APPLICATION OF THE PARTICLE BACKSCATTERING METHOD FOR THE CERTIFICATION OF THE OXIDE PROTECTIVE COATINGS AT THE SURFACE OF AL ALLOYS

E.A. Romanovsky, O.V. Bespalova, V.P. Petukhov, V.S. Kulikauskas, Institute of Nuclear Physics, Moscow St. Univ., 119899 Moscow, Russia,

A.M. Borisov, I.V. Souminov, O.N. Dunkin, A.V. Apelfeld, V.G. Sukharev, MATI - Russian State Technology University, 109383, Polbina St., 45, Moscow, Russia.

Abstract

The possibilities of the Rutherford (1.5 MeV ^{4}He$^+$) and Nuclear (7.7 MeV H$^+$) Backscattering Spectrometry for investigation and certification of the protective coatings at the surface of aluminium alloys obtained by micro-arc oxidation were studied.

1 INTRODUCTION

Nuclear micro-analysis is widely used for non-destructive testing of the surface layers of the industrial products. Micro-arc oxidation (MDO) is one of the most perspective methods of surface treatment receiving wide applications for obtaining of multifunctional coatings on metals and alloys. It is the development of the usual electrochemical process of anodizing [1,2], but has a number of differences. MDO is carried out in weak-alkaline electrolytes at the voltage of alternating pulsed currents of an order above that of anodizing (up to 1000 V) [3-9]. It does not require the preliminary prepared surface and allows to obtain thick (up to 300-400 μ) coatings without ecology-dangerous refrigerating equipment. MDO-coatings are characterised by very high hardness (up to 2000-2500 kg/mm^2), wear-resistance and controllable porosity (2-50%).

Micro-arc discharges migrate on the being processed surface loaded into the electrolyte and exercise thermal, plasmo-chemical and hydrodynamic influence upon matrix metal, coating and electrolyte. It results in the formation of the ceramic-like coatings with the elemental and phase composition, structure and properties adjustable in a wide range. The MDO-coatings on aluminium alloys consist of three layers usually: thin transitive inner layer, the main working intermediate layer with the maximum hardness and minimum porosity consisting, in main, of the corundum α-Al$_2$O$_3$ and the outer friable technological layer, which can be removed afterwards if it is necessary.

The technological experiments are carried out in order to obtain the required properties of coatings to optimise the treatment parameters. In the present paper the possibilities of the Rutherford (RBS) and Nuclear (NBS) Backscattering Spectrometry for investigation and certification of the MDO-coatings on the surface of Al alloys were studied. RBS and NBS were the parts of the technological experiments. Joint RBS and NBS analysis allowed to combine high depth resolution of RBS and increased (in comparison with RBS) sensitivity of NBS to an oxygen at higher depth [10,11].

2 EXPERIMENT

The polished samples of aluminium alloy D16 (Al + 3.8-4.9%Cu + 1.2-1.8%Mg + 0.3-0.9%Mn) of 10 mm diameter and 6 mm thickness were used in the technological experiments. MDO was carried out in continuously mixing water-silicate-alkaline electrolyte (NaOH+Na$_2$SiO$_3$*9H$_2$O). The samples were washed in the fat-dissolving soap solution and in running water beforehand. After MDO-treatment the samples were washed in running water again and then it were dried at the temperature not exceeding 70^{0}C. The sample was the first electrode and the bath made of stainless steel was the second electrode of the electrochemical cell. The basic parameters of MDO are the duration of the treatment τ, composition and the temperature of electrolyte, the averaged density of the current j and the ratio of the cathodic to anodic currents I$_c$/I$_a$ on the sample (it is under negative and positive potential alternately). In the technological experiments τ varied from 30 to 180 min. at 8≤j≤12 A/dm^2, the composition and concentration of the electrolyte varied from 1 to 2 g/l of NaOH and from 8.5 to 16.5 g/l of Na$_2$SiO$_3$*9H$_2$O, ratio I$_c$/I$_a$ varied from 0.54 to 1.81. The temperature of electrolyte was of 20 - 30^{0}C.

RBS and NBS spectra were obtained using 1.5 MeV ^{4}He$^+$ beam of INP MSU electrostatic generator EG-8 and 7.7 MeV proton beam of INP MSU cyclotron. The technique of the RBS-, NBS-experiments were presented in [12] in detail. The angle between the normal of the target and the beam and the scattering angle θ were chosen to be 0^0 and 160^0, respectively. The energy resolution of the Si-Li surface barrier detector was about 20 keV. The statistical error of the RBS and NBS spectra was <3%.

