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Regulation of AZ31 alloy biocorrosion by atomic layer deposition of oxide-based nanocoatings

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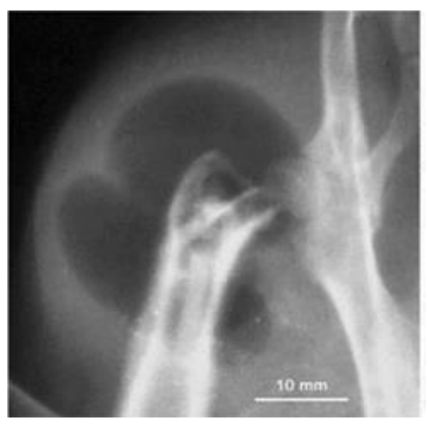
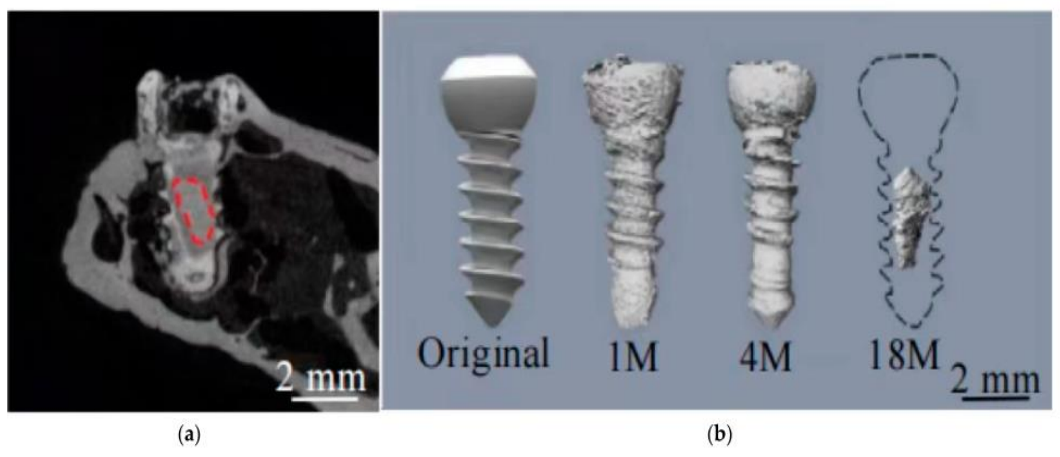
INTRODUCTION & AIM

In recent times, magnesium-based materials have emerged as a promising class of temporary implants due to their remarkable properties, including strength, biocompatibility, biodegradability, and bioactivity. However, the practical use of magnesium implants is constrained by a number of issues associated with accelerated biodegradation. In this context, it is crucial to regulate the rate of biocorrosion by implementing coatings. One of the most promising methods for preparing protective biocompatible coating is atomic layer deposition (ALD).

Hydrogen bubble formation during biodegradation of magnesium implant



Biodegradation of magnesium-based screw



The aim of this study is to synthesise thin oxide nanofilms of Al_2O_3, TiO_2, ZnO and zinc-titanium (ZTO) and aluminium-titanium (ATO) oxide nanocoatings on the surface of magnesium alloy AZ31 by atomic layer deposition and to investigate their physicochemical properties and anticorrosion properties.

ATOMIC LAYER DEPOSITION (ALD)

TiO_2 ($TiCl_4$ and H_2O) →

1. substrate – n(-OH)$_{(s)}$ + $TiCl_{4(g)}$ → (-O-)$_n$$TiCl_{4-n(s)}$ + $nHCl_{(g)}$
2. substrate –(-O-)$_n$$TiCl_{4-n(s)}$ + (4-n)$H_2O_{(g)}$ → (-O-)$_n$Ti (OH)$_{4-n(s)}$ + (4-n)$HCl_{(g)}$

