

## CORROSION AND WEAR BEHAVIOUR OF ALUMINA COATINGS OBTAINED BY VARIOUS METHODS

T. LAMPKE<sup>1</sup>, D. MEYER<sup>1</sup>, G. ALISCH<sup>1</sup>, B. WIELAGE<sup>1</sup>,  
H. POKHMURSKA<sup>1</sup>, M. KLAPKIV<sup>2</sup>, M. STUDENT<sup>2</sup>

<sup>1</sup> Chemnitz University of Technology, Institute of Materials Science  
and Engineering Erfenschlager Straße 73, 09125 Chemnitz, Germany;

<sup>2</sup> G. V. Karpenko Physico-Mechanical Institute of the National Academy of Sciences of Ukraine

Alumina coatings are widely used in a range of industrial applications to improve corrosion protection, wear and erosion resistance and thermal insulation of metallic surfaces. From various efficient and adjustable processes refined alumina surfaces with long-term use are obtained. It can be seen that cost-efficient arc-sprayed Al coatings post-treated by plasma-electrolytic oxidation (PEO) form Al<sub>2</sub>O<sub>3</sub>-layers with remarkable corrosion protection, hardness, bonding strength and abrasion resistance as well as extended service time. The properties of these coatings are compared to alumina coatings obtained by flame spraying and atmospheric plasma spraying.

**Key words:** *plasma electrolytic oxidation, arc-spraying, atmospheric plasma spraying, flame spraying, Al<sub>2</sub>O<sub>3</sub>.*

The application of technical components in extreme operating conditions often demands highly corrosion- and wear-resistant coatings to ensure the long-term functionality of technical systems. Thermal spraying of Al<sub>2</sub>O<sub>3</sub> via atmospheric plasma spraying (APS) or flame spraying are commercially used methods to create coatings meeting these requirements. Corrosion and wear resistance of thermally sprayed Al<sub>2</sub>O<sub>3</sub>-coatings are primarily determined by phase composition and porosity. Low porosity indicates high melting rates of the corundum spray particles. Quick solidification of the molten alumina particles leads to the formation of meta-stable  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and amorphous Al<sub>2</sub>O<sub>3</sub>, which show lower hardness compared to corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>). On the other hand, lower melting rates result in higher porosity and lower coating cohesion. In dependence on thermal spraying process parameters, a micro hardness values from 750 to 1650 HV can be found in the literature.

Another method to produce ceramic coatings is plasma-electrolytic oxidation (PEO, also called micro-arc oxidation (MAO) or spark discharge anodising), which is based on anodic oxide film formation on valve metals such as aluminium, magnesium, titanium, zirconium and their alloys under plasma conditions in low-concentrated alkaline electrolytes [1, 2]. This method is an alternative to electrochemical anodizing especially because of the very high hardness of the layers due to crystalline microstructure. PEO-treated aluminium parts show improved corrosion and wear resistance. The PEO process can also be applied as a post-treatment of thermally sprayed aluminium coatings to improve their performance characteristics.

The paper presents the results concerning the correlations between production, microstructure and functional properties of ceramic coatings obtained by different thermal spraying methods and PEO treatments of arc-sprayed aluminium coatings. The corrosion behaviour under potentiodynamic conditions as well as the abrasive wear mecha-

nism of the coatings are examined and discussed. The results show the high performance of alumina coatings produced by plasma-electrolytic oxidation of thermally sprayed aluminium coatings in comparison to conventionally produced alumina coatings.

**Experimental procedure. Thermal spraying.** To increase the mechanical bond strength of spray coatings, all substrates were pre-treated by abrasive blasting. Flame spraying was carried out with a CastoDyn 8000 powder flame spray system (Castolin Eutectic, Switzerland), APS with a 3K Magnum plasma-spray torch (GTV Verschleiss-Schutz GmbH, Germany), always on steel substrates ( $\varnothing 40 \times 8$  mm) with spray parameters given in Table 1. Corundum powder with defined grain fraction ( $-45 +20$ ) was used to prepare an  $\text{Al}_2\text{O}_3$  coating thickness from 150 up to 200  $\mu\text{m}$ .

