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BIOBASED ENGINEERING

Laser Surface Texturing of Bulk Metallic Glass for Orthopaedic Application

Osteoarthritis in weight bearing joints, such as the hip and knee, is the primary indicator for orthopaedic intervention in the UK. Joint replacements remain the only viable treatment for osteoarthritis, however implant metallics exhibit insufficiencies in their physical properties, producing high implant failure rates. Bulk metallic glasses (BMGs) have unique physical properties (high elasticity, high wear resistance) which can improve integration between biomaterials and host tissue. Laser surface texturing (LST) allows tuning of distinct surface properties, promoting favourable clinical outcomes (enhanced osseointegration). Following a comprehensive literature review on LST of BMGs, this work presents an experimental outline to assess how laser input parameters influence functional surface properties, in particular wettability, free energy, corrosivity, and surface chemistry. Future work will investigate both the antimicrobial properties of LST BMGs, and their propensity to modulate the host inflammatory response, with the goal of optimising LST parameters enhanced osseointegration of the peri-implant surface.

Keywords:
Bulk metallic glass, laser surface texturing, biomaterials, antimicrobial, regenerative.

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T. Green, W.N. Ayre, S. Bigot, E. Brousseau, and D. Bhaduri, ‘Laser Surface Texturing of Bulk Metallic Glass for Orthopaedic Application’, *Proceedings of the Cardiff University School of Engineering Research Conference 2024*, Cardiff, UK, 2024, pp. 1-4.

doi.org/10.18573/conf3.b

INTRODUCTION

Osteoarthritis (OA) is a degenerative joint disease, characterised by progressive degradation of articular cartilage and the subsequent lysis of subchondral bone. OA affects around 10 million people in the UK [1], and its prevalence is expected to rise as a result of an increasingly obese and aging population. OA afflicts patients with joint pain and reduced mobility, costing the nation ~1% of gross national product (GNP) through operative care and lost working days [2].

Biomaterials are products which are engineered to interact with biological systems of the body for therapeutic or diagnostic purposes. Orthopaedic implants are an example of a biomaterial, utilised for the purposes of fixation, reconstruction, and realignment, and remain the only viable long-term treatment strategy for patients with moderate to high levels of joint degradation. Unfortunately, around 10% of orthopaedic implants fail within 10 years [3].

Structural and articulating components of orthopaedic implants have been manufactured from polycrystalline metals such as titanium alloys, cobalt chromium, and stainless steel. Whilst these materials have relatively low fabrication costs and are bioinert in nature [4], they also exhibit fairly poor long-term wear and corrosion resistance and are poorly reflective of the elasticity of their surrounding tissue; acting to induce stress-shielding events and resulting in peri-implant bone resorption.

Metallic glasses are a group of alloys with amorphous molecular structure, inherited from their liquid state. Since their experimental discovery by the research team of Pol Duwez [5], developments in their manufacturing process and compositional design, have vastly increased the size at which fully amorphous alloys can be produced.

Bulk metallic glasses (BMGs), i.e. metallic glasses with a critical diameter >1 mm, have advantageous physical properties such as high strength and fracture toughness, low elastic moduli, high elasticity, and high wear and corrosion resistance, which find them suitable for orthopaedic applications [6].

Surface texturing via micro- and nano-patterning of biomaterial surfaces can be used to tailor surface properties such as wettability, surface energy and topography. Such texturing may enhance the performance of orthopaedic implants as modulation of surface properties can influence extent of integration between the peri-implant surface and native bone. Nanosecond (10^{-9} s) pulsed laser ablation is a laser surface texturing (LST) technique utilising short pulses of high intensity laser light to initiate melting and vaporisation at a material's surface and thus is capable of producing structured geometries, such as those presented in Fig. 1. Laser ablation demonstrates a number of advantages, e.g., high energy efficiency, low operation cost, and low contamination risk, over alternative surface texturing techniques such as sand-blasting and acid etching and photolithography.

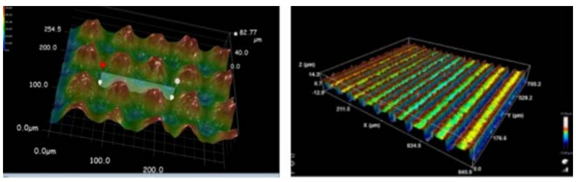

Fig. 1. Micro-pillar (left) and groove (right) surface patterning, produced via ns pulsed laser ablation [7,8].

LITERATURE REVIEW

Early investigations and single-pulse laser-texturing of BMGs
Early investigations into ns pulsed laser ablation of BMGs were focused on observing topological and morphological features following modulation of laser parameters. Perhaps the first of these studies determined that increasing laser fluence (energy density) or decreasing laser scanning speed would increase the depth of machined features (Fig. 2), albeit with an increased likelihood of crystalline precipitation [7]. Irradiation of a BMG with a single pulse induces crater formation, the depth and diameter of which are primarily determined by the laser fluence and pulse duration. Often concentric ripple-like structures are observed at the circumference of this crater, attributed to the Kelvin-Helmholtz instability, resulting from the motion of vapour across the material melt-pool [8]. Finally, redeposited material is observed towards and beyond the crater circumference, resulting from the generation of recoil pressure during material vaporisation, and subsequent melt ejection [9].

