

Effects of Chemical and Structural Heterogeneity on the Tribocorrosion Resistance of Metals in Aqueous Solutions

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Abstract

The corrosion-wear resistance tradeoff in conventional metals imposes a great challenge to their reliable long-term performance under extreme conditions where surface stress and corrosive environment coexist (i.e., tribocorrosion). In this work, strategies to introduce chemical and structural heterogeneity with controlled length-scale at nanometers were proposed and studied in three metallic systems (i.e., Zr-based, Al-based and Mg-based), in order to enhance their tribocorrosion resistance.

In the first study, ZrCuNiAl thin film metallic glasses (TFMG) with either homogeneous or heterogeneous local composition were deposited by magnetron sputtering through controlling processing conditions (i.e., argon (Ar) pressure). It was found that the mechanical properties, wear, corrosion and tribocorrosion resistance of ZrCuNiAl TFMG were significantly affected by nanoscale chemical heterogeneity. As a result, nanoscale chemical heterogeneity promoted ductility but reduced hardness, which in turn weakened wear resistance. While, in the 0.6 M NaCl solution, the resistance to pitting corrosion and tribocorrosion was improved because the presence

of nanoscale chemical heterogeneity facilitates to generate more protective passive layer with lower defect density and faster repassivated capability, compared to their homogenous counterparts.

In the second study, nanoscale chemical and structural heterogeneity were introduced in Al by forming Al/X nanostructured metallic multilayers (NMMs), where X=Mg, Cu, and Ti. Compared to the respective monolithic films, the alternating nanolayer configuration not only increased strength due to the presence of abundant interfaces but also reduced surface activity and pitting susceptibility. The electrochemical performance was significantly affected by the interaction, i.e., galvanic effect, between Al layer and underlayer constituents, which in turn led to different tribocorrosion behaviors. Specifically, transmission electron microscopy revealed that the materials loss in Al/Mg and Al/Cu NMMs primarily resulted from corrosion, while Al/Ti was dominated by severe plastic deformation during tribocorrosion as a result of sustained surface passivity.

Lastly, in the bulk biodegradable Mg alloys system, the surface was treated by femtosecond laser shock peening (fs-LSP) technique with ultra-low pulse energy to introduce structural heterogeneity. Treatment conditions (e.g., power density, direct ablation and confined ablation) significantly affected the ultimate peening effect and further surface performance. In this work, the optimized peening effect was obtained at 28 GW/cm² laser power density in the confined ablation with the assistance of the adsorption layer and confining medium. Combined with transmission electron microscopy and finite element analysis, the improvement of surface performance was

attributed to high dislocation density near the surface, rather than compressive residual stress. The existence of structural heterogeneity not only reduced corrosion kinetics but simultaneously improved the self-repassivation in the blood bank buffered saline solution at body temperature.

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General Audience Abstract

In various industrial applications such as marine infrastructure, nuclear power plants, and biomedical devices, the synergistic effect of wear and corrosion, known as tribocorrosion, is an inevitable material degradation phenomenon. To resist such aggressive degradation and prolong the service life of metals in complex environments, it is crucial to simultaneously enhance the wear and corrosion resistance, i.e., tribocorrosion resistance of metals. Unfortunately, the corrosion-wear resistance tradeoff in conventional metals imposes a great challenge. For example, most precipitation-hardened Al alloys impart high strength and wear but exhibit low resistance against localized corrosion as a sacrifice owing to the micro-galvanic coupling between the matrix and precipitates.

Several previous works pointed out that compositional and structural heterogeneity, even at the nanoscale, could simultaneously affect the mechanical properties and corrosion resistance of metals. However, few works have been performed to understand the effects of such heterogeneity and their length-scale during

tribocorrosion of metals. In this dissertation, by combining materials processing, advanced characterization, and tribocorrosion testing, the effects of chemical and structural heterogeneity, as well as their length-scale, on the deformation and degradation mechanisms of metals were studied using model systems of Zr-, Al- and Mg-based alloys, where the chemical and/or structural heterogeneity were introduced by tuning the materials processing conditions. Firstly, the nanoscale chemical heterogeneity was introduced into ZrCuNiAl thin film metallic glasses (TFMG) by adjusting argon (Ar) pressure during magnetron sputtering. Compared with the homogeneous composition, heterogeneous local composition in ZrCuNiAl TFMG improved ductility but sacrificed hardness and wear resistance. In 0.6 M NaCl solution, higher pitting corrosion and tribocorrosion resistance can be observed due to the generation of low defect density protective passive film with low defect density and with fast repassivation rates in heterogeneous ZrCuNiAl TFMG. Secondly, the architecture of nanostructured metallic multilayer in Al-based with different constituents, from noble to active metals (e.g., Cu, Ti and Mg), were studied the effects of chemical and structural heterogeneity on wear, corrosion and tribocorrosion performance. The results showed that the deformation and corrosion behaviors significantly depended on the distinct interfaces and chemical modulation at the nanoscale, caused by different constituents, which ultimately resulted in various tribocorrosion resistance in 0.6 M NaCl solution at room temperature. Transmission electron microscopy of deformed and degraded sample surfaces showed characteristic different deformation and degradation modes of all samples, governed by the

synergistic effects of the mechanical and corrosion properties of the constituting materials. Specifically, severe plastic deformation mainly led to material loss in Al/Ti NMMs owing to the noble surface reactivity, while corrosion was the dominant factor for material loss in Al/Mg and Al/Cu NMMs during tribocorrosion. Lastly, the ultra-low pulse energy femtosecond laser shock peening technique was successfully applied to introduce structural heterogeneity in the bulk biodegradable Mg alloys since in some cases the deposition is not feasible for bulk metals. The optimizing peening effect was firstly investigated and was achieved at confined ablation conditions under 28 GW/cm^2 laser power density. Results show that the high dislocation density near the surface was contributing to the surface strengthening effect, high corrosion and tribocorrosion resistance in a simulated body environment via transmission electron microscopy observation. The finite element analysis method investigated the compressive residual stress in current work that did not significantly affect the surface performance of Mg alloys. In summary, the study of this dissertation contributes to a good basis and design strategy of conventional metals for applications under complex environments.

Dedication

To my father and mother, Li Wang and Yingjie Meng

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Chapter 2: Dr. Wahyu Diyatmika synthesized Zr-based thin film metallic glasses samples and wrote the synthesis process. Dr. Hesham Mraied conducted potentiodynamic polarization and Mott-Schottky tests. I performed all other experiments, characterizations, manuscript writing and served as the first author. Prof. Jinn P. Chu and Prof. Lin Li gave valuable comments and edited the manuscript after review. The corresponding author Prof. Wenjun Cai edited the manuscript after review and finalized it.

Chapter 3: Kaiwen Wang performed the FEA simulation and wrote the simulated process. Zhengyu Zhang and Tianyou Mou performed the DFT calculation and wrote the calculated process. Prof. F. Marc Michel performed X-ray diffraction characterization and X-ray reflectometry and gave comments on these results. Dr. Jia Chen conducted TEM characterization. Dr. Weinan Leng performed X-ray photoelectron spectroscopy. I served as the first author and completed other experiments and the entire manuscript writing. Prof. Hongliang Xin presented some valuable comments and edited the manuscript after review. Prof. Wenjun Cai served as the corresponding author and edited/finalized the manuscript after review.

Chapter 4: Dr. Chang-Yu Hung and Dr. Jia Chen conducted TEM

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Table of Contents

Abstract.....	ii
General Audience Abstract	v
Dedication	viii
Acknowledgements	ix
Attribution	xiii
List of Figures.....	xviii
List of Tables.....	xxiv
Chapter 1. Introduction.....	1
1.1. Background of tribocorrosion	1
1.1.1. Tribocorrosion measurement.....	1
1.1.2. Synergistic effects during tribocorrosion	5
1.2. Microstructure design to control wear, corrosion and tribocorrosion	9
1.2.1. Amorphous microstructure.....	10
1.2.2. Multilayered microstructure.....	14
1.2.3. Gradient microstructure	18
1.3. Problem statement and research motivation	20
1.4. Organization of the dissertation	22
1.4.1. Study 1-Effects of nanoscale chemical heterogeneity on the wear, corrosion, and tribocorrosion resistance of Zr-based thin film metallic glasses (Chapter 2)...	22
1.4.2. Study 2-Ultrahigh tribocorrosion resistance of metals enabled by nano- layering (Chapter 3)	22

1.4.3. Study 3-Enabling High-Performance Surfaces of Biodegradable Magnesium Alloys via Femtosecond Laser Shock Peening with Ultralow Pulse Energy (Chapter 4)	23
References.....	24
Chapter 2. Effects of Nanoscale Chemical Heterogeneity on the Wear, Corrosion, and Tribocorrosion Resistance of Zr-based Thin Film Metallic Glasses	31
2.1. Introduction.....	32
2.2. Experimental methods	35
2.2.1. Materials synthesis	35
2.2.2. Characterization of mechanical properties.....	36
2.2.3. Electrochemical measurement	37
2.2.4. Dry scratch and tribocorrosion tests.....	37
2.2.5. Materials characterization	38
2.3. Results and discussion	39
2.3.1. Characterization of as-deposited Zr-TFMGs	39
2.3.2. Nanomechanical properties.....	42
2.3.3. Corrosion behavior.....	45
2.3.4. Dry scratch test.....	49
2.3.5. Tribocorrosion behavior	50
2.4. Conclusions.....	55
References.....	55

Chapter 3. Ultrahigh Tribocorrosion Resistance of Metals Enabled by Nano-

layering.....	65
3.1. Introduction.....	66
3.2. Experimental methods	69
3.2.1. Materials synthesis and characterization.....	69
3.2.2. Mechanical and tribological tests.....	70
3.2.3. Corrosion and tribocorrosion tests	71
3.3. Results.....	73
3.3.1. Microstructure characterization	73
3.3.2. Mechanical and wear properties.....	76
3.3.3. Corrosion behavior.....	78
3.3.4. Tribocorrosion behavior	82
3.3.5. Surface chemistry and microstructure after tribocorrosion.....	84
3.4. Discussion.....	88
3.5. Conclusions.....	89
References.....	90
 Chapter 4. Enabling High-Performance Surfaces of Biodegradable Magnesium Alloys via Femtosecond Laser Shock Peening with Ultralow Pulse Energy	 96
4.1. Introduction.....	97
4.2. Materials and methods	100
4.2.1. Sample preparation and characterization	100
4.2.2. fs-LSP experiment.....	101
4.2.3. Corrosion and tribocorrosion tests	103

4.2.4. Finite element simulations	105
4.3. Results and discussion	106
4.3.1. Surface morphology	106
4.3.2. Structure, surface morphology, and mechanical properties	108
4.3.3. Corrosion behavior.....	113
4.3.4. Tribocorrosion results.....	117
4.4. Conclusions.....	122
References.....	123
Chapter 5. Summary and Future Work.....	132
5.1. Summary of the thesis.....	132
5.2. Proposed future work.....	134
References.....	136

List of Figures

Figure 1.1. Schematics of common wear test set-ups with (a) ball on disc and (b) pin on disc	2
Figure 1.2. Schematic set-up of the tribocorrosion test, including WE-work electrode, CE-counter electrode, and RE-reference electrode.....	4
Figure 1.3. Schematic third-body approach of possible materials flows (arrows indication) and reactions during tribocorrosion	9
Figure 1.4. Schematics of (a) conventional polycrystalline microstructure with precipitates, (b) amorphous microstructure, (c) multilayered microstructure and (d) gradient microstructure	10
Figure 1.5. Schematic time-temperature-transformation (TTT) diagram	11
Figure 1.6. Surface morphologies of (a) Ti6Al4V, (b) Zr-based TFMG after dry wear, and (c) Ti6Al4V, (d) Zr-based TFMG after wet sliding in artificial saliva. Inserts show EDX results on the wear tracks.....	13
Figure 1.7. The mechanisms of (a) pitting corrosion, (b) corrosion products on the pits, (c) crevice corrosion and (d) filiform corrosion in Zr-based TFMGs.....	14
Figure 1.8. Bright field TEM images of Al/Ti with 2.5 nm individual layer thickness after 10 cycles of nanowear under 93 μm load.	17
Figure 1.9. Schematic of corrosion mechanism in multilayered and monolithic microstructure.	18
Figure 1.10. (a) The hydrogen evolution per area of untreated and treated AZ31 Mg	

alloy sheet in 3.5 wt% NaCl solution, (b) corrosion mechanisms under different depths	19
---	----

Figure 2.1. GIXRD patterns of as-deposited heter-Zr and homo-Zr TFMG samples.....	40
--	----

Figure 2.2. SEM images of (a, b) as-deposited surface (c, d) etched surface and (e, f) cross section after cleaving of heter-Zr and homo-Zr TFMG samples. Inset line profile in (c) shows the greyscale profile measured along the horizontal white arrow direction	41
--	----

Figure 2.3. Summary of (a) hardness and (b) elastic modulus of heter-Zr and homo-Zr TFMGs measured from nanoindentation tests	44
--	----

Figure 2.4. (a) Typical potentiodynamic polarization curves, and (b) time evolution of defect density of heter-Zr and homo-Zr samples in 0.6 M NaCl aqueous solution. Error bars in (b) represent one standard deviation from all repeated tests.....	48
--	----

Figure 2.5. (a, b) Surface SEM images and (c) COF of heter-Zr and homo-Zr samples after dry scratch test. Dashed lines in (b) indicate the edges of the wear track	50
---	----

Figure 2.6. (a) Current evolution and (b) coefficient of friction (COF) of heter-Zr and homo-Zr samples during tribocorrosion under OCP and anodic applied potential (400 mV above OCP). Dashed lines in (a) mark the start and finish of the scratch by the counterbody.....	51
--	----

Figure 2.7. (a-c) Surface and (d-f) cross-sectional SEM images of homo-Zr and heter-Zr samples after tribocorrosion test (OCP for homo-Zr; OCP and OCP + 0.4 V anodic applied potential for heter-Zr). Dashed lines in (a, d-f) indicate the edges of the wear	
---	--

track. Insets in (a-c) show the element compositions (at. %) obtained by EDS analysis on the wear tracks 53

Figure 2.8. Summary of material volume loss of heter-Zr and homo-Zr samples after dry scratch and tribocorrosion tests under OCP and anodic potentials. Error bar represents one standard deviation from all repeated tests.....54

Figure 3.1. (a) Schematic of Al/X NMM structure. (b) GIXRD and (c) XRR patterns of Al/Ti, Al/Mg and Al/Cu multilayers 73

Figure 3.2. (a-c) SEM, (d-f) AFM, (g), (i) bright-field TEM, and (h) inverse FFT TEM images of NMMs. Arrows in (g-i) indicate film growth direction. Insets in (g) and (i) are FFT images of the corresponding TEM images, while that in (h) is the corresponding bright-field TEM image 76

Figure 3.3. SEM images of indents under the corresponding loads (4 mN for Al/Mg and 5 mN for Al/Ti and Al/Cu NMMs) of all NMM samples 77

Figure 3.4. (a) Mechanical properties and (b) wear rates as a function of number of cycles for all NMM samples. (c) Surface height profiles and (d)-(f) surface topographies of all NMM samples after 10 cycles of wear under 90 μ N..... 78

Figure 3.5. Typical potentiodynamic polarization curves of (a) monolithic films and (b) NMMs in 0.6 M NaCl solution at room temperature. Results in (a) are replotted as dashed lines in (b) for direct comparison. (d-f) Mott–Schottky plots and (c) n-type defect density of all NMMs 81

Figure 3.6. Surface SEM images and corresponding EDS elements mappings of all NMMs after (a-c) PD and (d-i) tribocorrosion tests. Insets in (a-f) show the

corresponding EDS element maps	82
Figure 3.7. Evolution of (a) open circuit potential, (b) coefficient of friction (COF) of all multilayers during tribocorrosion tests. (c) Typical wear track cross-sectional surface depth profiles and (d) summary of experimentally measured wear volume and FE model predicted corrosion current of all NMMs after tribocorrosion tests. The profiles in (c) were measured perpendicular to the sliding direction on the worn surface of all samples	84
Figure 3.8. SEM images of surface morphology and the corresponding EDS analysis (insets) in areas far away from the wear track of (a) Al/Ti, (b) Al/Mg, and (c) Al/Cu NMM samples after tribocorrosion tests.....	85
Figure 3.9. Photoelectron spectroscopy (XPS) results (a) Al/Ti, (b) Al/Mg, and (c) Al/Cu NMMs before and after tribocorrosion test.....	86
Figure 3.10. (a-c) Surface SEM images and (d-i) cross-sectional bright-field TEM images of all NMMs after tribocorrosion tests	88
Figure 4.1. (a) fs-LSP experimental setup. The inset image shows the schematic of a laser–sample interaction at the presence of a confining medium and an absorbent layer and (b) FE model geometry setup and meshing, where r, z, t in the coordinate system represents the radial, normal, and transverse direction, respectively. Inset graph shows the imposed laser pressure temporal profile	103
Figure 4.2. SEM surface morphology of (a) untreated and (b–f) fs-LSP-treated WE43 Mg samples under different conditions as listed in Table 4.1. Insert image in (a) show the surface of untreated WE43 after chemical etching	108

Figure 4.3. XRD (a) 2θ spectra and (b) zoomed-in spectra of the box area (a) of untreated and fs-LSP-treated WE43 Mg alloy. The fs-LSP treatment of WE43 was performed using quartz as a confining medium and a black tape as an absorbent layer at 28 GW/cm² power density 109

Figure 4.4. AFM images of WE43 Mg alloys (a) before and (b) after fs-LSP treatment, (c) surface roughness, and (d) micro-Vickers hardness of WE43 Mg samples with and without fs-LSP treatment using quartz as a confining medium and a black tape as an absorbent layer at 28 GW/cm² power density..... 110

Figure 4.5. (a, b) Bright-field TEM images and (c) selected area electron diffractions of the fs-LSP WE43 sample at various depths below the surface as marked in (a). Insert TEM images in (b) shows the bottom of fs-LSP treated WE43 sample 111

Figure 4.6. (a) SAED patterns of fs-LSP WE43 sample at various depths below the surface, (b) schematic representation of in-plane lattice rotation, and (c) the measured misorientation angle and calculated residual strain as a function of depth..... 112

Figure 4.7. (a) Typical PD curves and post PD test surface morphologies of (b) untreated and (c) fs-LSP WE43 Mg samples 114

Figure 4.8. EIS results of WE43 Mg alloys with and without fs-LSP treatments: (a) equivalent circuit model used for the model fitting and (b) Nyquist plots and model fit. Bode plots of the (c) impedance magnitude, $|Z|$, and (d) phase shift are presented as a function of frequency 116

Figure 4.9. (a) Evolutions of OCP, (b) COF, (c) typical wear track depth profiles, and (d) the summary of volume loss of untreated and fs-LSP WE43 samples during

tribocorrosion tests. The profiles in (c) were measured perpendicular to the sliding direction on the tribocorroded surface of all samples 118

Figure 4.10. Surface SEM images after tribocorrosion tests of (a) untreated WE43 and (b) fs-LSP WE43 samples and corresponding EDS element mappings 119

Figure 4.11. FE simulated results of (a) von Mises stress and (b) effective plastic strain during laser peening. FE simulated (c) von Mises stress and (d) maximum residual stress depth profile after laser removal on WE43 surface after fs-LSP treatment using pressure profile defined in Fig. 4.1 inset..... 121

Figure 4.12. FE simulated results of 2D stress components (a) during laser peening and (b) after laser removal using coordinate system defined in (a)..... 122

Figure 4.13. FE simulated results of 2D logarithmic strain components (a) during laser peening and (b) after laser removal using coordinate system defined in (a) 122

List of Tables

Table 2.1 Summary of global and local compositions of heter-Zr and homo-Zr samples from EDS analysis. The boundary areas of heter-Zr are marked by red lines in Fig. 2.2(c) while areas away from these boundaries are referred as interior.	40
Table 2.2 Summary of electrochemical parameters from PD tests of homo-Zr and heter-Zr sampels in 0.6 M NaCl.....	48
Table 2.3 Summary of mechanical properties, dry scratch, and tribocorrosion test results of heter-Zr and homo-Zr samples. H and E represent hardness and elastic modulus respectively, obtained from nanoindentation tests. d, w, and V represents the wear track depth width, and total material loss in volume respectively, measured after dry scratch and tribocorrosion tests.	54
Table 3.1 Summary of bi-layer thickness and mechanical properties of all Al/X NMM samples.....	72
Table 3.2 Summary of key mechanical and corrosion properties of monolithic samples.	72
Table 3.3 Summary of wear, corrosion, and tribocorrosion properties of all Al/X NMM samples. Wear test data were taken from all samples after 10 cycles of wear. Each value is reported as average and standard deviation from at least three separate tests.	87
Table 4.1 Summary of femtosecond laser shock peening processing parameters.....	103
Table 4.2 Summary of surface compositions (measured by EDS analysis) of untreated and fs-LSP-treated samples before and after corrosion	114

Table 4.3 Summary of equivalent circuit model fitting parameters defined in Fig. 4.8(a)

..... 116

Chapter 1. Introduction

1.1. Background of tribocorrosion

In a variety of practical applications where metals are used, such as marine infrastructure, nuclear power plants, biomedical implants, mining equipment, manufacturing and food processing devices [1-3], tribocorrosion of metallic materials is a serious issue that affects their long-term performance. Tribocorrosion can be defined as the material degradation phenomenon caused by the simultaneous action of mechanical loading (i.e., wear) and chemical attack (i.e., corrosion). In an aqueous environment, the degradation rate of metals is often faster than in the case of pure wear or pure corrosion because of the synergistic effect in tribocorrosion [4]. Wear can occur in such systems owing to particle impact (erosion), or solid-body interaction (sliding and fretting wear) in the corrosive environment [5], which is supposed to cause nearly \$300 billion economic loss per year in the United States [6]. Owing to the enormous economic losses and potential safety hazards caused by tribocorrosion, it is vital to evaluate, understand and improve the tribocorrosion resistance of metals. The following subsections will briefly review the common tribocorrosion measurement methods and mechanisms.

1.1.1. Tribocorrosion measurement

To study metal's degradation in tribocorrosion, both wear and corrosion

behaviors of metals need to be investigated. On one hand, wear is affected by many factors such as applied normal load, surface roughness, sliding velocity, temperature, and material properties [6]. It can be evaluated using different testing methods such as ball or pin-on-disc, ball or pin-on-plate, etc, as shown in Fig. 1.1.

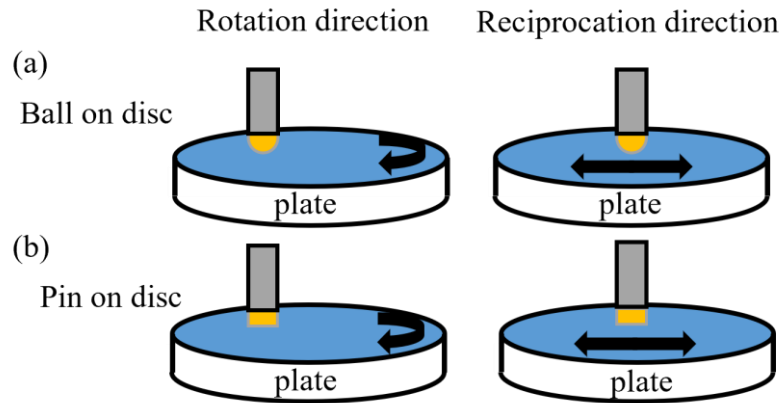


Figure 1.1. Schematics of common wear test set-ups with (a) ball on disc and (b) pin on disc.

During wear test, the coefficient of friction (COF) is defined as $COF = F_f/F_n$, where F_f is the frictional force and F_n is the applied normal force. Subsequently, the materials loss (e.g., weight loss or volume loss) caused by wear can be used to determine the wear rate as [7]:

$$\text{Wear rate} = \frac{\text{Wear volume}}{\text{Total sliding distance} \times \text{Normal load}} \quad (1.1)$$

On the other hand, corrosion is an electrochemical process that occurs when the metal interacts with its surroundings. It is typically comprised of one or more anodic and cathodic reactions. More basic principles of corrosion, especially its thermodynamics can be found in [8]. There are many forms of corrosion, such as uniform, pitting, galvanic corrosion, etc. Uniform corrosion (e.g., atmospheric

corrosion) [9] refers to an uniform metal dissolution rate on all areas of the metal surface, such as the case of Mg alloy corroding in water. Pitting corrosion [10], as a common type of localized corrosion for passive metals, causes small but deep pits on the surface due to the failure of the passive film. Galvanic corrosion [8] is usually found in dissimilar metals coupled in corrosive environments. One of the metals in the couple becomes the anode, corroding quicker than the other, while the other metal becomes the cathode. For example, in common commercial Al alloys, the microgalvanic coupling could be established between the Al matrix and the precipitates or second particles, further promoting the pitting corrosion development [11]. In aqueous solutions at room temperature, active metals (e.g., magnesium (Mg)) will be dissolved due to the oxidation, but some metals, known as passive metals (e.g., aluminum (Al), zirconium (Zr)), are able to generate a thin oxide film (i.e., passive film with ~ few nm thickness) that can protect the surface from further corrosion process.

Experimentally, corrosion measurement such as potentiostatic, potentiodynamic, and electrochemical impedance spectroscopy tests are often utilized to estimate the corrosion kinetics of metallic materials. Generally, a three-electrode configuration will be established which contains a working electrode (i.e., metallic specimen), a counter electrode and a reference electrode, to measure corrosion behaviors. These corrosion measurement methods can also be extended to evaluate the tribocorrosion performance of metals in combination with wear measurement. The typical schematic of tribocorrosion set-up is shown in Fig. 1.2. Three common methods [5] will be briefly reviewed here:

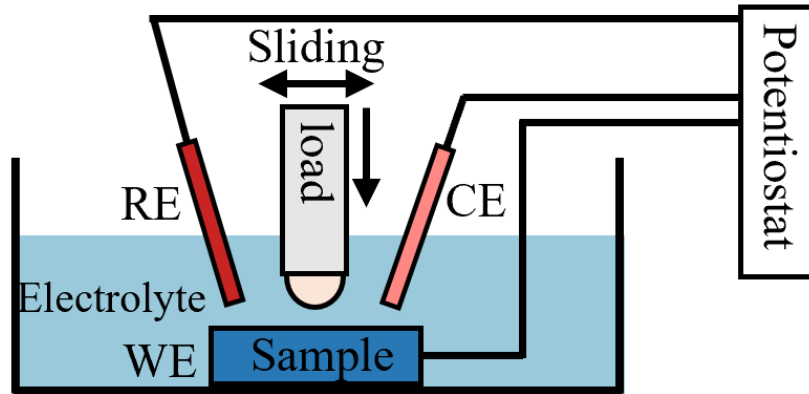


Figure 1.2. Schematic set-up of the tribocorrosion test, including WE-work electrode, CE-counter electrode, and RE-reference electrode.

1) Tribocorrosion test under open circuit potential

For the tribocorrosion test under open circuit potential (OCP), the equilibrium potential established between the working electrode and the corrosive environment is measured by the reference electrode when there is no flowing current or external voltage. After a stable potential is reached at the sample surface, the OCP may shift during wear to represent the active or passive characteristics of the metal. For example, a negative OCP shift can be found in pure Al during sliding due to the galvanic coupling established between the worn and unworn regions [12]. Unlike passive metals, the OCP of active metals is not sensitive to sliding owing to the similar surface state between the deformed and undeformed regions [13]. However, the kinetics of the corrosion reactions are not revealed by this approach.

2) Tribocorrosion test under constant potential

Unlike the tribocorrosion test under OCP set-up, this type of test will apply a constant potential above (anodic potential) or below (cathodic potential) the OCP, i.e.,

potentiostatic condition. The applied potential determines the directions of electrochemical polarization. The current is mainly controlled by the kinetics of metal oxidation at the anodic potential, whereas the current is primarily determined by the kinetics of the cathodic process at the cathodic potential. Thus, electrochemical kinetics can be acquired by measuring the current as a function of sliding time. For example, in Al-Mn thin film, the rapid sliding frequency was found to cause a higher anodic current in the wear track [14]. As a result, the relationship between the metal's mass loss caused by chemical reaction and the current in the anodic area may then be estimated using Faraday's law:

$$m = \frac{I \times M \times t}{n \times F} \quad (1.2)$$

where m is the metal mass oxidized during time t , I is anodic current, F is Faraday's constant ($\sim 96,500$ C/mol), n is the number of electrons transferred per ion and M is the atomic mass of the metal.

3) Tribocorrosion test through potentiodynamic polarization

In potentiodynamic polarization, the anodic and cathodic branches of the electrochemical process could be collected at a constant scan rate throughout a predefined potential range. After that, the corrosion current density or corrosion rate can be estimated by Tafel extrapolation method (if the polarization behavior follows Tafel relationship). In this type of test, the effect of friction on the various electrochemical processes that occur as a function of potential can be observed [15].

1.1.2. Synergistic effects during tribocorrosion

Based on the ASTM G119 standard [16], the total materials loss rate caused by

tribocorrosion (T) can be described by:

$$T = W + C + S, \quad (1.3)$$

where W is the material loss rate caused by pure wear, C is the material loss rate caused by pure corrosion, and S is the wear-corrosion synergy. In terms of synergistic effect S, it involves wear-accelerated corrosion (ΔC_w) and corrosion-accelerated wear (ΔW_c), described by:

$$S = \Delta C_w + \Delta W_c, \quad (1.4)$$

$$\Delta C_w = C_w - C, \quad (1.5)$$

$$\Delta W_c = T - (W + C_w), \quad (1.6)$$

where C_w is the corrosion rate during wear. With respect to ΔC_w , it suggests that the mechanical wear will serve as the dominant factor in the synergistic effect and affect the corrosion rate since the freshly exposed surface will continue to be oxidized as a result of mechanical wear during tribocorrosion. Contrarily, the dominant factor in synergistic effect is corrosion in ΔW_c and the rate of mechanical wear is significantly dependent on corroded surface. Due to the fact that current tribocorrosion testing methods are unable to give us measurement of the three components independently, additional mechanical wear and corrosion tests are required. For instance, firstly, C needs to be obtained by pure corrosion tests from potentiodynamic polarization. Secondly, the value T can be measured through wear in a corrosive environment without applied potential or current. Thirdly, it is necessary to acquire C_w by tribocorrosion test using potentiodynamic polarization. Finally, W is obtained by wear in a corrosive environment under an appropriate cathodic region [7]. As a result, some specific

synergism factors can be calculated, such as the total synergistic factor, corrosion augmentation factor and wear augmentation factor, as given by:

$$\text{Total synergistic factor} = \frac{T}{(T-S)}, \quad (1.7)$$

$$\text{Wear augmentation factor} = \frac{W+\Delta W_c}{W}, \quad (1.8)$$

$$\text{Corrosion augmentation factor} = \frac{C_w}{C}. \quad (1.9)$$

It is worth noting that the wear rate might alter even at cathodic potentials, such as embrittlement by hydrogen, based on some investigations [17, 18]. Thus, wear at cathodic potential needs to be utilized with caution when it is used as a reference for pure wear without corrosion effect.

Apart from the above description of the synergistic effect, a mechanistic model was established which contains mechanical wear and wear accelerated corrosion [5, 19], as given by:

$$V_{\text{tot}} = V_{\text{mech}} + V_{\text{chem}}. \quad (1.10)$$

where V_{tot} is the total material loss volume after tribocorrosion, V_{mech} is the material loss volume caused by mechanical wear, and V_{chem} is the volume loss caused by wear accelerated corrosion. V_{chem} can be calculated by Faraday's law through potentiostatic test [20]. In fact, V_{chem} is attributed to corrosion in passive regions and wear accelerated corrosion in depassivated regions, while the volume loss due to corrosion in passive regions can be neglected compared to the latter. Noteworthily, V_{mech} and V_{chem} are not entirely separate mechanical and corrosion mechanisms, instead they are affected by each other as well as materials surface properties. For example, corrosion products may modify wear behaviors and wear accelerated corrosion is possible to be affected by

materials properties and tribocorrosion testing parameters (e.g., applied loading) [2, 21].

