Laser Shock Processing as an Advanced Technique for the Surface and Mechanical Resistance Properties Modification of Bioabsorbable Magnesium Alloys

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INTRODUCTION

- Laser shock processing (LSP) is increasingly applied as an effective technology for the improvement of mechanical properties in different types of metallic components, principally as a means of enhancement of their corrosion and fatigue life behavior. Specially wear resistance, stress corrosion cracking susceptibility and crack propagation rate seem to be material properties specially improved by LSP treatments.
- On the other hand, Mg and its alloys have gained increasing relevance as natural biomaterials as their mechanical properties are in the same range as those corresponding to natural bone as well as due to their inherent bioabsorbable properties.
- In the present paper, the application of the LSP technology to biocompatible bioabsorbable Mg alloys suitable for surgical implementation is envisaged, the experimental verification of the residual stresses fields induced under different processing conditions and the experimental characterization of the corresponding surface properties being specifically considered.

Laser Shock Processing as an Advanced Technique for the Surface and Mechanical Resistance Properties Modification of Bioabsorbable Magnesium Alloys

OUTLINE:

- Introduction / Motivation
- Reminder of Laser Shock Processing Principles
- Experimental LSP Setup at CLUPM
- Sample results on the treatment of Metallic Materials of Biomedical Interest
 - Induced Surface Roughness and Residual Stresses in Mg ingot specimens
 - Improvement of Corrosion Behaviour in Mg ingot specimens
 - Modified wettability and microorganisms adhesion tolerance in Mg samples
- Discussion and Outlook

MOTIVATION

Due to their excellent biodegradability characteristics, Mg and Mg-based alloys have become an emerging material in biomedical implants, notably for repair of bone as well as coronary arterial stents. However, the main problem with Mg-based alloys is their rapid corrosion in aggressive environments such as human body fluids

(M. Peuster et al.: [doi: 10.1017/S1047951106000011](https://doi.org/10.1017/S1047951106000011).)

(B. Denkena, A. Lucas.: [doi:10.1016/j.cirp.2007.05.029](https://doi.org/10.1016/j.cirp.2007.05.029))

REMINDER OF LSP PHYSICAL PRINCIPLES (1/2)

FREE MODE

FREE PLASMA EXPANSION

CONFINED MODE

IMPROVED PRESSURE AND IMPULSION

REMINDER OF LSP PHYSICAL PRINCIPLES (2/2)

PROCESS EXPERIMENTAL SETUP

Q-SWITCHED Nd:YAG LASER

($\lambda = 1064 \text{ nm}$; $E = 2.5 \text{ J/pulse}$)
($\lambda = 532 \text{ nm}$; $E = 1.5 \text{ J/pulse}$)

$\tau = 10 \text{ ns}$; $f = 10 \text{ Hz}$

PROCESS EXPERIMENTAL SETUP

PROCESS EXPERIMENTAL SETUP

EXPERIMENTAL PROCEDURE

$$\text{Equivalent Overlapping Density} \equiv \text{EOD} = \frac{\text{N}^\circ \text{ of pulses}}{\text{Total treated surface}} = \frac{\frac{x}{\Delta x} \frac{y}{\Delta y}}{\Delta s} = \frac{\frac{x}{d} \frac{y}{d}}{xy} = \frac{1}{d^2}$$

$$\text{Equivalent Energy Density} \equiv \text{EED} = \frac{\text{N}^\circ \text{ of pulses} \cdot \text{Pulse Energy}}{\text{Total treated surface}} = \frac{\frac{x}{\Delta x} \frac{y}{\Delta y} E}{\Delta s} = \frac{\frac{x}{d} \frac{y}{d} E}{xy} = \frac{E}{d^2}$$

$$\text{Equivalent Local Overlapping Factor} \equiv \text{ELOF} = \frac{\text{N}^\circ \text{ of pulses} \cdot \text{Pulse Area}}{\text{Total treated surface}} = \frac{\frac{\pi}{4} \phi^2}{d^2} = \frac{\pi}{4} \left(\frac{\phi}{d} \right)^2$$

EXPERIMENTAL RESULTS

Mg extruded ingot

YS = 34-55 MPa

E = 41-45 GPa

Table 1. LSP processing conditions parameters

Sample	Laser Focused Diameter Ø (mm)	LSP treatment EOD (cm ⁻²)	LSP treatment EED (J.cm ⁻²)	LSP treatment ELOF (-)
1+2	1.5	400	960	7.07
3+4	2.0	400	960	12.57