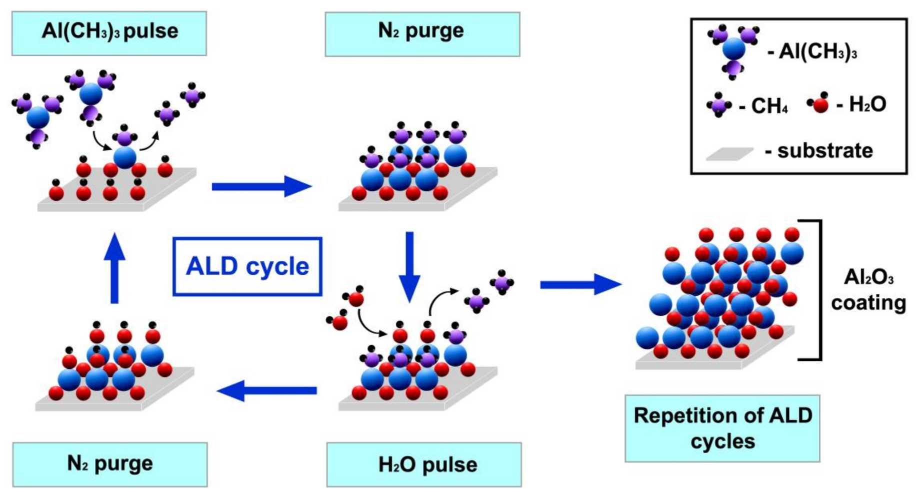
ZnO ($Zn(C_2H_5)_2$ and H_2O) →

1. substrate – $OH_{(s)}$ + $Zn(C_2H_5)_{2(g)}$ → substrate – O – Zn – $C_2H_{5(s)}$ + $C_2H_{6(g)}$
2. substrate – O – Zn – $C_2H_{5(s)}$ + $H_2O_{(g)}$ → substrate – O – Zn – $OH_{(s)}$ + $C_2H_{6(g)}$

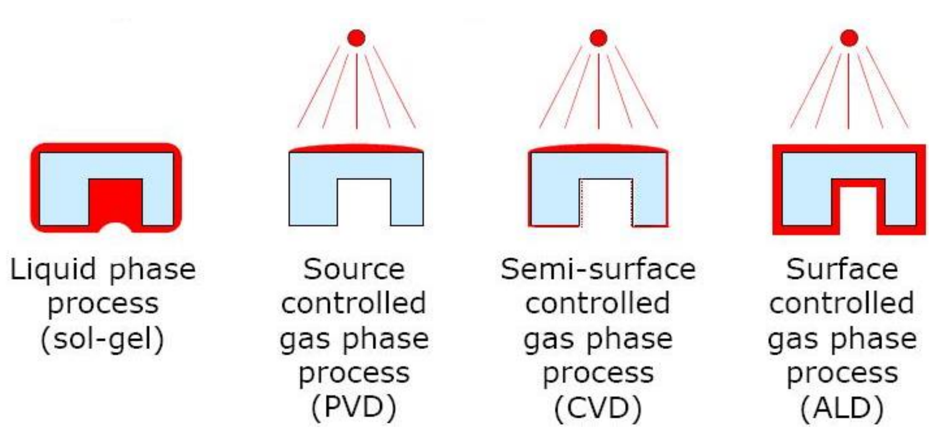
Al_2O_3 ($Al(CH_3)_3$ and H_2O) →

1. substrate – $OH_{(s)}$ + $Al(CH_3)_{3(g)}$ → substrate – O – Al – $(CH_3)_{2(s)}$ + $CH_{4(g)}$
2. substrate – O – Al – $(CH_3)_{2(s)}$ + $2H_2O_{(g)}$ → substrate – O – Al – $(OH)_{2(s)}$ + $2CH_{4(g)}$

