

SYNTHESIS AND PROPERTIES OF SOL-GEL COATINGS
DEPOSITED ON HYBRID MATERIALS

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Abstract

ZrO₂-Al₂O₃ and ZrO₂-Y₂O₃ coatings were synthesized using sol-gel technology with a complexing agent and HNO₃ acid catalyst. The resulting coatings were deposited on Nb/Al, Ti/Al substrates. The synthesized coatings were studied by X-ray photoelectron spectroscopy (XPS analysis), Atomic Force Microscopy (AFM) and XRD (X-ray phase analysis). The obtained data indicate that XPS analysis is very suitable for studying the deposited coatings. Interesting data on the phase composition and surface morphology were obtained from the XRD analysis and the AFM method.

Key words: hybrid materials, sol-gel, dip coating, oxide coatings

Introduction. In modern industry, during the operation of machines, equipment and devices under the influence of various physicochemical effects of the external environment, undesirable corrosion processes take place. They can be limited by applying new alloys, corrosion inhibitors or protective films and coatings on the surface that lead to a reduction in the intensity of corrosion.

As mentioned earlier, there are other intermetallic alloys studied in the recent past but not discussed in this work such as TiAl and MoSi based alloys. Extensive and thorough data on intermetallic compounds can be found in reviews

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by YAMAGUCHI et al. [1], VASUDEVAN and PETROVIC [2], including for TiAl and MoSi.

The study of intermetallic compounds is of extreme interest because their synthesis, properties and applications are important for various areas of modern materials science. The improvement at room temperature of mechanical properties such as wear, fatigue, creep of intermetallic compounds has been one of the most intensively researched areas in recent years.

Applications in biomedicine, engineering, nanotechnology and information technology are increasingly being sought. Regarding the application of spray pyrolysis in the preparation and study of intermetallic compounds, there are extensive studies aimed at understanding the behaviour of coatings at both room and high temperatures [3-5].

The chemical resistance of intermetallic compounds during oxidation processes is particularly important for their application at high temperatures.

In recent years, NiAl coatings have been widely used, with the help of which very reliable results have been obtained in studies in various working environments – air, inert gases, vacuum. The positive results for NiAl can also be considered a starting point for in-depth studies of FeAl coatings and TiAl. However, there is relatively little data regarding their use as coatings. Scientific research has revealed that very important for the effective use of FeAl and TiAl as coatings is the small sizes of their crystallites. High Velocity Oxygen Fuel (HVOF) coating is a thermal spray coating process, which is used to improve or restore the component's surface (properties or geometry). This surface engineering technique better enables life extension of equipment by increasing erosion and wear resistance, and corrosion protection. HVOF is well studied for FeAl, but the applied plasma technology, as well as the cold spray, are not sufficiently studied yet. The study of nitinol, which is used in medicine, is also of interest. Of particular importance for this application are its surface properties, which determine its biocompatibility [3-7].

Sol-gel synthesis is ideal for obtaining coatings on such materials. It offers many advantages such as low cost and low temperature processing, easy coating and flexibility in terms of doping. It provides the possibility to obtain homogeneous high purity and with controlled stoichiometry material. The effective and appropriate stabilization of the sol is still a problem.

Experimental. Current research is focused on the development of intermetallic compounds – Me_2Al , where $\text{Me} = \text{Nb}$ and Ti . Powder metallurgical technology was applied and laminated structures were synthesized by combining diffusion bonding and batch rolling. Significant changes have been registered as a result of an increase of the volume fraction of the intermetallic phases [8]. In this work the intermetallic substrates are marked with numbers 10, 11 and 12. This results in high strength at high temperatures. It was shown that the flexural strength measured at three points at 1300 °C reaches 8 MPa. Coatings obtained

