Investigations of TiO_2, Ti/TiO_2 and $Ti/TiO_2/Ti/TiO_2$ coatings produced by ALD and PVD methods on Mg-(Li)-Al-RE alloys substrates

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Abstract

Magnesium alloys are recently more and more popular in many sectors of the industry due to their unique properties, such as low density, high specific strength, vibration damping ability, also their recyclability, and excellent machinability. Nowadays, thin films have been attracting more attention in applications that improve mechanical and corrosion properties. The following alloys were used for the coated: Mg-4Al-2RE and the ultra-light magnesium-lithium alloy of the Mg-4Li-4Al-2RE type. A single layer of TiO_2 was deposited using the atomic layer deposition ALD method. Multilayer layers of the Ti/TiO_2 and $Ti/TiO_2/Ti/TiO_2$ type were obtained by the MS-PVD magnetron sputtering technique. Samples were investigated by scanning and transmission electron microscope (SEM, TEM) and their morphology by atomic forces microscope (AFM). Further examinations like electrochemical corrosion, roughness, and tribology were carried out. As a result of the research, it was found that the best electrochemical properties are exhibited by single TiO_2 layers obtained by the ALD method. Moreover, it was found that $Ti/TiO_2/Ti/TiO_2$ double film has better properties than Ti/TiO_2 film.improve their physicochemical properties is required.

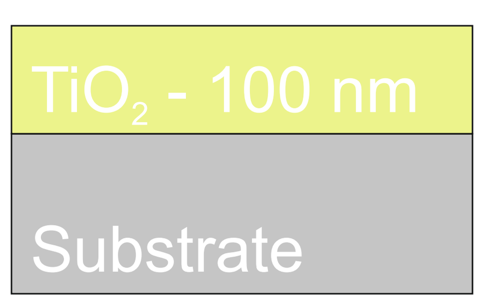
Materials

Substrate

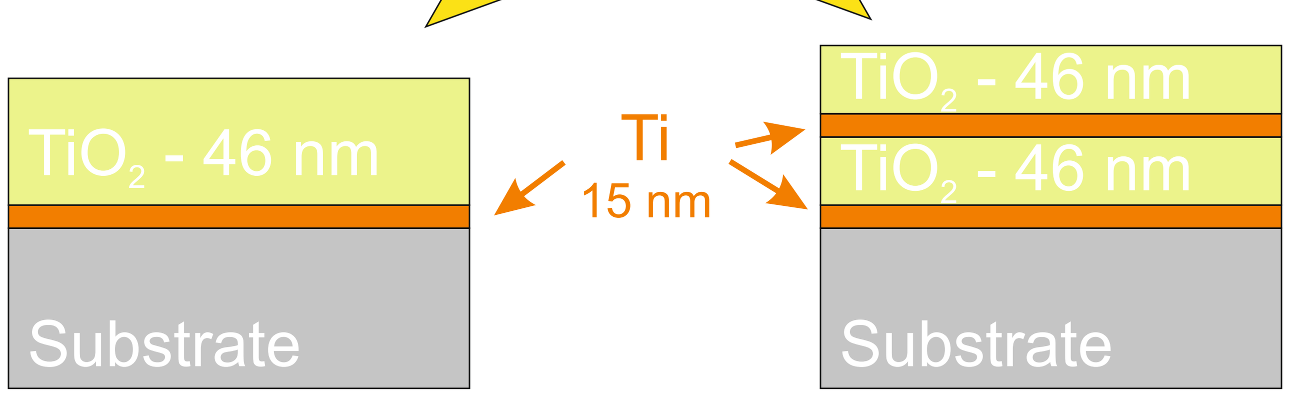
Mg-4Al-2RE

Mg-4Li-4Al-2RE

ALD coating



PVD coatings



Methodology

Structure

- Scanning Electron Microscope SEM
- Transmission Electron Microscope TEM
- EDS spectroscopy
- EELS spectroscopy
- Atomic Force Microscope AFM

Properties

- Corrosion resistance
  - Potentiodynamic method
  - EIS Method
- Wear resistance
  - Ball-on-disc

