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

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Processing, Fabrication, Properties, Applications

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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 chirurgical 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)
(B. Denkena, A. Lucas.: doi:10.1016/j.cirp.2007.05.029)
REMINDER OF LSP PHYSICAL PRINCIPLES (1/2)

FREE MODE

CONFINED MODE

FREE PLASMA EXPANSION

IMPROVED PRESSURE AND IMPULSION

Laser pulse

Pressure pulse

Confining Layer

Plasma/Vapour

Coating Layer

Bulk Material

Centro Láser
Universidad Politécnica de Madrid

International Conference on 
PROCESSING & MANUFACTURING OF ADVANCED MATERIALS 
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REMINDER OF LSP PHYSICAL PRINCIPLES (2/2)

Al 2024-T3
I₀ = 5.4 GW/cm²

Permanent Deformation
Damping
Elastic Precursor

Unit Strain
Depth (mm)
Time (µs)

Al2024-T351, λ = 1064 nm, 1.3 J/pulse,
Spot Diameter = 1.5 mm, water jet 2 bar, no paint

Minimum Residual Stress σₘᵢₙ (MPa)

625 pulses/cm²
900 pulses/cm²
2500 pulses/cm²

Depth (mm)
PROCESS EXPERIMENTAL SETUP

Q-SWITCHED Nd:YAG LASER

\[ \tau = 10 \text{ ns}; \ f = 10 \text{ Hz} \]
PROCESS EXPERIMENTAL SETUP
\[ \text{Equivalent Overlapping Density} \equiv \text{EOD} = \frac{N^\circ \text{ of pulses}}{\text{Total treated surface}} = \frac{x \cdot y}{\Delta x \Delta y} = \frac{x \cdot y}{d \cdot d} = \frac{1}{d^2} \]

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

\[ \text{Equivalent Local Overlapping Factor} \equiv \text{ELOF} = \frac{N^\circ \text{ of pulses} \cdot \text{Pulse Area}}{\text{Total treated surface}} = \frac{\pi \cdot \varphi^2}{4 \cdot d^2} = \frac{\pi}{4} \left( \frac{\varphi}{d} \right)^2 \]
Table 1. LSP processing conditions parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Laser Focused Diameter Ø (mm)</th>
<th>LSP treatment EOD (cm²)</th>
<th>LSP treatment EED (J.cm²)</th>
<th>LSP treatment ELOF (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1+2</td>
<td>1.5</td>
<td>400</td>
<td>960</td>
<td>7.07</td>
</tr>
<tr>
<td>3+4</td>
<td>2.0</td>
<td>400</td>
<td>960</td>
<td>12.57</td>
</tr>
</tbody>
</table>

Mg extruded ingot

YS = 34-55 MPa
E  = 41-45 GPa
**EXPERIMENTAL RESULTS**

Table 2. Surface Roughness Parameters Induced in LSP treated samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Laser Focused Diameter Ø (mm)</th>
<th>LSP treatment EOD (cm²)</th>
<th>Average Surface Roughness, $S_a$ (µm)</th>
<th>RMS Surface Roughness, $S_q$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (Ref)</td>
<td>0.0</td>
<td></td>
<td>1.59±1.0</td>
<td>2.06±1.0</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>400</td>
<td>12.02±1.0</td>
<td>15.04±1.0</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>400</td>
<td>11.46±1.0</td>
<td>14.43±1.0</td>
</tr>
</tbody>
</table>

According to ISO 25178 Standard

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

\[
S_q = \frac{1}{A} \iint_A |z(x,y) - z_{av}|^2 \, dA
\]
EXPERIMENTAL RESULTS

Residual stresses

According to ASTM E837-13 Standard

\[ \text{YS} = 34-55 \text{ MPa} \]
\[ E = 41-45 \text{ GPa} \]
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):

24 h Test

\[ \text{R1} + \text{R2} = 479.8 + 7009.0 = 7488.8 \, \Omega\text{.cm}^2 \]
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

Ø=2.0 mm

178 pulsos/cm²  223 pulsos/cm²  278 pulsos/cm²  400 pulsos/cm²
### HYDROPHOBICITY:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg mirror polished</td>
<td>74 ± 7</td>
</tr>
<tr>
<td>Mg + sand 600</td>
<td>118 ± 2</td>
</tr>
<tr>
<td>Mg + sand 600 + LSP 178</td>
<td>134 ± 3</td>
</tr>
</tbody>
</table>

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

### SURFACE GIBBS ENERGY LOWERING:

<table>
<thead>
<tr>
<th>Sample</th>
<th>S-L Surface Tension (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg mirror polished</td>
<td>43.5 ± 3.6</td>
</tr>
<tr>
<td>Mg + sand 600</td>
<td>21.2 ± 5.7</td>
</tr>
<tr>
<td>Mg + sand 600 + LSP178</td>
<td>18.8 ± 2.8</td>
</tr>
</tbody>
</table>

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

**PROTECTION AGAINST MICROORGANISMS ADHESION:**

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

Data supplied by Research Group on Microbian Adhesion. Univ. of Extremadura (SPAIN)
According to the presented results, the feasibility of introduction of compressive residual stresses fields in extruded ingot samples of pure Magnesium (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 (EOD = 400 cm⁻²) treatments with peak laser intensities in the range 8-15 GW/cm², providing equivalent energy densities (EED’s) in the range 75-150 J/cm².