Scheme of Al_2O_3 synthesis by ALD method

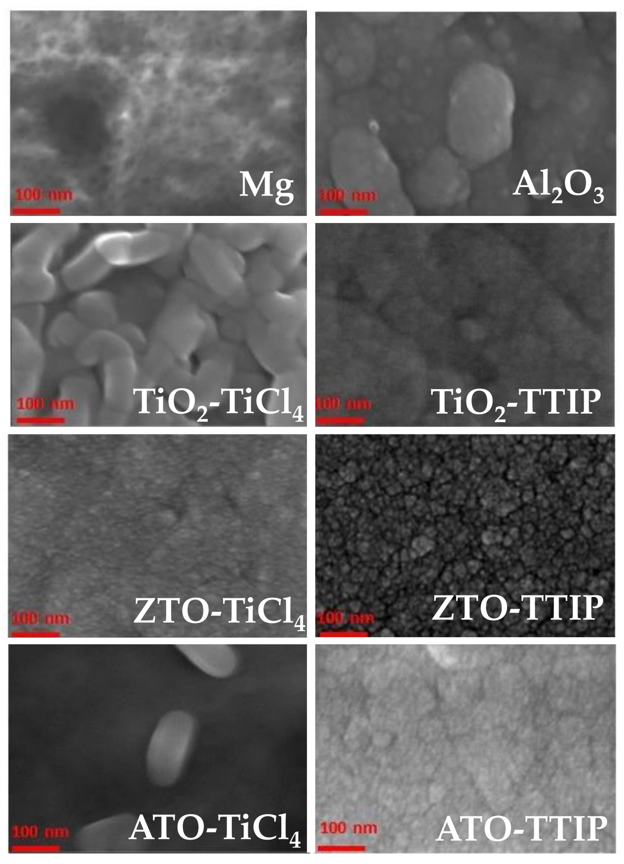


Coating thickness uniformity with different methods



RESULTS & DISCUSSION

Surface morphology of coatings (SEM – 300 000×)