Results

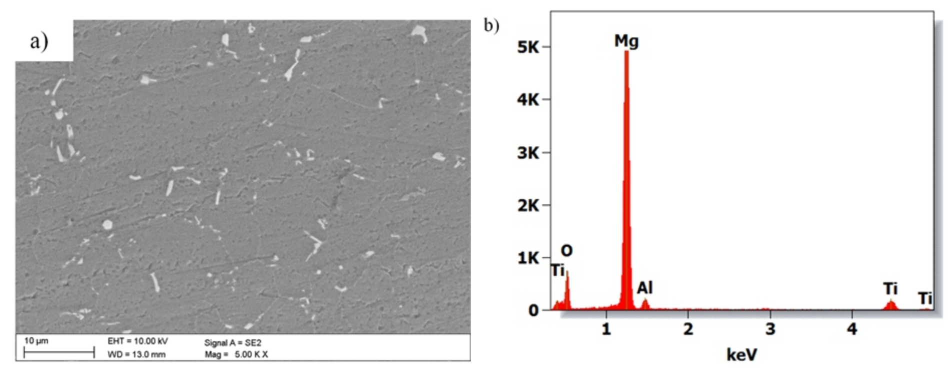


Fig. *a) Surface topography of Ti/TiO_2 coating on the AE42 alloy substrate, b) X-ray energy dispersive plot of the area according to figure a*

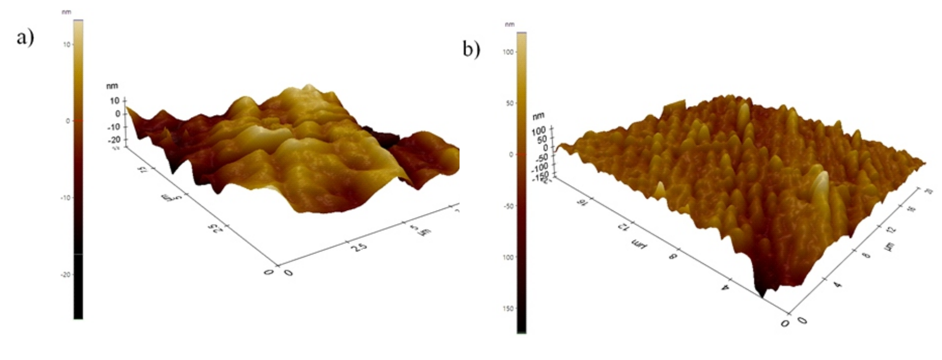


Fig. *Surface topography of AE42 alloy a) uncoated b) with Ti/TiO_2 coating, AFM*