As a result, this mechanical model was built-up under an approximately ideal tribocorrosion process, since it is possible that the passive film is partially removed rather than completely removed during the wear process, resulting in different surface reactivity. In addition, the contact mode could be converted from two-body to three-body [5, 22] due to the presence of wear debris.

To consider the effect of wear particles during sliding, a third-body approach was developed, as depicted in Fig. 1.3. In the mechanistic model, V_{mech} just takes into account the pure chipping of the metal during sliding. However, wear particles transfer to the third-body is able to affect the surface reactivity and further leads to different wear behaviors.

In summary, tribocorrosion is the result of wear and corrosion interacting simultaneously. In an aqueous environment, the synergistic effect generated in tribocorrosion can often cause materials to deteriorate at a faster rate than pure wear or pure corrosion. To understand the synergistic effect, three common approaches for assessing tribocorrosion were established. As a result, mechanistic models and third-body theory were developed to quantify and demonstrate the synergistic behaviors during tribocorrosion.

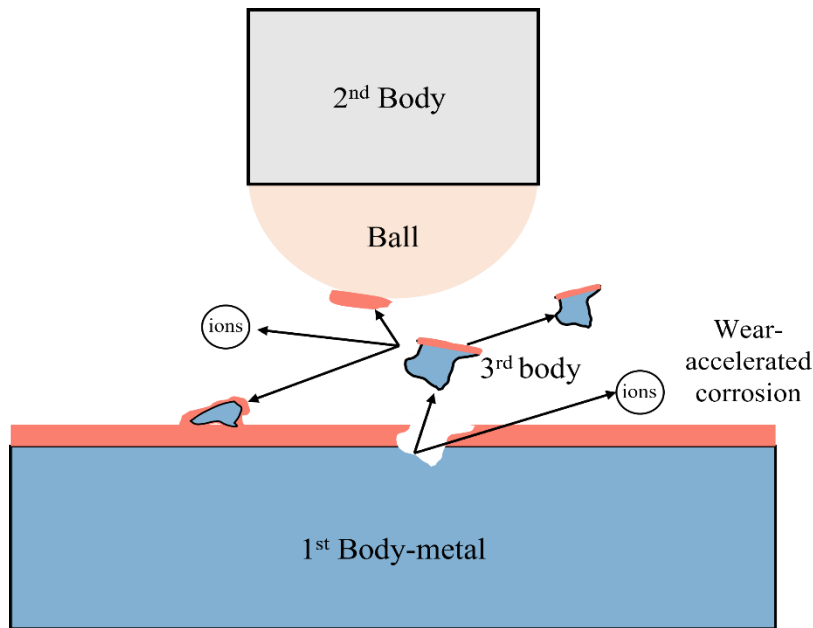


Figure 1.3. Schematic third-body approach of possible materials flows (arrows indication) and reactions during tribocorrosion.

1.2. Microstructure design to control wear, corrosion and tribocorrosion

Since tribocorrosion is caused by the integration of wear and corrosion, simultaneously increasing resistance to wear and corrosion of metallic materials is necessary. Unfortunately, there is typically a trade-off between wear and corrosion resistance in conventional microstructure due to the presence of chemical/structural heterogeneity (Fig. 1.4(a)), such as in Al alloys. Microstructure plays a vital role in the performance of metals. In this section, three microstructural designs (i.e., amorphous, multilayered and gradient microstructures), as shown in Fig. 1.4 (b-d), are proposed to introduce heterogeneity chemically or structurally to improve wear, corrosion and tribocorrosion resistance of metals in this thesis. Three metallic systems will be used as

examples, i.e., zirconium (Zr), aluminum (Al) and magnesium (Mg), representing metals with different corrosion characteristics. According to the Pourbaix diagram [8], in the neutral environment at room temperature, Zr and Al are stable metals with passive film generation while Mg is not thermodynamically passive.

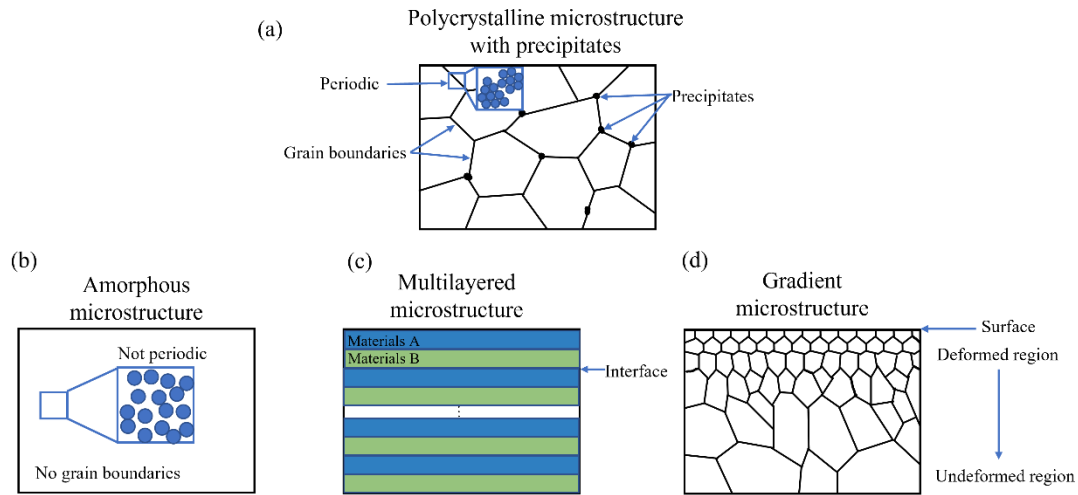


Figure 1.4. Schematics of (a) conventional polycrystalline microstructure with precipitates, proposed alternative (b) amorphous, (c) multilayered and (d) gradient microstructures.

1.2.1. Amorphous microstructure

Metallic materials with amorphous microstructure have been reported to exhibit excellent mechanical properties, wear and corrosion resistance owing to their short-range order, free of grain boundaries and crystal defects, which potentially perform high tribocorrosion resistance. Metallic glasses (MGs), as a type of amorphous microstructure family, are extensively explored and have a wide variety of applications such as biomedical materials, micro and nano-machines (MEMS) [23]. In general, a

high cooling rate is essential to prevent crystalline phases nucleation and retain the glassy state, as predicted by the TTT diagram in Fig. 1.5.

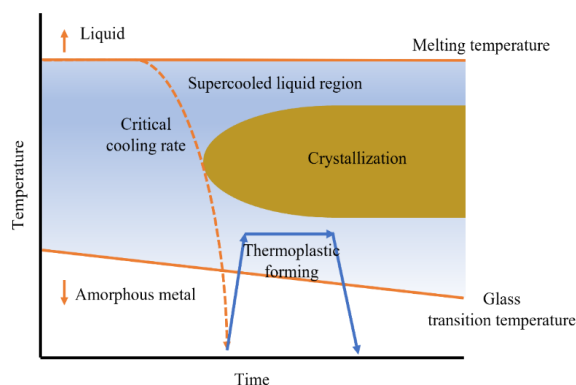


Figure 1.5. Schematic time-temperature-transformation (TTT) diagram.

To break through the critical size restriction, bulk metallic glasses (BMGs) with millimeter to centimeter thick were successfully cast at a very low critical cooling rate through multi-component composition design [24]. Those BMGs such as Zr-, Ti-, Pt-, Fe- and Pd-based systems performed good glass forming ability and remarkable hardness but limited ductility [25]. The deformation behavior of MGs is significantly dependent on external conditions [26]. At room temperature and high stress, MGs have a heterogeneous plastic deformation governed by localized shear bands, which is generally attributed to the localized atomic clusters (i.e., collectively reorganizing atoms under shear stress, known as shear transformation zone (STZ) theory) [27]. At a critical shear strain, the percolating propagation of STZs with high density will lead to the yielding of BMGs, from local shearing to macroscopic shear bands as a result of atom mobility increase and the occurrence of structural and/or thermal softening. As softening develops, these shear zones will serve as the preferred location for plastic flow, eventually resulting in brittle failure, consistent with the poor ductility of BMGs.

Thin film metallic glasses (TFMGs) with nanometer to several microns thick were firstly synthesized approximately 40 years ago [28]. As the physical vapor deposition technique is developed, TFMGs are promised to overcome the limitations of BMGs and perform superior wear and corrosion resistance [29]. For example, $\text{Zr}_{60}\text{Cu}_{24}\text{Al}_{11}\text{Ni}_5$ TFMGs coated on Zr-based BMGs perform high plasticity and can be subjected to the shear strain as large as 4000% [30]. Cai et al. [31] reported that $\text{Zr}_{60.14}\text{Cu}_{22.31}\text{Fe}_{4.85}\text{Al}_{9.7}\text{Ag}_3$ TFMG coated on Ti6Al4V substrate exhibited 1.8-2.8 times higher fretting resistance than the Ti6Al4V alloys under dry/wetting-sliding conditions, as shown in Fig. 1.6. Instead of the abrasion and oxidative wear features of the Ti6Al4V substrate (Fig. 1.6(a)), some wear debris was observed in the Zr-based TFMG (Fig. 1.6(b)) during dry wear, indicating that the wear resistance of Zr-based TFMG was connected to the formation and destruction of oxide layers (mainly Zr-oxide) during friction. During wetting wear or tribocorrosion, the passive layer formed on the Zr-TFMG (Fig. 1.6(c)) exhibited more protection than the substrate (Fig. 1.6(d)) and is the same wear mechanism as dry wear.

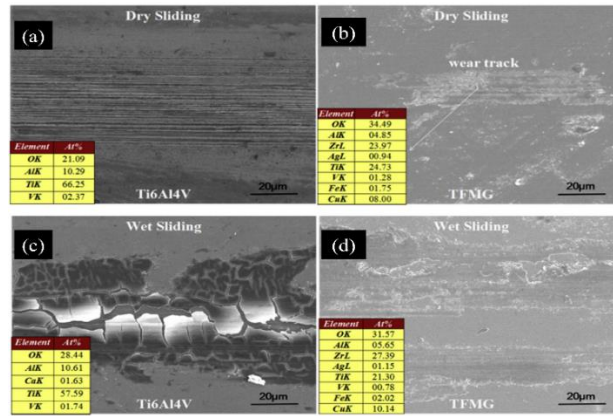


Figure 1.6. Surface morphologies of (a) Ti6Al4V, (b) Zr-based TFMG after dry wear, and (c) Ti6Al4V, (d) Zr-based TFMG after wet sliding in artificial saliva. Inserts show EDX results on the wear tracks [31]. Reprinted from ref. 31 with permission.

In terms of corrosion resistance, Chuang et. al [32] found that Zr–Cu–Ni–Al TFMG had a higher corrosion resistance than the bare AISI 420 substrate due to the amorphous microstructure and explained the potential corrosion mechanisms (e.g., pitting, crevice and filiform corrosion, as shown in Fig. 1.7. In Fig. 1.7(a) and (b), Zr and Al will be dissolved when the surface passivation layer was destroyed by pits, which will then produce corrosion products at the top of the pit as a result of copper reaction with oxygen. Besides pitting corrosion, crevice and filiform corrosion were also found in Zr-based TFMGs as shown in Fig. 1. 7(c) and (d). The corrosive solution penetrated and came into contact with the interface between passive layer and TFMG surface, resulting in a corroded region (Fig. 1.7(c)). Due to the limitation of oxygen content, this area acted as an anode and then the filaments extend outward in a random and uniform pattern, leaving behind corrosion products (Fig. 1.7(d)). In addition, Si, W,

B and N were found to have a positive effect on the corrosion properties of TFMGs as a result of the alteration of the atomic spacing and a further increase in the density of the film [33]. Since Zr-based systems exhibit strong glass forming capability and have great potential for a wide range of applications in dental implants, Zr-based TFMGs will be selected to be studied in chapter 2.

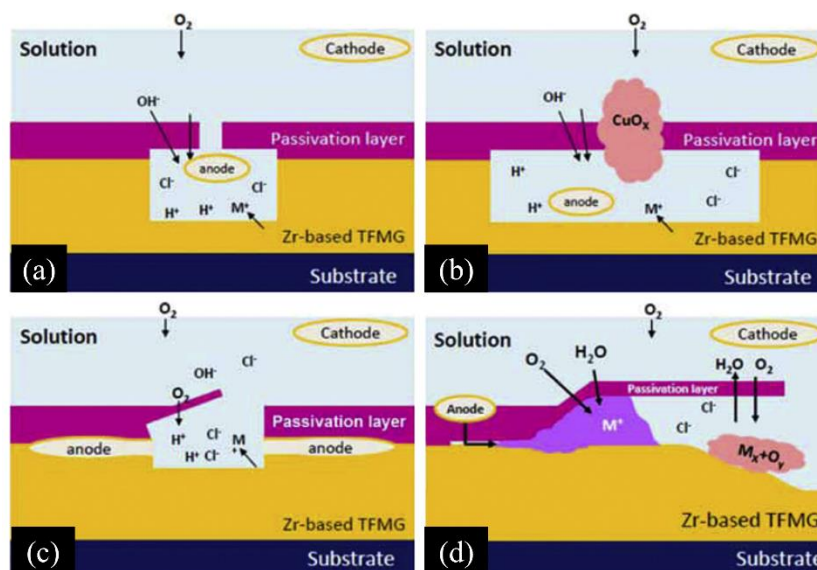


Figure 1.7. The mechanisms of (a) pitting corrosion, (b) corrosion products on the pits, (c) crevice corrosion and (d) filiform corrosion in Zr-based TFMGs [32].

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1.2.2. Multilayered microstructure

It is widely considered that hardness and wear resistance have a proportionate connection in bulk materials, i.e., higher wear resistance caused by higher hardness, as described in the classical Archard's law [34]. Thus, the basic idea underlying strengthening strategies for metallic materials is to impede dislocation movements,

such as grain size reduction [35], solid solution [36], precipitation strengthening [37], and strain hardening [38]. A metallic multilayered microstructure consisting of alternating layers of various materials is a promising hybrid microstructure design to obtain particular combination of properties, such as high hardness and wear resistance. For example, the strengthening effect can be obviously found in Zr/X (X=Cu, Ni and Ti) [39] and Al/X (X=Mg, Ti and Sc) [40-42] due to multilayered composites microstructure via accumulative roll bonding technique (ARB), a kind method of severe plastic deformation. Due to grain refinement, work hardening and high density phase boundary introduction, multilayered composites will be significantly harder than their pure counterparts, implying wear resistance improvement. In these bulk systems, multilayered microstructure also has been reported to have a favorable effect on corrosion resistance. Al/Mn multilayer with $\sim 0.3 \mu\text{m}$ grain size that produced by ARB exhibited a higher pitting corrosion resistance than its counterpart with coarse grain in 3.5 % NaCl solution [43]. The processing conditions (e.g., ARB), however, have a substantial impact on wear resistance or corrosion resistance in multilayered microstructures. As evidenced in certain contradictory results, the wear rate does not have a linearly increasing relationship with the cycles of ARB in pure Al sheets due to the competition between hardness increase, poor strain hardening capability and unstable grain boundaries [44]. In addition, micro-galvanic coupling [45], dislocation density and defects [46] are possible to generate a detrimental effect on corrosion resistance in multilayered microstructure.

With the assistance of other fabrication methods, such as physical vapor

deposition and electrodeposition, nanostructured metallic multilayers (NMMs) thin film exhibits excellent performance in resistance to wear, corrosion and even tribocorrosion. Unlike the bulk multilayered microstructure systems, the strengthening mechanism of NMMs is sensitive to the individual layer thickness and interface structure rather than grain size [47]. Generally, dislocation pile-up governs deformation behaviors when individual layer thickness (h) is over 100 nm, but confined layer slip (CLS) of single dislocations will be dominated at $h = 5\text{-}100$ nm. As h further reduction below 5 nm, the interfacial barrier strength (IBS) is the dominant factor, which is also affected by the modulus and lattice mismatch, stacking fault energy difference and interfacial coherency [48]. With respect to wear resistance, Izadi et al. [49] reported that hardness and wear resistance of Al/Ti NMMs were increased when equal-spaced individual layer thickness was reduced from 30 nm to 2.5 nm. High wear resistance of Al/Ti with 2.5 nm was attributed to increasing interface coherency and inducing subsurface work-hardening, as seen in the generation of chemical-mixed-like microstructures (Fig. 1.8).

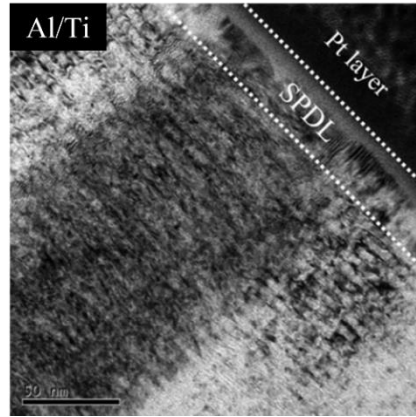


Figure 1.8. Bright field TEM images of Al/Ti with 2.5 nm individual layer thickness after 10 cycles of nanowear under 93 μN load [49]. Reprinted from ref. 49 with permission.

In view of less vulnerable microstructure (e.g., ultra-fine grain size, low surface roughness) in corrosive environment and presence of high density interfaces NMMs perform superior corrosion resistance [50], compared with monolithic thin film. The NMMs, however, will also suffer from the micro-galvanic coupling between adjacent layers after the top layer is corroded locally or damaged during tribocorrosion, as presented in Fig. 1.9. As a result, the design in materials selection, individual layers thickness, and interface structure of NMMs are significant to the wear, corrosion and tribocorrosion resistance. Al and its alloys are common structural materials in most industrial areas where high resistance to wear, corrosion and tribocorrosion are required. Therefore, Al-based multilayered microstructure will be introduced and studied in Chapter 3.

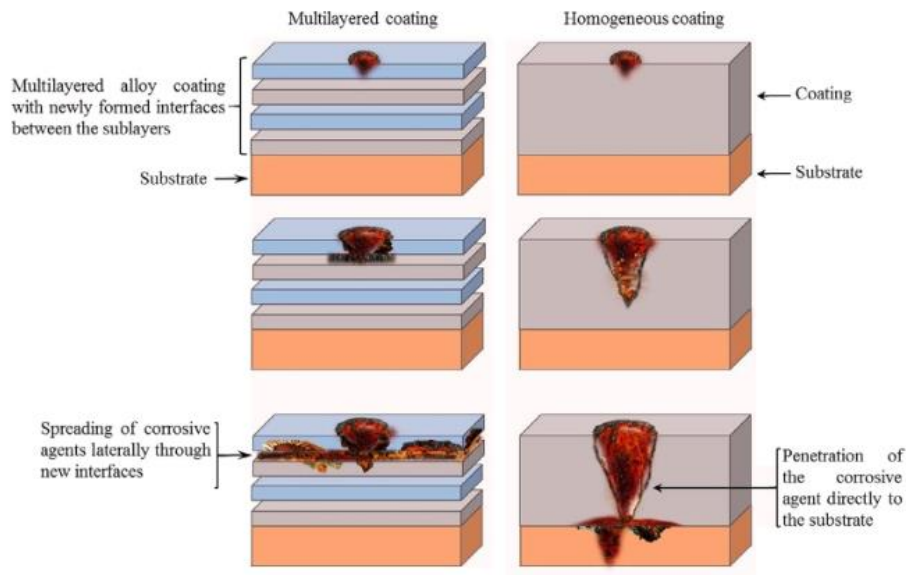


Figure 1.9. Schematic of corrosion mechanism in multilayered and monolithic microstructure [51]. Reprinted from ref. 51 with permission.

1.2.3. Gradient microstructure

As briefly reviewed above, both amorphous microstructure and multilayered microstructure may simultaneously boost wear and corrosion resistance. However, both microstructures involve compositional design and, in some cases, complex synthesis methods are needed if the length-scale needs to be controlled. To optimize performance of existing metallic materials without composition variation, gradient microstructure was proposed [52], which is a strategy of nanostructured surface layer on metallic materials via surface treatment such as surface mechanical attrition treatment (SMAT), shot peening (SP) and laser shock peening (LSP). For example, a gradient grain size from a few nanometers on the top surface (i.e., nanocrystalline surface layer) to several micrometers in the deep matrix was introduced by severe plastic deformation. Jamalian

et al. [53] reported an 82% improvement in the surface microhardness of AZ31 Mg sheet after severe SP treatment due to the presence of gradient grain size and microstructure. On the other hand, Zhang et al. [54] introduced gradient microstructure into AZ31 Mg alloys by ultrasonic shot peening (USSP, used S440 stainless steel balls) treatment and found a varied hydrogen evolution/corrosion rate as a function of depth below surface, as shown in Fig. 1. 10(a). The basic corrosion mechanisms (Fig. 1.10(b)) can be understood as the following: (1) the embedded Fe particles during treatment will couple to the matrix and induce micro-galvanic corrosion, leading to a high corrosion rate in the initial stage, (2) the corrosion rate on the surface below 40 μm was reduced by 40% because of the presence of high density grain boundaries (i.e., nanocrystalline surface layer) and beneficial compressive residual stresses.

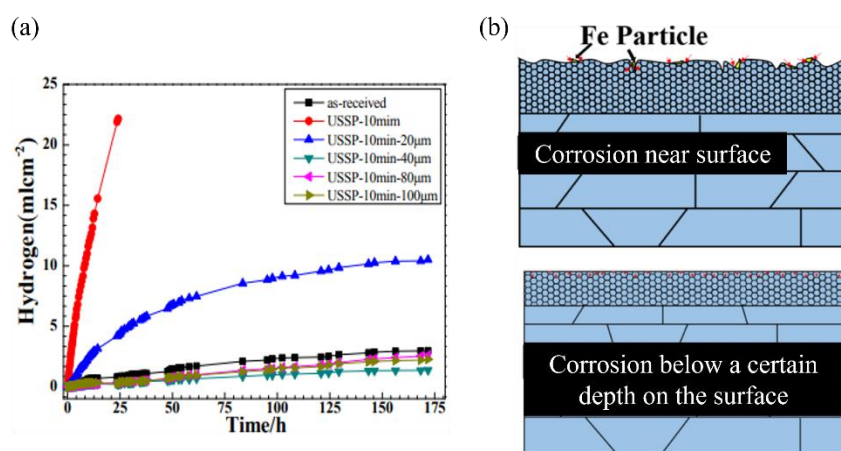


Figure 1.10. (a) The hydrogen evolution per area of untreated and treated AZ31 Mg alloy sheet in 3.5 wt% NaCl solution, (b) corrosion mechanisms under different depths [54]. Reprinted from ref. 54 with permission.

Siddaiah et. al [55] applied nanosecond LSP treatment to enhance the tribocorrosion resistance of AZ31B Mg alloys and found that LSP with low laser intensity was able to

increase tribocorrosion resistance by at least three times compared to untreated sample. However, such effects of gradient microstructure on corrosion and tribocorrosion are significantly affected by processing parameters, post-surface roughness, energy and contamination.

Mg and its alloys are regarded as a candidate for the next generation of orthopedic implant materials due to their biodegradability but are limited by their high degradation rate and low tribocorrosion resistance in physiological environments [56]. The ideal relationship between tissue and implant material is to ensure sufficient mechanical support at the beginning of the healing process and complete degradation in vivo once the tissue has healed. Hence, to achieve it, it is reasonable to consider the introduction of gradient microstructure into Mg alloys, and a detailed study will be discussed in Chapter 4.

1.3. Problem statement and research motivation

Due to the synergic effects of wear and corrosion during tribocorrosion, metals with high wear and corrosion resistance simultaneously are desired. Unfortunately, there is typically a tradeoff between strength and corrosion resistance, even for important passive metals such as Al alloys. For example, pure Al exhibits good corrosion resistance owing to the formation of a protective passive film in neutral solutions (pH 4-9), but it is highly susceptible to wear due to its low hardness. On the other hand, most precipitation-hardened Al alloys impart high strength and wear resistance, but none of them have very good resistance against localized corrosion. This

is because the presence of precipitates and secondary particles strengthens the material but, at the same time, enhances corrosion by catalyzing oxygen reduction, increasing the corrosion potential, and localizing the electrochemical activity due to their micro-galvanic coupling with the Al matrix [57]. In other words, most metals are difficult to attain high wear and high corrosion resistance at the same time due to the presence of heterogeneity exhibited in chemistry, structure or both. Controlling heterogeneity (e.g., content, length-scale) appears to be a significant aspect of improving tribocorrosion resistance of metals. Ralston et al. [58] showed that, in Al-Cu-Mg alloys, the tendency of micro-galvanic coupling between the precipitates and matrix was reduced when the precipitate size was below ~ 3 nm and strengthening was ensured at the same time.

However, most previous studies evaluated 'invisible' heterogeneity on wear or corrosion separately, few works have been done to study the effects of such heterogeneity control on the tribocorrosion resistance of metals. Thus, the research purpose of this dissertation is to study the effects of chemical or structural heterogeneity and their length-scale on the tribocorrosion resistance of metals in three systems (i.e., Zr-based, Al-based and Mg alloys), with an ultimate goal of understanding their effects on the deformation and degradation mechanisms of metals through integrated approaches of materials processing, tribocorrosion testing and advanced materials characterization. Such developed understandings will provide a guideline for future materials design for applications under extreme conditions where mechanical and chemical attack occurs simultaneously on the surface.

1.4. Organization of the dissertation

1.4.1. Study 1-Effects of nanoscale chemical heterogeneity on the wear, corrosion, and tribocorrosion resistance of Zr-based thin film metallic glasses (Chapter 2)

In this study, deposition parameters (i.e., low and high Ar pressure application) during magnetron sputtering were tailored to produce Zr-based thin film metallic glasses (TFMG) with different nanoscale chemistry and microstructure. The mechanical properties of Zr-based TFMG were estimated by nanoindentation tests. Corrosion and tribocorrosion tests were performed on all samples in simulated seawater at room temperature. Surface morphology, the composition of the samples and cross-section were characterized using scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS) and focus ion beam (FIB), respectively, prior to and post tribocorrosion testing. The results found that the presence of nanoscale chemical heterogeneity apparently led to hardness reduction but high ductility, and further affected wear behaviors. In addition, the resistance to pitting corrosion and tribocorrosion was enhanced by chemical heterogeneity because of the formation of a protective passive film with low defect density and a high repassivation capacity.

1.4.2. Study 2-Ultrahigh tribocorrosion resistance of metals enabled by nano-layering (Chapter 3)

In this work, the wear, corrosion and tribocorrosion resistance of nanostructured multilayers of Al/X (X= Mg, Cu, and Ti) were studied via experiments, to

fundamentally study the effects of nanoscale chemical and structural heterogeneity. Transmission electron microscopy (TEM) of deformed and degraded sample surfaces showed characteristically different deformation and degradation modes of all samples, governed by the synergistic effects of the mechanical and corrosion properties of the constituting materials. The results indicated that corrosion was the cause of material loss for both Al/Mg and Al/Cu NMMs during tribocorrosion due to significant micro-galvanic coupling effects, while severe plastic deformation was responsible for the loss of material in Al/Ti NMMs because of low surface reactivity. The detailed compositions of passive film in all Al-based NMMs were characterized and discussed by X-ray photoelectron spectroscopy, which was consistent with the mixed potential theory prediction except in Al/Ti NMMs.

1.4.3. Study 3-Enabling High-Performance Surfaces of Biodegradable Magnesium Alloys via Femtosecond Laser Shock Peening with Ultralow Pulse Energy (Chapter 4)

In this study, an effective surface treatment method, i.e., laser shock peening with the femtosecond laser (fs-LSP) was applied to simultaneously optimize the wear and corrosion resistance, i.e., tribocorrosion resistance of biodegradable Mg alloys. The different treatment conditions (e.g., power density, absorbent and confining layers) were firstly applied in order to investigate the optimized peening effect. The corrosion and tribocorrosion behaviors of Mg alloys were evaluated in stagnant blood bank buffered saline (pH of 7.0-7.2) under $\sim 37\text{ }^{\circ}\text{C}$, to simulate in vivo physiological

conditions. Materials characterization via transmission electron microscope (TEM) was combined with finite element (FE) simulations to reveal the underlying structural evolutions (i.e., gradient dislocation density) and residual stress generations during fs-LSP, which were responsible for the enhanced tribocorrosion resistance of WE43 Mg alloys.

References:

1. Landolt, D. and S. Mischler, *Tribocorrosion of passive metals and coatings*. 2011: Elsevier.
2. López-Ortega, A., R. Bayón, and J. Arana, *Evaluation of protective coatings for offshore applications. Corrosion and tribocorrosion behavior in synthetic seawater*. Surface Coatings Technology, 2018. **349**: p. 1083-1097.
3. Mathew, M., P. Srinivasa Pai, R. Pourzal, A. Fischer, and M. Wimmer, *Significance of tribocorrosion in biomedical applications: overview and current status*. Advances in tribology, 2009. **2009**.
4. López-Ortega, A., J. Arana, and R. Bayón, *Tribocorrosion of passive materials: a review on test procedures and standards*. International Journal of Corrosion, 2018. **2018**.
5. Mischler, S., *Triboelectrochemical techniques and interpretation methods in tribocorrosion: a comparative evaluation*. Tribology International, 2008. **41**(7): p. 573-583.
6. Davis, J.R., *Surface engineering for corrosion and wear resistance*. 2001: ASM international.
7. Siddaiah, A., R. Ramachandran, and P. Menezes, *Tribocorrosion: Fundamentals*,

- Methods, and Materials*. 2021: Academic Press.
8. Jones, D.A., *Principles and prevention of corrosion*. 1996.
 9. Ellor, J.A. and J. Repp, *Uniform Corrosion*. Corrosion Tests Standards, Application Interpretation, 2005: p. 205-210.
 10. Frankel, G., *Pitting corrosion of metals: a review of the critical factors*. Journal of the Electrochemical society, 1998. **145**(6): p. 2186.
 11. Liao, C.-M., J. Olive, M. Gao, and R. Wei, *In-situ monitoring of pitting corrosion in aluminum alloy 2024*. Corrosion, 1998. **54**(6): p. 451-458.
 12. Mraied, H. and W. Cai, *The effects of Mn concentration on the tribocorrosion resistance of Al–Mn alloys*. Wear, 2017. **380**: p. 191-202.
 13. Ponthiaux, P., F. Wenger, D. Drees, and J.-P. Celis, *Electrochemical techniques for studying tribocorrosion processes*. Wear, 2004. **256**(5): p. 459-468.
 14. Chen, J. and W. Cai, *Effect of scratching frequency on the tribocorrosion resistance of Al-Mn amorphous thin films*. Wear, 2019. **426**: p. 1457-1465.
 15. Chen, J., J. Wang, F. Yan, Q. Zhang, and Q.-a. Li, *Effect of applied potential on the tribocorrosion behaviors of Monel K500 alloy in artificial seawater*. Tribology International, 2015. **81**: p. 1-8.
 16. ASTM International, P.A.I., *ASTM G119-09 Standard Guide for Determining Synergism Between Wear and Corrosion*. 2016.
 17. Akonko, S., D. Li, and M. Ziomek-Moroz, *Effects of cathodic protection on corrosive wear of 304 stainless steel*. Tribology Letters, 2005. **18**(3): p. 405-410.
 18. Bidiville, A., M. Favero, P. Stadelmann, and S. Mischler, *Effect of surface chemistry on the mechanical response of metals in sliding tribocorrosion systems*. Wear, 2007. **263**(1-6): p. 207-217.
 19. Uhlig, H.H., *Mechanism of fretting corrosion*. 1954.