EXPERIMENTAL RESULTS

Table 2. Surface Roughness Parameters Induced in LSP treated samples

Sample	Laser Focused Diameter $\varnothing$ (mm)	LSP treatment EOD (cm ⁻²)	Average Surface Roughness, S_a (μm)	RMS Surface Roughness, S_q (μm)
0 (Ref)			1.59±1.0	2.06±1.0
1	1.5	400	12.02±1.0	15.04±1.0
3	2.0	400	11.46±1.0	14.43±1.0

$$S_a = \frac{1}{A} \iint_A |z(x,y) - z_{av}| dA$$

$$S_q = \sqrt{\frac{1}{A} \iint_A |z(x,y) - z_{av}|^2 dA}$$

According to ISO 25178 Standard

EXPERIMENTAL RESULTS

Residual stresses

YS = 34-55 MPa

E = 41-45 GPa

According to ASTM E837-13 Standard

EXPERIMENTAL RESULTS

IMPROVED CORROSION BEHAVIOUR (Assessed through EIS):

Dulbecco's Phosphate Buffered Saline (Ref. Sigma Aldrich: D8662-500ML)

EXPERIMENTAL RESULTS

IMPROVED CORROSION BEHAVIOUR (Assessed through EIS):

Element	Freedom	Value	Error	Error %
R1	Free(±)	479.8	6.193	1.2907
R2	Free(±)	7009	135.89	1.9388
CPE1-T	Free(±)	1.2031E-05	4.321E-07	3.5916
CPE1-P	Free(±)	0.79244	0.0071257	0.89921

Chi-Squared: 0.0028524
Weighted Sum of Squares: 0.18256

24 h Test

$$R1 + R2 = 479.8 + 7009.0 = 7488.8 \Omega \cdot \text{cm}^2$$

EXPERIMENTAL RESULTS

IMPROVED CORROSION BEHAVIOUR (Assessed through EIS):

144 h Test

$$R1 + R2 = 484.3 + 14082.0 = 14567.3 \, \Omega \cdot \text{cm}^2$$

EXPERIMENTAL RESULTS

$\varnothing=2.0$ mm

178 pulsos/cm²

223 pulsos/cm²

278 pulsos/cm²

400 pulsos/cm²

EXPERIMENTAL RESULTS

HYDROPHOBICITY:

Mg mirror polished

Mg + sand 600

Mg + sand 600 + LSP 178

Sample	Contact Angle (deg)
Mg mirror polished	74 ± 7
Mg + sand 600	118 ± 2
Mg + sand 600 + LSP178	134 ± 3

Data supplied by Research Group on Microbian Adhesion. Univ. of Extremadura (SPAIN)

EXPERIMENTAL RESULTS

SURFACE GIBBS ENERGY LOWERING:

Mg mirror polished

Mg + sand 600

Mg + sand 600 + LSP 178

Sample	S-L Surface Tension (mJ/m ²)
Mg mirror polished	43.5 ± 3.6
Mg + sand 600	21.2 ± 5.7
Mg + sand 600 + LSP178	18.8 ± 2.8

Data supplied by Research Group on Microbian Adhesion. Univ. of Extremadura (SPAIN)

EXPERIMENTAL RESULTS

PROTECTION AGAINST MICROORGANISMS ADHESION:

Mg mirror polished

Mg + sand 600

Mg + sand 600 + LSP 178

- **Microorganism type:** *Staphylococcus epidermidis* ATCC35983.
- **Suspension medium:** PBS (Phosphate buffered saline).
- **Microorganism concentration:** 1 McFarland ($\approx 3.10^8 \text{ mL}^{-1}$).
- **Adhesion method:** Static, 37°C, slight orbital agitation.
- **Contact time:** 1 h.