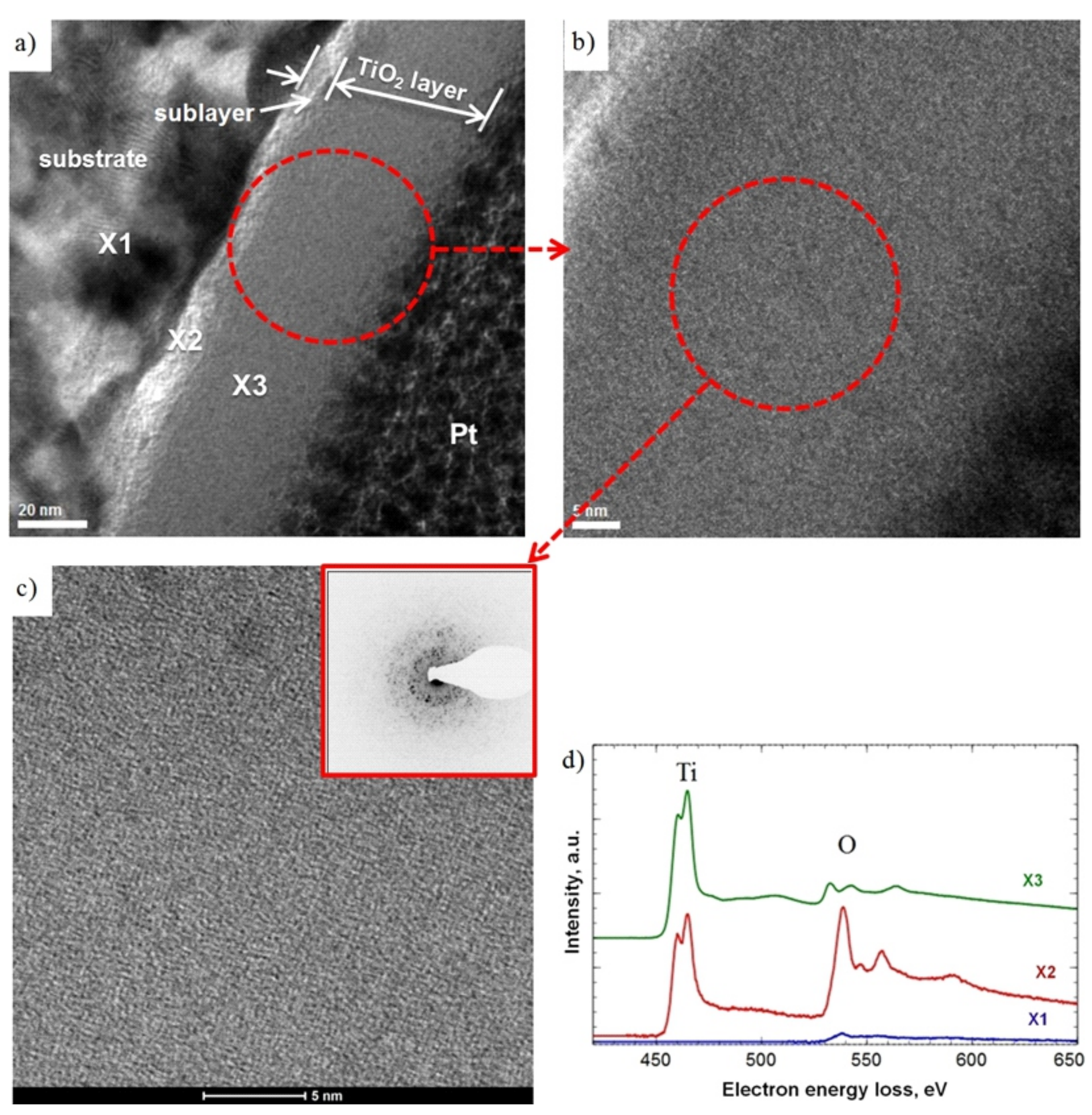


Fig. *Structure (TEM) of TiO_2 coating obtained: a-c) bright field (c with diffraction pattern); d) EELS energy loss spectrum from areas X1, X2, and X3 according to figure a*

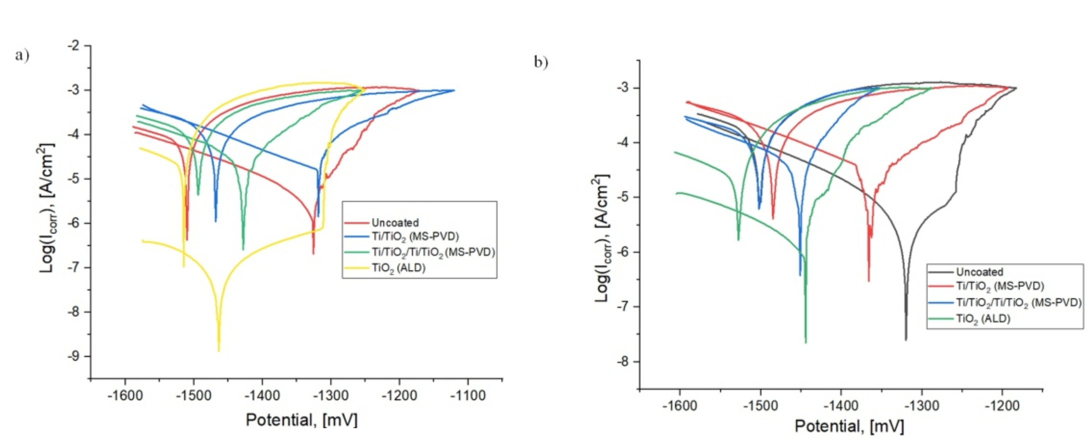


Fig. *Potentiodynamic polarization curves for a) AE42 b) LAE442*

Table *Poteotentiodynamic polarization parameters for samples in 0.05 m NaCl solution*