20. Vieira, A., L. Rocha, N. Papageorgiou, and S. Mischler, *Mechanical and electrochemical deterioration mechanisms in the tribocorrosion of Al alloys in NaCl and in NaNO₃ solutions*. Corrosion Science, 2012. **54**: p. 26-35.
21. Cao, S. and S. Mischler, *Modeling tribocorrosion of passive metals—A review*. Current Opinion in Solid State Materials Science, 2018. **22**(4): p. 127-141.
22. Landolt, D., S. Mischler, and M. Stemp, *Electrochemical methods in tribocorrosion: a critical appraisal*. Electrochimica acta, 2001. **46**(24-25): p. 3913-3929.
23. Chen, M., *A brief overview of bulk metallic glasses*. NPG Asia Materials, 2011. **3**(9): p. 82-90.
24. Johnson, W., *Bulk amorphous metal—An emerging engineering material*. Jom, 2002. **54**(3): p. 40-43.
25. Inoue, A. and A. Takeuchi, *Recent development and application products of bulk glassy alloys*. Acta Materialia, 2011. **59**(6): p. 2243-2267.
26. Schuh, C.A., T.C. Hufnagel, and U. Ramamurty, *Mechanical behavior of amorphous alloys*. Acta Materialia, 2007. **55**(12): p. 4067-4109.
27. Argon, A., *Plastic deformation in metallic glasses*. Acta metallurgica, 1979. **27**(1): p. 47-58.
28. Schwarz, R. and W. Johnson, *Formation of an amorphous alloy by solid-state reaction of the pure polycrystalline metals*. Physical Review Letters, 1983. **51**(5): p. 415.
29. Korkmaz, S. and İ.A. Kariper, *Glass formation, production and superior properties of Zr-based thin film metallic glasses (TFMGs): A status review*. Journal of Non-Crystalline Solids, 2020. **527**: p. 119753.
30. Yu, C.-C., C. Lee, J.P. Chu, J. Greene, and P.K. Liaw, *Fracture-resistant thin-film metallic glass: Ultra-high plasticity at room temperature*. APL Materials, 2016.

- 4(11): p. 116101.
31. Cai, C.-N., C. Zhang, Y.-S. Sun, H.-H. Huang, C. Yang, and L. Liu, *ZrCuFeAlAg thin film metallic glass for potential dental applications*. Intermetallics, 2017. **86**: p. 80-87.
 32. Chuang, C.-Y., Y.-C. Liao, J.-W. Lee, C.-L. Li, J.P. Chu, and J.-G. Duh, *Electrochemical characterization of Zr-based thin film metallic glass in hydrochloric aqueous solution*. Thin Solid Films, 2013. **529**: p. 338-341.
 33. Yiu, P., W. Diyatmika, N. Bönninghoff, Y.-C. Lu, B.-Z. Lai, and J.P. Chu, *Thin film metallic glasses: Properties, applications and future*. Journal of applied physics, 2020. **127**(3): p. 030901.
 34. Archard, J., *Contact and rubbing of flat surfaces*. Journal of applied physics, 1953. **24**(8): p. 981-988.
 35. Farhat, Z., Y. Ding, D. Northwood, and A. Alpas, *Effect of grain size on friction and wear of nanocrystalline aluminum*. Materials Science Engineering: A, 1996. **206**(2): p. 302-313.
 36. Ryen, Ø., B. Holmedal, O. Nijs, E. Nes, E. Sjölander, and H.-E. Ekström, *Strengthening mechanisms in solid solution aluminum alloys*. Metallurgical Materials Transactions A, 2006. **37**(6): p. 1999-2006.
 37. Tang, S., T. Xin, W. Xu, D. Miskovic, G. Sha, Z. Quadir, S. Ringer, K. Nomoto, N. Birbilis, and M. Ferry, *Precipitation strengthening in an ultralight magnesium alloy*. Nature communications, 2019. **10**(1): p. 1-8.
 38. Liang, C., C. Li, X. Lv, and J. An, *Correlation between friction-induced microstructural evolution, strain hardening in subsurface and tribological properties of AZ31 magnesium alloy*. Wear, 2014. **312**(1-2): p. 29-39.
 39. Hsieh, P., Y. Hung, and J. Huang, *Transformation into nanocrystalline or*

- amorphous materials in Zr–X binary systems using ARB route*. Scripta materialia, 2003. **49**(2): p. 173-178.
40. Liu, H., B. Zhang, and G. Zhang, *Microstructures and mechanical properties of Al/Mg alloy multilayered composites produced by accumulative roll bonding*. Journal of Materials Science Technology, 2011. **27**(1): p. 15-21.
 41. Yang, D., P. Cizek, and P. Hodgson, *Ultrafine equiaxed-grain Ti/Al composite produced by accumulative roll bonding*. Scripta materialia, 2010. **62**(5): p. 321-324.
 42. Quadir, M., O. Al-Buhamad, L. Bassman, and M. Ferry, *Development of a recovered/recrystallized multilayered microstructure in Al alloys by accumulative roll bonding*. Acta Materialia, 2007. **55**(16): p. 5438-5448.
 43. Wei, W., K.X. Wei, and Q.B. Du, *Corrosion and tensile behaviors of ultra-fine grained Al–Mn alloy produced by accumulative roll bonding*. Materials Science Engineering: A, 2007. **454**: p. 536-541.
 44. Talachi, A.K., M. Eizadjou, H.D. Manesh, and K. Janghorban, *Wear characteristics of severely deformed aluminum sheets by accumulative roll bonding (ARB) process*. Materials Characterization, 2011. **62**(1): p. 12-21.
 45. Pei, Y., Y. Gui, T. Huang, F. Chen, J. Guo, S. Zhong, and Z. Song, *Microstructure and corrosion behaviors of AZ63 magnesium alloy fabricated by accumulative roll bonding process*. Materials Research Express, 2020. **7**(6): p. 066525.
 46. Naeini, M.F., M.H. Shariat, and M. Eizadjou, *On the chloride-induced pitting of ultra fine grains 5052 aluminum alloy produced by accumulative roll bonding process*. Journal of Alloys Compounds, 2011. **509**(14): p. 4696-4700.
 47. Misra, A., J. Hirth, and R. Hoagland, *Length-scale-dependent deformation mechanisms in incoherent metallic multilayered composites*. Acta materialia, 2005. **53**(18): p. 4817-4824.

48. Wang, J. and A. Misra, *An overview of interface-dominated deformation mechanisms in metallic multilayers*. Current Opinion in Solid State and Materials science, 2011. **15**(1): p. 20-28.
49. Izadi, S., H. Mraied, and W. Cai, *Tribological and mechanical behavior of nanostructured Al/Ti multilayers*. Surface Coatings Technology, 2015. **275**: p. 374-383.
50. Xie, T., S. Mao, C. Yu, S. Wang, and Z. Song, *Structure, corrosion, and hardness properties of Ti/Al multilayers coated on NdFeB by magnetron sputtering*. Vacuum, 2012. **86**(10): p. 1583-1588.
51. Rashmi, S., L. Elias, and A.C. Hegde, *Multilayered Zn-Ni alloy coatings for better corrosion protection of mild steel*. Engineering science technology, an international journal, 2017. **20**(3): p. 1227-1232.
52. Lu, K. and J. Lu, *Nanostructured surface layer on metallic materials induced by surface mechanical attrition treatment*. Materials Science Engineering: A, 2004. **375**: p. 38-45.
53. Jamalain, M. and D.P. Field, *Effects of shot peening parameters on gradient microstructure and mechanical properties of TRC AZ31*. Materials Characterization, 2019. **148**: p. 9-16.
54. Zhang, J., P. Peng, J. She, B. Jiang, A. Tang, F. Pan, and Q. Han, *A study of the corrosion behavior of AZ31 Mg alloy in depth direction after surface nanocrystallization*. Surface Coatings Technology, 2020. **396**: p. 125968.
55. Siddaiah, A., B. Mao, A.K. Kasar, Y. Liao, and P.L. Menezes, *Influence of laser shock peening on the surface energy and tribocorrosion properties of an AZ31B Mg alloy*. Wear, 2020. **462**: p. 203490.
56. Staiger, M.P., A.M. Pietak, J. Huadmai, and G. Dias, *Magnesium and its alloys as*

- orthopedic biomaterials: a review*. Biomaterials, 2006. **27**(9): p. 1728-1734.
57. Zhu, Y., J.D. Poplawsky, S. Li, R.R. Unocic, L.G. Bland, C.D. Taylor, J.S. Locke, E.A. Marquis, and G.S. Frankel, *Localized corrosion at nm-scale hardening precipitates in Al-Cu-Li alloys*. Acta Materialia, 2020. **189**: p. 204-213.
58. Ralston, K., N. Birbilis, M. Weyland, and C. Hutchinson, *The effect of precipitate size on the yield strength-pitting corrosion correlation in Al-Cu-Mg alloys*. Acta Materialia, 2010. **58**(18): p. 5941-5948.

Chapter 2. Effects of Nanoscale Chemical Heterogeneity on the Wear, Corrosion, and Tribocorrosion Resistance of Zr-based Thin Film Metallic Glasses

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2.1. Introduction

Metallic glasses (MGs) exhibit good elastic limit [1], high strength [2, 3], and excellent wear [4, 5] and corrosion resistance [6, 7] largely owing to the lack of long-range order, the absence of grain boundary, and in many cases, the retention of high alloying content in homogenous solid solution [8, 9]. With the reduction of the critical cooling rate, MGs can be cast into bulk metallic glasses (BMGs) to optimize mechanical properties such as strength and fracture toughness, however, they often suffer from a very limited ductility and serrated plastic flow [9-12]. Thin film metallic glasses (TFMGs), i.e. MGs with typically hundreds of nanometers to several microns thickness, offset the shortcomings of BMGs by retarding strain localization via interface-mediated plasticity and hence have drawn great interest lately as they can be readily applied as coatings for various engineering applications which requires both good mechanical properties and high corrosion resistance on the surface [13-15]. For instance, Pd-based TFMGs with attractive forming ability have been used in micro-electro-mechanical systems (MEMS) [16]. Zr-based TFMGs, the focus of this work, have been applied in dental implant due to their high strength, exceptional fracture toughness and corrosion resistance [17]. In many of these applications, simultaneous wear and corrosion resistance, i.e. tribocorrosion resistance, are essential for the product's long-term durability and safe operation.

The hardness of Zr-based TFMGs prepared by physical vapor deposition ranges from ~ 5.5 GPa to as high as ~ 16.2 GPa at room temperature [18-20]. Such high hardness typically translates into wear resistance superior to many conventional

engineering metals in various applications [21, 22]. For example, Tsai et al. found that the cutting durability of surgical blades coated with $\text{Zr}_{48}\text{Cu}_{36}\text{Al}_8\text{Ag}_8$ and $\text{Zr}_{53}\text{Cu}_{30}\text{Ni}_9\text{Al}_8$ TFMGs was much higher than that of commercial AISI 440C martensitic stainless steel [23]. Cai et al. showed that the fretting wear rate of $\text{Zr}_{60.14}\text{Cu}_{22.31}\text{Fe}_{4.85}\text{Al}_{9.7}\text{Ag}_3$ TFMGs was approximately 2.8 times lower than that of Ti6Al4V alloys under the same dry sliding conditions [17]. However, since wear of Zr-based TFMGs is a complex dynamic process, often associated with subsurface shear band formation and contingent crystallization [24], the opposite has also been reported [25]. For example, Fu et al. [25] studied the sliding behavior of Zr-based MGs using molecular dynamics simulation and found that no exceptional friction and wear characteristics were observed.

A recently proposed four R's design paradigm has pointed out the importance of tailoring the properties of MGs via controlling their nanoscale compositional and structural heterogeneity [26,27], where the four R's represent (1) retaining more soft spots that participate in soft vibrational modes, (2) restraining shear-band propagation and nucleation, (3) rejuvenating glass structure into a more deformable state, and (4) relocating to alloy compositions rich in structural inhomogeneity. Based on such hypothesis, the macroscopic properties of MGs can be tailored by tuning the nanoscale chemical heterogeneity during processing. Indeed, several experimental and simulation studies of BMGs and TFMGs have indicated that nanoscale heterogeneity strongly affects both of their mechanical and corrosion properties [28–30]. It should also be pointed out that while MGs are inherently inhomogeneous with a wide spectrum of atomic-packing heterogeneities, the term 'nanoscale heterogeneity' used herein

specifically refers to quasi-periodic compositional fluctuations over a length scale of hundreds of nanometers, hence a higher degree of heterogeneity than those intrinsic to conventional homogenous MGs. For example, Rashidi et al. [28] reported that the chemical heterogeneity was induced during the introduction of Sn to Cu₄₇Zr₄₇Al₆ bulk metallic glass, resulting in increased shear band formation and enhanced ductility. Wang et al. [29] studied the effects of nanoscale chemical heterogeneity on the mechanical properties of Cu-Zr MGs via multiscale computer simulation and found that the organization of nanometer-scale shear transformation into shear-band patterns is dependent on the length-scale of the spatial heterogeneity. An optimum correlation length of ~5 nm was identified to result in the highest plastic strain to failure and lowest strain localization.

In terms of corrosion resistance, the chemical heterogeneity is often found to exhibit an adverse effect on the corrosion resistance of MGs owing to its obstruction to uniform passive film growth [31]. Zhang et al. [30] found that the Al₃Ni or Al₁₁Ce₃ intermetallics precipitation has negative effect on pitting resistance of Al-based MG whereas no detrimental effect was observed in nanoscale α -Al precipitation. Mudali et al. [32] pointed out that chemical inhomogeneous cluster zones in Zr-based BMGs served as attractive sites for aggressive ions and further accelerate the corrosion in locations containing less noble alloy components. Generally speaking, chemical homogeneity and an absence of surface defects are desired to achieve a more uniform corrosion mode and lower corrosion rate than those with high degrees of structural disorder and compositional fluctuations [33-35]. These previous work indicate the

contradictory effects of chemical heterogeneity on the mechanical and corrosion properties of MGs. While most studies have evaluated these two properties separately, few work has been performed to simultaneously evaluate its effects on TFMGs during simultaneous mechanical and chemical loads. In this work, the effects of nanoscale chemical heterogeneity on the wear, corrosion, and tribocorrosion properties of ZrCuNiAl TFMGs were investigated by examining two types of samples: heterogeneous and homogeneous Zr-TFMGs. The former exhibit domains with compositional fluctuations of $\sim 1.1\%$ Zr and $\sim 0.5\%$ Cu, separated at $\sim 413.0 \pm 64.7$ nm. On the other hand, the homo-Zr samples exhibited chemical homogeneity even at the nanoscale (to the resolution limit of scanning electron based energy dispersive X-ray spectroscopy). The goals of the present study include: 1) quantification of the wear, corrosion, and tribocorrosion resistance of Zr-based TFMGs, 2) evaluation of the effects of chemical heterogeneity on mechanical properties and the passive film property, and 3) understanding the effects of chemical heterogeneity on the depassivation and repassivation kinetics of Zr based TFMGs during tribocorrosion in 0.6 M NaCl solution.

2.2. Experimental methods

2.2.1. Materials synthesis

A base pressure of 7×10^{-5} Pa was achieved prior to film depositions. Zr₅₁Cu₃₄Ni₈Al₇ films of ~ 200 nm thickness were deposited on Si substrates using radio frequency (RF) magnetron sputtering at RF power of 100 W, deposition time of 30 min,

working distance of 10 cm, direct-current substrate bias of 50 V, and substrate rotation of 20 rpm without intentional substrate heating. The target is a quaternary Zr-based alloy with a composition similar to that of the film. Two sets of Zr-TFMG samples were prepared, with heterogeneous (hereafter referred as heter-Zr) and homogeneous (hereafter referred as homo-Zr) chemical distribution, by adjusting Ar pressure to be around 5 mTorr ($\sim 6.7 \times 10^{-1}$ Pa) and 3 mTorr ($\sim 4 \times 10^{-1}$ Pa) respectively, while Ar flow rate was kept constant at 20 sccm. These samples were then used for scratch, corrosion, and tribocorrosion tests later on. It is believed that such different Ar pressure leads to variations in the chemical heterogeneity of the deposits [36,37]. A more detailed description of the synthesis procedure can be found in [13,38].

2.2.2. Characterization of mechanical properties

The mechanical properties of the samples were measured by nanoindentation tests (Hysitron Ti900) using a standard diamond Berkovich indenter following the Oliver and Pharr method [39]. Prior to indentation, the tip-area function was calibrated using a fused quartz sample. A trapezoidal loading function was applied, with 5 s loading/unloading time and 2 s holding time at 2-3 mN. Special care was taken during the indentation to minimize the substrate effect by ensuring that the maximum indentation depth was less than ~20% of the total film thickness [40]. The reported results represent average values obtained from more than ten repeated tests for each sample sets.

2.2.3. Electrochemical measurement

Potentiodynamic polarization (PD) tests were conducted in a typical three electrode configuration at ambient temperature in naturally aerated 0.6 M NaCl aqueous solution ($\text{pH} \sim 6.4 \pm 0.3$) using a Gamry Reference 600® potentiostat. The as-deposited samples, mixed metal oxide coated titanium mesh, and a commercial silver-silver chloride electrode (1 M KCl internal solution) served as the working (WE), counter (CE), and reference electrode (RE) respectively. An exposed area of $\sim 1 \times 1.5 \text{ cm}^2$ was prepared on the samples using a protective stop-off lacquer. PD tests were conducted after 1 h of immersion of the sample in the electrolyte for stabilizing the open circuit potential (OCP). The scan was performed at a rate of 0.167 mV/s, starting at a potential $\sim 200 \text{ mV}$ cathodic to OCP and terminated when a rapid increase in the anodic current density took place, reaching 1 mA/cm^2 . Tafel extrapolation was performed by selecting a linear portion of the PD curve approximately 100 mV above and below the corrosion potentials (E_{corr}) to determine the corrosion current densities (i_{corr}) of both samples. To examine the behavior of the passive film, Mott-Schottky (MS) analysis were conducted for five days. MS tests were conducted from 0 to 300 mV vs. OCP in the anodic region at 1 kHz frequency, 10 mV rms amplitude, and 10 mV/s potential sweeping rate.

2.2.4. Dry scratch and tribocorrosion tests

Dry scratch tests of both samples were conducted using a multifunctional tribometer (Rtec Instruments, CA, USA). Dry scratch tests were performed under 0.2 N normal load, 0.2 mm/s sliding velocity, over 5 mm total scratch length for 25 s in air.

A diamond tip (12.5 μm radius) was used as the counter body, and the contact between the tip and sample was maintained for 5 s before each test. Tribocorrosion tests were performed under 0.2 N normal load, 0.2 mm/s sliding velocity, over 5 mm total scratch length for 25 s against diamond tip (12.5 μm radius) counter body. During the tribocorrosion test, a three-electrode setup was used, where the as-deposited sample (with $\sim 1 \times 1.5 \text{ cm}^2$ exposed area), activated titanium mesh, and 1 M KCl Ag/AgCl electrode were used as the WE, CE, and RE, respectively, immersed in 0.6 M NaCl aqueous solution. This setup was connected to a potentiostat/galvanostat/zero resistance ammeter (Gamry Reference 600™ system). The electrolyte used was ~ 40 ml of 0.6 M NaCl aqueous solution, open to air. During the tribocorrosion test, both of samples were tested under two different applied potential conditions: an anodic potential of 400 mV above OCP (OCP + 0.4 V) and OCP. Before each test, the current/potential was stabilized for ~ 10 -20 min. Unless specified otherwise, all results reported here were averaged from at least three repeated tests.

2.2.5. Materials characterization

The composition and morphology of sample surfaces and cleaved cross-sections were characterized by a field-emission scanning electron microscopy (FESEM, LEO 1550) with an Oxford INCASynergy energy dispersive X-ray spectroscopy (EDS). To reveal any compositional heterogeneity, the as-deposited samples were etched in 1 ml HNO_3 : 5 ml $\text{C}_2\text{H}_6\text{O}$ solution for 30 s at room temperature. A grazing incidence X-ray diffractometer (GIXRD, Panalytical X'pert) with a wavelength of 1.54 Å Cu $\text{K}\alpha$ under

45 kV and 40 mA were used to characterize the microstructure of as-deposited thin film samples. After dry scratch and tribocorrosion tests, the cross-sections of wear tracks were studied using focus ion beam microscopy (FIB, Helios600) at 30 kV and 0.9 nA current. A protective Pt layer (~ 0.3 - $1.5\ \mu\text{m}$) was deposited on the sample surfaces prior to milling of the cross-sectional samples.

2.3. Results and discussion

2.3.1. Characterization of as-deposited Zr-TFMGs

Fig. 2.1 presents the GIXRD patterns of the as-deposited thin films, where the typical broad hump diffraction peaks were observed at 2θ angle of $\sim 36^\circ$, confirming the amorphous nature of both samples, similar to prior report [41]. Fig. 2.2(a) and (b) show the surface morphology of the as-deposited heter-Zr and homo-Zr samples. Both samples exhibited a mirror finish to the naked eye and are featureless under SEM. After etching process, the homo-Zr sample remains featureless, as shown in Fig. 2.2(d). However, networks of deep etched grooves were observed in heter-Zr sample (indicated by arrow in Fig. 2.2(c)), suggesting the presence of nanoscale chemical heterogeneity within and outside the groove region that result in different etching rates on the surface. EDS analysis of heter-Zr reveal a compositional fluctuation of 1.1 at.% Zr and 0.5 at.% Cu within and outside the groove region, as summarized in Table 2.1. A similar but more dramatic chemical heterogeneity has been reported in $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ MG [42] where two amorphous phases were formed by liquid phase separation, with compositional differences of ~ 8.5 at.% Cu, 12.9 at.% Zr and 4.4 at.% Al.

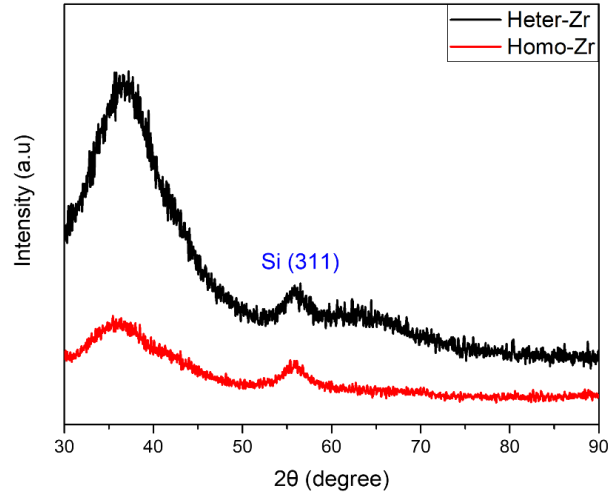


Figure 2.1. GIXRD patterns of as-deposited heter-Zr and homo-Zr TFMG samples.

Table 2.1 Summary of global and local compositions of heter-Zr and homo-Zr samples from EDS analysis. The boundary areas of heter-Zr are marked by red lines in Fig. 2.2(c) while areas away from these boundaries are referred as interior.

Sample ID	Zr (at. %)	Cu (at. %)	Ni (at. %)	Al (at. %)
Homo-Zr (global)	50.3 ± 0.32	33.8 ± 0.68	8.9 ± 0.32	6.9 ± 0.62
Heter-Zr (global)	52.6 ± 0.54	33.9 ± 0.35	7.4 ± 0.04	6.1 ± 0.69
Heter-Zr (Interior)	51.7 ± 0.68	34.0 ± 0.42	7.7 ± 0.23	6.5 ± 0.12
Heter-Zr (boundary)	52.8 ± 0.05	33.5 ± 0.17	7.3 ± 0.22	6.5 ± 0.33

To evaluate whether such mild chemical heterogeneity would affect the mechanical properties of TFMGs, both samples were cleaved via clippers with the thin film on the tensile side. Fig. 2.2(e) and (f) show the fractography of both samples. It can be seen that while homo-Zr exhibited clearly brittle fracture with a smooth fractured surface, heter-Zr exhibited a more corrugated fractured surface, indicating its better fracture resistance and potentially higher ductility. These results confirm the high

sensitivity of both chemical and mechanical properties of Zr-TFMG due to variations of processing conditions (i.e. Ar working pressure).

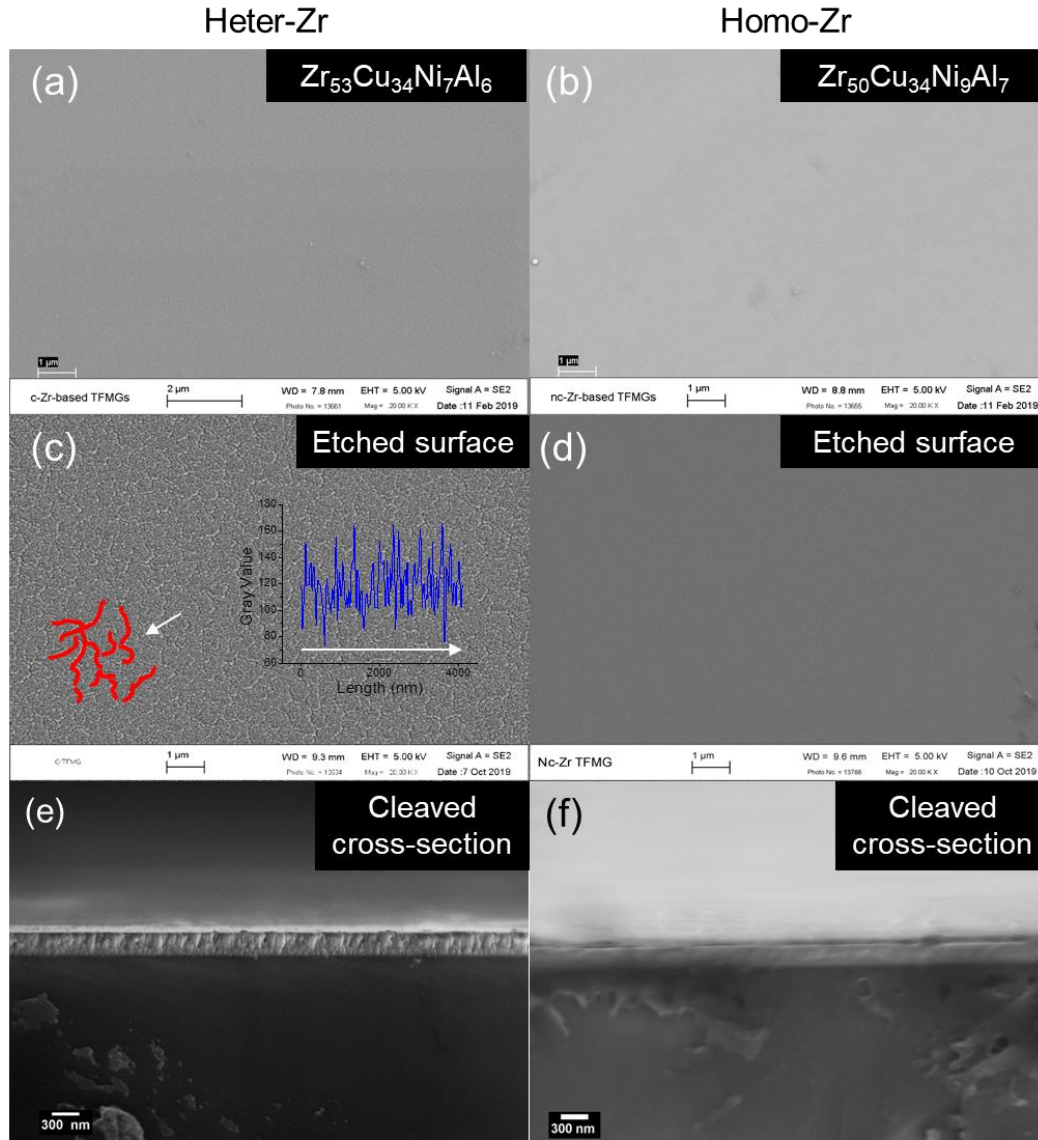


Figure 2.2. SEM images of (a, b) as-deposited surface (c, d) etched surface and (e, f) cross section after cleaving of heter-Zr and homo-Zr TFMG samples. Inset line profile in (c) shows the greyscale profile measured along the horizontal white arrow direction.

The microstructure of thin films deposited by PVD is often found to be dominated

by growth instabilities originating from a competition between surface diffusion and self shadowing, which can be tailored by controlling various deposition parameters such as deposition angle, substrate rotation, and the working pressures of Ar [36,37,43]. For example, Denis et al. [43] studied the effects of different working pressures of Ar from 0.4 to 10 Pa, and observed a thin film growth mode transition in Au-based thin film metallic glasses. As reported in previous research [44], under higher Ar working pressure, the probability of ion collisions between Ar and deposited elements is increased, resulting in more cluster growth. Under low Ar working pressure, the kinetic energy of atoms will be well reserved to overcome the shadowing effect (i.e. adatoms transferring from surface peaks to valleys), causing the formation of more homogeneous microstructure [43,45]. In addition, high working pressure can minimize the preferential ejection effect during sputtering owing to the diverse mass of the sputtering elements, resulting in slightly higher Zr concentration in the heter-Zr sample [44].

2.3.2. Nanomechanical properties

The hardness and elastic modulus of both samples were obtained after a series of nanoindentation tests under 2-3 mN normal load. These normal loads were chosen to maximize the indentation depth (to avoid indentation size effect) [46,47] yet minimize the substrate effect based on the thin film thickness. The typical indentation depths of both samples were around 30 nm. Fig. 2.3 and Table 2.3 summarize the mechanical properties of both sample sets. Both hardness (H) and elastic modulus (E) values

obtained are comparable to those reported before for similar Zr-based TFMGs or BMGs [48,49]. It can be also seen that the heter-Zr samples exhibit lower H and higher E values than those of homo-Zr samples. The contradictory mechanical properties (i.e. higher elastic modulus but lower hardness) of heter-Zr could not be explained using a simple rule of mixture (ROM) of modulus and hardness [50]. The difference in modulus could be related to the different relaxation state of the glassy films, consistent with prior report [51]. Upon deposition, the heter-Zr samples produced by higher Ar working pressure (lower kinetic energy of deposition) possess a longer time for the deposited atoms to relax, reaching a lower energy state that gives rise to a higher modulus. The homo-Zr samples, on the other hand, involve relatively fast surface diffusion of the deposited atoms, retaining a higher energy state and thus a lower modulus. In addition, the smaller average interatomic distance (d/K) in heter-Zr could also contribute to its higher modulus than homo-Zr [52]. According to the diatomic gas model [53], the average interatomic distance (d/K) can be measured from XRD results following $K\lambda = 2d\sin\theta_m$, where λ is the wavelength Cu-K α (0.154 nm), θ_m is the angle of the broad peak, d is the atomic spacing of a diatomic gas, and K is assumed to be an unknown constant for an amorphous solid ($K = 1.23$ for a diatomic gas). The average interatomic distance of heter-Zr ($d/K \sim 0.244$) is smaller than that of homo-Zr ($d/K \sim 0.247$), indicating denser atomic packing state as well as to stronger atomic interaction in heter-Zr.

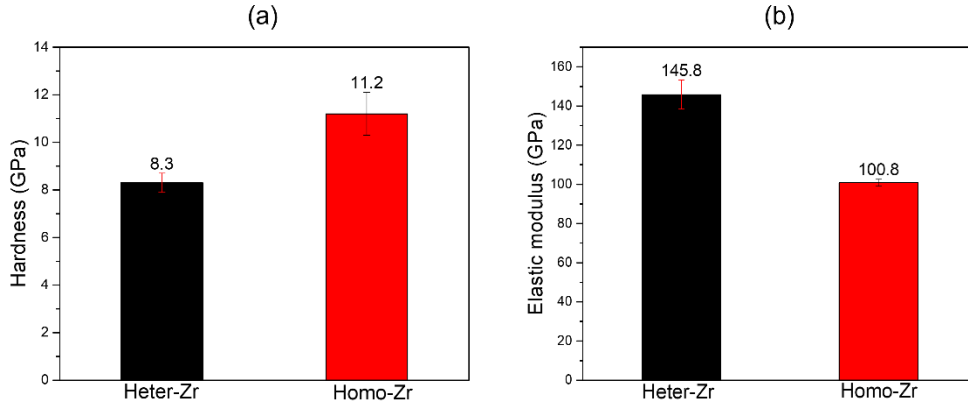


Figure 2.3. Summary of (a) hardness and (b) elastic modulus of heter-Zr and homo-Zr TFMGs measured from nanoindentation tests.