**Table 1. Spray parameters for atmospheric plasma, flame- and arc-spraying**

Spraying parameters	Value			Unit
	Flame-spraying	APS	Arc-spraying	
Power		50		kW
Voltage	–		27	V
Current	–	465	80	A
Powder feed rate	20	20	–	$\text{g}\cdot\text{min}^{-1}$
Wire feed rate	–	–	$2 \times 75$	$\text{mm}\cdot\text{s}^{-1}$
$\text{O}_2/\text{C}_2\text{H}_2$ pressure	0.05/0.07	–	–	MPa
Ar/He flow	–	30/20	–	$\text{l}\cdot\text{min}^{-1}$
Spray air pressure	0.25	–	0.3	MPa
Spraying distance	100	250	100	mm

Aluminium-based coatings ( $\text{AlMg}_3$ ) were applied on aluminium substrate (Al99.5) using an OSU arc-spraying equipment (Sulzer, Switzerland) under optimised spraying parameters yielding low-porosity coatings (Table 1). Two different specific coating thicknesses were sprayed. The first specimens set  $s_1$  contained samples with a coating thickness of 100...200  $\mu\text{m}$ ; for the  $s_2$  specimens set, the thickness of sprayed coatings was between 400 and 500  $\mu\text{m}$ .

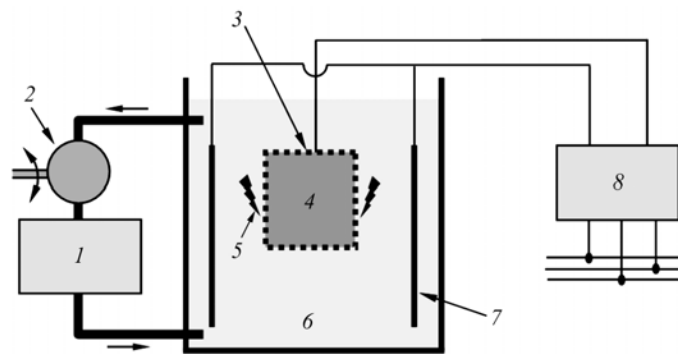


Fig. 1. Schematic diagram of PEO process: 1 – cooling system; 2 – pump; 3 – electrode 2; 4 – Al-coated substrate; 5 – spark discharges; 6 – electrolyte; 7 – electrode 1; 8 – power supply.

**Plasma-electrolytic oxidation.** The arc-sprayed aluminium coatings were plasma-electrolytically post-treated using a typical PEO setup (Fig. 1). The oxide coatings were synthesised under pulsed AC (current density:  $15 \text{ A}\cdot\text{dm}^{-2}$ ). The temperature of the

aqueous electrolyte (containing  $2 \text{ g}\cdot\text{l}^{-1} \text{ Na}_2\text{SiO}_3$  and  $3 \text{ g}\cdot\text{l}^{-1} \text{ KOH}$ ) was kept within a range from 18 to  $25^\circ\text{C}$ . The process time was 150 min. The duration of the oxidation treatment was selected with the consideration that in the case of thin-sprayed coatings, the whole coating and a certain layer of the substrate material were oxidised. In the case of thick coatings, only a partial oxidation of the sprayed coating occurred.

**Characterisation.** For materialographic investigations of the cross-sections, the optical light microscope (LM) Olympus PMG 3 and the scanning-electron microscope (SEM) LEO 1455VP were used. The composition of the coating phases was determined by X-ray diffraction (XRD, Siemens D5000) using  $\text{Cu-K}_\alpha$  radiation ( $2\theta$  between  $20$  and  $120^\circ$ ). To estimate the corrosion resistance of the alumina coatings, an electrochemical potentiodynamic corrosion test was carried out in a  $0.1 \text{ M NaCl}$  solution at  $25^\circ\text{C}$  in steps of  $1 \text{ mV/s}$ . The microhardness of the coatings was measured according to Vickers scale under a load of  $100 \text{ g}$ . Coatings abrasive wear resistance was characterised with ASTM G65 wear test (Rubber Wheel test).

**Experimental results and discussion. Microstructure.** The average thickness of the flame- and plasma-sprayed alumina coatings was  $190 \mu\text{m}$ . As expected, flame-sprayed coatings exhibit large pores and poor substrate bonding due to the low melting rate and low kinetic energy of the corundum spray particles (Fig. 2). A higher melting rate and higher kinetic energy of the plasma-sprayed particles results in more homogeneous and well substrate-bonded coatings with lower porosity (Fig. 2). The arc-sprayed aluminium coatings show a typical lamellar structure with interlamellar oxidation and good adhesion to the substrate. The average coating porosity is in the range of  $5\text{...}6\%$ . As example, general views of the as-sprayed  $\text{AlMg}_3$  coatings of both applied thicknesses are given in Fig. 3.

