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Report on the dissertation of Michal LATKIEWICZ

for a Ph.D. Thesis submitted to AGH University of Science and Technology, Faculty of Foundry Engineering, in Krakow, Poland and Laboratoire Interdisciplinaire Carnot de Bourgogne, Université de Bourgogne, Dijon France.

Title: Influence of microstructure on corrosion behavior of electrodeposited micro and nano-crystalline Cobalt-Molybdenum alloys.
Author: Michal LATKIEWICZ

Dear Committee Members,

I kindly accept the invitation of review on this Ph-D thesis. In the following, please find my report on the dissertation 'Influence of microstructure on corrosion behavior of electrodeposited micro and nano-crystalline Cobalt-Molybdenum alloys' (2018) of Michal LATKIEWICZ.

The Ph-D Work summarized in this thesis deals with the development of nanocrystalline coatings and the understanding of their structure and corrosion behavior.

The thesis is divided into five main parts dealing with the general introduction of the subject, a first bibliographic chapter relative to metallurgical aspects of metal surface engineering for Co-Mo nanocrystalline coating, a second one on samples and experimental methods and techniques, a third one on the structure, mechanical properties and electrochemical behavior of Co-Mo nanocrystalline coatings, a fourth one on the development of new Co-Mo/TiO_2 nanocomposite coatings and finally the last chapter focuses on the understanding of the growth mechanism of Co-Mo/TiO_2 nanocomposite coatings and its corrosion behavior.

First, **a general introduction** focuses on the main objective of this Thesis and presents the different following chapters.

Then, a **first and well-developed bibliographic chapter** provides a strong overview of the different kind of methods used for the deposition of metallic coatings. It describes the various techniques that allow obtaining alloys as a function of their desired properties. A special attention has been done on nanostructured coatings and especially, on Co-Mo nanocrystalline coatings. And finally, their potential applications are discussed.

The **second part** of the thesis focuses more on the description of the sample and experimental used set-up as well as its methods. The experimental conditions for the electrodeposition Co-Mo nanocrystalline coatings and the large panel of characterization techniques are presented. They vary from surface analysis with optical, atomic force and electronic microscopies, profilometry, then chemical analysis

with XPS, and also mechanical investigation (hardness measurement), structural analysis (X-Ray diffraction) and finally the different electrochemical techniques and corrosion tests. This chapter shows the wide range of the possible approaches regarding the understanding of the mechanisms underlaying the formation of the nanostructured alloy coatings.

The **third part** of the thesis focuses more on the structure, the mechanical properties and the electrochemical behavior of Co-Mo nanocrystalline coatings. The optimization of the electrodeposition conditions has allowed obtaining hard and compact Co-Mo nanocrystalline coatings. The structure, the mechanical properties and the electrochemical behavior in the Ringer solution of Co-Mo nanocrystalline coatings were studied using the different techniques. Results have shown that the properties of the Co-Mo coating strongly depend on the experimental parameters chosen during the electrolytic deposition, such as the deposition time, the deposition potential of the coatings, as well as the chemical composition of the electrolyte.

The **fourth chapter** of the thesis presents the structure, mechanical properties and corrosion behavior of Co-Mo / TiO_2 nano-composite coatings electrodeposited on pure cobalt. In fact, the previous results obtained with Co-Mo nanocrystalline coatings has led the author to prefer to deposit Co-Mo/TiO_2 nano-composite coatings. Such coatings have never been realized previously. The electroplating of these new nano-composite coatings significantly reduces the level of residual stresses, allows a good adhesion of the coating and the formation of a compact layer (no appearance of cracks). In addition, the oxidation of such layer takes place in the outermost part of the coating. Therefore, the bulk properties of the coating are not affected after long-term ageing in oxidative solution.

Finally, **the last fifth chapter of the thesis** focuses on the understanding of the growth mechanisms of the nano-composite coatings. The structure of Co-Mo/TiO2 nano-composite coatings electrodeposited for short and long-term potentiostatic conditions on pure cobalt disk and wire electrode have been investigated. Main results have shown that the corrosion behavior of the coatings electrodeposited on a wire electrode is quite similar to the coatings electrodeposited on disk electrode. However, lower content of Mo in the coatings electrodeposited on a wire electrode results in differences in the electrochemical behavior, which indicates slightly weaker resistance to corrosion than for the coatings electrodeposited on a disk electrode.

A **general conclusion** allows to summarize the main aspects of the thesis.

To summarize the thesis of Michal LATKIEWICZ contains a lot of new and very interesting results which have been (for some) and could kept on being published in highly-ranked scientific journals. The amount of observed effects is large for a Ph-D Thesis. The quality of the presented data is high and related discussions to the alloy coatings are addressed in a proper way using state-of-the-art theory.

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Evaluation

Due to the large amount of results and the quality of their presentation, I think that this thesis can be accepted and doctoral degree can be awarded to author after successful defense.
I would like to thank you again for this kind invitation as an external reviewer on this nice and valuable work and thesis manuscript.
Do not hesitate to contact me if you have any additional question concerning my report.

Sincerely

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