On the other hand, the difference in hardness speaks to the importance of nanoscale chemical variation induced by processing. Such observations are in qualitative agreement with prior experimental and simulation work of Wang et al. [29,54]. Notably, for spatially homogenous MG samples the plastic deformation is controlled by stress driven nucleation of a catastrophic shear band, which requires higher stress and leads to brittle failure, consistent with our results of homo-Zr. As the spatial heterogeneity increases, the deformation mechanism transforms to strain percolation of multiple shear bands from local soft regions, resulting in a decrease in strength (or hardness) and an increase in ductility, similar to those seen in heter-Zr films. Furthermore, the different elastic modulus mismatch between the thin film and substrate could be another factor for the different ductility of the two samples [48]. The elastic modulus of standard Si is 187 ± 8 GPa, exhibiting a lower elastic modulus mismatch with heter-Zr ($E_{\text{heter-Zr}} = 145.8 \pm 7.36$ GPa) than with homo-Zr ($E_{\text{homo-Zr}} = 100.8 \pm 1.8$ GPa). More compatible elastic modulus between the thin film and the

substrate can reduce the interfacial stress discontinuities and minimize brittle failure [55].

Based on the mechanical differences, heter-Zr and homo-Zr samples are expected to lead to different tribological behavior. While bulk materials' wear rate is typically inversely related to their surface hardness according to the classical Archard's law [56], for thin film materials, it has been reported that the ratio between hardness and elastic modulus (H/E) serves as a better indicator for wear resistance. Typically a higher H/E ratio is associated with better wear resistance [48]. It can be seen from Table 2.3 that the H/E value of the homo-Zr sample (0.1) is higher than that of heter-Zr sample (0.06), suggesting a better wear resistance of the former. As shown in the next section, such a prediction is in agreement with the dry scratch test results.

2.3.3. Corrosion behavior

Fig. 2.4(a) shows the typical PD curves of both samples tested in 0.6 M NaCl solution. Table 2.2 summarizes all measured electrochemical parameters from the PD tests. The polarization resistance (R_p) was calculated by the Stern-Gray equation as [57].

$$i_{\text{corr}} = \frac{\beta_a \beta_c}{2.3 \times R_p (\beta_a + \beta_c)}$$

where β_a and β_c are the slopes of the anodic and cathode curve respectively. It can be seen that while both samples exhibit similar OCP, i_{corr} of homo-Zr is slightly lower than that of heter-Zr. The homo-Zr sample exhibited a pitting potential of ~ 1.05 V vs. Ag/AgCl, while heter-Zr showed no apparent sudden increase of corrosion current as

those seen at pitting potential of homo-Zr in the whole scan range. Such results suggest that the heter-Zr samples exhibit a higher pitting resistance than its homo-Zr counterpart in 0.6 M NaCl aqueous solution albeit its slightly lower i_{corr} . Visual inspections (results not shown here) of both samples after tribocorrosion at anodic potential from the next section further confirms the higher pitting tendency of homo-Zr than heter-Zr. Such observation contradicts the common belief that chemical heterogeneity imposes detrimental effects on corrosion resistance [58], but is in agreement with several prior research that indicates corrosion resistance of MGs containing passive elements increase after structural relaxation [31,59,60] due to the releasing of internal stress [31] and reduction of free volume in the as-prepared amorphous alloy [59]. Indeed, there is growing evidence to indicate that mild nanoscale chemical heterogeneity, introduced either during processing or low temperature annealing, behaves rather differently from their micron-sized counterparts in affecting corrosion resistance [61 – 63]. For example, Asami et al. [61] found that the corrosion resistance of amorphous Cr-Zr alloys was improved via nano precipitation when the size of Zr precipitates is less than 20 nm. An increased Cr concentration was found in the passive film to enhance its protectiveness over the whole surface. Interestingly, a similar critical size of ~20 nm (of Al-rich precipitate) was also identified in amorphous Al-Cr system [63], above which the corrosion resistance decreases. In this work, we assume that the higher resistance of heter-Zr to pitting initiation and growth is attributed to the uneven distribution of elements and the Zr-enriched boundary structure (i.e. marked by the red lines in Fig. 2.2(c)) [62]. Under neutral pH, according to the thermodynamic calculations of

dissolved ions vs. oxide stability (i.e. the Pourbaix diagram), the passive layers of both alloys are assumed to contain primarily ZrO_2 and Al_2O_3 . Since Al content is small in the alloy, and remains close to $\sim 6.5\text{--}6.9$ at. % in both homo-Zr, its effects on the different corrosion behavior is neglected here. The slight enrichment of Zr in the boundaries of heter-Zr (~ 2.5 at. % higher than that of homo-Zr) could promote the formation of a more compact ZrO_2 structure on the surface. Such 'network' of Zr-rich boundaries may act similarly (probably to a much less extent) as grain boundaries in crystalline passive alloys. For crystalline passive alloys, it is thought that smaller grain size, hence higher grain boundary density influences corrosion resistance by affecting the rate of ion transport through the passive film, as well as the passive film dissolution rate [64]. For nanocrystalline materials that have a much higher grain boundary density at the surface compared to their microcrystalline counterparts, these boundaries lead to higher average surface reactivity through increased electron state density and diffusional defect transport.

To further quantify the differences in the passive film property, MS analysis was conducted for five days for homo-Zr and heter-Zr samples, as shown in Fig. 2.4(b). The charge carrier density was calculated as [65]:

$$\frac{1}{C^2} = \frac{\pm 2}{\epsilon \epsilon_0 e N} \left(E - E_{fb} - \frac{kT}{q} \right)$$

where C is the capacitance, ϵ is the passive film dielectric constant, ϵ_0 is the permittivity of vacuum (8.85×10^{-14} F/cm), N is the charge carrier concentration, E is the applied potential, E_{fb} is the flat band potential, k is the Boltzmann constant (1.38×10^{-23} JK⁻¹), T is the absolute temperature and q is the elementary charge (1.602×10^{-19}

C). It can be seen that the heter-Zr samples contain $\sim$ five orders of magnitude lower defect density than homo-Zr. Since the defect density in the passive film is proportional to the sample's pitting susceptibility, a much higher pitting resistance is expected in heter-Zr.

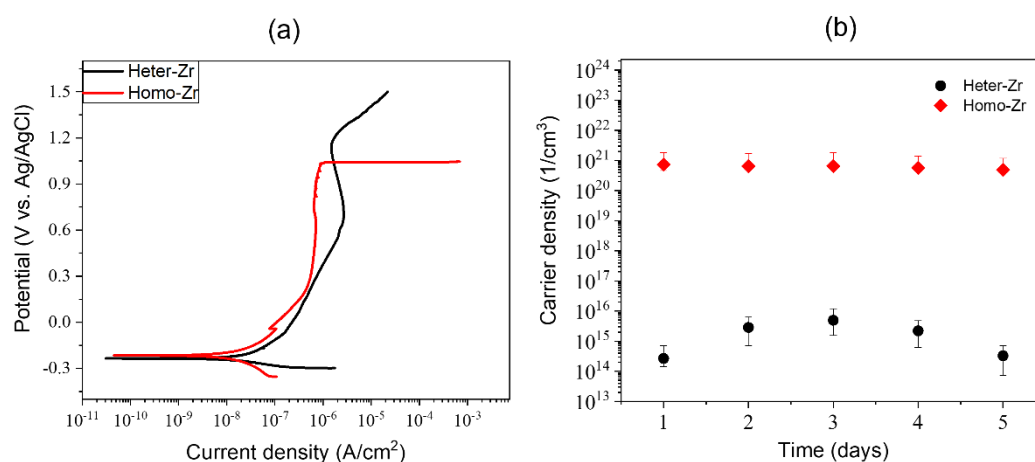


Figure 2.4. (a) Typical potentiodynamic polarization curves, and (b) time evolution of defect density of heter-Zr and homo-Zr samples in 0.6 M NaCl aqueous solution. Error bars in (b) represent one standard deviation from all repeated tests.

Table 2.2 Summary of electrochemical parameters from PD tests of homo-Zr and heter-Zr samples in 0.6 M NaCl.

Sample ID	E_{corr} (mV)	E_{pit} (mV)	$E_{\text{pit}} - E_{\text{corr}}$ (mV)	i_{corr} (nA/cm ²)	β_a (V/decade)	β_c (V/decade)	R_p ($\times 10^6 \Omega \text{ cm}^2$)
Homo-Zr	-204.3 ± 11.2	0.98 ± 0.1	205.3 ± 11.2	20.98 ± 25.6	0.61 ± 0.47	0.59 ± 0.46	2.17 ± 0.43
Heter-Zr	-202.7 ± 45.5	NA	NA	23.69 ± 12.5	0.24 ± 0.03	0.08 ± 0.01	1.68 ± 1.43

2.3.4. Dry scratch test

The surface morphologies of both samples after dry scratch test are shown in Fig. 2.5(a) and (b). Worn surfaces of both samples are quite smooth. On the worn surface of heter-Zr samples, pile-ups could be seen at the edges of the wear track, indicating extensive plastic deformation during abrasive wear [66]. On the other hand, no visible pile-up could be seen on homo-Zr samples. Instead, loose wear debris was frequently observed along the side of the wear track, indicating a lack of plastic deformation and more brittle failure on the surface, consistent with its higher hardness and lower compliance (lower E), and more brittle fracture than its heter-Zr counterparts. Cross-sectional SEM images (not shown) reveal that the heter-Zr sample exhibits a deeper and slightly narrower wear track than homo-Zr sample, ultimately resulting in higher material volume loss than homo-Zr sample, as summarized in Fig. 2.8, in agreement with the H/E ratio prediction [48]. The coefficient of friction (COF) of both samples is shown in Fig. 2.5(c). It can be seen that the heter-Zr sample exhibits a higher average COF (~ 0.46) than that of homo-Zr sample (~ 0.37) during dry scratch test, consistent with its higher wear rate [14].

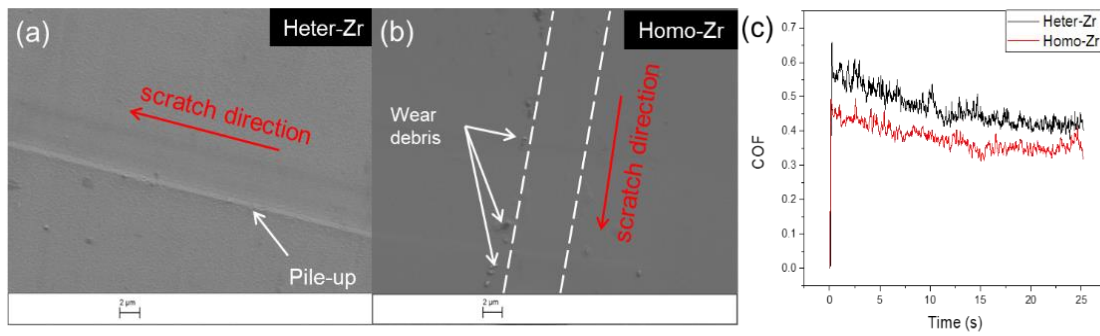


Figure 2.5. (a, b) Surface SEM images and (c) COF of heter-Zr and homo-Zr samples after dry scratch test. Dashed lines in (b) indicate the edges of the wear track.

2.3.5. Tribocorrosion behavior

Fig. 2.6(a) shows the evolution of current during the tribocorrosion tests of both samples. The dashed lines mark the start and finish of the scratch test. It can be seen that the overall current density of both samples is much higher under the anodic potential (0.4 V above OCP) than that under OCP. Under the anodic potential, the current remained almost constant before the indenter probed the surface, and shifted to more positive values during scratching, indicating positive wear-corrosion synergy (i.e. wear accelerate corrosion). Such positive shift of current is likely due to the depassivation on the wear track, where the surface passive film is locally destroyed or removed, exposing the more active, and unprotected thin film material. Once the test was finished, the current of both samples recovered their original state, indicating repassivation on the wear track. It is noted that the current evolution of homo-Zr under the anodic potential shows an abrupt increase before the initiation of the scratch test

due to early film dissolution (indicated by arrow in Fig. 2.6(a)). In addition, film delamination was observed by visual inspection at the end of the test, hence their results are not included in Fig. 2.6(b) and Fig. 2.7 later on. Overall, the much higher corrosion current rise during scratch as well as early film dissolution of homo-Zr indicates its poorer tribocorrosion resistance than that of heter-Zr under the testing condition.

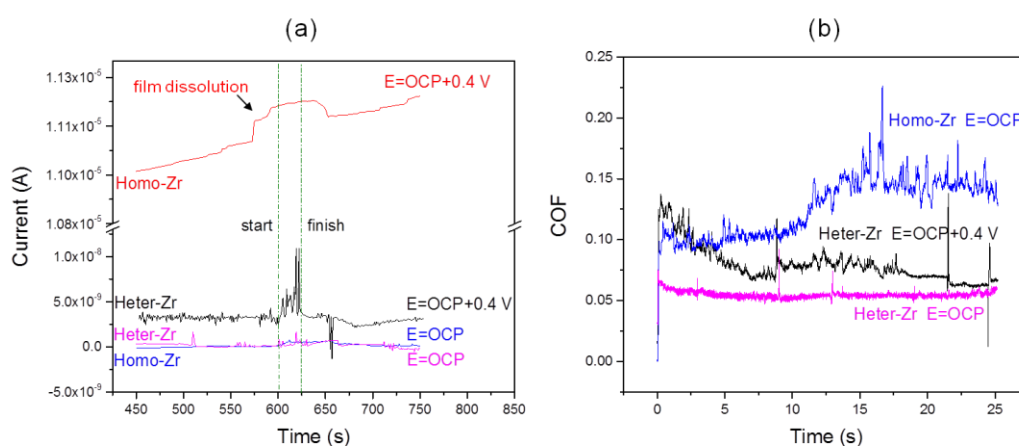


Figure 2.6. (a) Current evolution and (b) coefficient of friction (COF) of heter-Zr and homo-Zr samples during tribocorrosion under OCP and anodic applied potential (400 mV above OCP). Dashed lines in (a) mark the start and finish of the scratch by the counterbody.

During the tribocorrosion test, COF of both samples was much lower than that of the dry scratch test, as shown in Fig. 2.6(b), probably due to the lubrication effects of the electrolyte [67]. COF of homo-Zr under the anodic potential is not presented here due to film delamination during tribocorrosion. Interestingly, the average COF values of heter-Zr sample (~ 0.08 under OCP + 0.4 V and ~ 0.05 under OCP) is lower than that of homo-Zr sample (~ 0.13), suggesting that its passive film is more effective in

reducing friction. This is rather surprising as ZrO_2 has very low ionic potential and is generally associated with higher friction (i.e. abrasive rather than lubricious) [68]. More work is required to quantify the composition, structure, and properties of these passive films, which is left for future work.

Fig. 2.7 shows the surface SEM images of both samples after the tribocorrosion tests. The worn surfaces of heter-Zr and homo-Zr samples under OCP condition, as shown in Fig. 2.7(a) and (b), are similar to that observed under dry scratch test. Cross-sectional SEM images in Fig. 2.7(d-f) show that there is very little material loss for both samples and no film delamination. Table 2.3 summarizes the wear track dimensions and the calculated material volume loss. Under OCP, a narrower and shallower wear track was observed in heter-Zr, resulting in a tribocorrosion rate $\sim 38\%$ lower in heter-Zr sample than homo-Zr sample, as shown in Fig. 2.8. Under the anodic potential (0.4 V above OCP), the wear track of heter-Zr sample (Fig. 2.7(c)) appears to be deeper than that under OCP, with extensive shear bands formation, typical for MGs after plastic deformation [28,49,50]. EDS analysis (Fig. 2.7(a-c) insets) reveals that all elements including oxygen are uniformly distributed on the worn surfaces. A much higher oxygen concentration was observed on the wear track of heter-Zr under the anodic potential than under OCP. In addition to the higher oxidation driving force at the anodic potential, it is likely that the presence of extensive shear bands with excess free volume also promotes the surface chemical reactivity with oxygen [59].

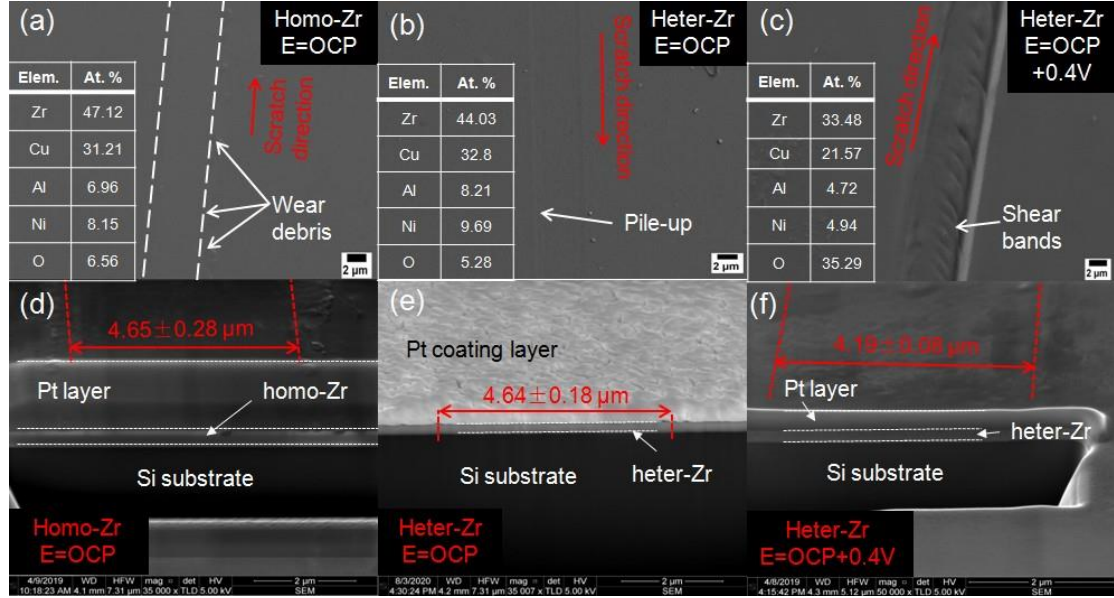


Figure 2.7. (a-c) Surface and (d-f) cross-sectional SEM images of homo-Zr and heter-Zr samples after tribocorrosion test (OCP for homo-Zr; OCP and OCP + 0.4 V anodic applied potential for heter-Zr). Dashed lines in (a, d-f) indicate the edges of the wear track. Insets in (a-c) show the element compositions (at. %) obtained by EDS analysis on the wear tracks.

To further quantify chemical wear during tribocorrosion under the anodic potential, the amount of material loss due to corrosion was calculated for both samples using Faraday's law as $V_{\text{chem}} = QM/nF\rho$, where Q is the total charge transferred from the start to finish during tribocorrosion test at $E = 0.4$ V above OCP, M is the atomic mass (≈ 73.77 g/mol), n is the valence (≈ 1.81), F is the Faraday's constant (96,500 C/mol), and ρ is the density (≈ 7.13 g/cm³) of Zr-based TFMG [69]. Fig. 2.8 shows the chemical wear (V_{chem}) of heter-Zr sample is around 4.62×10^{-9} mm³, which is about two orders of magnitude lower than that of homo-Zr sample ($V_{\text{chem}} = 1.43 \times 10^{-7}$ mm³). The chemical wear during tribocorrosion was dominated by their respective corrosion

properties, where homo-Zr exhibited higher material loss than heter-Zr, in consistent with their pure corrosion behavior. Overall, the results in this section showed that nanoscale chemical heterogeneity affects both the mechanical and electrochemical properties of Zr-TFMGs, which act synergistically to result in a better tribocorrosion resistance in heter-Zr than homo-Zr sample under the selected testing conditions.

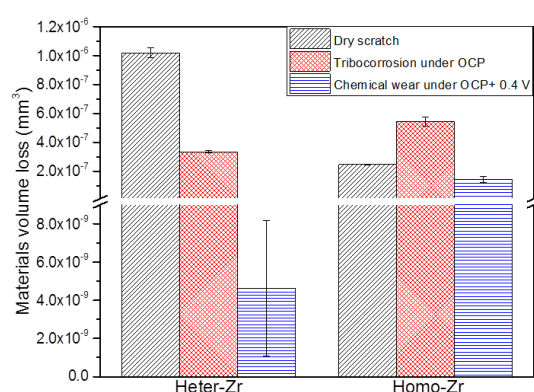


Figure 2.8. Summary of material volume loss of heter-Zr and homo-Zr samples after dry scratch and tribocorrosion tests under OCP and anodic potentials. Error bar represents one standard deviation from all repeated tests.

Table 2.3 Summary of mechanical properties, dry scratch, and tribocorrosion test results of heter-Zr and homo-Zr samples. H and E represent hardness and elastic modulus respectively, obtained from nanoindentation tests. d, w, and V represents the wear track depth width, and total material loss in volume respectively, measured after dry scratch and tribocorrosion tests.

Sample ID	H (GPa)	E (GPa)	H/E	Dry Scratch			Tribocorrosion			
				d (x10 ⁻⁵ mm)	w (x10 ⁻³ mm)	V (x10 ⁻⁷ mm ³)	d (x10 ⁻⁵ mm)	w (x10 ⁻³ mm)	V (x10 ⁻⁷ mm ³)	Corrosion potential
Heter-Zr	8.3 ± 0.4	145.8 ± 7.4	0.06	5.7 ± 1.4	3.59 ± 0.1	10.2 ± 0.3	2.7 ± 1.1	4.19 ± 0.08	5.66 ± 0.12	OCP+0.4V
							1.4 ± 0.7	4.64 ± 0.18	3.34 ± 0.1	OCP
Homo-Zr	11.2 ± 0.9	100.8 ± 1.8	0.1	1.4 ± 0.6	3.66 ± 0.5	2.47 ± 0.03	2.3 ± 0.8	4.65 ± 0.28	5.43 ± 0.33	OCP

2.4. Conclusions

In this work, the effects of chemical heterogeneity on the wear, corrosion, and tribocorrosion resistance of magnetron sputtered ZrCuNiAl TFMGs were evaluated by comparing two sets of sample: heter-Zr and homo-Zr. The presence of nanoscale (~ 413 nm) chemical heterogeneity ($\sim 1.1\%$ Zr and 0.5% Cu) was found to significantly affect the mechanical properties, resulting in lower hardness and higher ductility in heter-Zr than homo-Zr. As a result, the dry scratch wear resistance of homo-Zr was higher than that of heter-Zr samples. On the other hand, such nanoscale chemical heterogeneity affects the pitting corrosion in the opposite trend, where heter-Zr was found to outperform homo-Zr. Mott-Schottky analysis showed that the presence of nanoscale chemical fluctuations of Zr and Cu at the surface promoted the formation of a more protective passive film with lower defect density during corrosion. Finally, the tribocorrosion resistance of heter-Zr samples was found to be better than that of homo-Zr sample while the chemical wear was dominated by their respective electrochemical properties. The results of the present work may shed light on future structural optimization strategies for improving reliability of TFMGs under combined surface stress and corrosion conditions.

References:

1. L. Tian, Y.Q. Cheng, Z.W. Shan, J. Li, C.C. Wang, X.D. Han, J. Sun, E. Ma, Approaching the ideal elastic limit of metallic glasses, *Nat. Commun.* 3 (2012).
2. H. Ma, J. Xu, E. Ma, Mg-based bulk metallic glass composites with plasticity and

- high strength, Appl. Phys. Lett. 83 (14) (2003) 2793 – 2795.
3. J. Eckert, J. Das, K.B. Kim, F. Baier, M.B. Tang, W.H. Wang, Z.F. Zhang, High strength ductile Cu-base metallic glass, Intermetallics 14 (8) (2006) 876 – 881.
 4. D.R. Maddala, A. Mubarak, R.J. Hebert, Sliding wear behavior of Cu₅₀Hf_{41.5}Al_{8.5} bulk metallic glass, Wear 269 (7) (2010) 572 – 580.
 5. R. Salehan, H.R. Shahverdi, R. Miresmaeili, Effects of annealing on the tribological behavior of Zr₆₀Cu₁₀Al₁₅Ni₁₅ bulk metallic glass, J. Non-Cryst. Solids 517 (2019) 127 – 136.
 6. M. Gao, W. Lu, B. Yang, S. Zhang, J. Wang, High corrosion and wear resistance of Al-based amorphous metallic coating synthesized by HVAF spraying, J. Alloys Compd. 735 (2018) 1363 – 1373.
 7. G. Perumal, H.S. Grewal, A. Ayyagari, S. Mukherjee, H.S. Arora, Enhancement in bio-corrosion resistance of metallic glass by severe surface deformation, Appl. Surf. Sci. 487 (2019) 1096 – 1103.
 8. T.C. Hufnagel, C.A. Schuh, M.L. Falk, Deformation of metallic glasses: recent developments in theory, simulations, and experiments, Acta Mater. 109 (2016) 375 – 393.
 9. J.J. Kruzic, Bulk metallic glasses as structural materials: a review, Adv. Eng. Mater. 18 (8) (2016) 1308 – 1331.
 10. A. Inoue, N. Nishiyama, New bulk metallic glasses for applications as magnetosensing, chemical, and structural materials, MRS Bull. 32 (8) (2007) 651 – 658.

11. M.F. Ashby, A.L. Greer, Metallic glasses as structural materials, *Scr. Mater.* 54 (3) (2006) 321 – 326.
12. S.X. Song, H. Bei, J. Wadsworth, T.G. Nieh, Flow serration in a Zr-based bulk metallic glass in compression at low strain rates, *Intermetallics* 16 (6) (2008) 813 – 818.
13. C.C. Yu, C.M. Lee, J.P. Chu, J.E. Greene, P.K. Liaw, Fracture-resistant thin-film metallic glass: ultra-high plasticity at room temperature, *Apl Mater* 4 (11) (2016).
14. J.P. Chu, J.S.C. Jang, J.C. Huang, H.S. Chou, Y. Yang, J.C. Ye, Y.C. Wang, J.W. Lee, F.X. Liu, P.K. Liaw, Y.C. Chen, C.M. Lee, C.L. Li, C. Rullyani, Thin film metallic glasses: unique properties and potential applications, *Thin Solid Films* 520 (16) (2012) 5097 – 5122.
15. J.P. Chu, T.Y. Liu, C.L. Li, C.H. Wang, J.S.C. Jang, M.J. Chen, S.H. Chang, W.C. Huang, Fabrication and characterizations of thin film metallic glasses: antibacterial property and durability study for medical application, *Thin Solid Films* 561 (2014) 102 – 107.
16. W. Diyatmika, J.P. Chu, B.T. Kacha, C.C. Yu, C.M. Lee, Thin film metallic glasses in optoelectronic, magnetic, and electronic applications: A recent update, *Curr Opin Solid St M* 19 (2) (2015) 95 – 106.
17. C.N. Cai, C. Zhang, Y.S. Sun, H.H. Huang, C. Yang, L. Liu, ZrCuFeAlAg thin film metallic glass for potential dental applications, *Intermetallics* 86 (2017) 80 – 87.
18. J.C. Ye, J.P. Chu, Y.C. Chen, Q. Wang, Y. Yang, Hardness, yield strength, and plastic flow in thin film metallic-glass, *J. Appl. Phys.* 112 (5) (2012).

19. M.H. Chuang, C. Wang, B.K. Chao, W.L. Kao, J.J. Shyue, C.H. Hsueh, Mechanical properties and microstructure of Zr-Ti-Ni thin film metallic glasses modified with minor SF₆, *Compos Part B-Eng* 129 (2017) 243 – 250.
20. Y.L. Deng, J.W. Lee, B.S. Lou, J.G. Duh, J.P. Chu, J.S.C. Jang, The fabrication and property evaluation of Zr-Ti-B-Si thin film metallic glass materials, *Surf. Coat. Technol.* 259 (2014) 115 – 122.
21. Y. Wang, L.L. Shi, D.L. Duan, S. Li, J. Xu, Tribological properties of Zr₆₁Ti₂Cu₂₅Al₁₂ bulk metallic glass under simulated physiological conditions, *Mat Sci Eng C-Mater* 37 (2014) 292 – 304.
22. H.W. Jin, R. Ayer, J.Y. Koo, R. Raghavan, U. Ramamurty, Reciprocating wear mechanisms in a Zr-based bulk metallic glass, *J. Mater. Res.* 22 (2) (2007) 264 – 273.
23. P.H. Tsai, T.H. Li, K.T. Hsu, J.W. Chiou, J.S.C. Jang, J.P. Chu, Effect of coating thickness on the cutting sharpness and durability of Zr-based metallic glass thin film coated surgical blades, *Thin Solid Films* 618 (2016) 36 – 41.
24. P.J. Blau, Friction and wear of a Zr-based amorphous metal alloy under dry and lubricated conditions, *Wear* 250 (2001) 431 – 434.
25. X.Y. Fu, D.A. Rigney, M.L. Falk, Sliding and deformation of metallic glass: experiments and MD simulations, *J. Non-Cryst. Solids* 317 (1 – 2) (2003) 206 – 214.
26. E. Ma, J. Ding, Tailoring structural inhomogeneities in metallic glasses to enable tensile ductility at room temperature, *Mater. Today* 19 (10) (2016) 568 – 579.
27. J. Ding, S. Patinet, M.L. Falk, Y.Q. Cheng, E. Ma, Soft spots and their structural

- signature in a metallic glass, *Proc. Natl. Acad. Sci. U. S. A.* 111 (39) (2014) 14052 – 14056.
28. R. Rashidi, M. Malekan, R. Gholamipour, Microstructure and mechanical properties of a Cu-Zr based bulk metallic glass containing atomic scale chemical heterogeneities, *Mat Sci Eng a-Struct* 729 (2018) 433 – 438.
 29. N. Wang, J. Ding, F. Yan, M. Asta, R.O. Ritchie, L. Li, Spatial correlation of elastic heterogeneity tunes the deformation behavior of metallic glasses, *Npj Comput Mater* 4 (2018).
 30. S.D. Zhang, Z.M. Wang, X.C. Chang, W.L. Hou, J.Q. Wang, Identifying the role of nanoscale heterogeneities in pitting behaviour of Al-based metallic glass, *Corros. Sci.* 53 (9) (2011) 3007 – 3015.
 31. Y. Masumoto, A. Inoue, A. Kawashima, K. Hashimoto, A.P. Tsai, T. Masumoto, The effect of structural relaxation on the corrosion behavior of amorphous (Ni-Pd) 82si18 alloys, *J. Non-Cryst. Solids* 86 (1 – 2) (1986) 121 – 136.
 32. U.K. Mudali, S. Baunack, J. Eckert, L. Schultz, A.J.J.O.A. Gebert, Compounds, pitting corrosion of bulk glass-forming zirconium-based alloys, *J. Alloys Compd.* 377 (1 – 2) (2004) 290 – 297.
 33. U. Koster, D. Zander, Triwikantoro, A. Rudiger, L. Jastrow, Environmental properties of Zr-based metallic glasses and nanocrystalline alloys, *Scr. Mater.* 44 (8 – 9) (2001) 1649 – 1654.
 34. C.W. Chu, J.S.C. Jang, S.M. Chiu, J.P. Chu, Study of the characteristics and corrosion behavior for the Zr-based metallic glass thin film fabricated by pulse

- magnetron sputtering process, *Thin Solid Films* 517 (17) (2009) 4930 – 4933.
35. D. Zander, U.J.M.S. Koster, E. A, Corrosion of amorphous and nanocrystalline Zr based alloys, *Mater. Sci. Eng. A* 375 (2004) 53 – 59.
 36. S.G. Mayr, K. Samwer, Tailoring the surface morphology of amorphous thin films by appropriately chosen deposition conditions, *J. Appl. Phys.* 91 (5) (2002) 2779 – 2784.
 37. K. Khojier, H. Savaloni, E. Shokrai, Z. Dehghani, N.Z. Dehnavi, Influence of argon gas flow on mechanical and electrical properties of sputtered titanium nitride thin films, *J Theor Appl Phys* 7 (1) (2013).
 38. J.P. Chu, C.Y. Wang, L.J. Chen, Q. Chen, Annealing-induced amorphization in a sputtered glass-forming film: in-situ transmission electron microscopy observation, *Surf. Coat. Technol.* 205 (8 – 9) (2011) 2914 – 2918.
 39. W.C. Oliver, G.M. Pharr, An improved technique for determining hardness and elastic-modulus using load and displacement sensing indentation experiments, *J. Mater. Res.* 7 (6) (1992) 1564 – 1583.
 40. G.M. Pharr, J.H. Strader, W.C. Oliver, Critical issues in making small-depth mechanical property measurements by nanoindentation with continuous stiffness measurement, *J. Mater. Res.* 24 (3) (2009) 653 – 666.
 41. J.H. Chu, H.W. Chen, Y.C. Chan, J.G. Duh, J.W. Lee, J. Jang, Modification of structure and property in Zr-based thin film metallic glass via processing temperature control, *Thin Solid Films* 561 (2014) 38 – 42.
 42. K.B. Kim, J. Das, F. Baier, M.B. Tang, W.H. Wang, J. Eckert, Heterogeneity of a