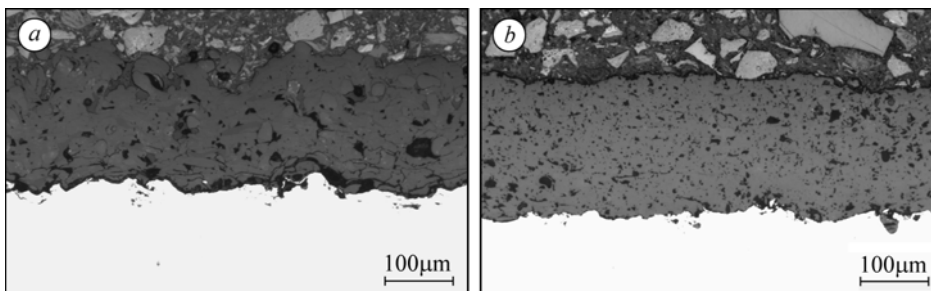


Fig. 2. Flame-sprayed (a) and plasma-sprayed (b)  $\text{Al}_2\text{O}_3$  coatings.

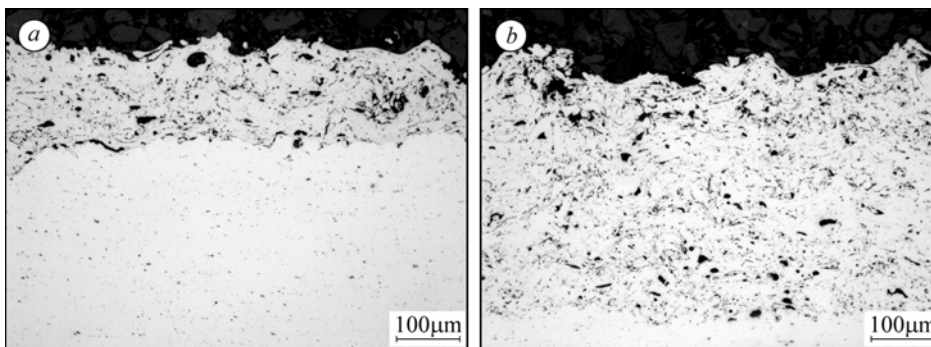


Fig. 3. Arc-sprayed  $\text{AlMg}_3$  coatings with different thicknesses (a:  $s_1$  – thin; b:  $s_2$  – thick).

The PEO process is carried out with parameters that provide the formation of oxide layers with average thicknesses similar to flame- and plasma-sprayed alumina coatings. The interface between the PEO coating and the substrate of the thin-sprayed

coatings (set  $s_1$ ) is beneath the original interface between spray coating and substrate. Under the same PEO process parameters, the thick-sprayed coatings (set  $s_2$ ) are only partially oxidised (Fig. 4). The oxidation process starts from the surface of the sprayed coating and propagates in the direction of the substrate (Fig. 5).

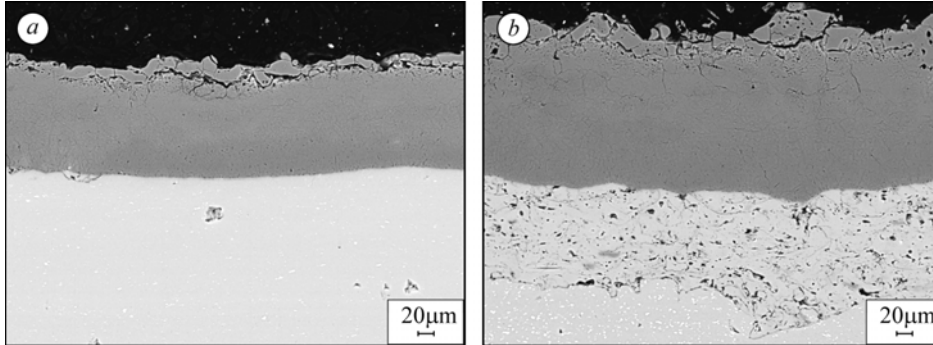


Fig. 4. PEO coatings on arc-sprayed AlMg<sub>3</sub>:  $a - s_1$ ;  $b - s_2$ .