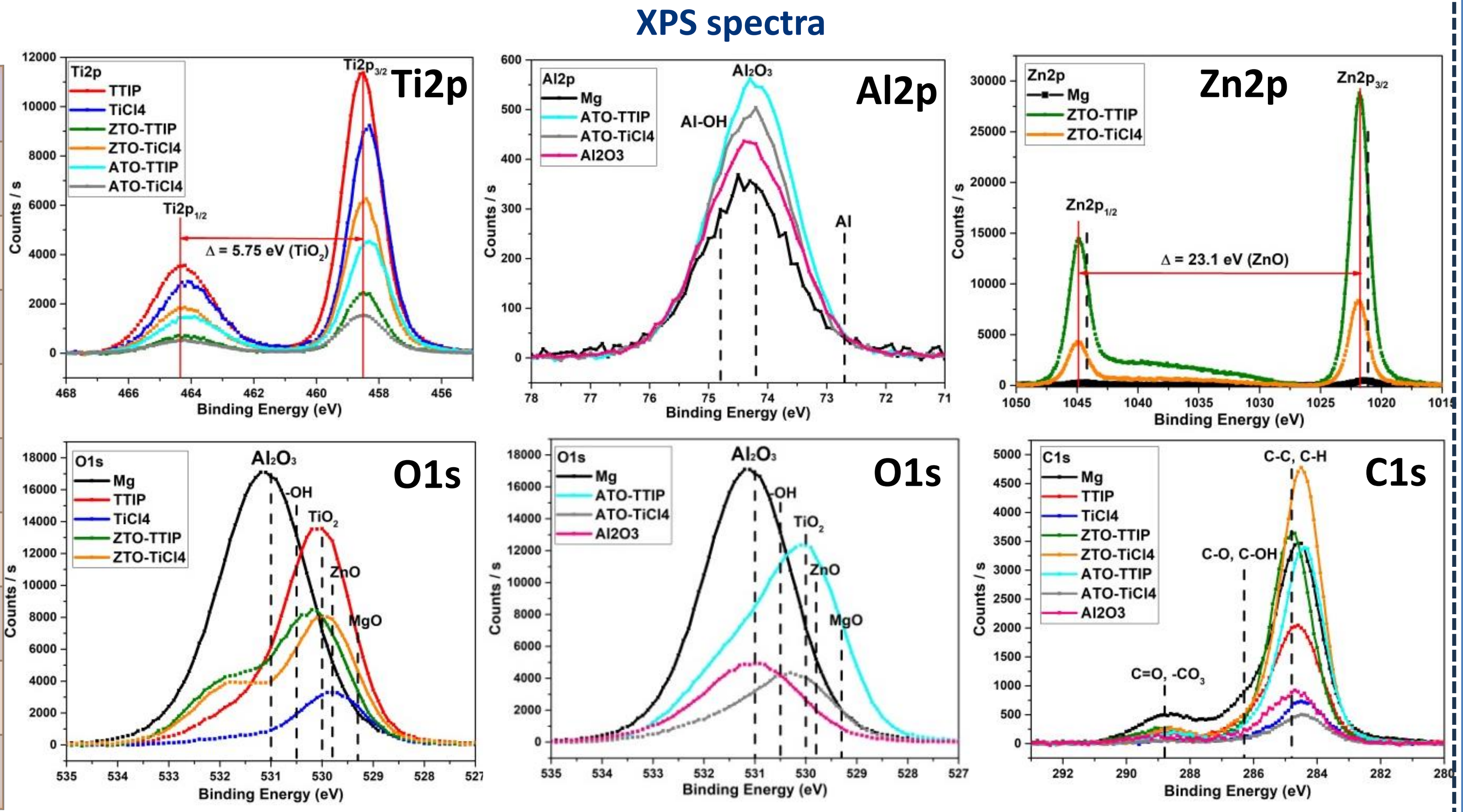


Elemental composition of coatings

Elemental quantitative analysis of coatings (XPS/EDX)

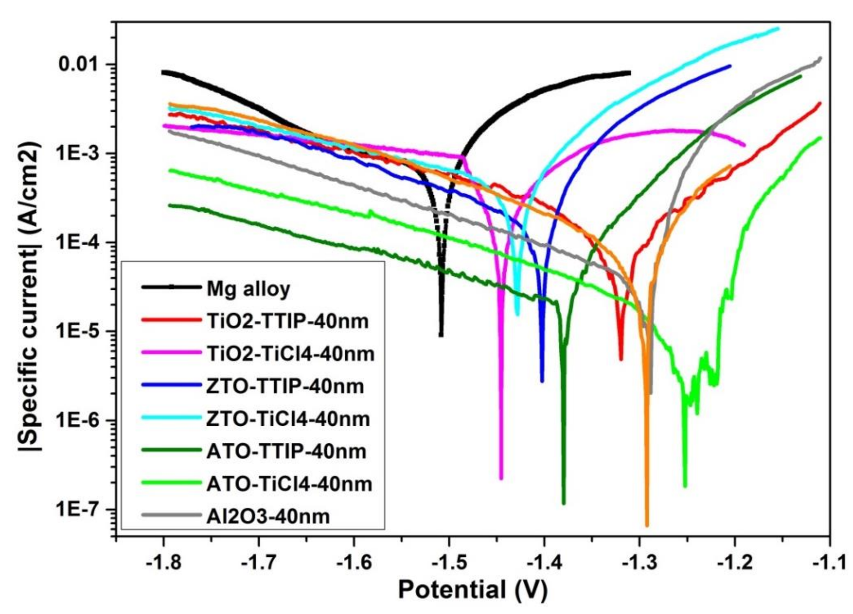
Sample	Mg, %	Zn, %	Ti, %	Al, %	O, %	Cl, %	C, %
Mg alloy	15.65/-	0.44/-	-/-	4.06/-	50.51/-	-/-	29.34/-
ZnO	-/-	44.53/-	-/-	-/-	36.55/-	-/-	18.83/-
TiO_2-TTIP	-/73.75	-/0.44	24.92/3.91	-/3.87	51.12/18.01	-/-	23.96/-
TiO_2-$TiCl_4$	-/54.94	-/0.35	24.66/5.81	-/3.09	49.86/35.32	-/0.49	25.48/-
ZTO-TTIP	-/86.83	26.74/1.08	4.38/0.23	-/2.80	37.22/9.06	-/-	31.66/-
ZTO-$TiCl_4$	0.86/89.72	8.34/0.49	11.71/0.37	-/3.06	36.99/6.35	-/0.02	42.10/-
ATO-TTIP	-/85.01	-/0.32	8.43/0.36	19.43/4.41	47.48/9.90	-/-	24.66/-
ATO-$TiCl_4$	-/70.86	-/0.52	9.97/1.20	20.34/6.10	54.39/21.22	-/0.09	15.29/-
Al_2O_3	-/61.17	-/0.34	-/-	32.98/11.30	56.3/27.19	-/-	10.72/-