- Cu_{47.5}Zr_{47.5}Al₅ bulk metallic glass, *Appl. Phys. Lett.* 88 (5) (2006).
43. P. Denis, S. Liu, H. Fecht, Growth mode transition in Au-based thin film metallic glasses, *Thin Solid Films* 665 (2018) 29–35.
 44. Y. Liu, T. Fujita, A.E. Hirata, S. Li, H. Liu, W. Zhang, A. Inoue, M.J.I. Chen, Deposition of multicomponent metallic glass films by single-target magnetron sputtering, *Intermetallics* 21 (1) (2012) 105–114.
 45. S.V. Ketov, R. Joksimovic, G. Xie, A. Trifonov, K. Kurihara, D.V.J.H. Louzguine-Luzgin, Formation of nanostructured metallic glass thin films upon sputtering, *Heliyon* 3 (1) (2017) e00228.
 46. S. Qu, Y. Huang, W.D. Nix, H. Jiang, F. Zhang, K.C. Hwang, Indenter tip radius effect on the Nix-Gao relation in micro- and nanoindentation hardness experiments, *J. Mater. Res.* 19 (11) (2004) 3423–3434.
 47. R. Yang, Q. Zhang, P. Xiao, J. Wang, Y.L. Bai, Two opposite size effects of hardness at real nano-scale and their distinct origins, *Sci. Rep.* 7 (2017).
 48. A. Leyland, A. Matthews, On the significance of the H/E ratio in wear control: a nanocomposite coating approach to optimised tribological behaviour, *Wear* 246 (1–2) (2000) 1–11.
 49. D.T.A. Matthews, V. Ocelik, J.T.M. de Hosson, Tribological and mechanical properties of high power laser surface-treated metallic glasses, *Mat Sci Eng a-Struct* 471 (1–2) (2007) 155–164.
 50. J. Kim, H.S. Oh, W. Kim, P.-P. Choi, D. Raabe, E.S.J.A.M. Park, Modulation of plastic flow in metallic glasses via nanoscale networks of chemical heterogeneities,

- Acta Mater. 140 (2017) 116–129.
51. W.H. Wang, Dynamic relaxations and relaxation-property relationships in metallic glasses, Prog. Mater. Sci. 106 (2019).
 52. A. Obeydavi, A. Shafyei, A. Rezaeian, P. Kameli, J.W. Lee, Microstructure, mechanical properties and corrosion performance of Fe₄₄Cr₁₅Mo₁₄Co₇C₁₀B₅Si₅ thin film metallic glass deposited by DC magnetron sputtering, J. Alloys Compd. 527 (2020) 119718.
 53. A. Caron, R. Wunderlich, D.V. Louzguine-Luzgin, G. Xie, A. Inoue, H.J. Fecht, Influence of minor aluminum concentration changes in zirconium-based bulk metallic glasses on the elastic, anelastic, and plastic properties, Acta Mater. 58 (6) (2010) 2004–2013.
 54. N. Wang, J. Ding, P. Luo, Y. Liu, L. Li, F.J.M.R.L. Yan, Chemical variation induced nanoscale spatial heterogeneity in metallic glasses, Materials Research Letters 6 (12) (2018) 655–661.
 55. J. Lee, M.-L. Liou, J.-G.J.S. Duh, C. Technology, The development of a Zr-Cu-Al-Ag- N thin film metallic glass coating in pursuit of improved mechanical, corrosion, and antimicrobial property for bio-medical application, Surf. Coat. Technol. 310 (2017) 214–222.
 56. J.F. Archard, Contact and rubbing of flat surfaces, J. Appl. Phys. 24 (8) (1953) 981–988.
 57. M. Stern, A.L.J.J.o.t.e.s. Geary, Electrochemical polarization I. A theoretical analysis of the shape of polarization curves, J. Electrochem. Soc. 104(1) (1957) 56–

- 63.
58. M.J. Duarte, A. Kostka, J.A. Jimenez, P. Choi, J. Klemm, D. Crespo, D. Raabe, F.U.J.A.m. Renner, Crystallization, phase evolution and corrosion of Fe-based metallic glasses: an atomic-scale structural and chemical characterization study, *Acta Mater.* 71 (2014) 20–30.
59. W.H. Jiang, F. Jiang, B.A. Green, F.X. Liu, P.K. Liaw, H. Choo, K.Q. Qiu, Electrochemical corrosion behavior of a Zr-based bulk-metallic glass, *Appl. Phys. Lett.* 91 (4) (2007).
60. F.F. Marzo, A.R. Pierna, M.M. Vega, Effect of irreversible structural relaxation on the electrochemical behavior of Fe_{78-x}Si₁₃B₉Cr(*x*=3,4,7) amorphous alloys, *J. Non-Cryst. Solids* 329 (1–3) (2003) 108–114.
61. K. Asami, B.-P. Zhang, M. Mehmood, H. Habazaki, K.J.S.m. Hashimoto, Effects of nanoscale heterogeneity on the corrosion behavior of non-equilibrium alloys, *Scr. Mater.* 44 (8–9) (2001) 1655–1658.
62. W.C. Johnson, P. Zhou, A. Lucente, J.J.M. Scully, M.T. A, Composition profiles around solute-lean, spherical nanocrystalline precipitates in an amorphous matrix: implications for corrosion resistance, *Metall. Mater. Trans. A* 40 (4) (2009) 757–767.
63. M. Mehmood, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami, K. Hashimoto, The effect of heat treatment on the corrosion behavior of sputter-deposited aluminum-chromium alloys, *Corros. Sci.* 41 (3) (1999) 477–499.
64. K.D. Ralston, N. Birbilis, Effect of grain size on corrosion: a review, *Corrosion-Us*

- 66(7) (2010).
65. J. Chen, J. Xiao, J. Poplawsky, F.M. Michel, C. Deng, W.J.C.S. Cai, The origin of passivity in aluminum-manganese solid solutions, *Corros. Sci.* (2020) 108749.
66. B. Sun, Y. Hu, D. Wang, Z. Zhu, P. Wen, W. Wang, C. Liu, Y.J.A.M. Yang, Correlation between local elastic heterogeneities and overall elastic properties in metallic glasses, *Acta Mater.* 121 (2016) 266–276.
67. D.D. Liang, X.S. Wei, T.C. Ma, B. Chen, H.R. Jiang, Y. Dong, J. Shen, Sliding tribocorrosion behavior of Fe-based bulk metallic glass under corrosive environments, *J. Non-Cryst. Solids* 510 (2019) 62–70.
68. A. Erdemir, A crystal chemical approach to the formulation of self-lubricating nanocomposite coatings, *Surf. Coat. Technol.* 200 (5–6) (2005) 1792–1796.
69. J. Chen, W.J. Cai, Effect of scratching frequency on the tribocorrosion resistance of Al-Mn amorphous thin films, *Wear* 426 (2019) 1457–1465.

Chapter 3. Ultrahigh Tribocorrosion Resistance of Metals Enabled by Nano-layering

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3.1. Introduction

The design of new metals and alloys resistant to both wear damage and corrosion degradation becomes increasingly demanded in complex service conditions, such as biomedical implants, hydraulic systems, nuclear power plants, marine and off-shore infrastructures, etc. [1–7]. Recently, nanostructured metallic multilayers (NMMs) consisting of alternating layers of different metals or alloys have attracted significant interests due to their potential to simultaneously achieve improved mechanical and electrochemical properties compared to their monolithic counterparts [8,9]. Hence it is critical to understand how the structure and properties of the constituting materials and interfaces of NMMs can be tailored to simultaneously optimize their wear and corrosion resistance, i.e. tribocorrosion resistance. Previous research shows that the individual layer thickness (h) of NMMs governs their mechanical and tribological behavior [10–12]. The wear rate of NMMs typically increases with decreasing hardness per Archard's law [13–15], although an optimum individual layer thickness of NMM for the highest wear resistance is not known a priori [16,17]. In addition to layer thickness effect, the elastic/plastic incompatibility between the constituting materials [18], the structure and properties of the heterophase interfaces [14,19], as well as residual stress [16,20] also play important roles on the tribological response of NMMs.

Apart from their excellent mechanical and tribological properties, many NMMs exhibit improved corrosion resistance compared to their monolithic counterpart of equal thickness due to the formation of less susceptible microstructure (e.g. finer grains and smoother surfaces) and the ability to effectively block ionic diffusion due to the

presence of interfaces [8,9,21,22]. However, such low corrosion rate is often short-lived. As soon as localized corrosion penetrates through the top layer, the ensuing galvanic coupling between adjacent layers often leads to preferred corrosion of the more active layers thus destructing the overall structural integrity. For example, in Zn/Ni NMMs, only Ni layers could be found after extended corrosion testing in 5 wt.% sodium chloride solution while all Zn sublayers were dissolved [22]. Hence optimizing corrosion resistance of NMMs requires an effective strategy that minimizes the micro-galvanic coupling between the constituting layers [23].

Even though there is no unified theory at the moment, the abundant evidence above indicates exciting opportunities to optimize tribocorrosion resistance of metals by forming nanostructured multilayers. For NMMs, the individual layer thickness not only controls its mechanical response due to length-scale dependent dislocation-mediated plasticity, but also represents the wavelength of chemical modulation, hence governs its electrochemical kinetics. Recent studies show that materials' corrosion resistance could be enhanced by controlling the chemical modulation below a critical length scale on the order of a few nm. For example, Ralston et al. [24] showed that when the precipitate size is below ~4 nm in Al-Cu-Mg alloys, the precipitates become 'invisible' during corrosion, i.e., they harden the material without forming unfavorable micro-galvanic coupling with the matrix. It was suggested that a continuous protective passive film could not be formed if the chemical heterogeneity length scale exceeds this threshold. Based on these separate observations on mechanical and corrosion properties, NMMs with individual layer thickness of a few nm, can potentially allow for achieving

extensive ultra-fine chemical modulation across adjacent layers and hence represent a new class of material system for exploring fundamental chemistry and physics at the scale of a few atoms. However, the underlying deformation and degradation mechanisms of NMMs, and how the synergistic effects of the mechanical and electrochemical properties of the individual layers govern the overall tribocorrosion behavior, remains largely unknown.

This work aims to develop a fundamental understanding of equal-spaced Al/X (X = Mg, Ti, and Cu) NMMs, their structure, and their deformation and degradation mechanisms during tribocorrosion. Aluminum (Al) is chosen as the top layer for its high corrosion resistance and passivity in 0.6 M NaCl aqueous solution, while Mg, Ti, and Cu were chosen to represent increasing thermodynamic driving force for corrosion, with more negative (-2.37 V vs. SHE), comparable (-1.63 V vs. SHE) and more positive (+ 0.34 V vs. SHE) standard electromotive force potential than that of Al (-1.66 V vs. SHE) [25]. Notably, the galvanic series of the four metals in seawater follows a slightly different trend: ranking from Mg, Al, Cu, to Ti with increasing corrosion potential (i.e. from active to noble) [26]. An individual layer thickness of ~3 nm was chosen for all samples. Specifically, nanoindentation and nanowear, potentiodynamic polarization, and tribocorrosion tests were performed to evaluate the effects of constituting materials on the tribological, corrosion, and tribocorrosion properties of Al/X NMMs. The microstructure and surface chemistry of NMMs before and after tribocorrosion were characterized using scanning and transmission electron microscopies, and X-ray photoelectron spectroscopy, respectively.

3.2. Experimental methods

3.2.1. Materials synthesis and characterization

Equal-spaced Al/X (X = Mg, Ti, and Cu) NMMs samples with alternating layers of Al and X were deposited on (100) Si substrate using direct current (DC) magnetron sputtering under a working pressure of 5 mTorr Argon atmosphere (PVD PRODUCTS, Wilmington, MA). The sputtering targets of 99.99% Al, 99.995% Ti, 99.99% Mg and 99.99% Cu were cleaned ~8 min at power of 200 W, 250 W, 50 W and 50 W respectively prior to sputtering to remove native oxides and surface contaminants. The substrate was subjected to a bias etch of ~5 min and then placed ~180 mm below the targets and rotated at 40 rpm during sputtering. All deposition started with metal X on Si substrate, followed by Al, as shown in Fig. 3.1(a). The individual thickness is ~3 nm and the total film thickness is $\sim 1.74 \pm 0.1 \mu\text{m}$ (Table 3.1). Additional monolithic thin films of Al, Ti, Mg and Cu (~1 μm total thickness) were also prepared for comparison, as summarized in Table 3.2.

Grazing incidence X-ray diffraction (GI-XRD) and X-ray reflectometry (XRR) were conducted using PANalytical X'Pert PRO diffractometer with Cu K α radiation (1.5406 $\text{\AA}$) at 45 kV and 40 mA. The incident angle was selected as 0.8 $^\circ$ and the step size of GI-XRD and XRR was 0.01 $^\circ$ and 0.005 $^\circ$, respectively. The size of the mask on the incident beam was 10 mm for GI-XRD and 4 mm for XRR, and a 0.18 $^\circ$ parallel plate collimator slit was used for the latter. The surface roughness of NMMs was measured using atomic force microscopy (AFM, Bruker) and the surface morphology and composition by a field-emission scanning electron microscopy (FE-SEM, LEO

1550) equipped with an Oxford INCASynergy energy dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, USA) analysis was performed using Al K α radiation source at constant pass energy of 69 eV, 0.125 eV step size and 25 total sweeps. Carbon 1s spectra at 285 eV was used for calibration. Transmission electron microscopy (TEM, JEOL 2100) was performed under 200 kV. TEM samples were prepared via the standard lift-out method using a focused ion beam microscopy (FIB, Helios600) with ~200 nm carbon coating followed by 2-3 μ m Pt protective coating.

3.2.2. Mechanical and tribological tests

Nanoindentation tests were performed by Hysitron Ti900 triboindenter using a standard Berkovich-type diamond tip following the Oliver and Pharr method [27]. A trapezoidal loading function with 5 sec loading/unloading time, 2 sec holding time, 4 and 5 mN maximum load was applied for all tests. The tip area function was calibrated using a standard fused quartz sample before indentation. The maximum load was chosen to ensure that the maximum penetration depth was less than ~15 % of the total film thickness in all tests to minimize the substrate effect [28]. All the reported results are the average of more than ten repeated tests for each sample sets. Nanowear tests were carried out by Hysitron Ti900 triboindenter over areas of 2 $\times$ 2 μ m² on all samples using a standard conical-spherical diamond indenter at a constant nominal load of 90 μ N for up to 15 cycles. Hysitron Triboview software was used to determine the wear depth and worn area.

3.2.3. Corrosion and tribocorrosion tests

All electrochemical tests were conducted using Gamry Reference 600 potentiostat/galvanostat/ZRA. The effective exposed area was $\sim 1 \text{ cm}^2$ on all specimens. Potentiodynamic polarization (PD) tests were carried out in naturally aerated 0.6 M NaCl aqueous solution ($\text{pH} \sim 6.4 \pm 0.3$) at ambient temperature using a three electrode cell where the specimen, activated titanium mesh, and a commercial silver-silver chloride electrode (1 M KCl internal solution) served as the working (WE), counter (CE), and reference electrode (RE) respectively. Prior to the PD tests, open circuit potential (OCP) was stabilized for 5-10 min. The PD test started from $\sim 150 \text{ mV}$ below OCP and terminated at $\sim 1.5 \text{ V}$ above OCP, at a constant scan rate of 1 mV/s . The corrosion current densities (i_{corr}) were evaluated by Tafel extrapolation over a linear portion of the polarization curve which is approximately 100 mV above and below OCP. Mott-Schottky analysis was performed from -0.5 V vs. OCP to 1 V vs. OCP , by using 10 mV/s scan rate with a constant frequency of $1,000 \text{ Hz}$ after stabilization for 30 min.

The tribocorrosion tests were conducted in 0.6 M NaCl aqueous solution at room temperature using a multifunctional tribometer (Rtec, CA, USA) [7]. The specimen ($\sim 1 \text{ cm}^2$ exposed area), mixed metal oxide coated titanium mesh, and Ag/AgCl electrode served as the WE, CE, and RE, respectively. An alumina ball (Al_2O_3 , 4 mm diameter) was employed as the counterpart under a normal load of 0.5 N (or $\sim 0.47 \text{ GPa}$ contact pressure). Prior to each test, the OCP was stabilized for $\sim 15 \text{ min}$. During the test, the specimen moves in linear reciprocal motion at a sliding velocity of 0.2 mm/s for 25 sec over a 5 mm scratch length. Each test was carried out using a new Al_2O_3 ball to

minimize contamination. After the tribocorrosion tests, the depth profile of wear tracks was measured by a Dektak XT profilometer. All electrochemical and tribocorrosion results reported were averaged from at least three separate tests under each test condition.

Table 3.1 Summary of bi-layer thickness and mechanical properties of all Al/X NMM samples.

NMM sample	Bi-layer thickness		Mechanical properties		
	XRR (nm)	TEM (nm)	H (GPa)	E (GPa)	H _{ROM} (GPa)
Al/Ti	5.92 ± 0.08	5.64 ± 0.32	5.44 ± 0.52	91.37 ± 6.62	1.61
Al/Mg	6.48 ± 0.04	NA	3.81 ± 0.26	59.98 ± 2.21	0.74
Al/Cu	5.71 ± 0.11	5.48 ± 0.43	6.3 ± 0.54	97.64 ± 6.05	1.43

Table 3.2 Summary of key mechanical and corrosion properties of monolithic samples.

Monolithic sample	Mechanical properties		Electrochemical properties	
	H (GPa)	E (GPa)	E _{corr} (V)	i _{corr} (μA/cm ²)
Al	0.67 ± 0.17	77.62 ± 14.2	-0.73 ± 0.06	0.83 ± 0.15
Ti	2.55 ± 0.46	68.35 ± 4.01	-0.28 ± 0.01	0.42 ± 0.16
Mg	0.8 ± 0.14	34.28 ± 1.98	-1.78 ± 0.05	42.24 ± 46.05
Cu	2.18 ± 0.07	58.23 ± 4.36	-0.21 ± 0.01	1.2 ± 0.54

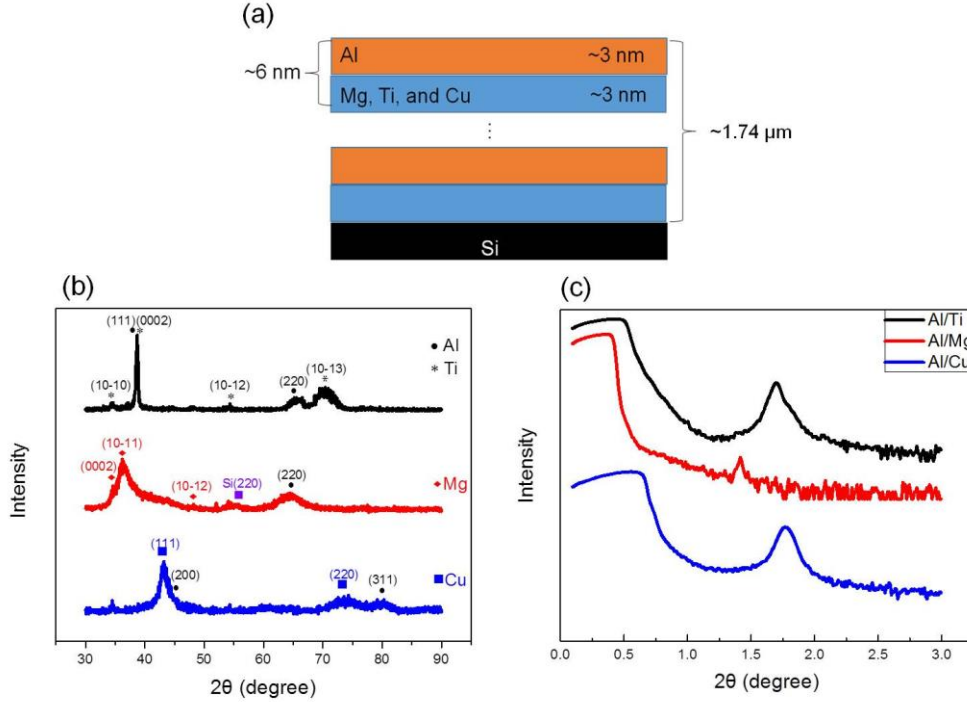


Figure 3.1. (a) Schematic of Al/X NMM structure. (b) GIXRD and (c) XRR patterns of Al/Ti, Al/Mg and Al/Cu multilayers.

3.3. Results

3.3.1. Microstructure characterization

Fig. 3.1(b) shows the GIXRD patterns of all as-deposited NMMs. In Al/Ti NMM, both face-centered-cubic Al ($Fm\bar{3}m$) and hexagonal Ti ($P6_3/mmc$) phases were detected. The high diffraction intensity at $\sim 38.6^\circ$ indicates the presence of strong Al (111) and Ti (0002) fiber texture in the film growth direction. In Al/Mg NMM, most diffractions were from hexagonal Mg phase ($P6_3/mmc$) with only one diffraction from Al (220). A small hump around $\sim 55.8^\circ$ was also observed from the Si substrate. In Al/Cu NMM, in addition to the face-centered-cubic Cu phase ($Fm\bar{3}m$), fcc Al diffractions were also detected. The presence of fewer diffractions of each phase than those of

traditional polycrystalline metals is common for deposited thin films due to the presence of strong crystallographic texture, which formed during thin film growth as a result of surface and interface energy minimization, as well as strain-energy minimization [29, 30].

XRR patterns of all samples are shown in Fig. 3.1(c). X-rays were completely reflected on each multilayer at increased critical angles of $\sim 0.2^\circ$, 0.25° to 0.32° for Al/Mg, Al/Ti, and Al/Cu NMMs respectively, in agreement with their increasing density from Al/Mg ($\rho_{\text{Al/Mg}} \approx 2.22 \text{ g/cm}^3$), Al/Ti ($\rho_{\text{Al/Ti}} \approx 3.6 \text{ g/cm}^3$), to Al/Cu ($\rho_{\text{Al/Cu}} \approx 5.83 \text{ g/cm}^3$). With the angle increase, the reflective intensity is weakened until the appearance of Bragg peaks because of interfacial roughness between the layers. However, there is no obvious oscillation before reaching the Bragg peaks, probably due to the extremely small layer thickness or surface roughness [31,32]. The bi-layer periodicity ($d = h_{\text{Al}} + h_{\text{x}}$) can be calculated by $d = 2\pi/q$ [33,34], where the lattice vector q can be obtained from the Bragg angle θ following the equation $q = 4 \pi \sin \theta / \lambda$. Table 1 summarizes the calculated d , which is $\sim 6 \text{ nm}$ for all samples.

All as-deposited samples appear mirror-finish to naked eye. SEM images in Fig. 3.2(a)-(c) show only nanoscale surface nodules on all samples. AFM analysis in Fig. 3.2(d)-(f) revealed the arithmetic average roughness (Ra) of all NMMs was $\sim 4.4\text{-}5.5 \text{ nm}$. The directly measured bi-layer thicknesses from TEM results are listed in Table. 3.1, in good agreement with x-ray results. Fig. 3.2(g) shows typical bright-field TEM image of Al/Ti NMM, where the film growth direction aligns with Al [111]. Semi-coherent interfaces were observed between the Al and Ti layers, with the orientation

relationship of Al $\{111\}$ // Ti $\{2000\}$ and Al $\langle 110 \rangle$ // Ti $\langle 1120 \rangle$. Bright-field TEM image (Fig. 3.2(h) inset) shows that there is no detectable phase contrast between the Al and Mg layers in Al/Mg NMMs, likely due to their similar atomic weight and epitaxial growth. Inverse FFT image of Al/Mg NMM in Fig. 3.2(h) shows the presence of largely coherent interfaces between the Al and Mg layers, with an orientation relationship of (110) Al // $(10^{-1}1)$ Mg, resulting in an in-plane strain of $\sim 14.5\%$. Fig. 3.2(i) shows the orientation relationship of Cu $\{111\}$ // Al $\{200\}$ parallel to the film growth direction in Al/Cu NMM, in agreement with the x-ray results (Fig. 3.1(c)). Additional high resolution TEM analysis (results not shown here) shows the interfaces in Al/Cu are semi-coherent. The grain sizes (d) of all NMMs were estimated by the linear intercept method from TEM images to be 178.5 ± 13.3 nm for Al/Ti, 127.6 ± 16.1 nm for Al/Mg, and 74.5 ± 15.2 nm for Al/Cu NMMs. Given that in all NMMs, d is much bigger than h (3 nm), it is assumed that the dominating structural length scale for mechanical properties is h [35].

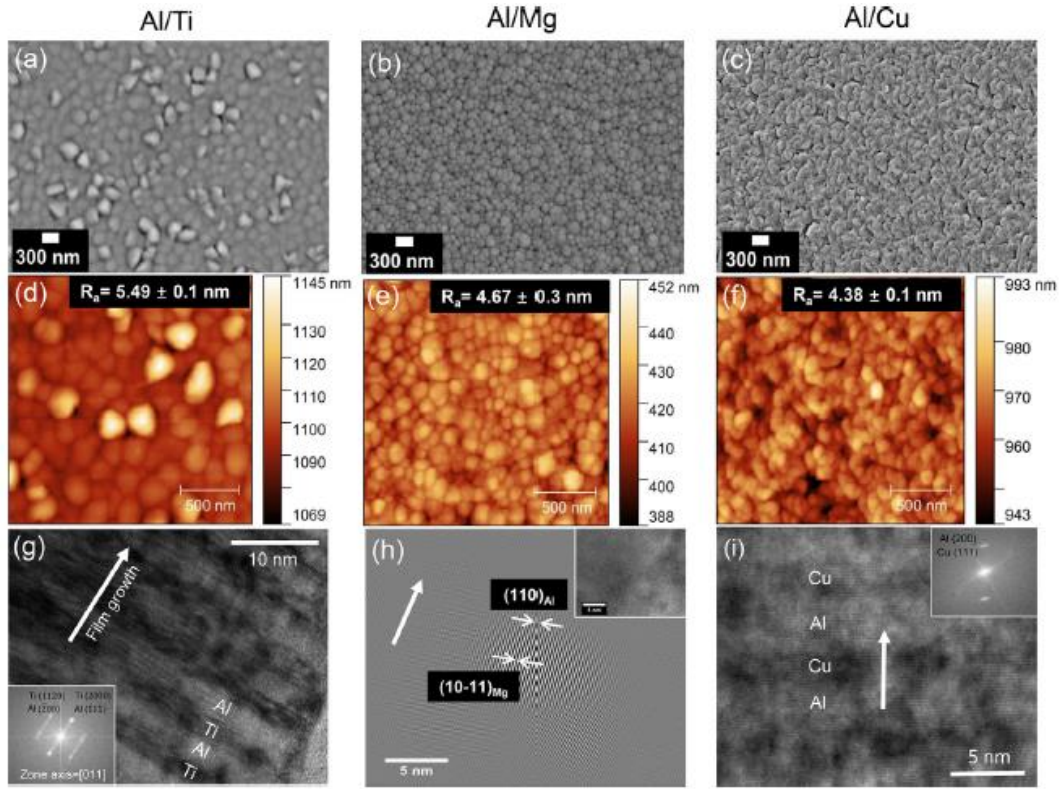


Figure 3.2. (a-c) SEM, (d-f) AFM, (g), (i) bright-field TEM, and (h) inverse FFT TEM images of NMMs. Arrows in (g-i) indicate film growth direction. Insets in (g) and (i) are FFT images of the corresponding TEM images, while that in (h) is the corresponding bright-field TEM image.

3.3.2. Mechanical and wear properties

The hardness (H) and elastic modulus (E) of all NMMs measured by nanoindentation tests are summarized in Fig. 3.4(a) and Table 3.1. For comparison, the mechanical properties of monolithic films measured using the same method are listed in Table 3.2. SEM images of typical indents on all NMM samples can be found in Fig. 3.3(a-c) in the Supplemental Materials. No surface crack or apparent pile-up was observed in all samples after nanoindentation, indicating relatively high strength and strain hardening exponent [36]. Results in Tables 3.1 and 3.2 show that the hardness of

all NMMs is $\sim 3\text{-}5$ times greater than their corresponding rule-of-mixture hardness H_{ROM} , similar to those reported previously [37,38]. Interestingly, pure Ti film is harder than pure Cu film, yet Al/Cu NMM is harder than Al/Ti NMM. It is also noted that the presence of any potential residual stress could also affect the hardness and other properties of NMMs, the measurement and analysis of which is left for future work.

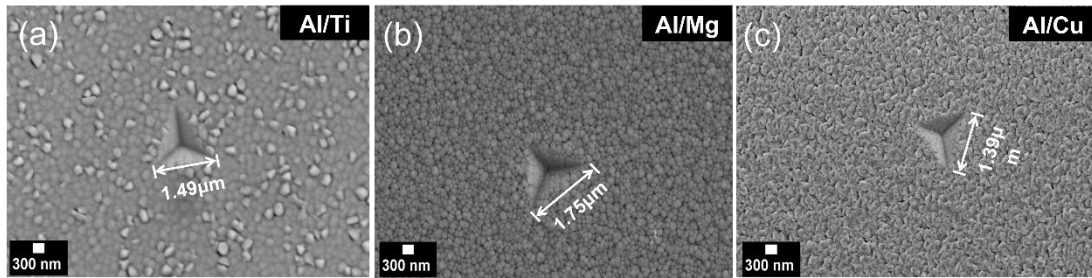


Figure 3.3. SEM images of indents under the corresponding loads (4 mN for Al/Mg and 5 mN for Al/Ti and Al/Cu NMMs) of all NMM samples.

Nanowear tests were carried out on all NMM samples under a constant load of 90 μN for up to 15 cycles. Fig. 3.4(b) shows that the wear rates (i.e. total volume loss normalized by the number of cycles) decreased with the number of cycles due to subsurface work-hardening until reaching a quasi-steady state after ~ 10 cycles, during which Al/Cu and Al/Mg NMMs exhibit the lowest and highest wear rate respectively. Fig. 3.4(d)-(f) show the typical surface topographies after 10 cycles. The corresponding surface height profiles and wear properties are summarized in Fig. 3.4(c) and Table 3.3 respectively. Al/Cu NMMs exhibited the best wear resistance due to their highest hardness, in consistent with the Archard's law [13]. However, a deviation from this behavior was observed during the running-in period (at two cycles of wear), probably due to the different surface roughness of Al/Ti and Al/Cu. Higher roughness in Al/Ti

leads to a smaller real contact area, hence lower material loss than that of Al/Cu NMM.