The thickness and through porosity of MDO-coatings with the technological layer as well as the thickness and the microhardness of the hard working MDO-coatings

were measured by the non-nuclear methods also. The soft technological layer was removed using emery paper. The thickness was measured by eddy current layer thickness gauge type V-60 (INCO, Poland) serving for the fast and nondestructive measurements of dielectric coatings deposited on aluminium and copper and its alloys. Measuring range of the gauge is 0-300μ with the accuracy of ±6%. For the determination of porosity the chemical reaction $2Al+6HCl=2AlCl_3+3H_2$ was used. The yields of hydrogen from the coated and initial uncoated samples immersed into 2% HCl solution were compared. The microhardness of the coatings was measured with a Vickers indenter, using loads 50 - 150 g.

3 ANALYSYS

The measured RBS and NBS spectra were analysed and the concentration profiles of the elements were obtained using the original code NBS [13]. It is applicable as for RBS as NBS conditions and serves for the determination of the best-fit concentration profiles of the target elements and the best-fit value of the energy dependences of the nuclear differential backscattering cross sections.The code NBS allows to look over the model spectra for each target component separately and facilitates in some cases the fitting of the adequate structure of near-surface layer. NBS has also convenient user interface for OS Windows'95.

4 RESULTS AND DISCUSSION

The depth range of the RBS-analysis of aluminium oxide was of 2μ. The elemental composition of MDO-coatings was found to be approximately constant in this depth range with increase of treatment time τ from 30 to 180 min. RBS spectra corresponded to the oxide Al_2O_3 with the admixture of Cu (the main alloying element of D16) as well as small amount of Ca contamination, Fig.1. We suppose that Ca appeared in the coating during the washing in the running water. The concentrations of the
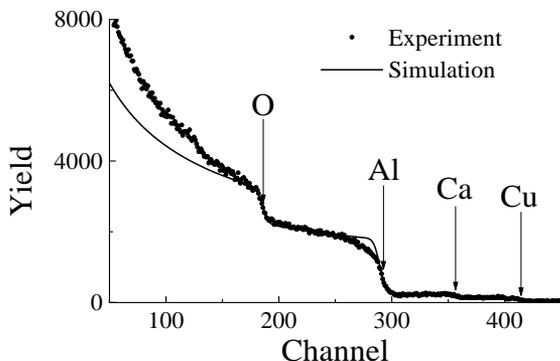

Figure 1: 1.5 MeV [4]He^{+} RBS spectrum for working MDO-coating obtained in electrolyte (1.5 g/l NaOH + 12.5 g/l $Ma_2SiO_3*9H_2O$), j=12 A/dm^{2}, I_c/I_a=1, τ=180 min. The best-fit composition: Al_2O_3+Cu(0.5 at.%) + Ca(3.3 at.%).

above mentioned admixtures in the surface layer of the coatings significantly decreased (≈2 times) after removal of technological layer. Admixtures of Mg and Mn (the alloying elements of D16) as well as Na and Si (components of electrolyte) were not displayed because of its small concentrations and the vicinity of its masses to the one of Al.

The depth of the NBS-analysis of aluminium oxide was of 100μ. It corresponds to the characteristic thickness of the MDO-coatings. For NBS of MDO-coatings the energy dependences of the proton differential cross sections σ(E) at θ=160[0] for the elements comprising the coatings are necessary. The NBS spectra for stoichiometry oxides WO_3 and Al_2O_3 were measured in order to determine $σ_O(E)$ and $σ_{Al}(E)$. The comparison of the simulated NBS spectra of WO_3 with experimental ones, taking into account the Rutherford proton cross section for W, allowed to determine $σ_O(E)$. We also measured $σ_O(E)$ at the same angles θ as [14]. The obtained data were in good agreement with $σ_O(E)$ [14]. We used the cross section $σ_O(E)$ for the measurements of $σ_{Al}(E)$ from NBS-spectra of Al_2O_3. The NBS-spectrum of the Al_2O_3 (Fig. 2) differs from RBS one (Fig. 1) due to the
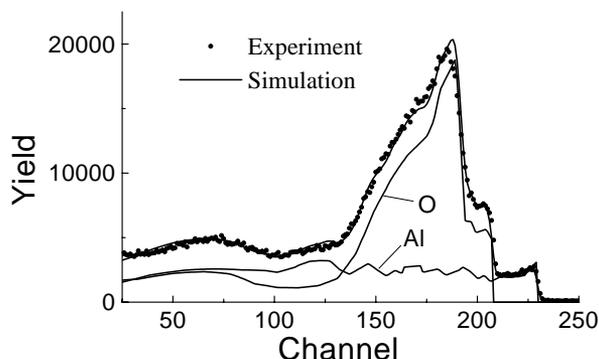

Figure 2: 7.7 MeV H^{+} NBS spectrum for Al_2O_3. Spectra for Al and O are the deconvolution of simulated spectrum for Al_2O_3.

non-Rutherford proton scattering on oxygen and aluminium. The wide resonance of $σ_O(E)$ at 6,8 ≤ E ≤ 7,7 MeV provides the increased sensitivity of NBS to the oxygen in films of the thickness up to 50 μ. The maximum value of $σ_O$ in the range 6,8 ≤ E ≤ 7,7 MeV is 100 times over than one calculated according to the Rutherford law. The cross section $σ_{Al}(E)$ is also nonmonotonic and is 2 times over than the Rutherford cross section.