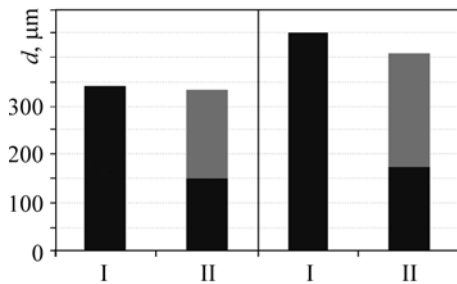


Fig. 5. Thickness of arc-sprayed (I) and arc-sprayed and PEO-treated (II) coatings (two representative examples of set  $s_2$ ):  
 ■ – AlMg<sub>3</sub> coating; ■ – Al<sub>2</sub>O<sub>3</sub> coating.

AlMg<sub>3</sub>-PEO coatings show a ratio of approximately 65%.

XRD analyses of alumina exhibit various modifications of the alumina phases and differences in the phase composition between thermally sprayed as well as PEO coatings (Fig. 6). The flame-sprayed alumina mainly consists of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> followed by  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The inverted case can be observed for plasma-sprayed coatings including the partial presence of amorphous Al<sub>2</sub>O<sub>3</sub>.

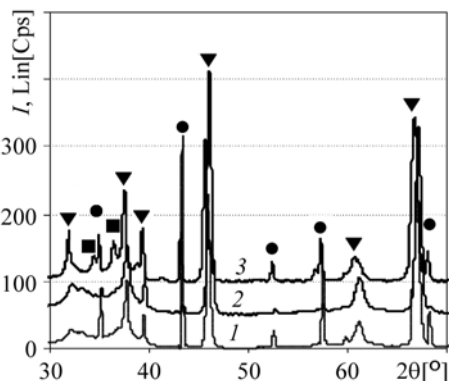


Fig. 6. X-ray diffractograms of alumina coatings obtained by flame spraying (1), APS (2) and PEO of arc-sprayed Al coatings (3).

The structure of the resulting PEO coatings can be generally classified into three different layers: the required and usable mechanical properties of PEO coatings are achieved in the bottom layer part, a dense, thick “working layer”. The top layer is characterised by a high porosity, numerous cracks and a poor inner cohesion. Between these two layers, a transition zone can be distinguished. The ratio of the working layer thickness to the total PEO coating thickness depends on the chemical composition of the Al alloy to be oxidised [3].

PEO coatings consist of  $\alpha$ -,  $\gamma$ - and  $\delta$ -phase. The ratio of  $\alpha$ - to  $\gamma$ - and  $\delta$ -Al<sub>2</sub>O<sub>3</sub> depends on the original Al alloy composition as well as on the parameters of the anodising process. High contents of stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are normally associated with high microhardness and high wear resistance and this is therefore the preferred phase in the PEO coatings to be produced [4]. PEO coatings that are produced on arc-sprayed AlMg<sub>3</sub> show a high  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, followed by lower amounts of  $\alpha$ - and  $\delta$ -Al<sub>2</sub>O<sub>3</sub>. The shown diffractograms give information about the phase composition in the upper

layer of the alumina coatings due to the limited penetration of X-ray. It must be assumed that the amount of  $\alpha$ - $\text{Al}_2\text{O}_3$  in the inner dense working layer of the PEO coatings is higher than in the outer parts. Owing to high PEO process temperatures, the preferentially formed meta-stable  $\gamma$ - $\text{Al}_2\text{O}_3$  gets converted in  $\alpha$ - $\text{Al}_2\text{O}_3$  [5, 6].

The average microhardness of ceramic coatings is shown in Table 2. Microhardness of alumina coatings increases from flame sprayed via APS to PEO coatings. The inversely proportionality of microhardness to associated coatings porosity was noticed.

The microhardness distributions along the perpendicular direction to the PEO coating substrate interfaces are given in Fig. 7. Generally, it is influenced by PEO process parameters and by the chemical composition of the oxidised material [3]. It is obvious that the highest microhardness of up to 1800 HV0.1 is achieved in the working layers of the PEO coatings. The characteristic distribution of microhardness corresponds to the content of  $\alpha$ - $\text{Al}_2\text{O}_3$  phase. Additionally, a reduction of the internal coating cohesion in the external part of the PEO layer due to higher porosity leads to a decrease in microhardness.

**Corrosion behaviour.** The results of the potentiodynamic corrosion tests are given in Fig. 8. Flame-sprayed and APS coatings exhibit the same open circuit potential (OCP), but slight differences in corrosion current density, which starts to increase strongly from  $-600$  to  $-400$  mV. PEO coatings show a lower OCP, but there is no increasing current density analogous to flame-sprayed and APS coatings. The inner dense working layer inhibits the diffusion of ions and no corrosion can occur.