Physical and functional properties of ns laser-textured BMGs
Recent work has focused on texturing of larger BMG surface areas, as well as how LST may influence certain surface properties. It has been suggested that increasing laser scanning speed can improve the resolution of textured surface features via a reduction in melt ejection and its resulting redeposition. Further augmentations in scanning speed, however, may subsequently lower feature definition due to a loss of the laser-material interaction time [10], as such texturing of defined surface geometries (e.g., cross-hatch, grooves, dimples), requires parameter optimisation.

Interestingly, a change from classical concave to convex, and a return to concave texturing has been reported, dependent on pulse overlap and applied pulse energy. The concave-convex transition occurs through a change in the surface tension gradient, and a resulting switch in the direction of the Marangoni effect producing a regime of laser texturing via 'pulling' of the surface [11].

LST in the nanosecond regime influences surface wettability, however the mechanism by which this occurs remains debated. Jiao, et al. [12] suggested that the wettability of the commercially available BMG Vitreloy 105 (Vit105) decreased following LST, resulting from a removal of hydrophilic carbonyl (C=O) and carboxyl (O=C-O) groups, and a degeneration of the surface oxide layer. It was stipulated, however, that wettability may still be increased by laser texturing, albeit in a morphology-dependent manner. In contrast, subsequent work has suggested that ns LST enhances surface wettability, by increasing surface oxidation [10]. Separately, surface hardening of up to ~39% of a Ti-based BMG following LST was attributed to surface oxidation [13].

Whilst the above highlights the potential for ns LST to modulate surface properties in an input-parameter dependent manner, additional investigation is imperative to assess these relationships before they can be optimised for orthopaedic application.

Biological response to ns laser-textured BMGs
In consideration of the antimicrobial performance of LST BMGs, increasing pulse power and decreasing scanning speed is reported to increase surface roughness and wettability, as well as promote ion (Cu2+ and Ni2+) release and production of reactive oxygen species (ROS) on Zr-BMG

surfaces textured with a pulse overlap of 66%. Bacterial colony formation of *S. aureus* was observed to be reduced following LST, albeit only significantly so on surfaces with scanning speeds between 10-100 mm/s [14]. Unfortunately, laser texturing at these scanning speeds was also associated with an increase in crystalline precipitate formation, which can negatively affect the material's physical property performance. Further work is needed to establish the antimicrobial mechanism of LST BMGs.

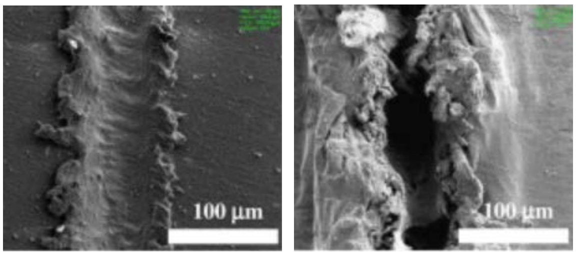

Fig. 2. A reduction in pulsed laser scanning speed from 300 mm/s (left) to 30 mm/s (right), at constant fluence (12 J/cm2), is associated with increased machining depth and material redeposition [7].

Regarding the regenerative capacity of LST BMGs, MG-63 human osteoblasts cultured on dimple and groove-patterned Vit105 have been shown to exhibit increased cell viability, compared to cells cultured on smooth samples. Furthermore, cells on groove-patterned samples exhibited a significant increase ($p<0.05$) in proliferation when compared to as-cast surfaces. This increase in proliferative activity was correlated with cell alignment along textured grooves (Fig. 2), providing evidence to suggest that the BMG provides both a biocompatible material surface, and that considered application of LST may promote regenerative phenotypic responses [15].

Overall, several distinct gaps remain within the literature regarding ns LST of BMGs for orthopaedic application. Foremost is a lack of a systematic investigation into how laser parameters influence BMG surface characteristics, and consequently functional surface properties. Additionally, the literature review outlined above remains the only research regarding biological responses to ns LST of BMGs. Thus, considerable investigation into both the antimicrobial and regenerative potential of these surfaces is required to enhance their clinical performance.

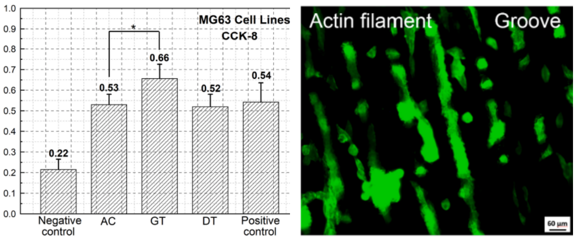

Fig. 3. MG-63 osteoblasts exhibit increased proliferation on ns LST groove-patterned Vit105 surfaces (left). Cells undergo contact guidance and align along groove patterning (right) [8].