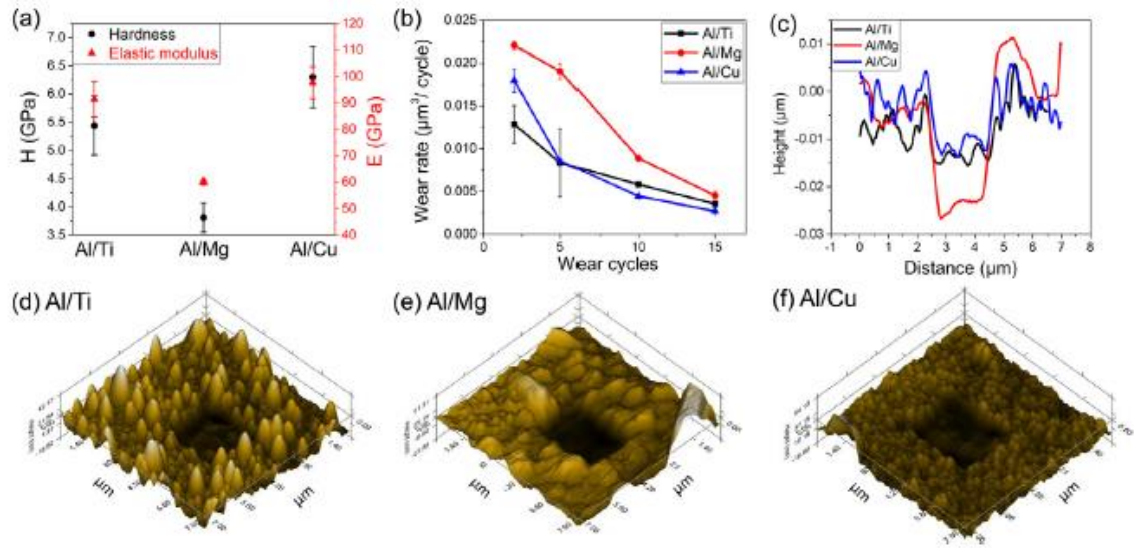


Figure 3.4. (a) Mechanical properties and (b) wear rates as a function of number of cycles for all NMM samples. (c) Surface height profiles and (d)-(f) surface topographies of all NMM samples after 10 cycles of wear under 90 μN .

3.3.3. Corrosion behavior

Fig. 3.5(a) and (b) present the typical Tafel plots of all samples after PD tests in 0.6 M NaCl aqueous solution at room temperature. The measured E_{corr} and i_{corr} are summarized in Tables 3.2 and 3.3. It is noted here while current rather than current density was preferred for Tafel plots of galvanic couples, in the present work, each NMM sample is treated as a 'composite' material and the measured current density is calculated by normalizing the corrosion current by the exposed sample area. In Fig. 3.5(a), E_{corr} of monolithic Ti and Cu are more positive while that of Mg more negative than that of Al, which is in agreement with previous results [39-41]. The values of E_{corr} increase in the order of Mg, Al, Ti, and Cu, in consistent with their reduction potential

trend from the EMF series under the standard state. i_{corr} is the smallest for pure Ti and highest for Mg. Among all monolithic samples, Al exhibited active corrosion in the anodic branch, Cu and Mg exhibited pitting behavior at E_{pit} , while Ti exhibited an active-pseudo passive behavior, with a transition potential around 0.4 V vs. Ag/AgCl.

Fig. 3.5(b) shows that the i_{corr} of all NMM samples increases in the order of Al/Ti, Al/Cu, and Al/Mg while E_{corr} increases in the order of Al/Mg, Al/Ti, and Al/Cu. The anodic polarization branches of all NMMs are characteristically different. For both Al/Mg and Al/Cu NMMs, an active-passive type of behavior was observed, where the anodic corrosion current density first increased with potential from E_{corr} , then reversed to a lower value over a range of more positive potentials. Interestingly, for both samples, two primary passive potential E_{pp} was observed, at ~ -1.62 V and ~ -0.74 V vs. Ag/AgCl for Al/Mg NMMs, and ~ -0.03 V and 0.57 V vs. Ag/AgCl for Al/Cu NMMs. Such behavior is likely due to the switching of corrosion mode between a passive state, contributed mainly by the outmost Al layer, and an active corrosion state by the underneath Mg and Cu layers as corrosion progressed through the thickness of the NMMs. On the other hand, the anodic branch of Al/Ti exhibited a stable passive state over the majority of the anodic potential with i_{corr} of $\sim 0.042 \mu\text{A}/\text{cm}^2$, smaller than that of either Al or Ti. This i_{corr} value is around two orders of magnitude smaller than those reported of Al/Ti bilayers and multilayers with micrometer-sized individual layer thickness [42,43].

Mott-Schottky (MS) results are shown in Fig. 3.5(c-f). The capacitance of the Helmholtz layer is assumed to be much bigger than the semiconductor capacitance of

the passive layer, hence the measured capacitance C is taken as the semiconductor capacitance of the passive layer to calculate the defect densities according to [44,45], $\frac{1}{C^2} = \frac{\pm 2}{\varepsilon \cdot \varepsilon_0 \cdot q \cdot N} \times (E - E_{fb} - \frac{kT}{q})$, where ε is the passive film dielectric constant (10 for Al_2O_3), ε_0 is the permittivity of vacuum ($\varepsilon_0 = 8.85 \times 10^{-14}$ F/cm), N is the donor or acceptor density, E_{fb} is the flat band potential, k is the Boltzmann constant (1.38×10^{-23} JK⁻¹), T is the absolute temperature, and q is the elementary charge (1.602×10^{-19} C). According to this relationship, a positive slope of the MS curve indicates the presence of n-type defect such as oxygen vacancies and cation interstitials (e.g. Al^{3+}), while a negative slope indicates p-type defect such as cation vacancies. Fig. 3.5 shows that while only n-type defects are present in Al/Ti over the whole potential range, both Al/Mg and Al/Cu experiences a transition from n-type to p-type when the potential increases above OCP. It is likely the active corrosion of Mg and Cu in the later lead to the dissolution of metallic ions at the surface, leaving behind cation vacancies. Fig. 3.5(c) shows the n-type defect density of all NMMs measured from the cathodic potential region (between the dashed lines in Fig. 3.5(d-f)), hence corresponds to that of the intact surface Al layer. It can be seen that the defect density of all samples is $\sim 10^{20}/cm^3$, with Al/Ti slightly higher than the rest. These values are about two orders of magnitude lower than those measured in pure Al and Al 3003 alloy [44].

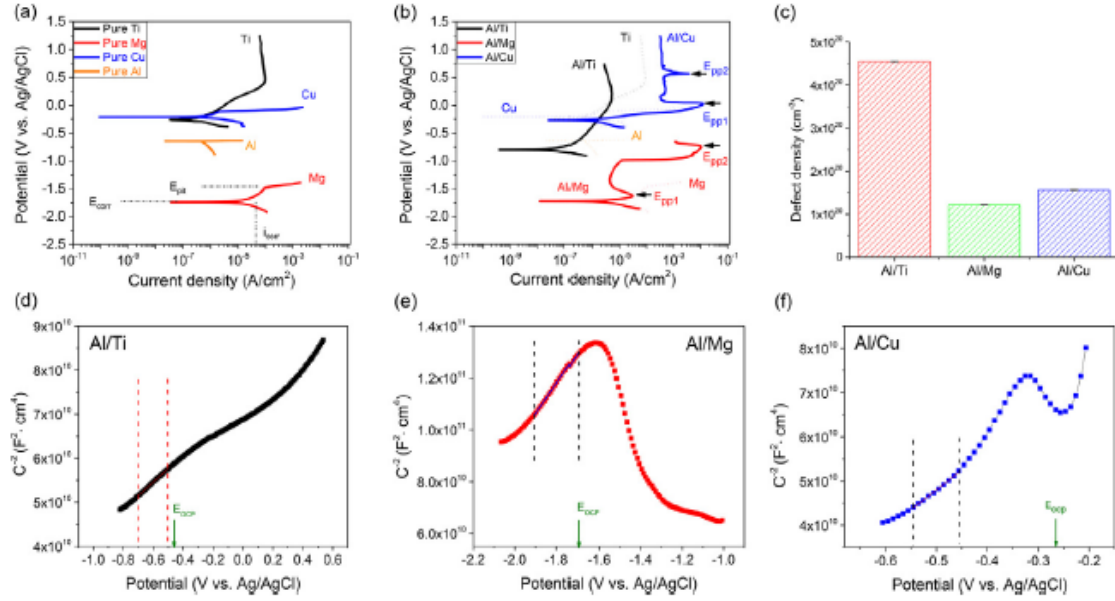


Figure 3.5. Typical potentiodynamic polarization curves of (a) monolithic films and (b) NMMs in 0.6 M NaCl solution at room temperature. Results in (a) are replotted as dashed lines in (b) for direct comparison. (d-f) Mott–Schottky plots and (c) n-type defect density of all NMMs.

The corroded surface morphology and elemental mappings were shown in Fig. 3.6(a-c), which are in good agreement with their PD results. The corroded surface of Al/Ti NMM (Fig. 3.6(a)) resembled that of the as-deposited sample, confirming its lack of either active or localized corrosion. On the other hand, the majority of Al/Mg NMM is gone after PD tests, as shown in Fig. 3.6(b), exposing large areas of Si substrate. On the corroded surface of Al/Cu, extensive nanometer-sized nodules could be seen, as marked by arrow in Fig. 3.6(c). EDS mapping in Fig. 3.6(c) suggests that these nodules are enriched in Cu. Similar surface enrichment of Cu has also been reported in Al-Cu-Li [46] and Al-Cu [47] alloys, due to dealloying of copper-rich inclusions being redistributed on the aluminum surface.

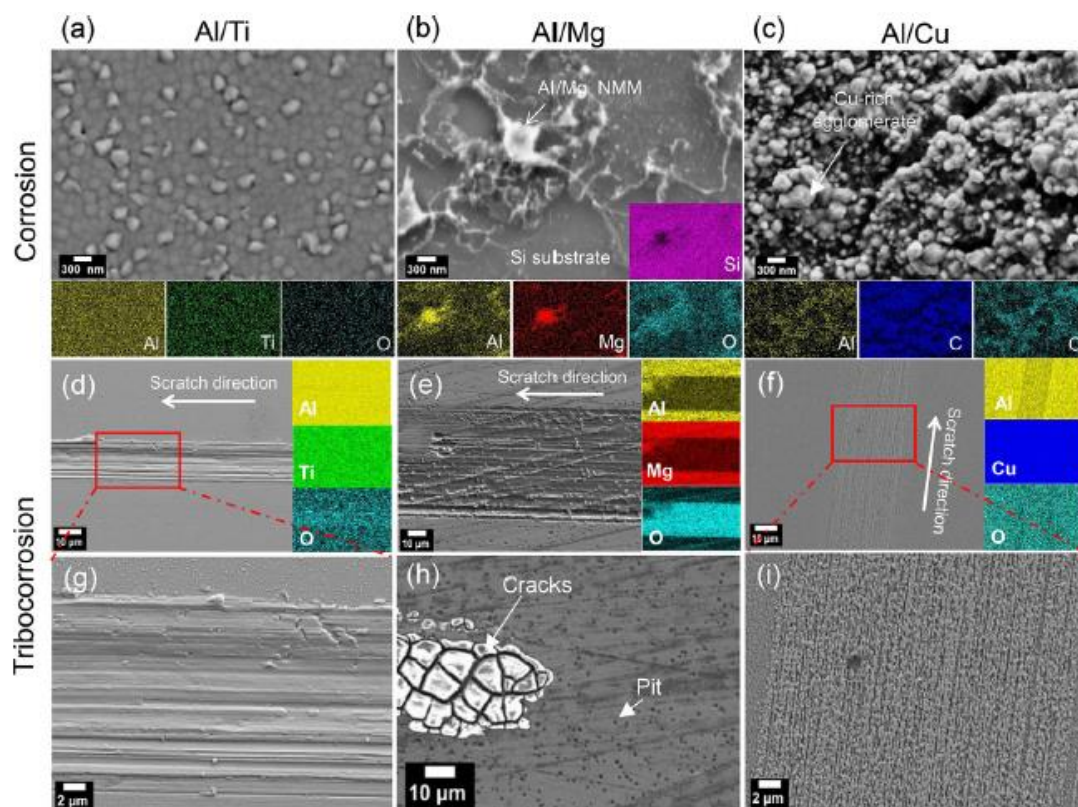


Figure 3.6. Surface SEM images and corresponding EDS elements mappings of all NMMs after (a-c) PD and (d-i) tribocorrosion tests. Inserts in (a-f) show the corresponding EDS element maps.

3.3.4. Tribocorrosion behavior

Fig. 3.7(a) shows the typical OCP evolution of all samples during tribocorrosion tests in 0.6 M NaCl solution. In all samples, OCP shifted to the cathodic direction upon getting in contact with the counter body at the beginning of the test, and restored the original value once the test was ended. The magnitude of this cathodic potential shift was large for Al/Ti NMM (~ 86 mV) and quite small for Al/Mg (~ 8 mV) and Al/Cu NMM (~ 1.6 mV). This observation is consistent with the PD corrosion results, where unlike Al/Mg and Al/Cu, passivity, instead of galvanic corrosion, was dominating in

Al/Ti. During tribocorrosion, the mechanical removal of the protective passive film by the counter body, i.e. the depassivation process, led to the shift of the corrosion potential in the more active direction. Once the test was finished, OCP shifted back to its original steady state value, indicating a repassivation of the worn area. On the other hand, the small potential shift of Al/Mg and Al/Cu indicates a lack of surface passivity. Hence depassivation by the counter body has small effect on OCP. The repassivation time, i.e. the time required for OCP to restore its initial value at the end of the test was ~ 73 s for Al/Ti, followed by ~ 82 s for Al/Cu and ~ 388 s for Al/Mg. As a comparison, the repassivation time of pure Al film is ~ 45 s from [7], much shorter than that of all NMMs, likely due to its chemical homogeneity. Coefficient of friction (COF) of all samples was presented in Fig. 3.7(b). Al/Ti NMM exhibited the highest average COF (~ 0.38), followed by Al/Cu (~ 0.27) and Al/Mg (~ 0.16). Fig. 3.7(c) and (d) show the wear track profiles and total material volume loss of all NMMs after tribocorrosion tests respectively. Among all samples, the wear track of Al/Mg NMM was the widest and deepest, in agreement with their low hardness and high corrosion rate. Al/Cu NMM exhibited the smallest material loss, hence the best tribocorrosion resistance, most likely due to its highest wear resistance. Al/Ti NMM, although showing the highest corrosion resistance, was slightly inferior to Al/Cu under the chosen tribocorrosion testing condition. It should also be pointed out that if a different tribocorrosion condition was chosen so that the mechanical wear occurs at a much smaller frequency than those conducted here, Al/Ti will be expected to be the most tribocorrosion-resistant since material loss will be dominated by corrosion and less frequently by wear.

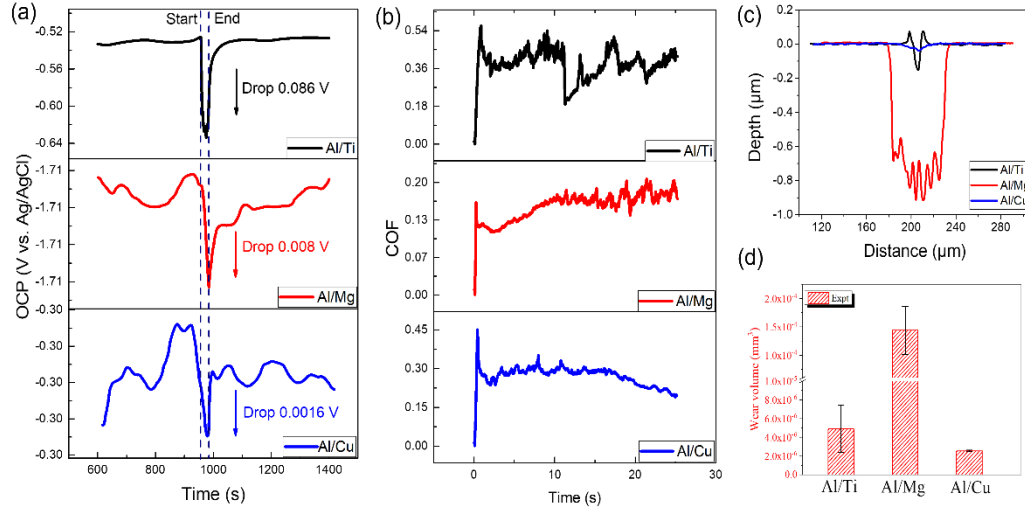


Figure 3.7. Evolution of (a) open circuit potential, (b) coefficient of friction (COF) of all multilayers during tribocorrosion tests. (c) Typical wear track cross-sectional surface depth profiles and (d) summary of experimentally measured wear volume and FE model predicted corrosion current of all NMMs after tribocorrosion tests. The profiles in (c) were measured perpendicular to the sliding direction on the worn surface of all samples.

3.3.5. Surface chemistry and microstructure after tribocorrosion

Fig. 3.6(d-i) shows the surface morphologies and corresponding EDS mappings of all NMM samples after tribocorrosion tests. The wear track of Al/Ti NMMs is characterized by deep grooves and high pile-ups near the edge of the track, suggesting largely abrasive wear during scratch. The inset EDS mappings in Fig. 3.6(d) show uniform distribution of Al and Ti elements in either the worn or unworn area with a higher O composition within the wear track (~2.36 at%) than that outside (~0.84 at%). This observation is consistent with prior corrosion and tribocorrosion results, indicating the formation of a protective (hydr)oxide layer on the wear track. For Al/Mg NMM,

EDS analysis in Fig. 3.6(e) inset revealed that the majority of the sample was removed in the worn area, leaving behind a high O concentration most likely from SiO₂ layer on the Si substrate. Within the wear track, in locations where the NMM is still present (Fig. 3.6(h)), extensive cracks were seen on the tribocorroded surface, similar to dehydration cracks formed on corrosion products of many Mg alloys [48]. Away from the wear track, extensive pits were seen, of ~200-600 nm diameter. For Al/Cu NMM, Fig. 3.6(f) and (i) show that its wear track has extensive fine scratch lines along the sliding direction. In addition, the wear track contains high nanoscale surface roughness with higher Cu concentration than the rest of the sample. This partial dissolution of Al in Al/Cu NMM could be related to the anodic nature of Al in the Al-Cu galvanic couple, in consistent with those observed after pure corrosion (Fig. 3.6(c)). The surface morphology and EDS analysis far away from the wear track of all NMM samples after tribocorrosion tests are presented in the Fig. 3.8, which are similar to those observed during pure corrosion (Fig. 3.6(a-c)).

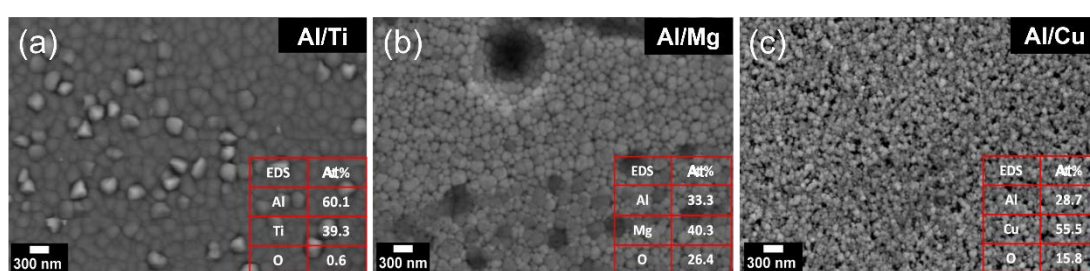


Figure 3.8. SEM images of surface morphology and the corresponding EDS analysis (insets) in areas far away from the wear track of (a) Al/Ti, (b) Al/Mg, and (c) Al/Cu NMM samples after tribocorrosion tests.

Additional XPS analysis, as shown in Fig. 3.9, indicate that in all as-deposited samples, the surface contains mainly alumina (Al_2O_3) and metallic forms of Al and X ($\text{X} = \text{Ti}, \text{Mg}, \text{and Cu}$), as expected [49]. Al_2O_3 is also the main surface component after tribocorrosion in all samples. In Al/Mg NMM (Fig. 3.9(b)), $\text{Mg}(\text{OH})_2$ was also detected from both the worn and unworn areas, resulting from active corrosion of Mg. In both Al/Cu and Al/Ti NMMs, no copper oxide or titanium oxide was detected, likely due to the cathodic protection provided by the more active Al layers [26].

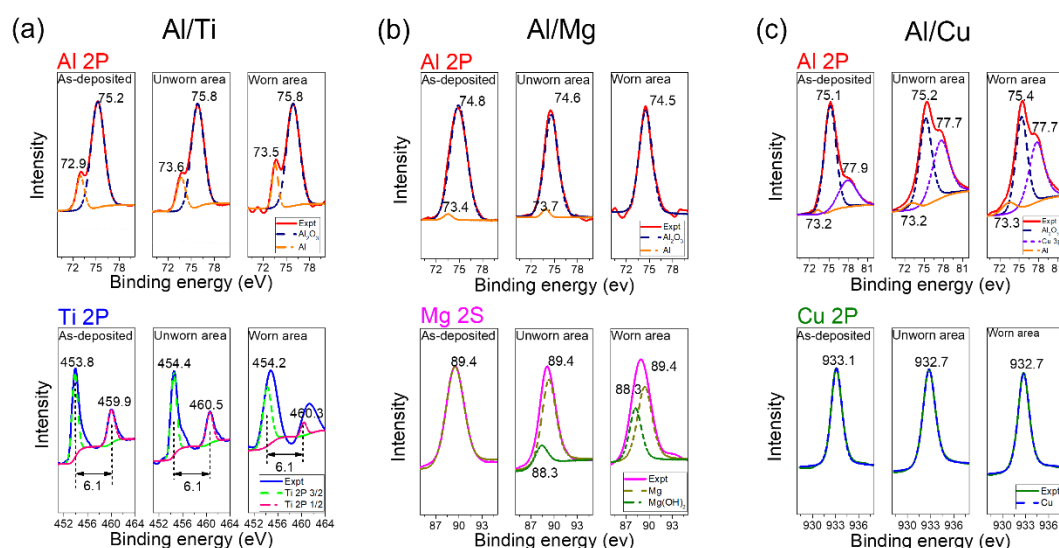


Figure 3.9. Photoelectron spectroscopy (XPS) results (a) Al/Ti, (b) Al/Mg, and (c) Al/Cu NMMs before and after tribocorrosion test.

Table 3.3 Summary of wear, corrosion, and tribocorrosion properties of all Al/X NMM samples. Wear test data were taken from all samples after 10 cycles of wear. Each value is reported as average and standard deviation from at least three separate tests.

Sample ID	Wear			Corrosion		Tribocorrosion		
	D ($\times 10^{-4}$ mm)	W ($\times 10^{-3}$ mm)	V ($\times 10^{-11}$ mm ³)	E _{corr} (V)	i _{corr} (μ A/cm ²)	D ($\times 10^{-4}$ mm)	W (mm)	V ($\times 10^{-6}$ mm ³)
Al/Ti	0.15 $\pm$ 0.006	2.4 $\pm$ 0.1	5.81 $\pm$ 0.24	-0.62 $\pm$ 0.17	0.041 $\pm$ 0.02	1.21 $\pm$ 0.92	0.014 $\pm$ 0.001	4.88 $\pm$ 2.52
Al/Mg	0.22 $\pm$ 0.005	2.6 $\pm$ 0.1	8.89 $\pm$ 0.23	-1.7 $\pm$ 0.04	3.89 $\pm$ 1.2	5.87 $\pm$ 0.51	0.049 $\pm$ 0.01	144 $\pm$ 42.4
Al/Cu	0.11 $\pm$ 0.006	2.3 $\pm$ 0.05	4.44 $\pm$ 0.24	-0.28 $\pm$ 0.01	1.55 $\pm$ 0.94	0.17 $\pm$ 0.017	0.031 $\pm$ 0.003	2.54 $\pm$ 0.10

Fig. 3.10(d-i) show TEM images of the tribocorroded NMMs. Plastic deformation dominates the subsurface of Al/Ti NMM and a severe plastically deformed (SPD) layer of ~ 450 nm was formed, where extensive shear-induced mixing erased the well-defined interface contrast between the Al and Ti layers. On the other hand, corrosion degradation instead of plastic deformation dominates the worn surfaces of Al/Mg (Fig. 3.10(e, h)) and Al/Cu (Fig. 3.10(f, i)). It is noted here that within the wear track of Al/Mg, most of the film was gone (see Fig. 3.6(e)), and the TEM lift-out was performed at a location where the film was still present. In Al/Mg NMM, deep and narrow corrosion paths can be seen, extending a few hundred nm deep below the surface. In Al/Cu NMM, frequent undercuts can be seen under the Cu-rich phases that were redeposited on the surface after Al dissolution.

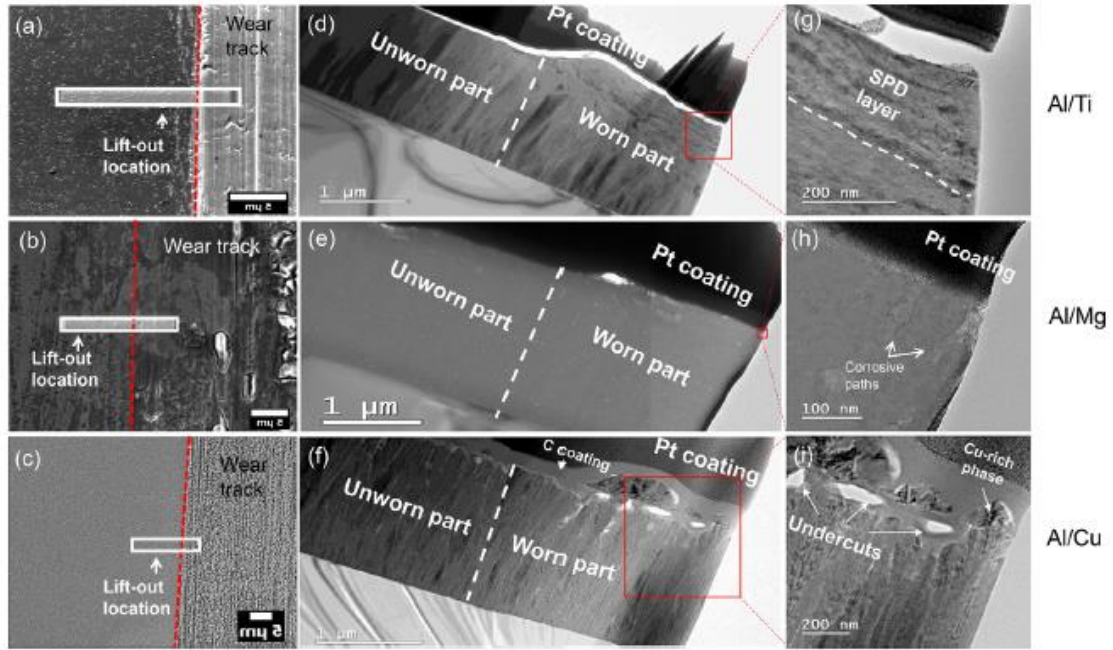


Figure 3.10. (a-c) Surface SEM images and (d-i) cross-sectional bright-field TEM images of all NMMs after tribocorrosion tests.

3.4. Discussion

According to the mixed potential theory (MPT) [26], the corrosion potential of a galvanic couple A/B ($E_{\text{corr}}^{\text{A/B}}$) is always in between those of uncoupled metal A ($E_{\text{corr}}^{\text{A}}$) and B ($E_{\text{corr}}^{\text{B}}$), and at potentials cathodic to $E_{\text{corr}}^{\text{A/B}}$, the cathodic current of the couple should be dominated by the one with higher cathodic current, likewise for the anodic current. In the present study, this was indeed the case for Al/Mg and Al/Cu NMMs. For example, in Al/Cu NMM, $E_{\text{corr}}^{\text{Al/Cu}}$ is in between that of $E_{\text{corr}}^{\text{Al}}$ and $E_{\text{corr}}^{\text{Cu}}$ (Fig. 3.5(b)). In addition, the cathodic branch of the Al/Cu PD curve is similar to that of Cu. However, a deviation from MPT was observed for Al/Ti NMM, where both the cathodic and anodic current of the couple was about one order of magnitude smaller than that of either uncoupled Al or Ti. The cathodic reaction during corrosion under this potential

range, is assumed to be dominated by hydrogen reduction as $2H^+ + 2e^- \rightarrow H_2$. A reduction of cathodic reaction rate of Al/Ti NMM indicates a reduction of the exchange current of hydrogen reaction ($i_{o,H^+/H_2}$) on the surface. Likewise, the reduction of anodic reaction rates indicates a reduction of $i_{o,Al^{3+}/Al}$ in the anodic reaction $2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 3e^-$. The fact that both cathodic and anodic kinetics is smaller on Al/Ti NMM than those on monolithic Al, whose outmost surface is the same, indicates that the nanolayered strategy is reducing the surface activity.

3.5. Conclusions

The experimental study was carried out to evaluate the effects of constituting materials on the tribocorrosion behavior of Al/X NMMs. It was found experimentally that the degradation and deformation mode of Al/X depends on both of their mechanical and electrochemical properties. While plastic deformation and wear rely heavily on stiffness mismatch between the constituents and the interface coherency, corrosion behavior was more complicated. In Al/Mg and Al/Cu NMMs where Al is the only passive element, micro-galvanic corrosion dominates material loss, as predicted from the mixed potential theory. On the other hand, in Al/Ti NMM where both constituents are passive metals, Al is the only specie that participates in the passive film formation during corrosion and tribocorrosion despite the wide passivity window of Ti and plastic deformation is the dominate factor for materials loss in Al/Ti during tribocorrosion.

References:

1. D. Landolt, S. Mischler, M. Stemp, Electrochemical methods in tribocorrosion: a critical appraisal, *Electrochimica Acta* 46 (24-25) (2001) 3913–3929.
2. K. Pondicherry, D. Fauconnier, P. De Baets, Synergism in multi-asperity abrasion-corrosion of martensitic and dual phase steels in three aqueous electrolytes, *Wear* (2020) 452.
3. S. Roy, J.M. Coyne, J.A. Novak, M.A. Edwards, Flow-induced failure mechanisms of copper pipe in potable water systems, *Corros Rev* 36 (5) (2018) 44 9–4 81.
4. Y.S. Kim, S.K. Lee, H.J. Chung, J.G. Kim, Influence of a simulated deep-sea condition on the cathodic protection and electric field of an underwater vehicle, *Ocean Eng* 148 (2018) 223–233.
5. M. Buciumeanu, A. Bagheri, J.C.M. Souza, F.S. Silva, B. Henriques, Tribocorrosion behavior of hot pressed CoCrMo alloys in artificial saliva, *Tribol Int* 97 (2016) 423–430.
6. H. Mraied, W. Wang, W. Cai, Influence of Chemical Heterogeneity and Microstructure on the Corrosion Resistance of Biodegradable WE43 Magnesium Alloys, *Journal of Materials Chemistry B* (2019).
7. H. Mraied, W.J. Cai, The effects of Mn concentration on the tribocorrosion resistance of Al-Mn alloys, *Wear* 380-381 (2017) 191–202.
8. T.T. Xie, S.D. Mao, C. Yu, S.J. Wang, Z.L. Song, Structure, corrosion, and hardness properties of Ti/Al multilayers coated on NdFeB by magnetron sputtering, *Vacuum* 86 (10) (2012) 1583–1588.