**Table 2. Microhardness of alumina coatings (*S* – standard deviation)**

	$\text{Al}_2\text{O}_3$ coating		
	Flame-sprayed	APS	PEO
HV0.1	1055	1235	1462
<i>S</i> , %	9.1	8.8	7.0

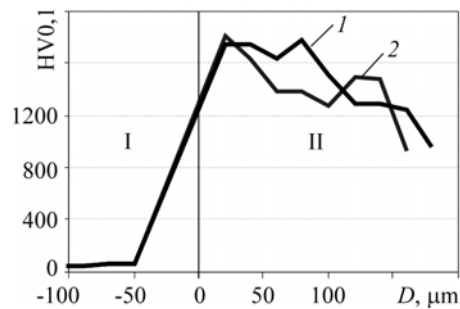


Fig. 7. Distribution of microhardness in PEO layers synthesised on arc-sprayed  $\text{AlMg}_3$  coatings (1 and 2 – two representative lines of set  $s_2$  coatings): I – arc-sprayed  $\text{AlMg}_3$ ; II – PEO  $\text{Al}_2\text{O}_3$  coating.

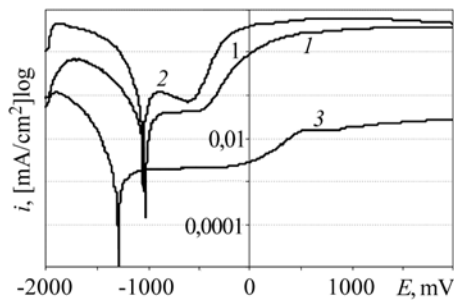


Fig. 8.

Fig. 8. Potentiodynamic graphs of alumina coatings obtained from flame spraying (1), APS (2) and PEO of arc-sprayed Al coating (3).

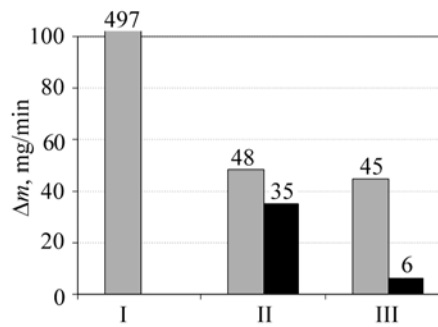


Fig. 9.

Fig. 9. Mass loss rate of  $\text{Al}_2\text{O}_3$  coatings in ASTM G65 wear test: I – flame sprayed; II – APS; III – arc sprayed, PEO treated. ■ – 0...0.5 min testing time; ■ – 0.5...5 min testing time.

**Wear behaviour.** Very high mass loss rates of flame-sprayed alumina coatings (497 mg/min) lead to completely worn surfaces during the initial testing period where the substrate material is visible (Fig. 9). Due to the low melting ability of corundum spray particles during flame spray process the coating cohesion and mechanical stability are very low. APS and PEO coatings show a distinctly higher resistance against abrasive wear. Due to easy abrasion of the rough top layer, the wear rate in the initial testing period is higher than in the residual testing time. Both testing periods show a similar wear for both coating types (48/45 mg/min). In the following testing cycles the APS coatings wear rate levels out to 35 mg/min; the wear rate of the PEO coatings is minimised to 6 mg/min, which indicates a remarkable six times higher resistance against abrasive wear to compare with the APS-coatings. Fig. 10 shows the surface top view and the cross-section of the completely oxidised PEO coating (an example of coating from set  $s_1$ ) after 5 min of the ASTM G65 test. The worn surface is smooth and uniform. There are no cracks and defects caused by the abrasive load detectable within the residual working zone.

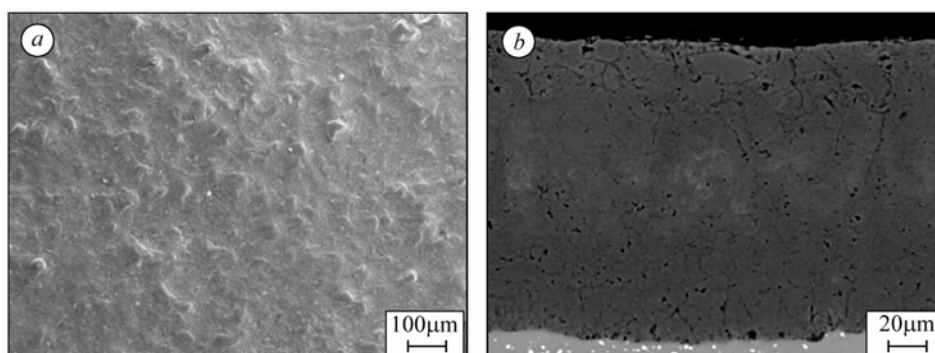


Fig. 10. Completely oxidised arc-sprayed coating after ASTM G65 wear test: *a* – surface top view; *b* – cross-section).

