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Corrosion Behaviors of Oxygen Plasma Immersion Ion Implantation Treated Magnesium

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Abstract

Oxygen PIII was performed on magnesium to modify their corrosion resistance, which was investigated in PBS and chloride ion enriched PBS (PBS(Cl-)). Significantly enhanced corrosion resistance against PBS were achieved for high dose implanted Mg, and the $I_{corr.}$ of treated Mg with oxygen dose more than 1 x 1016 ions.cm-2 was strongly decreased by almost five orders compared with untreated Mg. This is ascribed to increased Mg-O bonding states formed on the surface layer of magnesium by the PIII process, as discerned by XPS and XRD measurements, as well as to a more homogenous surface morphology, due to the ion bombardment effect, as observed by AFM. Such modifying layer cannot withstand more aggressive PBS(145mM Cl- pH6.4), even for 2 x 1016 ions.cm-2 implanted samples.

Outline

1.Introduction

Attractive mechanical and lightweight properties make magnesium welcomingly used in:

automobile, aerospace, electronic fields and so on.....

however, poor corrosion resistance limits the widespread scope.

Biomedical application of magnesium takes this advantage of degradation:

orthopaedic and trauma surgery (the first half of 20th century)

degradable cardiovascular stents (newly creative concept)

Attempts to modify the corrosion resistance of Mg:

of great scientific and technical importance.

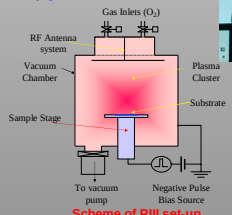
Way:

plasma immersion ion implantation (PI^2) predestinated by none-line-of-sight capable to treat a complex geometry

2. Experimental

Oxygen PIII treatment

PIII Instrument in SWJTU



Scheme of PIII set-up

Plasma generation

O_2 plasma ← r.f.

Implantation process

Pulsed bias voltage (20kV)

PIII Instrumental Conditions

Samples	Target bias Voltage: Voltage (KV)	Frequency (Hz)	Pulse width (μ s)	r.f. (W)	O_2 pressure (Pa)	Time (min.)	O_2 implanted doses ($\times 10^{16}$ions/cm^2)
PIII-1						30	2.5
PIII-2						60	5
PIII-3	20	245	6.5	500	0.2	120	10
PIII-4						240	20

Characterization:

Surface chemical states ← XPS(Model PHI 5600, Perkin-Elmer, USA)

Phase & structure ← XRD(X'Pert Pro MPD, Philips, Netherlands)

Surface morphology ← AFM(SPI 3800N, SEIKO)

Investigation:

Corrosion behaviors:
Potentiodynamic polarization(IM6)
SEM(Quanta200, FEI)

IM6 electrochemical workstation (Zahner, Germany) in SWJTU

3.Results and discussions

Surface chemical states characteristics: XPS

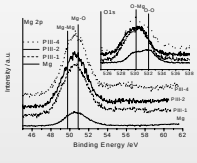


Fig.1. Mg 2p and O1s core level XPS spectra of untreated Mg and Oxygen PIII processed Mg.

Mg 2p:
Deconvoluted into : Mg-O (50.8 eV) and Mg-Mg (49.7eV)
Higher energy shift: increased Mg-O bonds.
O1s:
consist of: Mg-O (531.0eV) and O-O (532eV)
low energy shoulder of Mg-O and lower shifts :Mg-O bonds increased
Conclusion: increased Mg-O bonds with increased oxygen doses implanted was achieved by the oxygen PIII process.

Phase and structure characteristics: XRD

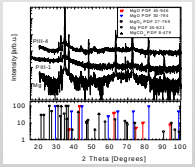


Fig.2. Surface layer XRD pattern of untreated magnesium and samples PIII-1 and PIII-4.

➢ **XRD pattern is dominated by the bulk magnesium**

➢ **Characteristic oxide peaks appearing at 36.9 ° , 73° and 81.5° on both untreated Mg and treated Mg**

- Very thin of the modified layer;
- Low implantation dose;
- incompletely oxidized states.

