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STRUCTURAL ANALYSIS OF ALUMINA THIN LAYER PREPARED BY CONTROLLED OXIDATION PROCESS

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ABSTRACT

Alumina thin layers were prepared by controlled oxidation process of aluminium obtained by PVD technique. As support steel sampled have been used. The structural analyses and stress state were performed by SEM and XRD techniques. The roughness of surface was pointed out by using an instrument that allows obtaining of 3D surface profile. The structural data allow conducting by a typical soft of the PVD technique such as to obtain alumina thin layer having certain physical and optical properties.

KEYWORDS: aluminium, oxidation, alumina, structure, roughness, XRD, SEM

1. INTRODUCTION

Mild steel is widely used as a structural material in a number of engineering applications because of its good machinability, high thermal conductivity and superior mechanical strength. However, it is highly prone to suffer from corrosion and wear as a consequence of which its service life is limited. Therefore, a number of approaches have been adopted to improve its corrosion and wear resistance properties [1, 2].

A generic way to protect metals from corrosion is to apply protective films or coatings, which also permit the desired properties of the substrate to be coated through the chemical modification of the coatings such as mechanical strength, optical appearance, bioactivity, etc. [3, 4].

Interest in the preparation of alumina coatings has steadily increased due to its excellent corrosion resistance, decorativeness and physico-chemical properties. Several procedures can be employed for coating alumina on various substrates – like steels – such as hot dipping [5, 6], thermal spraying [7], sputter deposition [8, 9], physical vapor deposition (PVD) [10, 11], etc. The major advantages of PVD technique are the almost unlimited variation in the chemical composition of the coating material, the principal tolerance of all substrate materials and also, represent an easy way of layered film structures taking out.

The goal of this research was to prepare the alumina thin films by controlled oxidation process of aluminium which was obtained by PVD technique on steel substrates. Following, the surface morphology and structural properties of thin layers of alumina have been examined.

2. MATERIALS AND METHODS

2.1. Preparation of samples

All chemicals were purchased from commercial sources and have the highest purity available. They were used without further purification. The mild steel plates were used as the substrates. Before film deposition, the steel surfaces were mechanically polished with fine grained emery paper. Afterwards, the polished substrates were rinsed with acetone and alcohol. Then, they were ultrasonically cleaned sequentially in acetone and doubly-distilled water each for 15 min. Finally, the specimens were dried in air at room temperature. During the experiments three samples were placed in the PVD installation to obtain thin layers of aluminium (99.999%) on their surfaces. Aluminium films, 1 μm thickness were vacuum deposited on mild steel into a PVD installation by means of AV1003. The pressure of the evaporator was $5 \cdot 10^{-5}$ Torr during deposition. The thickness of obtained layers was measured with an interferential microscope LEITZ LINIK type. The thermal oxidation process of evaporated aluminium films was done in an horizontal, radiatively heated quartz furnace. The process was performed at three different temperatures, namely 300, 400 and 500 °C, during one hour with a rate of 10° min^{-1}. After that the samples were cooled in air. In Fig. 1 the heating diagram is presented.

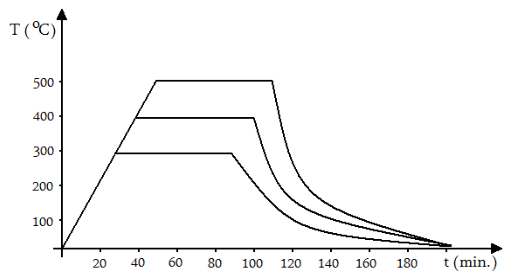


Fig. 1. Heating and cooling diagrams of aluminium coatings

2.2. *Microscopical and structural characterization of alumina samples*

The morphological characteristics of the surface of alumina samples were examined by means of scanning electron microscopy (SEM). The micrographs were recorded by means of Quanta 200 Philips FEI device. The crystallographic characteristics of specimens were analyzed through X-ray diffraction method (XRD) by means of DRON-3M diffractometer. This diffractometer uses the CuK_α radiation with λ = 1.542 Å at 40 kV and 30 mA [15, 16]. The XRD patterns were recorded at 2θ angular range between 30 and 80°, with a scanning rate of 0.02° min^{-1} and acquisition time of 0.1 s/step. The behaviour of alumina by interaction with a polychromatic beam was examined by reflectance measurements recorded by means of Perkin Elmer (type Lambda) 35 UV-VIS Spectrophotometer with double beam in the spectral range of 190÷1100 nm. The surface roughness of the coated layers was examined by means of profilometer UMT CETR 200 (USA) using a PRO 500 profile tester in contact mode.