## CONCLUSIONS

Alumina coatings obtained with flame spraying, atmospheric plasma spraying and plasma-electrolytic oxidation of arc-sprayed aluminium were examined and discussed. Due to the non-porous inner layer, PEO coatings exhibit a very high resistance against corrosion. It has been shown that PEO coatings indicate the highest resistance against abrasive wear with non-fixed abrasive, which depends on the microstructure and phase composition of the oxidised layers. The suitability of PEO coatings for technical components in extreme operating conditions is shown.

The degree of oxidation of arc sprayed coatings could technically lead to a variance in the bond strength of the coatings. Further investigations are necessary to clarify this correlation. Owing to special modifications of the thermal spray process (e.g. particle-reinforced aluminium), the range of applications of PEO coatings can be extended. The implementation of cold-gas spraying (CGS) allows the use of polymeric substrate materials for PEO treatment.

**РЕЗЮМЕ.** Покриви на основі оксиду алюмінію широко використовують у промисловості для поліпшення корозійного захисту, зносо- та ерозійної тривкості, а також теплоізоляції металевих поверхонь. Різними методами отримано удосконалені покриття. Показано, що економічно ефективні алюмінієві покриття, сформовані методом електродугового розпилення, а потім оброблені плазмово-електролітичним оксидуванням, утворюють шари  $Al_2O_3$  з високими антикорозійними характеристиками, твердістю, силою зчеплення та абразивною тривкістю і продовженим ресурсом роботи. Порівняно їх властивості з покриттями на основі оксиду алюмінію, одержаними методами полумєневого та атмосферного плазмового розпилення.

*РЕЗЮМЕ.* Покрытия на основе оксида алюминия часто применяют в промышленности для улучшения коррозионной защиты, износо- и эрозионной стойкости, а также теплоизоляции металлических поверхностей. Различными методами получены усовершенствованные покрытия. Показано, что экономически эффективные алюминиевые покрытия, сформированные методом электродугового распыления, а потом обработанные плазменно-электролитическим оксидированием, образуют слои  $Al_2O_3$  с высокими антикоррозионными характеристиками, твердостью, силой сцепления, абразивной стойкостью и длительным ресурсом работы. Сравнены их свойства с покрытиями на основе оксида алюминия, полученными методами пламенного и атмосферного плазменного распыления.

*Acknowledgement. The authors would like to thank the “Deutsche Forschungsgemeinschaft” (DFG) for supporting the research project WI 688/87-1.*

1. *Plasma* electrolysis for surface engineering / A. L. Yerokhin, X. Nie, A. Leyland, et al. // *Surface and Coatings Technology*. – 1999. – **122**, № 2–3. – P. 73–93.
2. *Deposition* of duplex  $Al_2O_3$ /Aluminium coatings on steel using a combined technique of arc spraying and plasma electrolytic oxidation / W. Gu, D. Shen, Y. Wang, et al. // *Applied Surf. Scien.* – 2006. – **252**, № 8. – P. 2927–2932.
3. *Peculiarities* of abrasive wear of PEO layers obtained on arc sprayed aluminium coatings / B. Wielage, H. Pokhmurska, T. Grund, D. Meyer // *Proceedings ITSC 2008*, DVS-Verlag, ISBN 978-2-87155-979-2. – P. 594–596.
4. *Plasma* electrolytic oxidation of arc sprayed aluminium coatings / V. Pokhmurskii, G. Nykforchyn, M. Student, et al. // *J. of Therm. Spray Technol.* – 2007. – **16**, № 5–6. – P. 998–1004.
5. *Tailored* aluminium oxide layers by bipolar current adjustment in the Plasma Electrolytic Oxidation (PEO) process / F. Jaspard-Mécuson, T. Czerwiec, G. Henrion, et al. // *Surface and Coatings Technology*. – 2007. – **201**, № 21. – P. 8677–8682.
6. *Sundararajan G. and Rama Krishna L.* Mechanisms underlying the formation of thick alumina coatings through the MAO coating technology // *Ibid.* – 2003. – **167**, № 2–3. – P. 269–277.

*Received 09.03.2010*