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Katowice, 25.10.2018

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REVIEW

of the doctoral dissertation of mgr Michał Latkiewicz,

titled **„Influence of microstrcuture on corrosion behaviour of electrodeposited micro and nano-crystalline cobalt-molybdenium alloys"**

completed at the Faculty of Foundry Engineering

of the AGH University of Science and Technology

under the direction of dr hab. Halina Krawiec and dr hab. Vincent Vignal

1. General description of the doctoral dissertation

Electrodeposition is one of the most frequently used surface engineering processes for metal alloys. It is widely used e.g. in the electronic, motor, aircraft, space, and construction industries. Coatings produced by electrodeposition may be characterised by a variety of exceptional service, mechanical, electrical, magnetic or optical properties - e.g. appropriate corrosion resistance, hardness, creep resistance or friction resistance. Particularly interesting properties are exhibited by nano-crystalline and amorphous coatings for metals or alloys, including Co-Mo coatings. Due to the use of Co-Mo coatings in many industrial sectors, such as biology, the power industry, nanotechnologies or the aircraft industry, the materials are subjected to combinations of mechanical, corrosive, and biological factors. Thus, the requirements set for those materials with respect to their chemical and phase composition, microstructure, mechanical properties, and appropriate behaviour in contact with the human organism, are exceptionally demanding and strict. For this reason, they are the object of interest of many scientific centres, as many phenomena accompanying the production and property-shaping processes are very complex and despite extensive research, not fully explained. This makes the subject of mgr Michał Latkiewicz's doctoral dissertation

up-to-date and original. This is particularly noticeable in the production of nano-crystalline Co-Mo coatings by electrodeposition and with the use of a wide range of structural methods for assessing the influence of the structure, chemical and phase composition, and corrosion factors on the behaviour of Co-Mo coatings in simulated physiological solutions. In his work, Mr Michał Latkiewicz presents a comprehensive approach to the issue in question, from the production of the material to the assessment of its properties, and the results obtained in this work make, in my opinion, a major contribution to the development of Co-Mo coating technologies and to the exploration of the course of the phenomena accompanying corrosion damage in physiological solutions. The subject of the dissertation is an excellent example of a research problem related to surface engineering.

Taking into account the complex aspects of shaping coating surfaces, in his doctoral dissertation, Mr Michał Latkiewicz assessed the coating's microstructure, chemical and phase composition, and selected corrosion properties. An interesting variation in the initial condition of the substrate (pure Co)–Co-Mo coating system was obtained by the use of surface engineering methods, in particular by varying the parameters of the coating deposition process. The use of a broad spectrum of research methods, in turn, allowed Mr Michał Latkiewicz
to enrich data on the properties of nano-crystalline Co-Mo coatings and nano-composite Co-Mo/TiO_2 coatings, but also to characterise their behaviour as biomaterials.

2. Detailed description of the doctoral dissertation

The doctoral dissertation has 222 pages. The references are assigned to particular chapters: Chapter I - 142 literature references, Chapter II - 55 (5 self-citations), Chapter III - 29 (3 self-citations), Chapter IV - 24, Chapter V - 8 (1 self-citations). The selection of references unambiguously indicates detailed familiarity with the literature, both domestic and foreign.

The study part of the work (*Chapter I. Metallurgical aspects of metal surface engineering for Co-Mo nanocrystalline coatings)* in integrally linked to its subject and was based on an extensive review of publications, including monographs, concerning nano-crystalline Co-Mo coating technologies. In particular, the most important methods for producing the coatings were outlined [subsection II - Methods used for deposition of metallic coatings: *Galvanic coatings, Conversion coatings, Deposition from gas phase (chemical – CVD and physical – PVD), Thermal spraying, Ion implantation, Hot-Dip coatings, Hardfaced*

coatings, Plating, Electroplating (electrodeposition)], a short assessment of nanostructured coatings (subsection III - Nanostructured coatings) was given, and nanostructured Co-Mo coatings (subsection IV - Co-Mo nanostructuralline coatings) were extensively described. All the research was summed up in "*Conclusions*".

I deem the literature part of the doctoral dissertation to be very satisfactory. The author managed to present very concisely accurate, although very short, descriptions of major coating deposition methods, as well as to characterise in detail nanostructured coatings, including Co-Mo coatings. The result of the critical analysis of the literature and of its summary was the clear formulation of the aim of the work by Mr Michał Latkiewicz (*General Introduction*, page24):

„***The object of this thesis is to obtain Co-Mo nanocrystalline coatings and to understand their structure and corrosion behaviour***".

In my opinion, the aim of the thesis is correct in scientific terms, clearly formulated, and at the same time so general that it is possible to expect several different ways of reasoning. The test programme and the methods employed (*Chapter II. Samples and experimental methods and techniques*) are entirely appropriate to the tasks undertaken.

