally to the substrate surface, was found.

The available conglomerate fragment length patterns 1mkm (Figure 5c). The maximum height of speeches on the surface of Al_2O_3 layer is 142 nm. Thus the bulk of the surface microrelief performances takes up 50-70 nm (Figure 5d). Thus the main share of the microrelief of the surface is occupied by ledges 50-70 nm high (Figure 5d).

For the surface TiO_2 layer there is a typical uniform distribution of structure fragments, they are smaller compared to the layers that were considered above. Clearly there are observed limits of separation between performances. Fragments of the surface structure are formed in rows oriented in several directions (Figure 5e). The histogram of surface roughness indicates a uniform distribution of performances with a smooth transition from minimum to maximum values. The maximum height of speeches on the surface of TiO_2 layer is 140 nm. The major share of TiO_2 surface microrelief ledges takes up 60-100 nm.

Thus, the microtopography analysis of the surface layers formed revealed that the lowest surface roughness and uniformity of size of the fragments of the structure had a TiO_2 layer. These results confirm the analysis of surfaces of oxide layers by means of the infrared camera.

Our studies (based on previous processing [11-14]) allow us to further improve image analysis techniques for thermal imaging surfaces using parameter estimation of detected thermal radiation, resulting in multiple spectral bands. The estimation of the signal obtained with the use of IR-filter set for selection in the registered range that part of the spectrum where the signal / noise ratio is maximized. This is appropriate to combine frame by frame sequential thermal imaging frames obtained with different set towards registration IR-filters. In order to avoid excessive mismatch of experimental models, check carried out at the final stage transient thermal process, stimulated by a heat pulse (Figure1).

4. Conclusions

It is shown that the use of an infrared camera SC7600 gives a possibility to evaluate the structural stability of dielectric layers more correctly. Getting a clear correlation of the coating by using multispectral infrared image registration is considered.

It is established that the temperature field heterogeneity or homogeneity on the external surface of the investigated layers testifies indirectly to the character of the defect distribution. In turn, this allows us to identify the level of thermophysical properties with good quality.

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