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.
ACKNOWLEDGEMENTS

Work partly supported by MINECO (Spain; Projects MAT2012-37782, MAT 2012-37736-C05-01, MAT 2015-63974-C4) and Comunidad de Madrid (Spain; S2013/MIT-2862).
The CIBER of Bioingeniería, Biomateriales y Nanomedicina is supported by the ISCIII (Spain)

MAIN REFERENCES

The LSP Team at UPM Laser Centre
Thank you very much for your attention!

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RESULTS: Experimental Procedure for EIS determinations

King, A.D., Birbilis, N., Scully, J.R. 

- **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

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.

RESULTS: Experimental Procedure for EIS determinations

Equivalent circuit

R₁ = Rₛ + Rᶠ
R₂ = Rₜ
CPE₁ = CPE strpos

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

RESULTS: Experimental Procedure for EIS determinations

King, A.D., Birbilis, N., Scully, J.R.  

\[
Rs + R1 + R2 = 14578 \ \Omega \cdot \text{cm}^{-2}
\]

<table>
<thead>
<tr>
<th>Element</th>
<th>Freedom</th>
<th>Value</th>
<th>Error</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs</td>
<td>Free(\pm)</td>
<td>223.1</td>
<td>2.4399</td>
<td>1.0936</td>
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<tr>
<td>CPE1-T</td>
<td>Free(\pm)</td>
<td>9.9417E-06</td>
<td>1.4228E-06</td>
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<tr>
<td>CPE1-P</td>
<td>Free(\pm)</td>
<td>0.66474</td>
<td>0.013318</td>
<td>2.0035</td>
</tr>
<tr>
<td>R1</td>
<td>Free(\pm)</td>
<td>1599</td>
<td>318.17</td>
<td>19.898</td>
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<tr>
<td>CPE2-T</td>
<td>Free(\pm)</td>
<td>2.7137E-06</td>
<td>9.0302E-07</td>
<td>33.276</td>
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<td>CPE2-P</td>
<td>Free(\pm)</td>
<td>0.87521</td>
<td>0.005603</td>
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<tr>
<td>R2</td>
<td>Free(\pm)</td>
<td>12756</td>
<td>236.43</td>
<td>1.8535</td>
</tr>
<tr>
<td>RL</td>
<td>Free(\pm)</td>
<td>67822</td>
<td>13606</td>
<td>20.061</td>
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<tr>
<td>L</td>
<td>Free(\pm)</td>
<td>1.0633E06</td>
<td>2.0176E05</td>
<td>18.975</td>
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</table>

Chi-Squared: 0.004226  
Weighted Sum of Squares: 0.56206

\[
R1 + R2 = 14566.3 \ \Omega \cdot \text{cm}^{-2}
\]

<table>
<thead>
<tr>
<th>Element</th>
<th>Freedom</th>
<th>Value</th>
<th>Error</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Free(\pm)</td>
<td>484.3</td>
<td>17.923</td>
<td>3.7008</td>
</tr>
<tr>
<td>R2</td>
<td>Free(\pm)</td>
<td>14082</td>
<td>331.68</td>
<td>2.3553</td>
</tr>
<tr>
<td>CPE1-T</td>
<td>Free(\pm)</td>
<td>1.143E-05</td>
<td>3.7889E-07</td>
<td>3.3149</td>
</tr>
<tr>
<td>CPE1-P</td>
<td>Free(\pm)</td>
<td>0.74094</td>
<td>0.003619</td>
<td>0.99369</td>
</tr>
</tbody>
</table>

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: Ø=1,5 mm; τ=10 ns; f=10 Hz; E=1 J/pulse; I=1,41 GW/cm²
Swept Area: 15x15 mm²; 2500 pulses/cm²

Air

Water
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),
τ = 9 ns, F = 84 J/cm², radius = 1.5 mm

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Major Facilities (1/4)
Major Facilities (3/4)
Major Facilities (4/4)
MICROMANUFACTURING EXPERIMENTAL SETUP AT CLUPM
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<th><strong>Photron</strong></th>
<th>FASTCAM-Ultima512 ...</th>
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<td>1/500 sec</td>
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The UPM Laser Centre Approach to LSP Development

- **LASER-PLASMA INTERACTION SIMULATION AND DIAGNOSIS**
- **NUMERICAL SIMULATION OF SOLID BEHAVIOUR AND PROPERTIES TRANSFORMATION**
- **PROCESSING AND EXPERIMENTAL CHARACTERIZATION OF MATERIAL PROPERTIES**