The extensive testing resulting from the research objective set in the thesis was possible due to the preparation of appropriate test specimens. Cobalt was selected as the substrate, and the variation in the nano-crystalline coatings was obtained through the appropriate selection of electrolytes and electrodeposition parameters (number of rotations, time, potential). The properties of the coatings obtained were determined using advanced methods for examining the structure *(Light Microscopy* – LM, *Scanning Electron Microscopy* – SEM), surface topography (*Atomic Force M*icroscopy - AFM, *profilometry*), chemical composition (*X-Ray Photoelectron Spectrosopy* - XPS, *Electron Probe MicroAnalysis* – EPMA (EDS)), phase composition (X-*Ray Diffraction* - XRD), mechanical properties (*microhardness*), electrochemical techniques and corrosion resistance (Cyclic Voltammetry, Open Circuit Potential - OCP, Linear Sweep Voltammetry - LSW, Electrochemical Impedance Spectroscopy - EIS, Chronoanperometry, Electrochemical Microcell Technique – EMT).

Mr Michał Latkiewicz placed the main emphasis first on the production of appropriate coatings on cobalt and then on comprehensive structural examinations of the coatings and their behaviour as biomaterials. I believe that his approach was right and promised interesting results. The description of the test materials and the research methods employed raises no doubts.

The first part of the author's own research (Chapter III) in the doctoral dissertation concerns the characteristics of the structure, mechanical properties, and electrochemical properties of Co-Mo coatings. What is especially noteworthy in this part of the thesis is the optimisation of the conditions for the electrochemical deposition of Co-Mo coatings and for examining the chemical and phase composition of the coatings obtained (XPS).

In the second part of the author's own research (Chapter IV), Mr Michał Latkiewicz focused on producing and characterising nano-composite Co-Mo/TiO_2 coatings on Co substrates. This is a very interesting part of the doctoral dissertation, as nano-composite Co-Mo/TiO_2 coatings were described so extensively for the first time. Particularly noteworthy is the presentation of the results of the assessment of the coatings obtained with respect to their structure on cross sections (SEM, XRD), their thickness, and their surface morphology (AFM). However, the results of the corrosion tests of the coatings in Ringer's solution and in Artificial Saliva are the most interesting from a scientific point of view. This part of the research was analysed in detail.

In the next chapter (Chapter V), a nano-composite Co-Mo/TiO_2 coating growth mechanism is proposed. I regard this part of the thesis very highly - it is logical and well-documented with the results of structural and electrochemical examinations. The careful analysis of the results of the electrochemical examinations and the valid conclusions drawn from those results are particularly remarkable. This part of the research is exemplary. The author demonstrates his ability to approach the theoretical and practical aspects of his research synthetically and at the same time more elaborately in comparison with previous studies. The complex problem of the phenomena accompanying the growth of electrodeposited coatings is addressed in a model way. The author clearly expends considerable effort to generalise and systematise the relationships and interactions among various factors in the coating growth process. The analysis of the results is presented in a clear and communicative manner.

The entirety of the results is summed up in "*General Conclusions*". Mr Michał Latkiewicz briefly summarises and analyses all the results obtained, demonstrating that the aim of his thesis has been fulfilled. The conclusions formulated based on the results and their discussion are presented in a clear manner, demonstrating that the objective defined by Mr Michał Latkiewicz in his doctoral dissertation has been attained.

3. Assessment of the doctoral dissertation

In my opinion, the most important merits of the thesis include:

1. The development of a production process for nano-structured Co-Mo and nano-composite Co-Mo/TiO_2 coatings (definition of the parameters).
2. The application of various methods for assessing the properties of the coatings obtained - their structure, chemical and phase composition, and mechanical and corrosion properties.
3. The provision of a model description of the nano-composite Co-Mo/TiO_2 coating growth mechanism.

Whereas I evaluate the doctoral dissertation very positively, I wish to raise some issues for discussion, in particular:

1. On the basis of the results of your own research, please describe in points the most important relationships between the coatings (e.g. their structure, chemical and phase composition) and the electrodeposition parameters, from the point of view of their behaviour in Ringer's solution and in Artificial Saliva.
2. Please explain what use was made of the results of the quantitative chemical composition analysis of the coatings within the scope of the so-called light elements (C and O), which results were obtained by X-ray microanalysis with the use of an energy-dispersive spectrometer (EDS). Bearing in mind the X-ray microanalysis methodology, the results were obtained outside the analytical capacity of this method.

At the end of my review, I would like to express my view that in editorial terms, the thesis is written very carefully, in a simple and clear language. In general, I believe that Mr Michał Latkiewicz has accomplished fully and extensively the scientific objective being the subject of the doctoral dissertation. The conclusions contained in the thesis are fully documented.

Taking into account the relevance of the subject of the thesis in the light of research carried out across the world, as well as the clear formulation of the aim of the work and its fulfilment through well-planned and well-executed tests and analyses, including a discussion of the results obtained, I regard Mr Latkiewicz's doctoral dissertation very highly and I request that mgr Michał Latkiewicz be admitted to the further stages of the procedure for the conferment of a doctoral degree. Based on the opinion presented above, I declare that the work meets all requirements for doctoral dissertations, as set out in appropriate acts of law, and at the same time I request that the work should be granted a distinction.

Maria Szaniska