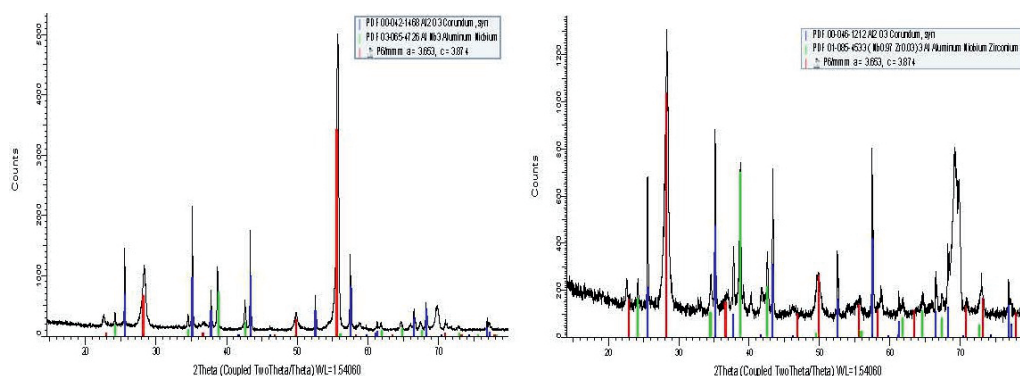


Fig. 1. XRD diffraction of the samples 10, 11 Nb/Al and 12 Nb/Al

by the sol-gel method were deposited on the thus obtained compounds by applying thin layers by dipping (dip-coating) with a withdrawal speed of 42.8 mm/minute. The stabilized sols used in the present study are $\text{ZrO}_2\text{-Al}_2\text{O}_3$ and $\text{ZrO}_2\text{-Y}_2\text{O}_3$ in a Zr:Y and Zr:Al molar ratio of 2:1, respectively. HNO_3 was used as a stabilizer and acid catalyst. The method for obtaining stabilized sols is presented in previous publications by PETKOV et al. [9].

Results and discussion. The phase composition was determined using X-Ray diffraction (rucker D8 Advanced Diffractometer, Cu-K α radiation). According to the XRD analyses, two phases were synthesized – predominantly Al_2O_3 corundum and NbZrO_3 , which are characterized by the presence of nanosized crystallites (Fig. 1). Intense peaks are characteristic of very thin layers. These data indicate that the modification of Al_2O_3 with ZrO_2 leads to the formation of chemically resistant oxide coatings at high temperatures.

The surface composition and electronic structure were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were carried out on AXIS Supra electron spectrometer (Kratos Analytical Ltd.) using achromatic Al-K α radiation with a photon energy of 1486.6 eV and charge neutralisation system. The binding energies (BE) were determined with an accuracy of ± 0.1 eV. The chemical compositions in the depth of the films were determined monitoring the areas and binding energies of C1s, O1s, Zr3d, Al2p, Fe2p, Y3d, and Ti2p photoelectron peaks. Using the commercial data-processing software of Kratos Analytical Ltd. the concentrations of the different chemical elements (in atomic %) were calculated by normalizing the areas of the photoelectron peaks to their relative sensitivity factors.

The chemical composition of the films was determined based on the areas and binding energies of the photoelectron peaks. The concentrations of the various chemical elements (in atomic %) were calculated by normalizing the photoelectron peak areas to their relative sensitivity factors.

Regarding the binding energy for the core level O1S, complex peaks are observed, which necessitated the application of deconvolution through appropriate