9. J. Creus, E.H. Top, C. Savall, P. Refait, C. Ducros, F. Sanchette, Mechanical and corrosion properties of dc magnetron sputtered Al/Cr multilayers, *Surf Coat Tech* 202 (16) (2008) 4047–4055.
10. A. Misra, J.P. Hirth, R.G. Hoagland, Length-scale-dependent deformation mechanisms in incoherent metallic multilayered composites, *Acta Mater* 53 (18) (2005) 4 817–4 824.
11. A. Misra, M. Verdier, H. Kung, J.D. Embury, J.P. Hirth, Deformation mechanism maps for polycrystalline metallic multiplayers, *Scripta Mater* 41 (9) (1999) 973–979.
12. A. Misra, H. Kung, Deformation behavior of nanostructured metallic multilayers, *Adv Eng Mater* 3 (4) (2001) 217–222.
13. J.F. Archard, Contact and rubbing of flat surfaces, *Journal of Applied Physics* 24 (8) (1953) 981–988.
14. S. Izadi, H. Mraied, W.J. Cai, Tribological and mechanical behavior of nanostructured Al/Ti multilayers, *Surf Coat Tech* 275 (2015) 374–383.
15. W. Wang, R.N. Singh, Tribological behavior of Ni/Sn metallic multilayer composites, *J Mater Eng Perform* 7 (1) (1998) 27–32.
16. S.K. Ghosh, P.K. Limaye, B.P. Swain, N.L. Soni, R.G. Agrawal, R.O. Dusane, A.K. Grover, Tribological behaviour and residual stress of electrodeposited Ni/Cu multilayer films on stainless steel substrate, *Surf Coat Tech* 201 (8) (2007) 4609–4618.
17. S.K. Ghosh, P.K. Limaye, S. Bhattacharya, N.L. Soni, A.K. Grover, Effect of Ni sub- layer thickness on sliding wear characteristics of electrodeposited Ni/Cu

- multilayer coatings, *Surf Coat Tech* 201 (16-17) (2007) 7441–7448.
18. W. Cai, P. Bellon, Subsurface microstructure evolution and deformation mechanism of Ag-Cu eutectic alloy after dry sliding wear, *Wear* 303 (1-2) (2013) 602–610.
19. Z.P. Luo, G.P. Zhang, R. Schwaiger, Microstructural vortex formation during cyclic sliding of Cu/Au multilayers, *Scripta Mater* 107 (2015) 67–70.
20. M. Linz, H. Winkelmann, K. Hradil, E. Badisch, F. Mucklich, Directional development of residual stress and surface fatigue during sliding contact, *Eng Fail Anal* 35 (2013) 678–685.
21. M. Rahsepar, M.E. Bahrololoom, Corrosion study of Ni/Zn compositionally modulated multilayer coatings using electrochemical impedance spectroscopy, *Corros Sci* 51 (11) (2009) 2537–2543.
22. J.Y. Fei, G.D. Wilcox, Electrodeposition of zinc-nickel compositionally modulated multilayer coatings and their corrosion behaviours, *Surf Coat Tech* 200 (11) (2006) 3533–3539.
23. S.R. Cross, R. Woollam, S. Shademan, C.A. Schuh, Computational design and optimization of multilayered and functionally graded corrosion coatings, *Corros Sci* 77 (2013) 297–307.
24. K.D. Ralston, N. Birbilis, M. Weyland, C.R. Hutchinson, The effect of precipitate size on the yield strength-pitting corrosion correlation in Al-Cu-Mg alloys, *Acta Mater* 58 (18) (2010) 5941–5948.
25. V.G. Shverina, V.K. Zaitsev, Standard Electrode-Potentials in Aqueous and Non-aqueous Solutions, *Zh Fiz Khim* 59 (7) (1985) 1696–1698.

- 26 D. Jones, Principles and Prevention of Corrosion, Prentice-Hall, Inc., New Jersey, USA, 1996.
27. W.C. Oliver, G.M. Pharr, AN IMPROVED TECHNIQUE FOR DETERMINING HARDNESS AND ELASTIC MODULUS USING LOAD AND DISPLACEMENT SENSING IN- DENTATION EXPERIMENTS, J. Mater. Res. 7 (6) (1992) 1564–1583.
28. R. Saha, W.D. Nix, Effects of the substrate on the determination of thin film mechanical properties by nanoindentation, Acta Mater 50 (1) (2002) 23–38.
29. C.V. Thompson, R. Carel, Texture Development in Polycrystalline Thin-Films, Mat Sci Eng B-Solid 32 (3) (1995) 211–219.
30. Y.F. Zhang, S. Xue, Q. Li, J. Li, J. Ding, T.J. Niu, R. Su, H. Wang, X. Zhang, Size dependent strengthening in high strength nanotwinned Al/Ti multilayers, Acta Mater 175 (2019) 466–476.
31. I. Kojima, B. Li, Structural characterization of thin films by X-ray reflectivity, Rigaku J 16 (2) (1999) 31.
32. J. Jensen, A. Oelkers, R. Toivola, D.C. Johnson, J. Elam, S. George, X-ray reflectivity characterization of ZnO/Al₂O₃ multilayers prepared by atomic layer deposition, Chemistry of materials 14 (5) (2002) 2276–2282.
33. J.Z. Hu, L. Chen, Effect of annealing on microstructure of Co/Cu multilayers, Journal of Materials Science-Materials in Electronics 26 (5) (2015) 3168–3173.
34. V.G. Sathe, D. Phase, Interfacial reactions in Mo–Zr multilayer structure: an X-ray reflectivity study, Vacuum 77 (3) (2005) 301–306.

35. A. Misra, J. Hirth, R. Hoagland, Length-scale-dependent deformation mechanisms in incoherent metallic multilayered composites, *Acta materialia* 53 (18) (2005) 4 817–4 824.
36. B. Taljat, G.M. Pharr, Development of pile-up during spherical indentation of elastic–plastic solids, *International journal of solids and structures* 41 (14) (2004) 3891–3904.
37. J.Y. Zhang, J.J. Niu, X. Zhang, P. Zhang, G. Liu, G.J. Zhang, J. Sun, Tailoring nanostructured Cu/Cr multilayer films with enhanced hardness and tunable modulus, *Materials Science and Engineering: A* 543 (2012) 139–144.
38. K.Y. Yu, Y. Liu, S. Rios, H. Wang, X. Zhang, Strengthening mechanisms of Ag/Ni immiscible multilayers with fcc/fcc interface, *Surf Coat Tech* 237 (2013) 269–275.
39. C. Kuphasuk, Y. Oshida, C.J. Andres, S.T. Hovijitra, M.T. Barco, D.T. Brown, Electrochemical corrosion of titanium and titanium-based alloys, *The Journal of prosthetic dentistry* 85 (2) (2001) 195–202.
40. F. Cao, G.-L. Song, A. Atrens, Corrosion and passivation of magnesium alloys, *Corros Sci* 111 (2016) 835–845.
41. A. Fateh, M. Aliofkhazraei, A. Rezvanian, Review of corrosive environments for copper and its corrosion inhibitors, *Arabian journal of Chemistry* (2017).
42. G.S. Wu, Fabrication of Al and Al/Ti coatings on magnesium alloy by sputtering, *Mater Lett* 61 (18) (2007) 3815–3817.
43. R.C. Zeng, K. Jiang, S.Q. Li, F. Zhang, H.Z. Cui, E.H. Han, Mechanical and corrosion properties of Al/Ti film on magnesium alloy AZ31B, *Front Mater Sci* 9 (1)

- (2015) 66–76.
44. J. Chen, J. Xiao, J.D. Poplawsky, F.M. Michel, C. Deng, W. Cai, The origin of passivity in aluminum-manganese solid solutions, *Corros Sci* 173 (2020) 108749.
 45. B. Zhang, Y. Li, F.J.C.s. Wang, Electrochemical corrosion behaviour of micro-crystalline aluminium in acidic solutions, *Corrosion science* 49 (5) (2007) 2071–2082.
 46. Y.K. Zhu, J.D. Poplawsky, S.R. Li, R.R. Unocic, L.G. Bland, C.D. Taylor, J.S. Locke, E.A. Marquis, G.S. Frankel, Localized corrosion at nm-scale hardening precipitates in Al-Cu-Li alloys, *Acta Mater* 189 (2020) 204–213.
 47. H. Yoshioka, Q. Yan, K. Asami, K. Hashimoto, Pitting Potential and Structure of Sputter-Deposited Al-Ti Alloys, *Mat Sci Eng a Struct* 134 (1991) 1054–1057.
 48. H. Mraied, W. Wang, W. Cai, Influence of chemical heterogeneity and microstructure on the corrosion resistance of biodegradable WE43 magnesium alloys, *J Mater Chem B* 7 (41) (2019) 6399–6411.
 49. J. Zähr, S. Oswald, M. Törpe, H. Ullrich, U. Füssel, Characterisation of oxide and hydroxide layers on technical aluminum materials using XPS, *Vacuum* 86 (9) (2012) 1216–1219.

Chapter 4. Enabling High-Performance Surfaces of Biodegradable Magnesium Alloys via Femtosecond Laser Shock Peening with Ultralow Pulse Energy

*This chapter has been adapted from a **published** manuscript by Wenbo Wang, Chang-Yu Hung, Leslie Howe, Jia Chen, Kaiwen Wang, Vinh X. Ho, Shannon Lenahan, Mitsuhiro Murayama, Nguyen Q. Vinh, and Wenjun Cai from the following reference: Wenbo Wang, et al. “Enabling High-Performance Surfaces of Biodegradable Magnesium Alloys via Femtosecond Laser Shock Peening with Ultralow Pulse Energy” ACS Applied Bio Materials, 4(11), 7903-7912. 2021. Reprinted with permission from the ACS.*

4.1. Introduction

Strong and corrosion-resistant metallic materials such as stainless steel, cobalt-, and titanium-based alloys have been successfully applied as permanent orthopedic implant materials owing to their reliable structural stability in physiological conditions [1,2]. However, these materials often exhibit a high mismatch in stiffness and elastic modulus as compared to natural bone, causing stress shielding complications that ultimately reduce the density of the surrounding bone and weaken the bone structure [3–5]. In addition, the high corrosion resistance indicates that they would remain in vivo permanently if no follow-up removal operation was performed, which could lead to enduring physical irritation or inflammatory discomfort [6,7]. Recently, biodegradable alloys have attracted significant interest in the orthopedic industry due to their suitable mechanical properties and high degradation rate, potentially eliminating both the stress fielding problem as well as the secondary removal surgery [8]. Specifically, magnesium (Mg) and its alloys stand out among various degradable metals [9,10], exhibiting outstanding biocompatibility with similar mechanical properties as human bone (i.e., $E_{\text{bone}} = 3\text{--}20$ GPa; $E_{\text{Mg}} = 41\text{--}45$ GPa), and excellent implant stability. In addition, Mg also serves as a nutritional element that is essential to human metabolism to facilitate bone tissue growth [11]. Unfortunately, the rapid degradation rate of Mg alloys in the physiological environment under a pH of $\sim 7.4\text{--}7.6$ makes it challenging to ensure adequate structural integrity over the required time for complete tissue and bone healing [12,13]. For example, WE43 alloy (part of a promising candidate alloy series for this type of application) has a typical corrosion rate

of $\sim 0.7\text{--}1$ mm/year [14,15]. Witte et al. [16] found that WE43 alloy completely degrades within 18 weeks in vivo. Electrons released from the dissolution of Mg (anodic reaction) are consumed by the cathodic reaction to generate H_2 gas [17]. The Mg^{2+} and OH^- ions formed in anodic and cathodic reactions could then combine to form $\text{Mg}(\text{OH})_2$ [18]. As indicated by the Pourbaix diagram, this corrosion product is normally unstable in the human body. Thus, Mg tends to corrode actively without protection in vivo. In addition, the low mechanical strength of Mg makes it susceptible to high wear rates, especially in a corrosive physiological environment [19]. The formation of extensive wear debris on bone screws and anchors could result in an undesirable inflammatory reaction and implant loosening due to osteolysis [20]. Therefore, it is critical to simultaneously enhance the surface corrosion and wear resistance, i.e., tribocorrosion resistance of Mg alloys, to enable their potential usage as degradable load-bearing implants.

Among various surface treatment techniques for metals, laser shock peening (LSP) has generated considerable interest lately as a noncontacting photon-modification method due to its high precision, simple operability, and excellent reliability and efficiency [21,22]. Compared to traditional contacting-type methods (e.g., surface mechanical attrition, burr grinding, mechanical shot peening), surfaces treated with LSP not only exhibit enhanced fatigue life and corrosion resistance but also reduced stress relaxation during thermal exposure due to lower amounts of cold work involved [23–27], making it highly desirable for biomedical applications. By employing nanosecond (ns) pulsed lasers, a high-intensity laser beam is irradiated onto

the metal surface at a short period (typically 10–100 ns) to produce a high-energy plasma, which subsequently generates high-pressure shock waves [21]. Peening effect occurs when the pressure exceeds the Hugoniot elastic limit of the targeted materials [28,29]. Several previous studies showed that enhanced surface hardness and corrosion resistance could be achieved in metals after ns-LSP treatment as results of surface microstructure refinement, phase transformation, and residual stress generation [24,29,30]. For example, Ge et al.[31,32] reported a 34.1% increase in ultimate tensile strength and an 85.4% decrease in the corrosion rate of AZ31B Mg alloys after ns-LSP treatment, mainly due to the formation of compressive residual stresses and a nanostructured subsurface layer.

While most work on LSP so far uses ns-lasers [32–34], few have studied the shock peening effect of femtosecond (fs) lasers [35], where laser pulses are delivered to the metal surface in an ultrashort amount of time (on the order of one quadrillionth of a second) at precisely defined positions. Compared with ns-LSP, fs-LSP is found to introduce higher surface hardness at lower energy input [36] and interact differently with the confinement medium and protective coating than ns-laser [35]. For instance, Lu et al. [37] found that the surface hardness of Mg–3Gd alloy is improved by 70% through fs-LSP with 430 μ J pulse energy, as compared to 45.1% using ns-LSP with 9 J pulse energy due to less thermally facilitated subsurface structure relaxation. Apart from the effective strength improvement, fs-LSP is also beneficial to corrosion resistance enhancement. Wang et al. [38] discovered that the fs-LSP surface treatment effectively impedes corrosion crack formation and pits growth on the NiTi shape

memory alloy. In addition, the smaller surface roughness generated by fs-LSP than that by ns-LSP could further attenuate the dissolution rate between peaks and recesses of a rough surface [39]. In this work, we demonstrate that the usage of fs-LSP with the laser power on the order of 10^{-2} μJ is highly effective in enhancing the surface properties of biodegradable WE43 alloys by employing a confining medium and an absorbent layer. Specifically, the effects of fs-LSP processing conditions (e.g., power density, confinement, and absorption material) on the hardness, corrosion, and tribocorrosion resistance of WE43 alloys were measured in a stagnant blood blank buffered saline (BBBS) environment at body temperature. Material's characterization is combined with finite element simulations to reveal the underlying structural evolutions and residual stress generations during fs-LSP, which are responsible for the enhancement of the surface performance of WE43 alloys for biomedical implant applications.

4.2. Materials and methods

4.2.1. Sample preparation and characterization

All specimens were cut from extruded WE43 plates (Hunan High Broad New Material Co., Ltd., China) into dimensions of $2 \times 2 \times 0.6 \text{ cm}^3$. The chemical composition of the alloy in wt % is ~ 1.54 zirconium (Zr), ~ 3.51 yttrium (Y), ~ 2.27 neodymium (Nd), ~ 1.45 gadolinium (Gd), and balance Mg. The average grain size of the as-received WE43 is $21.9 \pm 7.1 \text{ }\mu\text{m}$, determined from the line-intercept method from the scanning electron microscope (SEM) images of etched surfaces (see the Supporting Information, Figure S1). Before fs-LSP, each sample was ground with abrasive SiC

papers with sizes down to 1200 grit, polished using alcohol-based diamond polish suspension (Allied High-Tech Products Inc., California) from 3 to 0.25 μm , ultrasonically cleaned in ethanol for 10 min, and finally dried in air. The microstructure characteristics were performed by X-ray diffraction (XRD, Bruker D8 Discovery) on the samples before and after fs-LSP, at 40 kV and 40 mA with Cu K α radiation and a 1 mm slit. A scan speed of 0.2° s/step with a step increment of 0.02 and 0.003° was applied for the large and small θ range scans, respectively. An atomic force microscope (AFM, Bruker) was employed to evaluate the surface roughness over areas of $\sim 20 \times 20 \mu\text{m}^2$. Hardness was measured using a Vickers hardness tester (LECO LV 700AT) with a load of 1000 gf and a dwell time of 10 s from at least seven separate tests on each sample. The surface morphology and composition were measured by a field-emission scanning electron microscope (FE-SEM, LEO 1550) equipped with an Oxford INCASynergy energy-dispersive X-ray spectroscopy (EDS) system. Transmission electron microscopy (TEM) was performed for selected samples using a JEOL JEM-2100 operated at 200 kV. Samples for TEM measurements were prepared via the standard lift-out method using a focused ion beam microscope (FIB, Helios600) after e-beam deposition of ~ 200 nm and ion beam deposition of $\sim 3 \mu\text{m}$ Pt protective coating on the sample surface to minimize FIB-induced damage and Ga contamination.

4.2.2. fs-LSP experiment

The fs-LSP surface treatments of WE43 samples were conducted by a Ti:Sapphire laser (Spectra-Physics Mai Tai, VF-T1S laser) delivering femtosecond pulses with < 60

fs pulse duration, at 750 nm wavelength and 80 MHz repetition rate, using a setup shown in Fig. 4.1. The output power of the femtosecond laser was adjusted to 0.6 W for all treatments. The power density (I , GW/ cm²) was controlled by the spot size and the pulse energy of the laser beam using lenses with different focal lengths, i.e., $f = 50$ and 25 mm and estimated as: $I = \frac{4E}{\pi \cdot \Delta t \cdot D^2}$, where E is the pulse energy per single pulse, Δt is the pulse duration, and D is the diameter of the laser spot size. The samples were scanned at 0.5 mm/s in a zigzag pattern using a custom-made motorized x–y stage (Thorlabs, PT1-Z8). To obtain a homogeneous power density on the samples, 50% overlap between adjacent laser spots was used for all samples. Table 4.1 summarizes all samples tested under various processing parameters. For direct ablated samples (fs-LSP-air-7), the samples were directly treated by the laser in air without an absorbent layer or a confining medium. For other samples, deionized water (~3 mm thickness) or quartz (~2 mm thickness) were employed as a confining medium, while vinyl electrical black tape (3M-700) with ~0.177 mm thickness was used as an adsorbent layer.

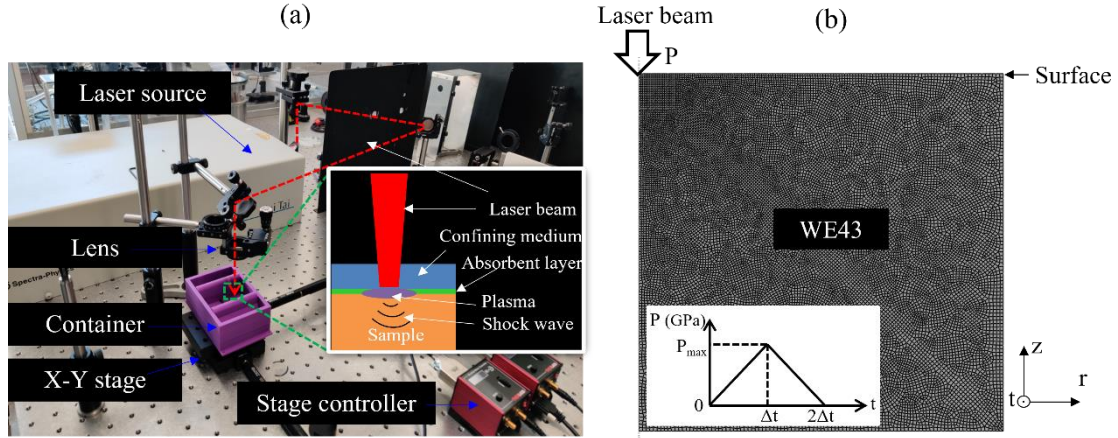


Figure 4.1. (a) fs-LSP experimental setup. The inset image shows the schematic of a laser–sample interaction at the presence of a confining medium and an absorbent layer and (b) FE model geometry setup and meshing, where r, z, t in the coordinate system represents the radial, normal, and transverse direction, respectively. Inset graph shows the imposed laser pressure temporal profile.

Table 4.1 Summary of femtosecond laser shock peening processing parameters.

Sample group ID	Focal length (mm)	Spot size (ϕ mm)	Power density (GW/cm ²)	Absorbent layer	Confining medium
fs-LSP-air -7	50	~ 0.05	7	NA	NA
fs-LSP-water-7	50	~ 0.05	7	NA	Water
fs-LSP-water-tape-7	50	~ 0.05	7	Black tape	Water
fs-LSP-quartz-tape-7	50	~ 0.05	7	Black tape	Quartz
fs-LSP-quartz-tape-28	25	~ 0.02	28	Black tape	Quartz

4.2.3. Corrosion and tribocorrosion tests

To evaluate the effect of fs-LSP on a metal surface, all electrochemical measurements were performed in the BBBS solution with pH of 7.0–7.2 at 37.01 ± 0.43 °C using a Gamry Reference 600 potentiostat/galvanostat/ZRA in the three-electrode configuration, where the specimen, activated titanium mesh, and a

commercial silver–silver chloride electrode (1 M KCl internal solution) served as the working (WE), counter (CE), and reference (RE) electrodes, respectively. Potentiodynamic polarization (PD) tests were carried out on all specimens with an effective exposed area of $\sim 0.5 \text{ cm}^2$. After stabilization at the open circuit potential (OCP) for ~ 5 min, the PD tests started from -0.2 V below OCP and terminated at 0.5 V above OCP under a constant scan rate of 1 mV/s . Electrochemical impedance spectroscopy (EIS) tests were conducted by applying a 10 mV root mean square of AC voltage under OCP from 100 mHz to 100 kHz with five points per decade in the BBBS solution, after 5 min of equilibrium time at OCP. All electrochemical results were collected and fitted using the Gamry E-chem software.

Tribocorrosion tests were performed using a multifunctional tribometer (MFT-5000, Rtec Instruments, California) with a built-in electrochemical cell in the three-electrode setup in the BBBS solution with the same pH, temperature, and WE exposed area as the corrosion tests. After $\sim 5 \text{ min}$ of OCP stabilization, tribocorrosion tests were started by applying a 0.5 N normal load at 0.1 mm/s sliding velocity for 2 min over a 3 mm stroke length. An alumina ball (Al_2O_3 , 4 mm diameter) was selected as the counterpart, and a new surface was used after each test to minimize contamination. A Dektak XT profilometer was used to measure the depth profile of wear tracks after the tribocorrosion tests. To ensure repeatability of results, all electrochemical and tribocorrosion tests were carried out at least three times for each sample group.

4.2.4. Finite element simulations

A two-dimensional (2D) axisymmetric finite element model was developed to simulate residual stress/strain generation from fs-LSP using the ABAQUS software, as shown schematically in Fig 4.1. The workpiece dimensions were set up as a square with 100 μm in both the r- and z-directions and a laser spot size of $\sim 20 \mu\text{m}$. The bottom and right sides were set as a fixed constraint with non-deformation boundary conditions. CAX4R (4-node bilinear axisymmetric quadrilateral, reduced integration and hourglass control) mesh elements were selected for finite computational domain, and the mesh S-4 size was refined from 1.0 to 0.5 μm toward the center of laser beam in both r- and z-directions after convergence analysis. The peak pressure (P) generated from the shock wave was estimated by Fabbro's model as [41]: $P(\text{GPa}) = 0.01 \sqrt{\frac{\alpha}{2\alpha+3}} \cdot \sqrt{Z} \cdot \sqrt{I}$, where I the power density (GW/cm^2), Z is the reduced shock impedance ($\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$) between the confining material and the workpiece, and α is the efficiency of the interaction ($\alpha = 0.1 - 0.2$). It should be noted that Fabbro's model is generally used in ns-LSP. In current simulation, the early stage of interaction between laser and target, i.e., two-temperature model, is not considered. Thus, the peak pressure of fs-LSP was estimated by Fabbro's model for simplicity [42]. Due to the ultrashort pulse duration, a linear triangle ramping pressure was utilized on the top surface, as shown in Fig 4.1(b) insert, instead of the conventional Gaussian temporal profile, and total loading time was adjusted to twice the pulse duration (Δt) [43]. The stable time increment during ABAQUS/Explicit analysis is smaller than the stress stabilization time in order to avoid numerical instability and obtain accurate results [44] The Johnson-Cook model was

used to simulate the rate-dependent mechanical behavior of WE43, as described by the flow stress, $\sigma = (A + B\varepsilon^n) \cdot \left(1 + C \ln\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}\right)\right) \cdot (1 - T^m)$, where A is the yield stress, B is work hardening modulus, C is the strain rate sensitivity, n is the work hardening coefficient, ε is the strain, $\dot{\varepsilon}$ is the strain rate, T is the dimensionless temperature, and m is the thermal soften coefficient. hardening modulus, C is the strain rate sensitivity, n is the work hardening coefficient, ε is the strain, $\dot{\varepsilon}$ is the strain rate, T is the dimensionless temperature, and m is the thermal soften coefficient. The materials parameters used in the present work are estimated from [45] and information from the vendor.

4.3. Results and discussion

4.3.1. Surface morphology

To examine changes in the surface morphology of samples under the fs-LSP process, electron microscopes have been used. Fig. 4.2 shows the SEM surface morphology of WE43 samples before and after fs-LSP treatments. There is no obvious difference between the surfaces of untreated and fs-LSP-air-7 samples (Fig. 4.2(a,b)), indicating that under direct ablation in air, the low laser energy was not adequate to stimulate electrons so that little ionization or plasma was generated. On the other hand, for fs-LSP-water-7 samples treated under confined ablation in water without an absorbent layer (Fig. 4.2(c)), except occasional dimple formation [40], the surface is dominated by the formation of circular corrosion product (most likely $\text{Mg}(\text{OH})_2$ -rich hydroxide) [46] with $\sim 20\text{--}30\ \mu\text{m}$ diameter as a result of Mg corrosion in water. When a black tape was used as an absorbent layer, more dramatic surface morphological

changes were observed. For sample fs-LSP-water-tape-7, Fig. 4.2(d) shows the formation of extensive craters on the surface, indicating that the energy absorption was significantly improved by the black tape to induce laser ablation. A similar treatment using an aluminum tape (results not shown here), however, leads to a negligible surface morphological change due to its higher surface reflectivity or lower (80%) laser energy absorption than that of black tape (100%). It was also observed that when either static or flowing water was used as the confining medium, H₂ gas bubbles frequently occur on the sample surfaces due to metal corrosion [47] greatly impeding uniform laser peening effect. Thus, the usage of water as a confining medium should be avoided for actively corroding metals such as Mg alloys. When quartz was used as the confining medium, fewer craters and more ripplelike structures and surface nodules were seen on the sample surface, as shown in Fig. 4.2(e). Under a higher laser power density of 28 GW/ cm², the sample surface shows uniform ripple, a.k.a. laser induced the formation of periodic surface structures [48] over the entire surface (Fig. 4.2(f)). During the laser–sample interaction, surface electrons are energized by the laser energy, with a higher possibility to escape as irradiative energy increases. Such an ionization process produces plasma. If the power of the laser is appropriate, the expansion of such plasma leads to plastic deformation and ripple formation instead of surface ablation due to evaporation, plume and cone formation, as seen in the fs-LSP-water-tape-7 sample [49–52]. Comparing surface morphologies of all samples in Fig. 4.2 shows that the fs-LSP-quartz-tape-28 samples are exhibited the most uniform formation of ripples. Hence, they were selected for the subsequent mechanical, corrosion, and tribocorrosion

studies in Sections 4.4.2–4.4.4, and abbreviated as fs-LSP WE43 for simplicity hereafter.

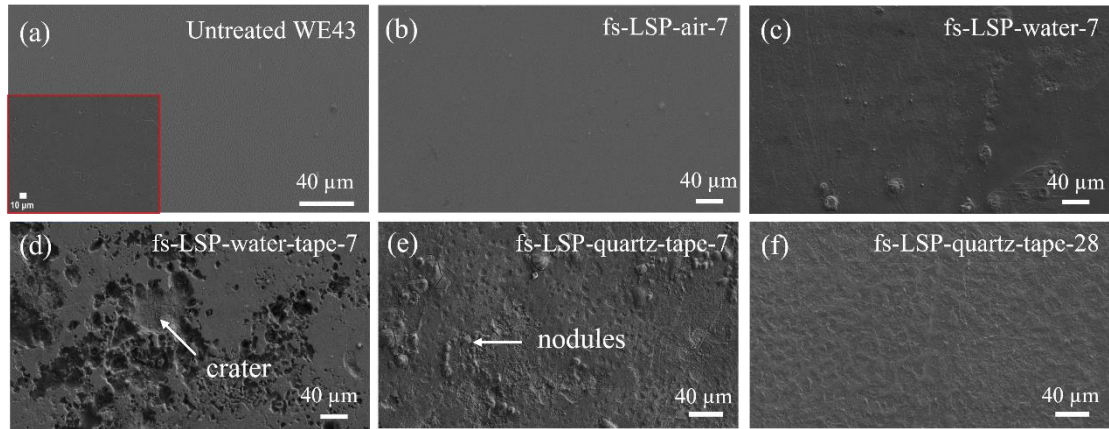


Figure 4.2. SEM surface morphology of (a) untreated and (b–f) fs-LSP-treated WE43 Mg samples under different conditions as listed in Table 4.1. Insert image in (a) show the surface of untreated WE43 after chemical etching.

4.3.2. Structure, surface morphology, and mechanical properties

The crystal structure of the untreated and fs-LSP WE43 samples was characterized by XRD and AFM. Both samples exhibited polycrystalline characteristics with an α -Mg matrix and $\text{Mg}_{41}\text{Nd}_5$, Mg_{24}Y_5 , and Mg_{12}Nd precipitates, and no new phase was generated after the fs-LSP treatment, as shown in Fig. 4.3. The diffraction peak of Mg (11 $\bar{2}$ 0) phase shifted slightly ($\sim 0.048^\circ$) toward the higher angle direction after fs-LSP, as compared to the untreated WE43 (indicated by arrows in Fig. 4.3(b)), which could be related to the formation of lattice strain at the surface [53]. In addition, the full width at half-maximum (FWHM) of this diffraction peak exhibited a slight broadening ($\sim 0.271^\circ$) for the fs-LSP sample than that ($\sim 0.261^\circ$) of the untreated WE43, which is typically caused by grain refinement, or generation of high dislocation density

and residual stress at the surface [54,55].

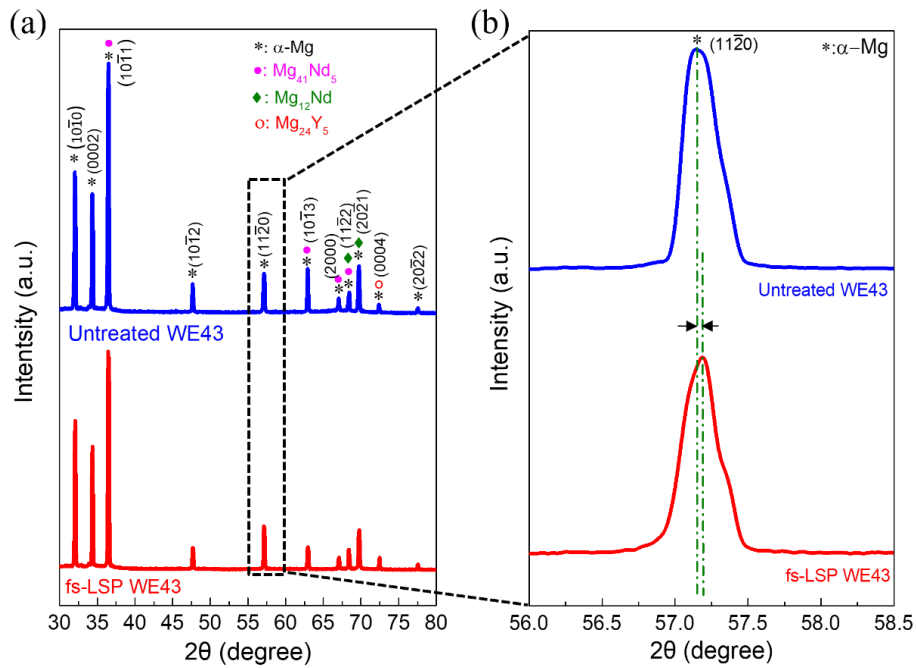


Figure 4.3. XRD (a) 2 θ spectra and (b) zoomed-in spectra of the box area (a) of untreated and fs-LSP-treated WE43 Mg alloy. The fs-LSP treatment of WE43 was performed using quartz as a confining medium and a black tape as an absorbent layer at 28 GW/cm² power density.

