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

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Abstract

The possibilities of the Rutherford (1.5 MeV '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/mm²), 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-Al₂O₃ 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+Na₂SiO₃·9H₂O). 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°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 Ic /Ia 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/dm², 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 Na₂SiO₃·9H₂O, ratio Ic /Ia varied from 0.54 to 1.81. The temperature of electrolyte was of 20 - 30°C.

RBS and NBS spectra were obtained using 1.5 MeV 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° and 160°, 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=2AlCl₃+3H₂ 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 Al₂O₃,
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
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° for the elements comprising the
coatings are necessary. The NBS spectra for stoichiometry oxides WO₃ and Al₂O₃ were measured in order to determine σ₀(E) and σₐ(E). The comparison of
the simulated NBS spectra of WO₃ with experimental ones, taking into account the Rutherford proton cross
section for W, allowed to determine σₐ(E). We also
measured σ₀(E) at the same angles θ as [14]. The
obtained data were in good agreement with σ₀(E) [14].
We used the cross section σ₀(E) for the measurements of
σₐ(E) from NBS-spectra of Al₂O₃. The NBS-spectrum of
the Al₂O₃ (Fig. 2) differs from RBS one (Fig. 1) due to the
non-Rutherford proton scattering on oxygen and aluminium. The wide resonance of σ₀(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 σ₀ in the range 6,8 ≤ E ≤ 7,7 MeV is
100 times over than one calculated according to the
Rutherford law. The cross section σₐ(E) is also
nonmonotonic and is 2 times over than the Rutherford
cross section.

Sharp excitation functions σₐ₀(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 Al₂O₃,

![Figure 1: 1.5 MeV 'He' RBS spectrum for working MDO-coating obtained in electrolyte (1.5 g/l NaOH +
12.5 g/l Ma₃SiO₅*9H₂O), j=12 A/dm², I/I₀=1, τ=180 min. The best-fit composition: Al₂O₃+Cu(0.5 at.%) + Ca(3.3
at.%).](image1)

![Figure 2: 7.7 MeV H⁺ NBS spectrum for Al₂O₃. Spectra for Al and O are the deconvolution of simulated spectrum
for Al₂O₃.](image2)
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$_2$O$_3$ 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 $\alpha$-Al$_2$O$_3$ determines the unique protective properties of the coatings.

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$_2$O$_3$)$_x$+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 metric scale in Fig.4, setting the density of the aluminium oxide equal to the density of the corundum $\alpha$-Al$_2$O$_3$ 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.

REFERENCES