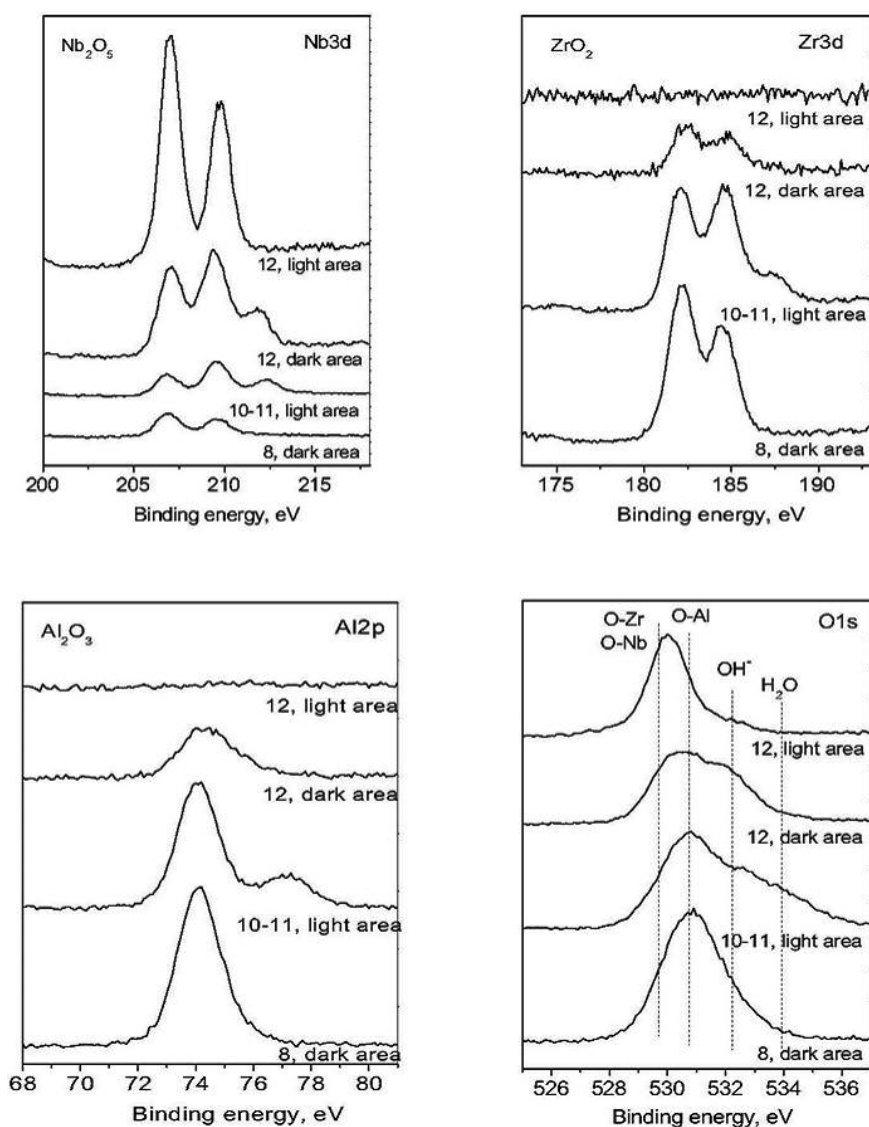


Fig. 2. XPS analysis of the samples 10, 11 and 8 substrates with sol-gel coatings

Lorentzian–Gaussian curves. The most intense peak for samples 10, 11 and 12 is characteristic of the O–Al bond – binding energy 530.7 eV.

The peak corresponding to the O–Zr and O–Nb bonds is located at a binding energy of 529.7 eV. In samples 12 – bright and dark area, a shift to lower binding energies is observed. A shoulder characteristic of the OH^- group at 532.2 eV is visible, as well as the presence of water at 534 eV, which are most likely the result of the preparation of the samples, in which sol-gel technology is used.

Regarding binding energies for Nb 3d – two intense peaks were registered – 207.1 eV for Nb 3d_{5/2} and 210.0 eV for Nb 3d_{3/2} for samples 8 – dark area, 10,

11 – light area and 12 – light and dark area. These binding energies correspond to compound Nb_2O_5 . as binding energy at 207 eV is described in the literature as the most characteristic for this compound [10–13]. Here, niobium is in its highest valence – fifth. Another phase appears in samples 10 and 11 light area and 12 dark area at a binding energy of 209.8 eV for Nb 3d5/2 and 210.8 eV for Nb 3d3/2, which corresponds to $\text{Nb}(\text{OH})_3$.

Binding energies for Zr 3d – 182.2 and 184.5 eV are characteristic of ZrO_2 [14,15] and appear in samples 8 – dark area, 10 and 11 – light area, as well as for sample 12 – light area, as for this sample the peaks are weak and broad.

The surface topography was investigated using Atomic Force Microscopy. AFM imaging was performed with the NanoScope V system (Bruker Inc., Germany) operating in non-contact mode in air at room temperature. Silicon cantilevers (Tap 300 Al-G, Budget Sensors, Innovative Solutions Ltd, Bulgaria) with an aluminum reflective coating with a thickness of 10 nm were used. The scan rate was set at 0.5 Hz and a scan size of $10 \times 10 \mu\text{m}$ and $5 \times 5 \mu\text{m}$ was applied. Images were taken in the highest possible AFM resolution mode, 512×512 pixels in JPEG format using Nano Scope software.

An Atomic Force Microscope was applied to measure the topography and surface roughness. The high-resolution imaging capability of AFM allows precise location of indentation locations and measurement of their depth [16].

The applied roughness analysis of each AFM image uses Ra, Rq, and Rmax values calculated according to the relative heights of each pixel of the topography of the sample under study [17].

The roughness analysis gives the value Ra which is the arithmetic mean of the absolute values Z_j of the surface height deviations measured from the mean plane while the image Rq is the root mean square of the height deviations taken from the image mean data plane [17].

The surface morphology of a 10, 11 Nb/Al specimen was characterized by Atomic Force Microscopy (AFM) and the resulting 3D images are presented in