XPS spectra

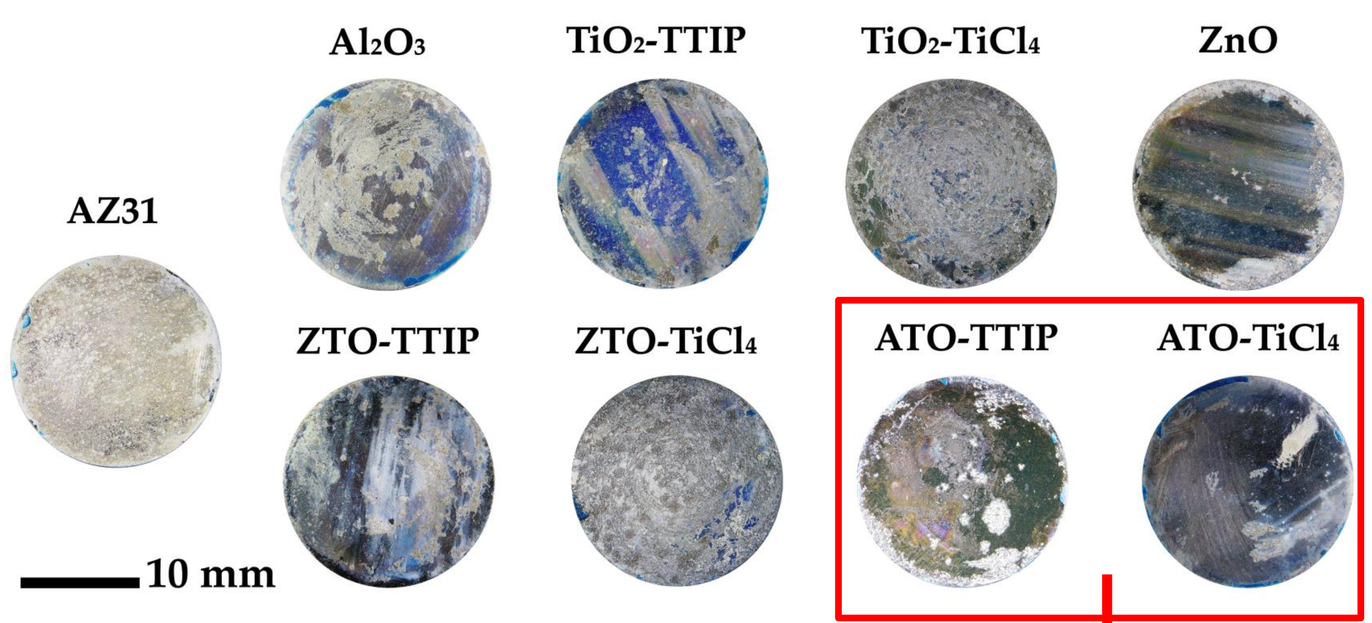


Anticorrosive properties of coatings in Ringer's solution

Polarization curves of AZ31 alloy samples with coatings



Optical photographs of AZ31 alloy samples with coatings after corrosion test



Results of the corrosion tests

Sample	Coating thickness, nm	I_{corr}, A/cm²	E_0, V	Corrosion rate, mm/year	Corrosion resistance, Ohm*cm²
Mg	0	$7.291 \cdot 10^{-4}$	-1.508	16.1	28.5
ZnO	40	$6.620 \cdot 10^{-5}$	-1.292	1.46	260
ZTO-TTIP	40	$2.145 \cdot 10^{-4}$	-1.403	4.73	94.2
ZTO-$TiCl_4$	40	$4.243 \cdot 10^{-4}$	-1.427	9.36	51.5
TiO_2-TTIP	40	$2.221 \cdot 10^{-4}$	-1.319	4.90	227
TiO_2-$TiCl_4$	40	$8.070 \cdot 10^{-4}$	-1.445	17.8	75.5
ATO-TTIP	40	$2.990 \cdot 10^{-5}$	-1.380	0.66	418
ATO-$TiCl_4$	40	$1.354 \cdot 10^{-5}$	-1.246	0.30	3230
Al_2O_3	40	$4.007 \cdot 10^{-5}$	-1.289	0.88	158

The samples with the ATO coating showed the most significant reduction in the rate of biocorrosion.

CONCLUSION

Among ALD aluminium, zinc, titanium oxides and their composite nanocoatings the Al_2O_3 and Al_2O_3-TiO_2 nanocoatings are the most effective in the reduction of biocorrosion rate of AZ31 alloy in the initial stages, while ensuring the material's biodegradability in subsequent stages.

FUNDING

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