Project: “Synthesis, Characterization and Testing of Hydrogen Permeation Barriers (HPBs) applied as a safety measure for future fusion reactors”

Project type: Post-doctoral research

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Summary of scientific and technical report,

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1. Summary

For the current reporting period, the metallic (W, Be, W:Be), oxides (Al_2O_3, Cr_2O_3, Er_2O_3 and SiO_2) and metal-oxides (W/B: Al_2O_3, Cr_2O_3, Er_2O_3 and SiO_2) co-depositions realized by means of Thermionic Vacuum Arc (TVA), magnetron sputtering (CMSII, RF – radio frequency, DC- direct current) and metallization (plasma jet), were investigated in relation to their structural parameters (morphology, adherence, hardness, desorption) in order to validate them, taking into account the configuration, as possible candidates for future laborious permeation measurements.

The primary motivation consisted in the fact that the surface morphology can influence the relevant parameters such as solubility, diffusivity and permeation. Therefore, the applicability of the depositions as permeation barriers could be in an incipient phase evaluated by realizing complex analysis on surface morphology that is highly influenced by the chemical and physical structure of the films.

In order to study the surface morphology and elemental composition, for the current reporting phase, numerous methods were applied such as: Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). Relevant parameters as roughness and hardness of deposited films were studied by Atomic Force Microscope (AFM) and Micro-Indentation technique (Vickers method). For calibrating the deposition rates and the thicknesses, the SEM method was applied for cross-section overview. Additionally, alternative methods were applied for layer thickness evaluation such as X-ray fluorescence (XRF) or depth profilometry by Glow Discharge Optical Emission Spectroscopy (GDOES). Structural integrity at micrometer scale was addressed by conducting X-ray laminography (XCL), where the region of interest was the deposition to substrate interface. Thermal Desorption Spectroscopy (TDS) method was applied for observing desorbed molecules from the films surface when the surface temperature is increased.

Therefore, by evaluating the morphology, structure, chemical bounds of the deposited layers, the configurations were further validated for future laborious permeation measurement campaigns included among the objectives proposed in the last phase of this project.

2. Microstructural, morphological, chemical and mechanical investigations of oxides and metallic-oxides depositions

In the second phase of the current project, multi-physics analyses of deposited films were necessary to validate them as high purity and non-defective structures. In the following subparagraphs, a brief presentation of the determined results was included. The proposed objectives in the current project phase were reached and the dissemination of the results was realized by participating in international conferences and by publishing in ISI ranked papers.

2.1 Morphological and compositional characterization by SEM, EDX, GDOES, XPS and XRF methods

Following the surface analysis by SEM, differences were observed between the studied deposited configurations such as: Uniform surfaces including isolated spherical particles (Al_2O_3, SiO_2); High roughness with (SiO_2:Be, Er_2O_3:Be, Al_2O_3:W) and without (Er_2O_3, Er_2O_3:W, SiO_2:W, Al_2O_3:Be) visible artefacts; Random nucleation with spherical (Cr_2O_3:Be) and pyramidal (Cr_2O_3:W) shapes; Quasi-homogenous structures (W, Be and W:Be). These variations could be attributed to the crystalline structure of the implied elements: Be (hexagonal close packed), W (body-centered cubic), Al_2O_3 (trigonal), SiO_2 (tetrahedral), Cr_2O_3 (trigonal), Er_2O_3 (cubic).

Elemental concentration was measured by EDX method. The results suggest that the content of oxygen (at. %) is near to the stoichiometry ratio, thus confirming the oxide-metallic state for the analyzed co-depositions. XRF method indicated that the depositions don’t contain impurities of other materials and it contributed to quantifying the deposited layer thickness. Were available, the thickness of W deposited by CMSII method was addressed and validated by GDOES method.

Also, the morphology and roughness were evaluated by AFM method. Scanned AFM images and roughness parameter as root mean square factor (RMS), were highly relevant to point out the changes between pure oxides and metallic-oxides configurations. Thus, the configurations including Er_2O_3 determined a mixed granularity of morphology, while beryllium determined an increase of general roughness and RMS. This results was also confirmed based on the SEM surface images on the Er_2O_3:Be configuration were artefacts could be observed, in comparison to pure oxide described as a smooth and homogeneous surface. The presence of Be in the configurations implying Er_2O_3 and SiO_2 determined up to 50% increase of the RMS parameter. Also, for these oxides, the tungsten determined a homogenization of surface, while Be tends to build up isolated nucleation, determining the artefacts observed by SEM imaging. High roughness was observed for the Cr_2O_3 consisting in flake-like structures, while the co-depositions with W and Be have the influence of mitigating them. The minimal variation of the RMS factor was observed in the co-depositions implying Al_2O_3 oxide, while the SEM imaging showed a uniform and smooth surface with isolated shapes as cones, observed also by AFM scanning.