METHODOLOGY OF THE PRESENT RESEARCH

Materials and laser system
A commercially available BMG, AMLOY-Zr02, with a nominal composition of $Zr_{65}Cu_{16}Ni_{12}Al_{4}Ti_{3}$, purchased from Heraeus (Germany) will be used for the present research on the LST of BMG. Laser surface texturing will be conducted using a Yb-doped fiber laser system (SPI lasers, UK) with a wavelength of 1064 nm and 32 µm nominal spot diameter. Laser parameters are defined by pre-set waveform specifications, as outlined in Table 1, and are to be chosen as experimentally appropriate.

Influence of independent laser parameters on surface properties - Initial investigations
Preliminary investigations will involve assessment of the influence of laser input parameters on surface characteristics, with the aim of accounting for confounding factors which may influence surface functional properties. This will be split into two sections:

i. Influence of pulse duration and applied fluence on surface characteristics.

Pulse duration, according to the waveforms outlined in Table 1, and fluence will be varied at a constant pulse overlap value. This analysis will allow pulse duration to be accounted for in the assessment of the effect of laser parameters on functional surface properties.

Waveform	Pulse duration (ns)	Frequency (kHz)	E_{max} (mJ)
11	220	35	0.57
16	140	51	0.39
22	65	80	0.25

Table 1. Preset laser waveform specifications.

ii. Influence of pulse overlap on surface characteristics.

For a given pulse duration (e.g., 220 ns, waveform 11), applied fluence will be kept constant, and the influence of varying pulse overlap on surface characteristics will be assessed. In each of these instances surface characterisation will entail consideration of resulting topographies via evaluation of surface roughness, as well as quantification of the depth and width of morphological features, and the height of redeposited material following melt ejection.

Influence of ns laser-texturing on functional surface properties.
In order to determine which laser input parameters most significantly influence BMG surface characteristics, a full-factorial design of experiments (DOE) approach will be utilised, according to Table 2.

Fluence (J/cm2)	Scanning speed (mm/s)
10	50
20	100
30	150
40	200
50	250
60	300
70	350

Table 2. DOE for investigation into influence of laser input parameters on BMG surface properties.

Additionally, particular sample groups i.e., low, mid, and high values, will be taken forward for assessment of functional surface properties, specifically: wettability, surface energy, corrosivity, and surface chemistry, as well as for analysis of surface crystallinity.

CONCLUSIONS AND FUTURE DIRECTIONS OF RESEARCH

Nanosecond pulsed laser ablation has been identified as an energy-efficient technique for reproducible biomaterial surface texturing, with low associated contamination risk. Variations in particular laser input parameters are associated with changes in surface characteristics, and consequently functional surface properties. The research proposed in this paper will systematically investigate these relationships, with the goal of enhancing the design and long-term osseointegration of orthopaedic implants.

To further meet this aim, future work will investigate the biological responses to ns LST AMLOY-Zr02. This will initially be achieved via assessment of the response of THP-1 derived macrophages, as a model for the host response, to differentially textured surfaces. Directing macrophages towards anti-inflammatory phenotypes is associated with enhanced osseointegration at the peri-implant surface and may improve clinical implant success rates.

Additionally, changes in bacterial adhesion and biofilm formation have been associated with variations in biomaterial wettability and surface roughness. As such, the antimicrobial activity of LST AMLOY-Zr02 will be assessed using the bacterial strains most associated with orthopaedic infection: *S. aureus* and *P. aeruginosa*. Optimisation of antimicrobial LST may provide two significant contributions to the application of biomaterials. Firstly, the reliance on antibiotics may be lessened, alleviating the occurrence and pathogenic antibiotic resistance. Additionally, the prevalence of post-operative infection, caused by the presence of dormant bacteria and the biomaterial surface may be reduced, thereby improving the likelihood of successful clinical outcomes such as enhanced peri-implant osseointegration and reduced rates of infection.

Conflicts of Interest
The authors declare no competing conflicts of interest.

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Cardiff Engineering Research Conference

E. Spezi and M. Bray (eds.) 2024. *Proceedings of the Cardiff University School of Engineering Research Conference 2024.* Cardiff: Cardiff University Press.
doi.org/10.18573/conf3

Cardiff University School of Engineering Research Conference 2024 was held from 12 to 14 June 2024 at Cardiff University.

The work presented in these proceedings has been peer reviewed and approved by the conference organisers and associated scientific committee to ensure high academic standards have been met.

Cardiff University Press | Gwasg Prifysgol Caerdydd

First published 2024

Cardiff University Press
Cardiff University, Trevithick Library
First Floor, Trevithick Building, Newport Road
Cardiff CF24 3AA

cardiffuniversitypress.org

Editorial design and layout by
Academic Visual Communication

ISBN: 978-1-9116-5351-6 (PDF)