Sample		E_{corr} [mV]	I_{corr} [µA/cm²]	R_{pol} [Ohm×cm²]
AE42 (MS-PVD)	Uncoated	-1328	3.799	4250
	Ti/TiO_2	-1320	16	716.3
	$Ti/TiO_2/Ti/TiO_2$	-1426	10.981	976.78
AE42 (ALD)	TiO_2	-1466	0.067	329×10^3
LAE442 (MS-PVD)	Uncoated	-1319	2.157	7690
	Ti/TiO_2	-1380	5.2	977.9
	$Ti/TiO_2/Ti/TiO_2$	-1452	11.205	522.63
LAE442 (ALD)	TiO_2	-1447	0.85	5729

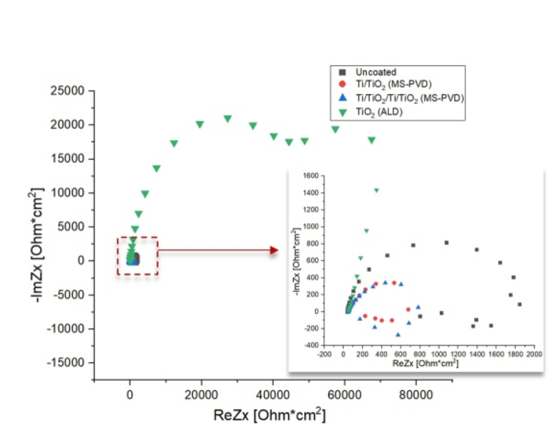


Fig. *Nyquist impedance diagram for AE42*

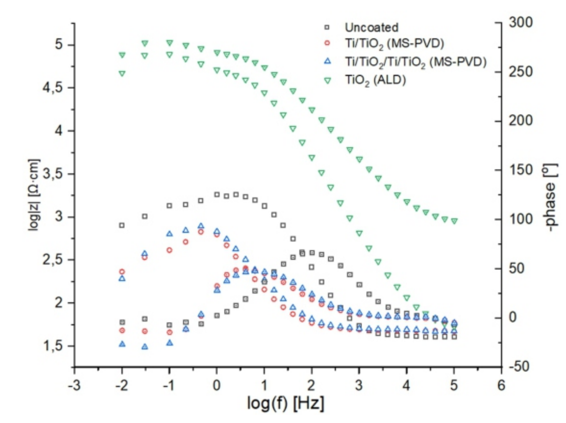


Fig. *Bode impedance diagram for AE42*

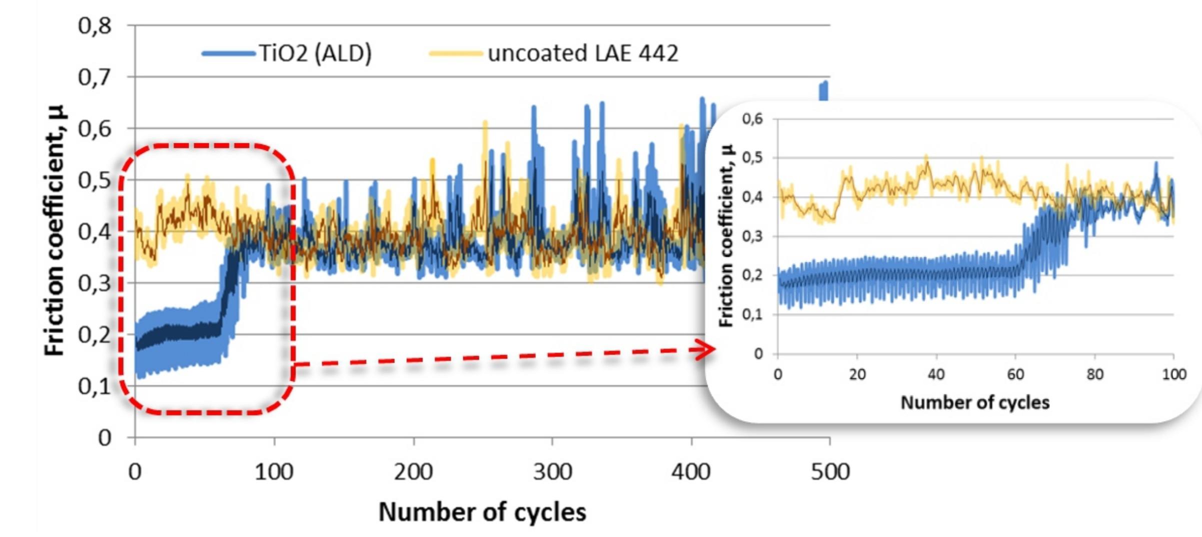


Fig. *Friction coefficient as a function of the number of cycles for uncoated Mg-4Li-4Al-2RE substrate material and TiO2 coating obtained by ALD method*