Thin oxide phase are formed by PIII

Surface morphology characteristics: AFM

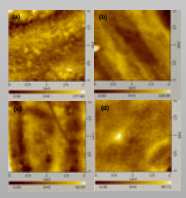


Fig.3. AFM images of untreated Mg (a) and oxygen PIII treated Mg : (b) PIII-1; (c) PIII-3; (d) PIII-4.

(a): porous albeit fine crystalline surface

(b) : more amorphous, irregular

(c) : smoother and more homogenous

(d) much smoother, amorphous and homogenous with none-porous

Surface morphology has been changed by PIII process

Corrosion behaviors : in PBS

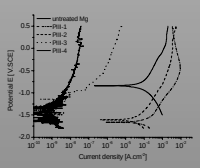


Fig.4. I/E curves of untreated Mg and oxygen PIII treated Mg in PBS.

➢**Up to 1V more negative $E_{corr.}$ than the untreated Mg**

➢ **$I_{corr.}$ was strongly decreased almost five orders for PIII-3 and PIII-4.**

No improvement has been observed ➢ on PIII-1 and PIII-2

Conclusion: High oxygen PIII does improve corrosion resistance of Mg against PBS significantly;
One threshold value for implanted dose exists.

Surface characteristics after corrosion :in PBS

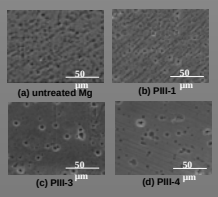


Fig.5. SEM images of untreated Mg, oxygen PIII treated Mg after corrosion tests in PBS

(a)a great amount of pits, big sizes and high depth, cracks on pits indicating accompanying intergranular corrosion.

corrosion also occurs along polishing groove lines.

(b) similar to the untreated Mg, just with slightly less pits.

(c) Much less pits with obviously lower depth

(d) Least amount of pits, with shallowest pitting

Conclusion: pitting is the dominant corrosion type for all samples, and corrosion resistance against pitting increase with higher oxygen implanted

Corrosion behaviors : in PBS(Cl$^-$) (145mM Cl$^-$ pH6.4)

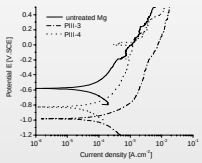


Fig.6. I/E curves of untreated Mg, oxygen PIII treated Mg in PBS(Cl-).

➢**$I_{corr.}$ doesn't change with oxygen implanted, no obvious improvement of corrosion resistance for oxygen implanted Mg compared to untreated Mg, although $E_{corr.}$ vary with implanted dose.**

The modified layer cannot withstand PBS(Cl$^-$), such Cl- and pH values are still very aggressive for Mg-O phase.

Surface characteristics after corrosion : In PBS(Cl$^-$)

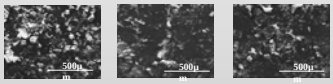


Fig.7. SEM photos of Mg, oxygen PIII treated Mg after corrosion tests in PBS(Cl-)

➢**covered by corrosion products, which do not dissolve in the solution;**
➢**Crack failure still can be observed on incompletely covered surface of untreated Mg.**

Severely corrosion occurred on whole surface.

Discussion

Process effect on corrosion performance

- **The increased corrosion resistance against PBS can be ascribed to increased Mg-O states as well as more uniform surface properties.**
- **the phosphate ions and water can readily oxidize or hydro-oxidize the metal Mg bonding, albeit can hardly reduce Mg-O bonds states**
- **the more homogeneous surface property obtained by ion bombardment reduces the risk of pitting nuclei formation.**
- **a higher thickness and more complete oxidation of the modified layer enhance further corrosion resistance against pitting in PBS.**
- **(145mM)Cl$^-$ at the lower pH(6.4) can still easily dissolve the Mg-O phase, and the formed pits can be hardly oxidized and repaired per se**

4. Summary

1. **Oxygen PIII was conducted onto Mg, Increased Mg-O bond states have been successfully achieved by obtaining increased oxygen doses and accented temperatures for longer treatment time.**
2. **Such modified oxide rich layer possesses significantly protective corrosion resistance against neutral none-Cl$^-$-containing PBS solution (pH7.4).**
3. **even the highest dose in our case can not withstand much more aggressive 145mM Cl$^-$ containing and acidified (pH 6.4)PBS.**
4. **Further work should focus on this subject to solve the stringent problem.**

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Thank you for attention!