Sharp excitation functions $σ_{Al,O}(E)$ are clearly displayed in NBS spectra of MDO-coatings (Fig.3). NBS spectra strongly depend on the τ and another parameters of MDO-treatment and become stationary at significantly large τ (≈3 hours) and, consequently, at large coating thickness. The stationary NBS spectrum of MDO-coatings was found to be close to the one of oxide Al_2O_3

without admixture. In the other words NBS yields from admixtures (Ca, Cu) were not observed within the statistical error in distinction from RBS. So we suppose that the different NBS spectra of MDO-coatings (see Fig.3) correspond to the different concentrations of the oxide Al_2O_3 in metallic matrix. Thus NBS allows to obtain data on the thickness and depth distribution of the main component of MDO-coatings - aluminium oxide. Note that the corundum α-Al_2O_3 determines the unique protective properties of the coatings.
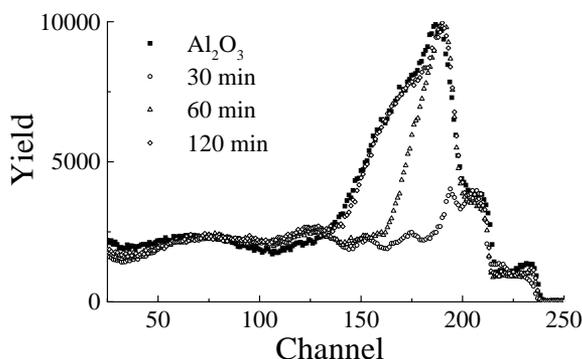

Figure 3: 7.7 MeV H^+ NBS spectrum for Al_2O_3 and MDO-coatings obtained in electrolyte (1.5 g/l NaOH + 12.5 g/l $Ma_2SiO_3*9H_2O$) at different time duration treatment, j=12 A/dm^2, I_c/I_a=1.

The typical structure of the hard working MDO-coatings presented by concentration profile of the aluminium oxide is shown in Fig.4. Correlation between oxide and aluminium of the matrix in model structure layers was characterised by relative concentration of an oxygen y in the compound $Al_{1-y}O_y$, where $y=3x/(4x+1)$ and x is the concentration of the aluminium oxide in the system $(Al_2O_3)_x+Al_{1-x}$. The thickness of the model structure layers was determined in units of 10^{15} at/cm^{-2}. We converted the thickness from these units into the
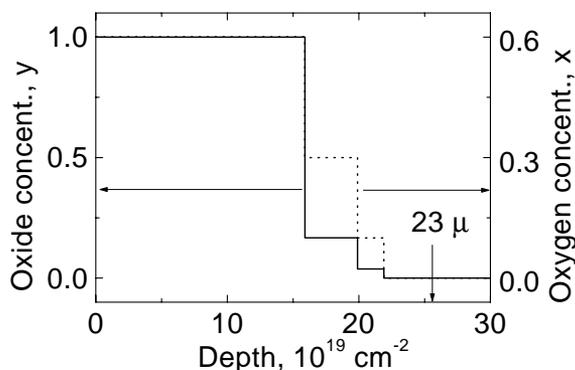

Figure 4: Aluminium oxide and oxygen concentration profiles in working MDO-coating obtained in electrolyte 2 g/l NAOH + 12.5 g/l $Ma_2SiO_3*9H_2O$, j=10 A/dm^2, I_c/I_a=1.42, τ=60 min. The thickness of layer measured by V-60 is of 23μ.

metric scale in fig.4, setting the density of the aluminium oxide equal to the density of the corundum α-Al_2O_3 without pores. The simulated NBS spectra were fitted to the experimental data within the statistical error by the variations of x, the quantity and the thickness of the structure layers.

The maximum oxygen concentration in atomic parts of 0.6 was observed in the near-surface layer of the working MDO-coatings. It corresponds to the 100% of the aluminium oxide in this layer. The intermediate layer at the boundary oxide-metal, where the oxygen concentration falls off, were observed also. The parameters of this structure are strongly influenced by the parameters of MDO-treatment. In particular, it was that the samples with the thinner intermediate layer are more hard and less porous.

5 CONCLUSION

It was shown in the present paper that one can use NBS to investigate the structure of the MDO-coatings on the surface of aluminium alloys. Consequently, the analysis of the regularities of MDO, optimisation of MDO technology parameters as well as the certification of the MDO-coatings are possible by NBS. RBS spectrometry was applied for the control of the admixtures in the surface layer of the coatings. Such a control is important for the application of the MDO-coated articles in the medicine, food industry etc.

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