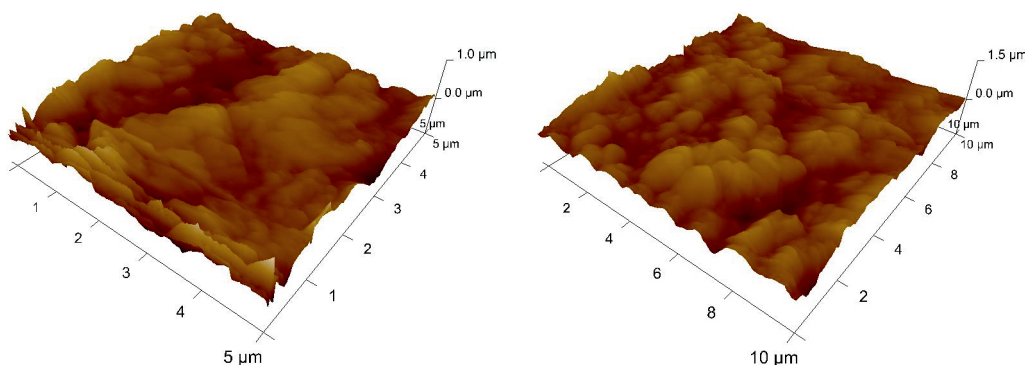


Fig. 3. 3D images for a 10, 11 sample at different scan areas of: $10 \times 10 \mu\text{m}^2$, $5 \times 5 \mu\text{m}^2$

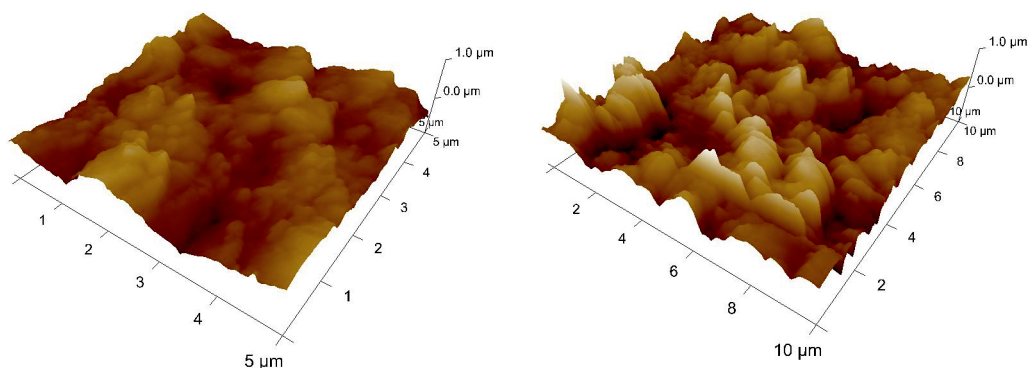


Fig. 4. 3D images for sample 10, 11 Nb/Al after the layer at different scan area of: $10 \times 10 \mu\text{m}^2$ and $5 \times 5 \mu\text{m}^2$

Fig. 3. The surface morphology of this specimen is rough and more homogeneous. From the diagonal section of the scanned surfaces, structured zones with heights of: 403 nm, 351 nm, and 301 nm are observed. The coatings on a surface labelled 10, 11 Nb/Al is rough and has values for Ra and Rq presented. With a scanning area of $10 \times 10 \mu\text{m}^2$ the value of Ra is 141 nm, and Rq is 176 nm, while with an area of $5 \times 5 \mu\text{m}^2$ we have a measured result of 116 nm for Ra and 144 nm for Rq. From the scanned area of $5 \times 5 \mu\text{m}^2$, it is clearly observed that the surface is structured with low and high areas in the nanometer scale (nm).

The surface morphology of a 10,11 Nb/Al sample after the layer was characterized by Atomic Force Microscopy (AFM) and the resulting 3D images are presented in Fig. 4. The surface morphology of this sample after the layer is eporough, compared to the morphology of sample 10, 11 Nb/Al in the layer. From the diagonal section of the scanned surfaces, structured zones with heights: 259 nm, 345 nm, 434 nm, and low zones: -387 nm and -394 nm are observed. The coating on the substrate labelled 10, 11 Nb/Al is characterized by an uneven surface (Fig. 4). Values for Ra and Rq were determined as follows. For a sample with an area of $10 \times 10 \mu\text{m}^2$, the Ra is 177 nm, and the Rq value is 228 nm, while for an area of $5 \times 5 \mu\text{m}^2$ the Ra value is 124 nm, and the Rq is found to be 155 nm. It is clearly observed that the surface is structured with low and high zones in the nanometer scale (nm).

Conclusions. From the results thus obtained, the following conclusions were specified.

Through the XRD analysis, the obtained phases of thin layers of $\text{Al}_2\text{O}_3/\text{ZrO}_2$, $\text{ZrO}_2/\text{Y}_2\text{O}_3$ with a thickness of $1 \mu\text{m}$ have been proven.

The elements Al, Zr and Y in the samples were proven by XPS analysis.

Through AFM analysis, it has been proven that the difference in Ra between the uncoated and coated part of the layer is 53 nm (Ra 177 – Ra 124), which means that the coated part has a finer and more homogeneous structure.

In the research conducted in this way, it is assumed that the highly refractory oxides will withstand temperatures above 1300 °C, which is the object of the following investigations.

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