Data supplied by Research Group on Microbian Adhesion. Univ. of Extremadura (SPAIN)

DISCUSSION AND OUTLOOK

- According to the presented results, the feasibility of introduction of compressive residual stresses fields in extruded ingot samples of pure Magnesium ($\text{Mg} > 99.9\%$) has been experimentally demonstrated. Maximum compressive residual stresses higher than 45% - 50% of the reported yield strength of the material have been achieved by moderate overlapping density ($\text{EOD} = 400 \text{ cm}^{-2}$) treatments with peak laser intensities in the range $8\text{-}15 \text{ GW/cm}^2$, providing equivalent energy densities (EED's) in the range $75\text{-}150 \text{ J/cm}^2$.
- Taking into account the relatively very low value of the elastic Young modulus and compressive yield stress of such material, the achieved compressive residual stresses values are considered to be well over the minimum values strictly needed for improvement of its surface corrosion resistance.
- Such improvement on corrosion resistance behavior induced by LSP treatments has been experimentally demonstrated by standard EIS tests. The effect has been shown to be stable and even to increase for long test times.
- Additionally, the application of the reported LSP treatments has been found to introduce a moderate increase in surface roughness. These moderate values of the introduced roughness are not considered to have an appreciable influence on the material susceptibilization to crack initiation and result in modified wettability and free energy properties (behavior needed for further study).
- In summary, the feasibility of inducing compressive residual stresses fields over an appreciable depth in this kind of “soft” material is considered to have been experimentally demonstrated under different operational conditions, thus assuring the expected result of improvement of crack propagation retardation and corrosion properties of the material.
- Considering that the presented work is the starting point for application of the LSP technology to different Mg-based bioabsorbable alloys, this technology is considered to be a key one able to change the technological expectations for the practical working limits in the biomedical implants field.

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MAIN REFERENCES

1. Ocaña, J.L. et al.: “Predictive assessment and experimental characterization of the influence of irradiation parameters on surface deformation and residual stresses in laser shock processed metallic alloys”. In: High-Power Laser Ablation V, Phipps C.R., Ed.. SPIE Vol. 5548, 642-653 (2004)
2. Ocaña, J.L. et al.: Materials Science Forum, 539-543, 1116-1121 (2007)
3. Morales, M. et al.: Surfaces and Coating Technology, 202 , 2257-2262 (2008)
4. Morales, M. et al.: Applied Surface Science, 255, 5181–5185 (2009)
5. Ocaña, J.L. et al.: “Design Issues of Engineered Residual Stress Fields and Associate Surface Properties Modification by LSP in Al and Ti Alloys”. Proceedings of the Fifth International WLT-Conference on Lasers in Manufacturing 2009. Munich, June 2009. A. Ostendorf et al. Eds.. pp. 387-392 (2009)
6. Martí-López, L. et al.: Applied Optics, 48, 3671-3680 (2009)
7. Ocaña, J.L. et al.: “Laser Shock Processing of Metallic Materials: Coupling of Laser-Plasma Interaction and Material Behaviour Models for the Assessment of Key Process Issues”. In International Symposium on High Power Laser Ablation 2010, C.R. Phipps, Ed. AIP Conference Proceedings, Vol. 1278, pp. 902-913 (2010)
8. Morales, M. et al.: Materials Science Forum, 638-642, 2682-2687 (2010)
9. Morales, M. et al.: International Journal of Structural Integrity, 2, 51-61 (2011)
10. Ocaña, J.L. et al.: Materials Science Forum, 706-709, 2565-2570 (2012)
11. Ocaña, J.L. et al.: Materials Science Forum, 783-786, 2376-2381 (2014)
12. Correa, C. et al.: International Journal of Fatigue, 70, 196–204 (2015)
13. Correa, C. et al.: International Journal of Fatigue, 79 ,1–9 (2015)
14. Correa, C. et al.: Materials & Design, 79, 106–114 (2015)
15. Ocaña, J.L. et al.: Journal of Materials Processing Technology, 223, 8–15 (2015)
16. Moreno-Díaz , C. et al.: Journal of Materials Processing Technology, 232, 9–18 (2016)
17. Ocaña, J.L. et al.: Advances in Materials and Processing Technologies, 3, 12-22 (2017)
18. Ocaña, J.L. et al.: Materials Science Forum, 879, 1408-1413 (2017)

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*Thank you very much
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RESULTS: Experimental Procedure for EIS determinations

King, A.D., Birbilis, N., Scully, J.R.
Electrochimica Acta, 121 (2014), 394-406.

- HFR Region associate to behaviour of native oxides or induced by LSP treatments
- MFR Region associate to charge transfer resistance
 (inversely proportional to metal substrate corrosion rate)
- LFR Region associate to adsorption/desorption of unstable species

RESULTS: Experimental Procedure for EIS determinations

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Equivalent circuit

R_s is the solution resistance.