3. RESULTS AND DISCUSSION

3.1. *Characterization of optical properties of alumina samples*

Optical properties of reflectance of alumina samples are determined through interaction between a polychromatic beam and material surface. The incident radiation has the wavelength ranged between 190 nm and 1100 nm.

Fig. 2 indicates the reflectance curves of the oxidated aluminium samples. The specimen subjected to oxidation at 400 °C indicates higher values of reflectance than those of samples subjected to 300 and 500 °C. For a certain value of wavelength, for example λ = 902 nm, the subjected sample to 300, 400 and 500 °C present reflectance values of R = 34.42%, 38.18% and 6.605%. Therefore, aluminium subjected to 500 °C exhibits more opaque and darker (low reflectance capacity) due to the oxide compounds formed on the material surface compared with the other two.

The curves from Fig. 2, corresponding to first two alumina samples (300 and 400 °C) indicate the formation of an inverse pick more evidently than in case of the last one at 500 °C. It means that a minimum value of reflectance (R ≈ 7%) appears at a maximum value of adsorbance at higher temperature. The reflectance plots follow sudden exponential increasing with wavelength in the visible region.

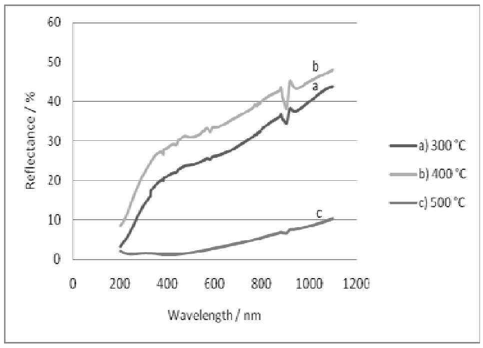
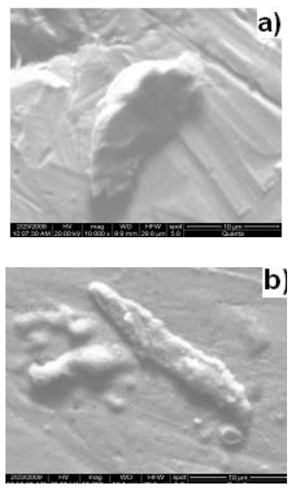


Fig. 2. UV-VIS-IR spectra of alumina subjected to 300 °C (a), 400 °C (b) and 500 °C (c)

3.2. Morphological study of alumina samples

The surface morphology of aluminium subjected to three temperature of oxidation at different magnifications is indicated in Fig. 3.



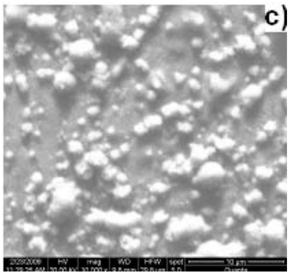
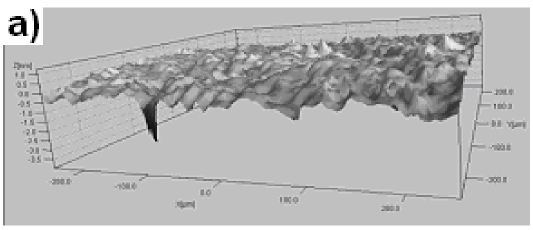


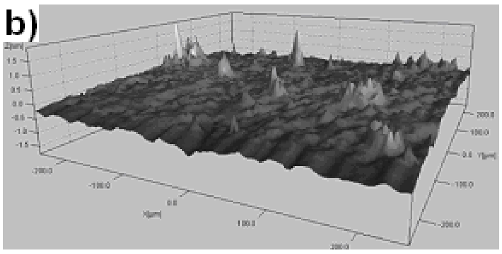
Fig. 3. SEM micrographs of alumina subjected to 300 °C (a), 400 °C (b) and 500 °C (c)