XPS investigations were carried out to access the bonding state of atoms at the surface and after quantitative analysis to find the element and chemical state relative concentrations. XPS characterized the co-deposited films as a mixture of oxidized and metallic states of the constituent elements. Most notably, for the Al-based configurations, the presence of Be determined the occurrence of metallic aluminum.

2.2 Volumetric (XCT), structural (XRD) and desorption (TDS); Mechanical studies by micro-indentation technique (Vickers method)

Multiscale studies were conducted as the current objective. Here we look forward into validating of the deposited films as high purity, dense and without containing any volume artefacts. Therefore, the volumetric measurements conducted by XCL contributed as a non-destructive structural analysis technique applied as an alternative to the limited to surface SEM technique. The most significant results stand for the W film deposited by CMSII method. Numerous porous formations in the W layer were observed at the surface and also in the surface to film interface.

Here we remind the fact that porous matrix in the deposition could favorize the presence of atomic traps during the deposition process. Taking this into account, TDS investigations were conducted and the following elements were analyzed: H_2, N_2, CO_2, O_2, Ar and H_2O. Thus, for the SiO_2 deposition, we observed the most desorbed notable quantities of elements. Other notable desorbed contaminants were reported for the following: Ar for Cr_2O_3, Er_2O_3, SiO_2; O_2 for Er_2O_3 and H_2O for Be.

Structural characterization was addressed by XRD method. Most notable result stand on the fact that the addition of W breaks the stability of k-Al_2O_3 but has no significant influence on the structure of sample Al_2O_3:W. It is worth noting that the k-Al_2O_3 coating exhibits very good mechanical and wear-resistant properties that can be harnessed for the protection of various surface, and in spite of the metastable nature of k-Al_2O_3, the phase transition to stable α-Al_2O_3 occurs at very high temperatures. Moreover, in such polycrystalline systems with significance structural disorder, broad peaks with a slight shift of the center position are present because of the small values of crystalline coherence length and high mechanical stress between crystallographic planes.

Hardness studies were conducted by means of Vickers microhardness instrument. Among the pure oxide layers, the highest hardness value was reported for alumina, while for the metallic layers was wolfram. Generally, for the co-deposited configurations, one observed a mitigation of hardness in comparison to the values reported for the bulk elements.

Based on the preliminary data, one could validate the W, Be and Al_2O_3 layers deposited by TVA and RF magnetron sputtering as being of high interest for future laborious permeation measurements included among the following activities of the project.

2.3 Results dissemination

International conferences:

M. Lungu et. al., "Synthesis and morphology characterization of Hydrogen Permeation Barriers (HPBs) candidates applicable as a safety measure for future fusion reactors", 18^{th} International Conference on Plasma-Facing Materials and Components for Fusion Applications (17^{th} - 21^{st}) May 2021, virtual conference, poster;

M. Lungu et. al., "RF Magnetron Sputtering Co-deposition and Characterization of Hydrogen Permeation Barrier Oxides in Tungsten & Beryllium Metallic Reinforced Matrix Composites", 19^{th} International Conference on Plasma Physics and Applications, August 31 – September 3, Magurele, Romania, poster;

M. Lungu et. al., "Microstructural and Microchemical Evaluation of Hydrogen Permeation Barriers-like Candidates Deposited with Thermionic Vacuum Arc and RF Magnetron Sputtering", European Materials Research Society (EMRS), Fall Meeting 20^{th}-23^{rd} September 2021, virtual conference, poster.

ISI papers:

M. Lungu, C. Staicu, F. Baiasu, A. Marin, B. Butoi, D. Cristea, O. G. Pompilian, C. Locovei and C. Porosnicu, „Deposition, morphological and mechanical evaluation of W and Be - Al_2O_3 and Er_2O_3 as mixed films in comparison with pure oxides", Coatings 2021, 11, 1430, https://doi.org/10.3390/coatings11111430, IF = 2.881;

V. Malinovschi, A. Marin, C. Ducu, V. Andrei, E. Coaca, V. Craciun, **M. Lungu**, „Influence of sodium aluminate concentration and process duration on microstructure, mechanical and electrochemical behavior of PEO coatings formed on CP-Ti", Surface and Coatings Technology, Vol. 418, 25 July 2021, 127240, https://doi.org/10.1016/j.surfcoat.2021.127240, IF = 4.158.

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