R_f is the resistance of the oxide/hydroxide films (air-formed, LSP, and corrosion products film, respectively).

R_{ct} is the charge-transfer resistance of the metal/electrolyte interface (which is inversely proportional to the corrosion rate).

CPE_f is the capacitance oxide/hydroxide films on magnesium surface (*).

CPE_{dl} represents the double-layer capacitance at the interface between magnesium alloy and the solution.

L_a and R_a represent respectively the inductance and the resistance of adsorbed/desorbed species on the electrode surface.

(*) In a real system, ideal capacitive behavior is not observed, so a constant phase element (CPE) is often used as a substitute for a capacitor C to fit more accurately impedance behavior of the electric double layer.

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Equivalent circuit

Simplified equivalent circuit (Ignoring the inductive arc of the Nyquist plots)

$$R_1 = R_s + R_f$$

$$R_2 = R_t$$

$$CPE_1 = CPE_{dl}$$

RESULTS: Experimental Procedure for EIS determinations

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$$R_s + R_1 + R_2 = 14578 \, \Omega \cdot \text{cm}^{-2}$$

Element	Freedom	Value	Error	Error %
Rs	Free(±)	223.1	2.4399	1.0936
CPE1-T	Free(±)	9.9417E-06	1.4228E-06	14.311
CPE1-P	Free(±)	0.66474	0.013318	2.0035
R1	Free(±)	1599	318.17	19.898
CPE2-T	Free(±)	2.7137E-06	9.0302E-07	33.276
CPE2-P	Free(±)	0.87521	0.055603	6.3531
R2	Free(±)	12756	236.43	1.8535
RL	Free(±)	67822	13606	20.061
L	Free(±)	1.0633E06	2.0176E05	18.975

Chi-Squared: 0.004226
Weighted Sum of Squares: 0.56206

$$R_1 + R_2 = 14566.3 \, \Omega \cdot \text{cm}^{-2}$$

Element	Freedom	Value	Error	Error %
R1	Free(±)	484.3	17.923	3.7008
R2	Free(±)	14082	331.68	2.3553
CPE1-T	Free(±)	1.143E-05	3.7889E-07	3.3149
CPE1-P	Free(±)	0.74094	0.0073619	0.99359

Chi-Squared: 0.0014439
Weighted Sum of Squares: 0.063533

Open challenges envisaged for real-scale process design and implementation

- Experimentally validated 2D model-based laser-plasma interaction and plasma dynamics assessment (i.e. locally dependent thermo-mechanical wave applied to treated material).
- In depth evaluation of confining layer breakdown thresholds, with detailed consideration of the effect of different types of protective coatings (specially in high EOD treatments). Possible application of highly adaptable solid media.
- Development of appropriate (experimentally tested) high rate (LSP typical) dynamic material behaviour models.
- In depth parametric analysis of processing windows and scaling laws for different approaches (i.e. high to minimum EOD, EED).
- Further experimental investigation of material transformations (i.e. microstructure, surface and mechanical properties,..) under LSP.
- In depth evaluation of thermal / mechanical stability of LSP induced material properties transformations.
- Further exploitation of the capability of LSP predictive assessment tools for the design of concrete purpose oriented applications (i.e. through-thickness compressive RSs fields for crack propagation arresting, surface defects remediation, preventive LSP treatment for extended life,.....).
-

EXPERIMENTAL RESULTS

Material: Al2024 T3
Pulses: $\varnothing=1,5$ mm; $\tau=10$ ns; $f=10$ Hz;
 $E=1$ J/pulse; $I=1,41$ GW/cm²
Swept Area : 15x15 mm²; 2500 pulses/cm²

SHOCK PROPAGATION AND DERIVED RESIDUAL STRESSES IN LSP

Evaluation of relative effects of thermal and mechanical waves on shocked material

Water / Aluminium; Nd:YAG (1064 nm),

$\tau = 9$ ns, $F = 84$ J/cm², radius = 1.5 mm

Morales, M. et al.: Materials Science Forum, 638-642, 2682-2687 (2010)

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Major Facilities (1/4)

Major Facilities (2/4)

Major Facilities (3/4)

Major Facilities (4/4)

Ellipsometry and Reflectometry

Reflectometry

MICROMANUFACTURING EXPERIMENTAL SETUP AT CLUPM

The UPM Laser Centre Approach to LSP Development