SEM image of alumina subjected to 300 °C emphasizes the structure of aluminium with a shiny surface which presents a few small scratches like material defects (Fig. 3a). Also, a developing of some agglomerations can be observed onto the material surface due to the oxidation phenomenon. At 300 °C no uniformly coating was shown (Fig. 3a). A division of the oxide agglomerations into small formations is indicates in Fig. 3b and c with increasing the temperature from 300 to 500 °C. Fig.3c shows an uniformly layer of oxides distributed onto the whole surface when the temperature is high (500 °C). The growing of the oxide layer onto aluminium surface determines a changing in colour of three samples while the temperature of oxidation is increased (Fig. 3a, b and d). For example, for 500 °C the surface colour is more darker than those subjected to 300 and 400 °C.

3.3. Topographical study of alumina samples

Fig. 4 shows images of the top surface of the alumina coatings. The deposited films has a rough appearance because of the crystal faces which form square pyramidal-like tips protruding from the ends of the columnar grains. The columns are all aligned in the same direction perpendicular to the substrate. This shows how the columnar grains form an uniform crystallographic texture in the growth direction. The degree of roughness of coatings deposited at 500 °C (Fig. 4c) is higher than that of coatings deposited at 400 and 300 °C (Fig. 4b and a). Consequently, column growth is smooth and uniform resulting in low surface roughness. The surface indicates in Fig. 4b is rougher than that from Fig. 4a. Therefore, the oxide particles developed on the substrate during oxidation process increase with temperature.





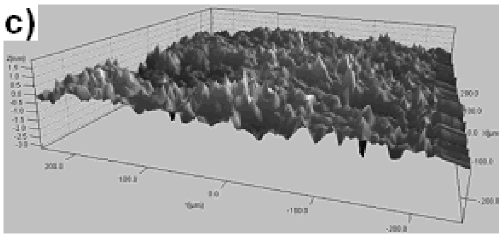


Fig. 4. Topographical images of the top surface of alumina coatings at 300 °C (a), 400 °C (b) and 500 °C (c)

The results of the topographical analysis are presented in Table 1. The material and void volume are inverse proportionally and varied in accordance with temperature. For each sample the material volume increases with temperature due to the oxide coating onto the surface. During the oxidation process the voids volume from the surface decreases due to the oxides developing.

Table 1. Characteristic parameters of alumina from topographical analysis

Nr. crt.	Material volume (μm^3)	Void volume (μm^3)
Alumina 300 °C	0.1772	0.1967
Alumina 400 °C	0.1772	0.1967
Alumina 500 °C	0.1772	0.1967

3.4. Structural characterization of alumina samples

In this work XRD method was used to determine the phase composition of grown alumina films by comparing diffractograms (detected intensity versus diffraction angle) in accordance with JCPDS card data for different alumina phases.

The structural characteristics of alumina films synthesized by the oxidation process at two temperatures are illustrated in Fig. 5. The crystallographic planes emphasize the crystalline structure of the films. Both XRD patterns show peaks associated with α, β and γ [12-14] alumina crystalline phases. But a difference of peak's intensity was shown due to the growing of crystalline grains on aluminium surface while the temperature is high. During oxidation process the crystalline network is rearranged and the internal stresses are reduced with increasing temperature.

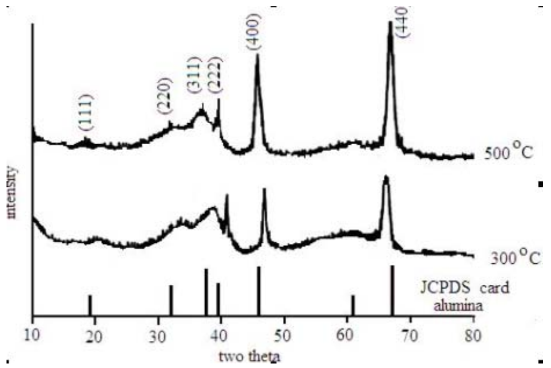


Fig. 5. X-ray diffraction patterns of alumina films synthesized by oxidation process at 300 °C and 500 °C

4. CONCLUSIONS

Based on experimental results regarding the oxidation of aluminium samples subjected to three different temperature (300, 400 and 500 °C) the structural, morphology, topographical and optical properties of alumina specimens were analyzed.