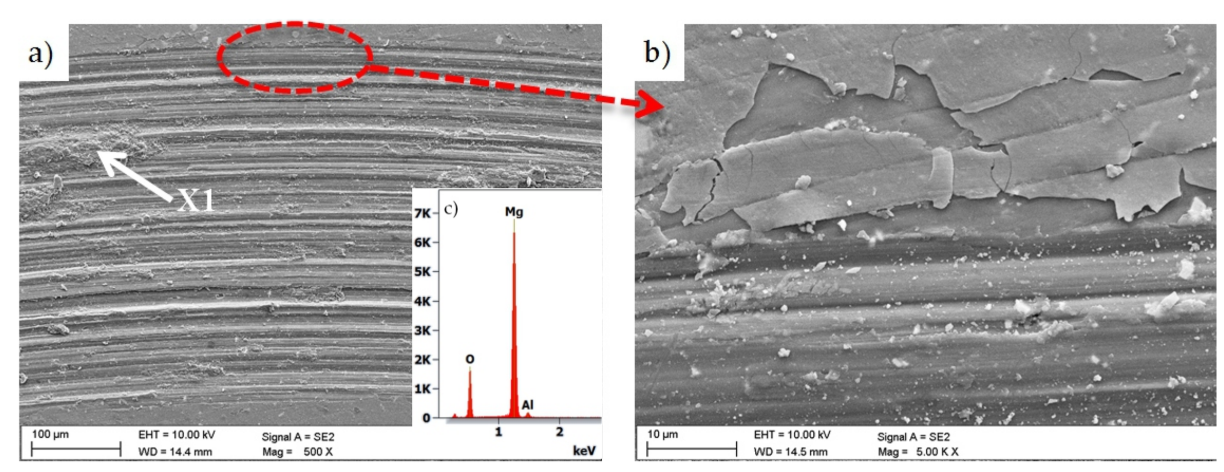


Fig. *(a,b) Wear trace after the "ball-on-plate" wear test for the TiO2 layer deposited in ALD process on Mg-4Li-4Al-2RE alloy substrate, (c) X-ray energy dispersive plot of the area X1 shown in figure a*

Summary

Magnesium alloys are among the lightest construction materials and are therefore increasingly popular in the industry. they are also characterized by low cost, good mechanical properties and the ability to dampen vibrations. One of the key factors limiting its wider application is its low corrosion resistance, which significantly reduces its application properties. The TiO_2 coating is often used as a corrosion protection due to its physical and chemical stability properties, especially in acidic environments. The magnetron method of depositing the Ti/TiO_2 coating on two magnesium alloys of the Mg-(Li)-Al-RE type allowed for the deposition of a relatively continuous layer without visible flaking and pores. The obtained coatings do not improve the corrosion resistance of the alloys. The best results of the potentiodynamic method and electrochemical impedance spectroscopy were obtained for samples coated with the use of the ALD method. These results are comparable to those of the uncoated samples. The layer applied by the ALD method also improves the tribological properties of the sample. In the case of PVD coatings, the results of corrosion resistance are much worse. There were likely discontinuities in the produced coating and therefore the substrate material was not tightly coated. As a result, the corrosion rate at the leakage point was greater than in the absence of the cathode coating. In the case of both the uncoated and those with the deposited coating, the samples of the alloy with lithium as an alloy additive, which lowers the corrosion resistance of magnesium alloys, showed lower corrosion resistance. The produced PVD coating also increased the surface roughness, which is also crucial in considering corrosion resistance. As the obtained coatings had discontinuities, and therefore did not ensure corrosion resistance, they cannot be used as the only protection of magnesium alloys against corrosion processes. However, due to the increased resistance to pitting corrosion, the substrates can be used as an intermediate composite layer together with the use of another coating that would ensure the tightness of the layer. Research should be aimed at optimizing the thickness of the layer or combining it with coatings made of other compounds, producing hybrid coatings, in order to eliminate discontinuities and reduce the roughness of the sample surface.

APMME 2021

APPLICATIONS OF PHYSICS IN MECHANICAL AND MATERIAL ENGINEERING

Częstochowa, 19th of February 2021