The reflectance is low during the oxidation process at 500 °C due to the oxide layer formed onto the surface of alumina.

The increasing of temperature emphasized a formation of some agglomerations onto the material surface due to the oxidation phenomenon shown by means of SEM images. Also, an uniformly layer of oxides are distributed onto the whole surface at 500 °C and a changing in colour was observed.

The surface roughness is varied proportionally with temperature. This analysisis confirmed by SEM and optical investigations. The voids are filled up during the oxidation process with oxide particles.

The crystalline structure of film is emphasized by the presence of specific crystalline phases of alumina.

REFERENCES

[1] Ruhi, G., Modi, O.P., Sinha, A.S.K., Singh, I.B., *Effect of sintering temperatures on corrosion and wear properties of sol-gel alumina coatings on surface pre-treated mild steel*, Corrosion Science, 50, 2008, pp. 639–649;

[2] Bull, S.J., Kingswell, R., Scott, K.T., *The sliding wear of plasma sprayed alumina,* Surface and Coating Technology, 82, 1996, pp. 218–225.

[3] Buchheit, R.G., Grant, R.P., Hlava, P.F., Mckenzie, B., Zender, G.L., *Local Dissolution Phenomena Associated with S Phase (Al_2CuMg) Particles in Aluminum Alloy 2024-T3, Journal of the Electrochemical Society, 144, 1997, pp. 2621-2628;*

[4] Bierwagen, G.P., He, L., Li, J., Ellingson, L., Tallman, D.E., *Consideration of a New Accelerated Evaluation Method for Coating Corrosion Resistance - Thermal Cycling Testing*, Progress in Organic Coatings, 39, 2000, pp. 67-78;

[5] Wang, D., Shi, Z., Zou, L., *A liquid aluminum corrosion resistance surface on steel substrate,* Applied Surface Science, 214, 2003, pp. 304-311;

[6] Wang, D., Shi, Z., *Aluminizing and oxidation treatment of 1Cr18Ni9 stainless steel,* Applied Surface Science, 227, 2004, pp. 255-260;

[7] Paredes, R.S.C., Amico, S.C., d'Oliveira, A.S.C.M., *The effect of roughness and pre-heating of the substrate on the morphology of aluminium coatings deposited by thermal spraying*, *Surface and Coatings Technology, 200, 2006, pp. 3049-3055;*

[**8] Boogard, A., van den Broek, J.J.**, *Crystallisation and electrical resistivity of sputter-deposited aluminium–germanium alloy films,* Thin Solid Films, 401, 2001, pp. 1-6;

[9] Kersten, H., Kroesen, G.M.W., Hippler, R., *On the energy influx to the substrate during sputter deposition of thin aluminium films,* Thin Solid Films, 332, 1998, pp. 282-289;

[10] Charrier, C., Jacquot, P., Denisse, E., Millet, J.P., Mazille, H., *Aluminium and Ti/Al multilayer PVD coatings for enhanced corrosion resistance*, Surface and Coating Technology, 90, 1997, pp. 29-34;

[11] Yang, D., Jonnalagadda, R., Rogers, B.R., Hillman, J.T., Foster, R.F., Cale, T.S., *Texture and surface roughness of PRCVD aluminum films,* Thin Solid Films, 332, 1998, pp. 312-318;

[12] Joo, H.U., Chae, S.A., Jung, W.S., *Is it possible to synthesize cubic aluminum nitride by the carbothermal reduction and nitridation method?*, Diamond and Related Materials, 17, 2008, pp. 352-355;

[13] Sun, J., Sun, Y.C., *Chemical liquid phase deposition of thin aluminum oxide films*, Chinese Journal of Chemistry, 22, 2004, pp. 661-667;

[14] Reyes-Reyes, M., Reyes-Gasga, J., Park, J.W., Lee, Y.K., *Study and characterisation of the substrate and thin film of the ZrO2-Y2O3/Al2O3 solid oxide fuel cells*, Acta Microscopica, 8, 1999, pp. 48-53.

[15] Gheorghies, C., *Analiza structurii fine a materialelor*, Ed. CERMI, Iasi, 2007

[16] Gheorghies, C., Cantaragiu, A. M., *Fizica radiatiilor X. Aplicatii*. Ed.CERMI, Iasi, 2007