The AFM surface topography of the samples is presented in Fig. 4.4(a,b) and the corresponding surface roughness (Ra) in Fig. 4.4(c). It can be seen that Ra increased after fs-LSP treatment due to the formation of ripples. Fig. 4.4(d) shows the surface hardness of the WE43 sample increased by 23.1% after fs-LSP treatment. To reveal the subsurface microstructure evolution after fs-LSP, the cross-section of fs-LSP-quartz-tape-28 samples was characterized by TEM and selected area electron diffraction (SAED) at various depths below the surface (Fig. 4.5). It can be seen that the amount

of plastic deformation at the surface has not resulted in significant grain refinement; instead, a higher dislocation density was present within the top $\sim 1\ \mu\text{m}$ below the surface (see Fig. 4.5(b)). In addition, the rotation of SAED patterns at various depths below the surface indicates the presence of a strain gradient, hence the formation of geometrically necessary dislocations after fs-LSP.

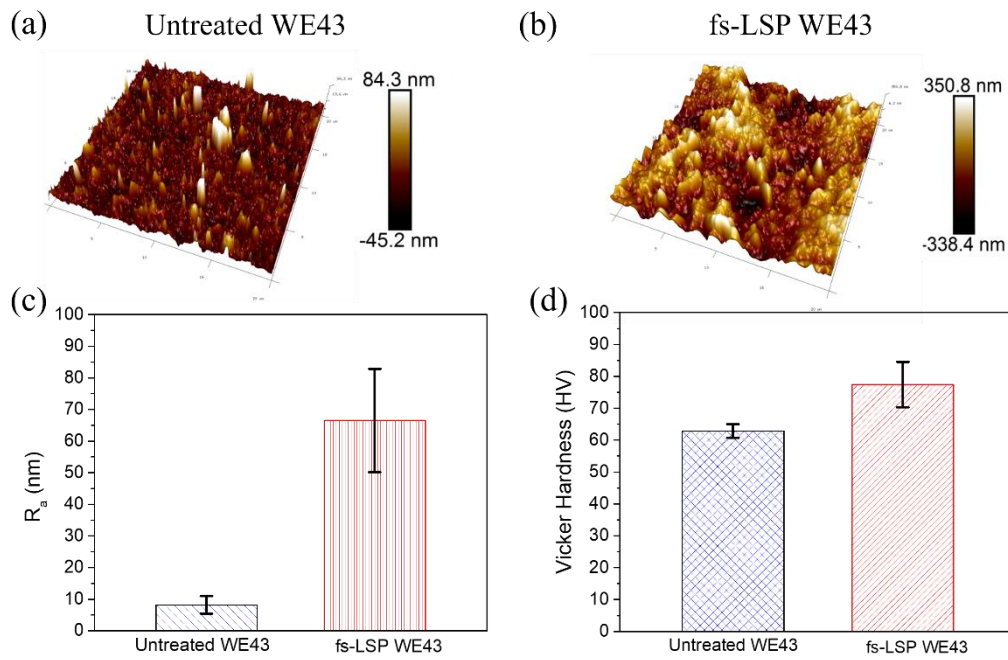


Figure 4.4. AFM images of WE43 Mg alloys (a) before and (b) after fs-LSP treatment, (c) surface roughness, and (d) micro-Vickers hardness of WE43 Mg samples with and without fs-LSP treatment using quartz as a confining medium and a black tape as an absorbent layer at $28\ \text{GW}/\text{cm}^2$ power density.

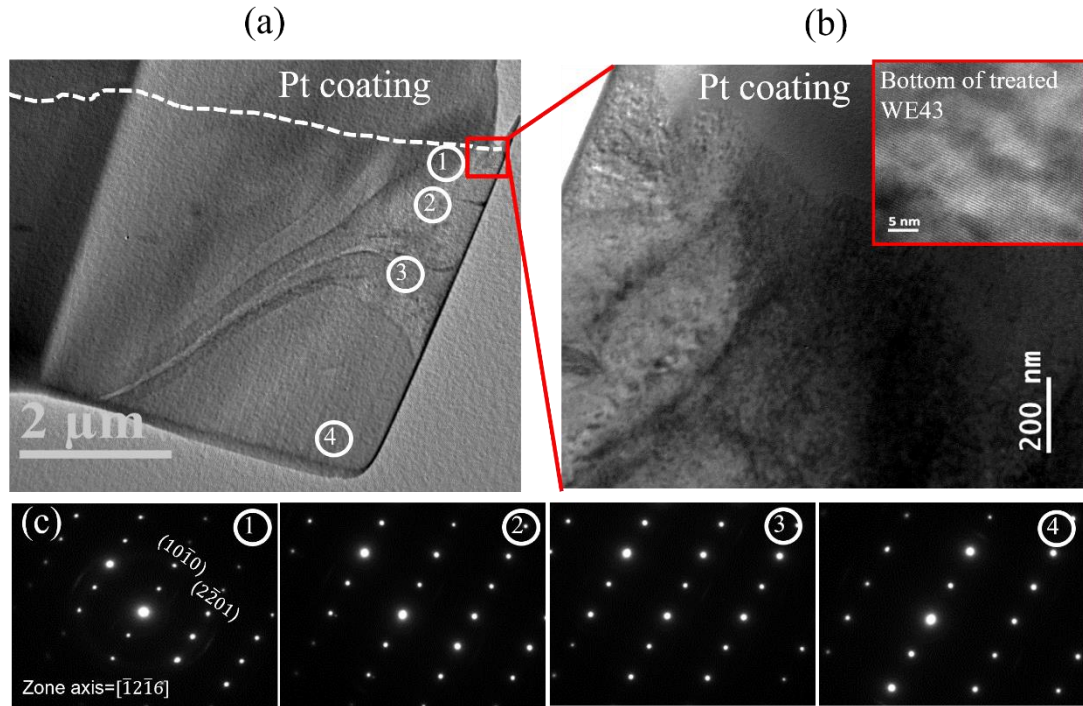


Figure 4.5. (a, b) Bright-field TEM images and (c) selected area electron diffractions of the fs-LSP WE43 sample at various depths below the surface as marked in (a). Insert TEM images in (b) shows the bottom of fs-LSP treated WE43 sample.

It should be noted that, for thin FIB lamellar, the TEM sample lift-out procedure would relieve most of (if any) out-of-plane strain inevitably. Nevertheless, the deformation induced by a Gaussian laser beam is radial symmetric on the WE43 surface; hence, stress/strain measured from a 2D cross-sectional plane (perpendicular to the surface) is enough to determine that in 3D based on symmetry operation. In addition, fs-LSP involves a surface deformation with an affected depth significantly less than the grain size ($\sim 22 \mu\text{m}$, as shown in Fig. 4.2(a)). Due to the presence of a strain gradient within the grain, the in-plane strain can be captured by accounting for the lattice rotation

[56] from the undeformed (i.e., areas far away from the surface) and the deformed configurations (i.e., areas right below the surface), similar to that observed during severe adhesive wear [57]. Specifically, comparing the SAED patterns from locations 1 and 4 indicate a total rotation of $\sim 0.5^\circ$, with the rotation axis perpendicular to the image plane, corresponding to a residual strain of $\sim 0.5\%$, specifically as shown in Fig. 4.6.

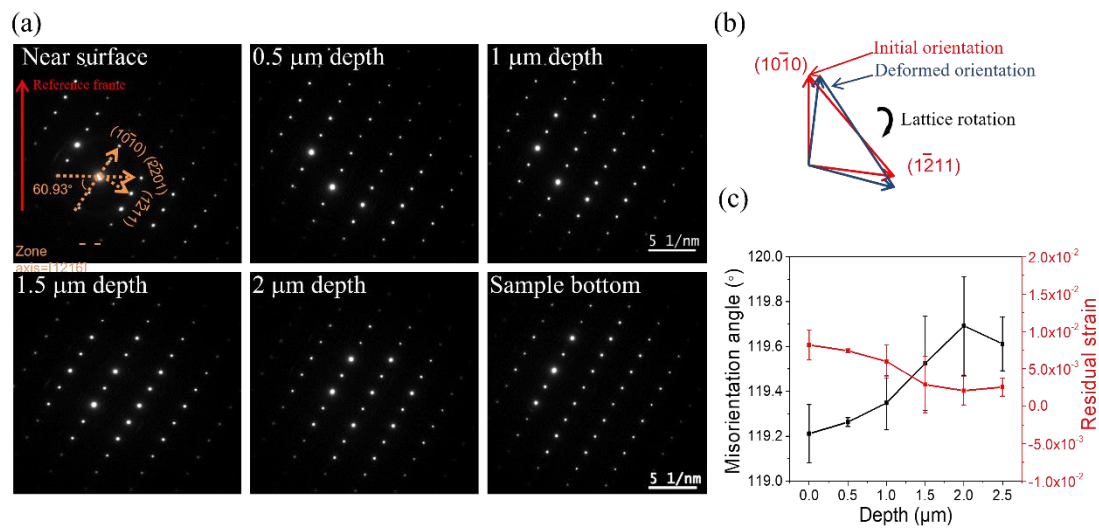


Figure 4.6. (a) SAED patterns of fs-LSP WE43 sample at various depths below the surface, (b) schematic representation of in-plane lattice rotation, and (c) the measured misorientation angle and calculated residual strain as a function of depth.

However, such interpretation of strain should be cautioned, as the bend contour (equal inclination fringe) in Fig. 4.5(a) indicates the presence of local curvature, which may also affect the appearance of the SAED patterns. Combined with the FE simulation results shown in later, it is concluded here that the residual elastic strain, if any, is insignificant in WE43 after fs-LSP.

4.3.3. Corrosion behavior

An improvement of the corrosion behavior of the Mg alloy has been obtained with fs-LSP. Fig. 4.7(a) presents typical PD results of untreated and fs-LSP WE43 samples under the BBBS solution at body temperature. It can be seen that the fs-LSP WE43 samples exhibited a shift toward positive of the corrosion potential (E_{corr}) and a reduction of corrosion current density (i_{corr}) than those of the untreated WE43 sample, indicating an enhancement of corrosion resistance due to reduced cathodic and anodic kinetics. Fig. 4.7(b,c) shows their corresponding morphologies of corroded surfaces. The formation of the corrosion product of the untreated WE43 was found to be localized, while that of the fs-LSP samples was more uniform. In both cases, dehydration cracks were observed on the corrosion product, most likely due to the evaporation of water from magnesium hydroxide on the surface [46]. Table 4.2 summarizes the surface composition before and after corrosion for both samples from EDS analysis. It can be seen that after corrosion, a higher oxygen content was observed on the fs-LSP sample than the untreated sample, consistent with their more uniform distribution of the corrosion product on the surface.

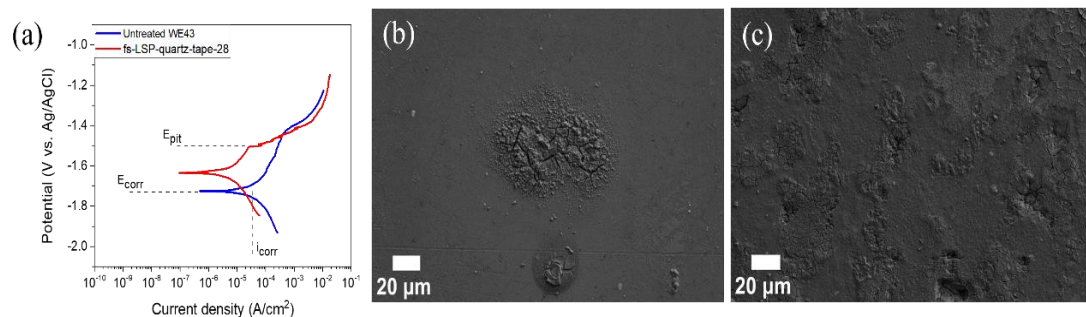


Figure 4.7. (a) Typical PD curves and post PD test surface morphologies of (b) untreated and (c) fs-LSP WE43 Mg samples.

Table 4.2 Summary of surface compositions (measured by EDS analysis) of untreated and fs-LSP-treated samples before and after corrosion.

Elements (at. %)	Untreated WE43		fs-LSP-quartz-tape-28	
	Before corrosion	After corrosion	Before corrosion	After corrosion
O	2.8 ± 0.2	22.8 ± 1.1	17.8 ± 1.2	30.3 ± 5.8
Mg	95.3 ± 0.3	75.1 ± 1.3	80.7 ± 1.1	67.9 ± 5.6
Y	1.2 ± 0.01	1.0 ± 0.01	1.0 ± 0.06	0.9 ± 0.06
Zr	0.2 ± 0.08	0.6 ± 0.07	0.1 ± 0.06	0.5 ± 0.04
Nd	0.4 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	0.3 ± 0.01
Gd	0.1 ± 0.03	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.03

To further understand their corrosion kinetics, EIS analysis was performed at OCP for both samples, and the results are shown in Fig. 4.8. An equivalent circuit model [58] shown in Fig. 4.8(a) was used to fit the experimental data, where R_s is the resistance of the electrolyte between the working and the reference electrodes, R_1 is the resistance of the electrolyte through the corrosion products, R_2 is the charge-transfer

resistance, C is the double-layer capacitance between the metal surface and electrolyte, and L and R_L are the inductance and the corresponding resistance of the inductor, respectively. In this model, CPE is the constant-phase element, representing nonideal capacitive behavior caused by surface inhomogeneity. Mathematically, CPE is defined as $Z = 1/Y \cdot (j\omega)^a$, where Y is a constant, j is the imaginary unit, ω is the angular frequency of the sinusoidal signal, and a is a coefficient between 0 and 1. All fitting parameters of the model are summarized in Table 4.3. Fig. 4.8(b) shows typical the Nyquist plots and model fitting curves of both samples. Two capacitance loops can be found in the high- and low-frequency ranges, where the larger diameter of the semicircle of the fs-LSP sample indicates a higher charge-transfer resistance, hence better corrosion resistance than the untreated sample. Additionally, the inductive loop (where Z_{imag} is negative) was observed on the untreated WE43 sample, which likely formed after pitting induced accelerated anodic dissolution [59]. Note that such an inductive loop might disappear after a protective passive layer is generated, which is indeed observed in the fs-LSP sample. At high frequencies, the electrolyte resistance R_s was estimated to be $\sim 77\text{--}85\ \Omega$ from Fig. 4.8(c). At lower frequencies, the polarization resistance of the fs-LSP sample was much higher than that of the untreated sample, in agreement with their PD behavior. In the phase-shift Bode plot, Fig. 4.8(d), the untreated WE43 sample exhibited a maximum phase angle close to 0° around 0.1 Hz, resembling the behavior from a simple Randles cell, indicating only one-time constant was dominating, likely from the electrode/ electrolyte double layer. On the other hand, the phase shift of the fs-LSP sample shows a small wave trough in the low-

frequency region, characteristic of an electrical circuit with two relaxation processes [60], where the additional relaxation process likely originated from the presence of an additional corrosion layer on the metal surface (i.e., electrode).

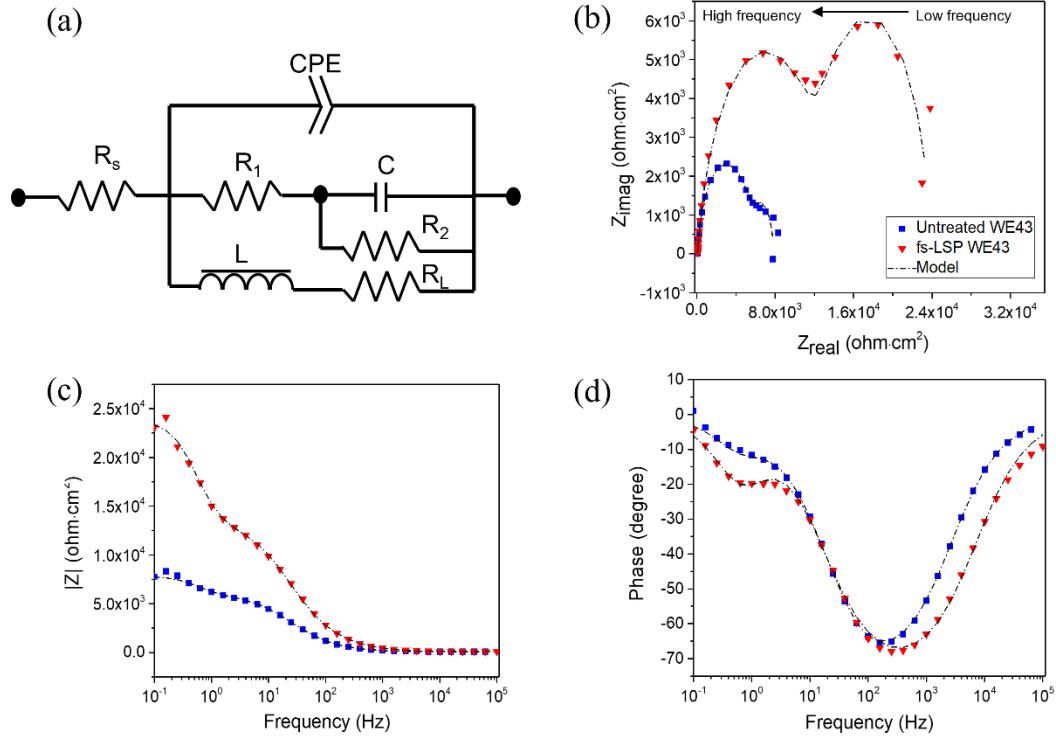


Figure 4.8. EIS results of WE43 Mg alloys with and without fs-LSP treatments: (a) equivalent circuit model used for the model fitting and (b) Nyquist plots and model fit. Bode plots of the (c) impedance magnitude, $|Z|$, and (d) phase shift are presented as a function of frequency.

Table 4.3 Summary of equivalent circuit model fitting parameters defined in Fig.

4.8(a).

Sample ID	R_s ($\Omega \cdot \text{cm}^2$)	Y_{01} ($\text{cm}^{-2} \text{s}^{-n} \Omega^{-1}$)	a_1	CPE ($\text{F} \cdot \text{cm}^{-2} \text{s}^{n-1}$)	R_1 ($\Omega \cdot \text{cm}^2$)	C ($\text{F} \cdot \text{cm}^{-2}$)	R_2 ($\Omega \cdot \text{cm}^2$)	L (H)	R_L ($\Omega \cdot \text{cm}^2$)
Untreated WE43	76.9	3.8×10^{-6}	0.84	1.98×10^{-6}	8.83×10^3	7.31×10^{-5}	3.28×10^3	48.49	1.85×10^4
fs-LSP-quartz-tape-28	84.7	1.6×10^{-6}	0.83	7.75×10^{-7}	1.64×10^4	2.09×10^{-5}	1.81×10^4	55.32	7.62×10^4

4.3.4. Tribocorrosion results

The tribocorrosion results are summarized in Figs. 4.9 and 4.10. Fig. 4.9(a) shows the OCP evolution of both samples during tribocorrosion tests in the BBBS solution under body temperature. Before the onset of sliding, the stabilized OCP of fs-LSP samples was higher (nobler) than that of the untreated WE43 sample, which is consistent with their PD results (Fig. 4.7(a)). As soon as the counter body sliding starts, the potential shifts toward the positive direction for the untreated WE43 sample, while a shift toward the more negative potential for the fs-LSP sample has been observed. Such different behavior can be understood as the following. For the untreated WE43 sample, the generated corrosion product layer was unprotected due to their discontinuity and defects [61]. The unworn area is thus actively corroded at a low corrosion potential. During tribocorrosion, the mechanical sliding imposes subsurface deformation within the wear track, similar to those imposed by LSP, hence leading to enhanced passivity and ennoblement of corrosion potential. On the other hand, the unworn surface of the fs-LSP sample was passivated due to laser peening, hence passivated during pure corrosion and exhibited a higher corrosion potential. Once scratched, the depassivation (i.e., mechanical removal of the passive film) on the wear track leads to the formation of more actively corroding surfaces, resulting in the potential drop during sliding. When the test was over, the fs-LSP sample recovered its original OCP value, i.e., repassivated, with a small repassivation time of ~ 32 s, indicating a fast-repassivation kinetics. The average coefficient of friction (COF) during tribocorrosion is shown in Fig 4.9(b). It can be seen that a slightly lower COF

has been observed in the fs-LSP sample than that of the untreated counterpart, indicating that the corrosion product affected by the laser peening is also lubricious.

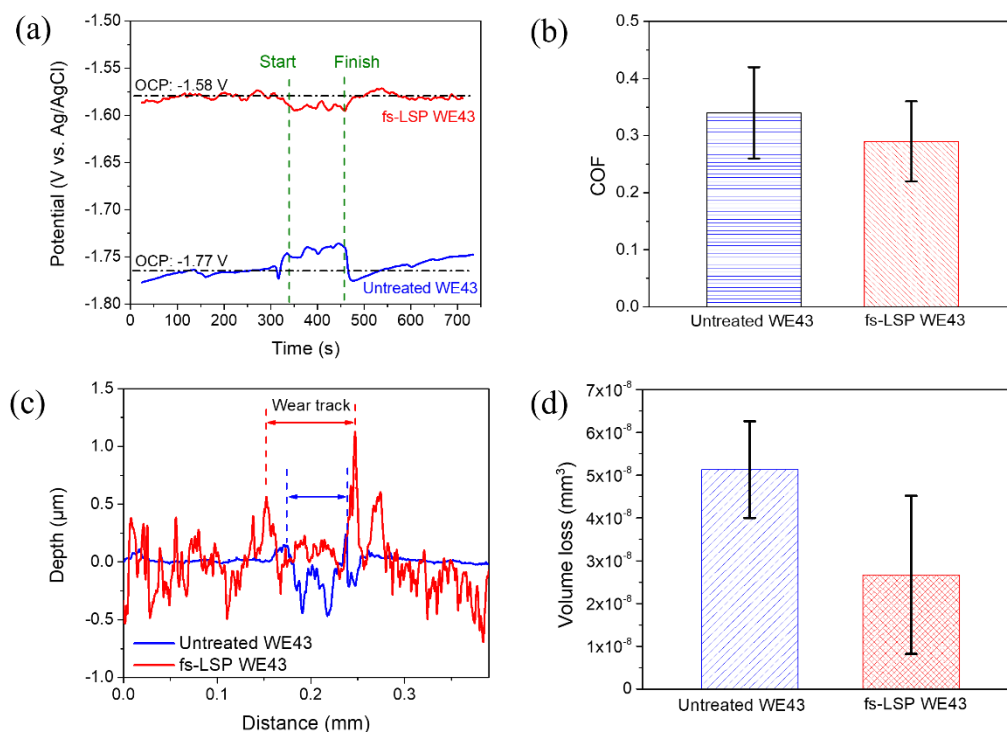


Figure 4.9. (a) Evolutions of OCP, (b) COF, (c) typical wear track depth profiles, and (d) the summary of volume loss of untreated and fs-LSP WE43 samples during tribocorrosion tests. The profiles in (c) were measured perpendicular to the sliding direction on the tribocorroded surface of all samples.

Fig. 10 shows the post-tribocorrosion surface morphology and the corresponding EDS mappings. In Fig. 10(a), the wear track of the untreated WE43 sample exhibited deep grooves and pileups near the edge of the track, indicating the characteristics of abrasive wear. On the other hand, the wear track of the fs-LSP sample was much shallower and smoother (Fig. 10(b)). In terms of element distribution, Mg, rare-earth elements, and oxygen are almost uniformly distributed on the surface of the untreated

sample, with higher concentrations of O, Y, and Zr on the corrosion products. On the other hand, the O distribution of the fs-LSP sample was patchy, at a length scale similar to that of the surface ripples ($\sim 20\text{--}30\text{ }\mu\text{m}$). The dimensions of wear tracks of both samples were evaluated and presented in Fig. 4.9(c), from which the total volume loss during tribocorrosion was calculated for both samples, as shown in Fig. 4.9(d). Approximately, 48% reduction in tribocorrosion rate was measured in the fs-LSP sample than that of the untreated one, indicating a significant enhancement of tribocorrosion resistance, in agreement with the enhancement of surface's mechanical and corrosion properties.

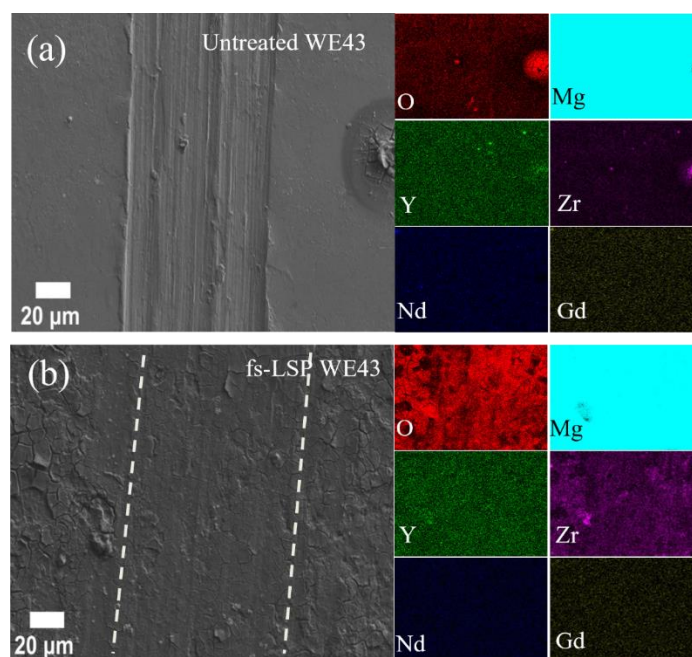


Figure 4.10. Surface SEM images after tribocorrosion tests of (a) untreated WE43 and (b) fs-LSP WE43 samples and corresponding EDS element mappings.

Finally, we briefly discuss the structural origin for the enhanced surface properties of WE43 after fs-LSP. While the improved surface hardness and corrosion resistance of Mg alloys through ns-LSP are typically attributed to grain refinement, generation of nanocrystalline layers, and beneficial residual stress [62], our TEM analyses (Fig. 4.5) indicate that there is no obvious grain refinement after fs-LSP. Hence, both surface hardening and corrosion resistance improvement in this work should be mainly attributed to the high dislocation density generated near the surface. On the one hand, the dense dislocation on the surface impedes dislocation motion, so the surface hardness is increased by strain hardening after fs-LSP, which further contributes to the shallow wear depth during tribocorrosion. On the other hand, the interception of dislocations at the surface is the preferred location for passive film growth according to the point-defect model [63]. It is believed that such high dislocation density considerably contributes to the rapid generation of a uniform and compact protective layer with high charge-transfer resistance on the fs-LSP sample surface during corrosion and also facilitates fast repassivation during tribocorrosion by modifying the surface activity. Another commonly observed structural modification during ns-LSP is the generation of residual stress. As shown the simulation results in Fig. 4.11, although present, both the affected depth and magnitude of residual stress are rather small during fs-LSP and hence are likely to play a less significant role than that of dislocations. Specifically, Fig. 4.11(a,b) shows the simulated subsurface von Mises stress (σ_{VM}) and effective plastic strain (ϵ_{pl}) distribution during laser peening.

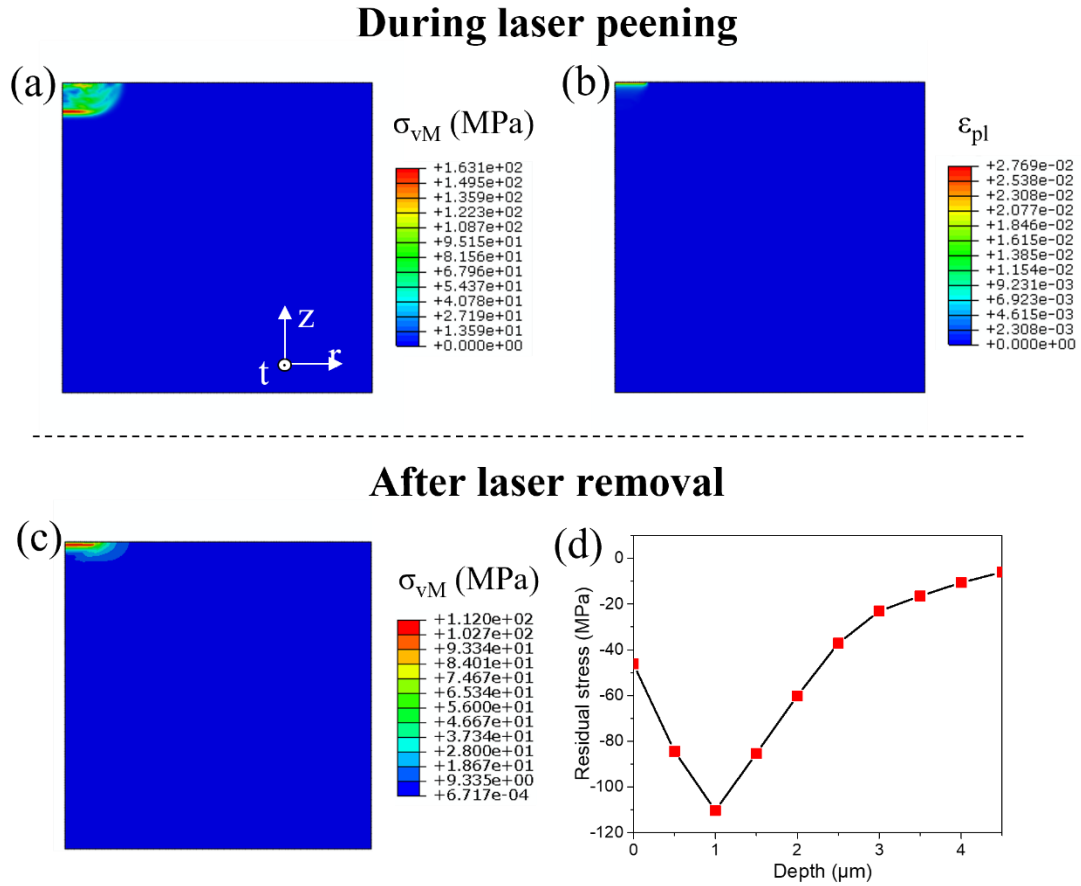


Figure 4.11. FE simulated results of (a) von Mises stress and (b) effective plastic strain during laser peening. FE simulated (c) von Mises stress and (d) maximum residual stress depth profile after laser removal on WE43 surface after fs-LSP treatment using pressure profile defined in Fig. 4.1 inset.

The main deformation (as shown in Fig. 4.12 for stress components in different directions) is a compression stress in the surface-normal direction. A maximum effective plastic strain of 2.77% was observed during peening (Fig. 4.11(b)), which became negligible (less than $\sim 0.02\%$) once the laser was removed, leaving behind an elastic strain that was dominated by a compressive strain component of 0.49% in the surface with normal direction (Fig. 4.13). It is noted that the simulated residual strain

magnitude and residual stress depth (Fig. 4.11(d)) are in great agreement with those measured experimentally from SAED analyses (Figs. 4.5 and 4.6).

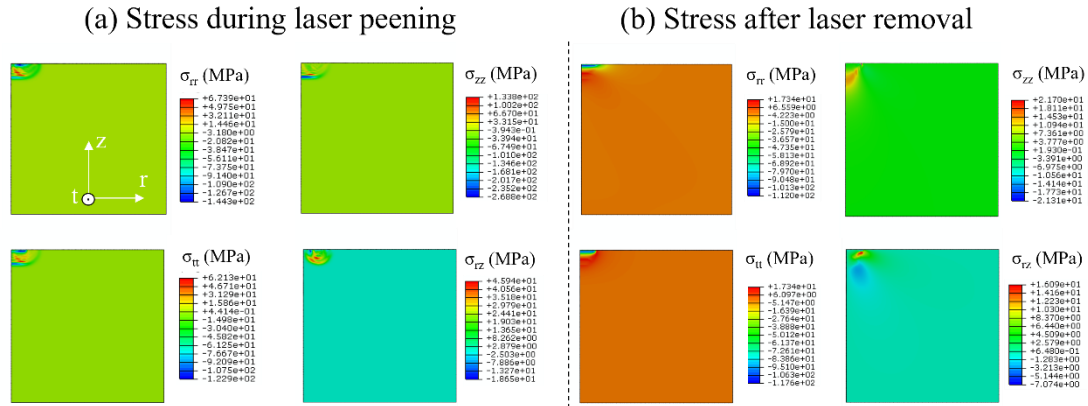


Figure 4.12. FE simulated results of 2D stress components (a) during laser peening and (b) after laser removal using coordinate system defined in (a).

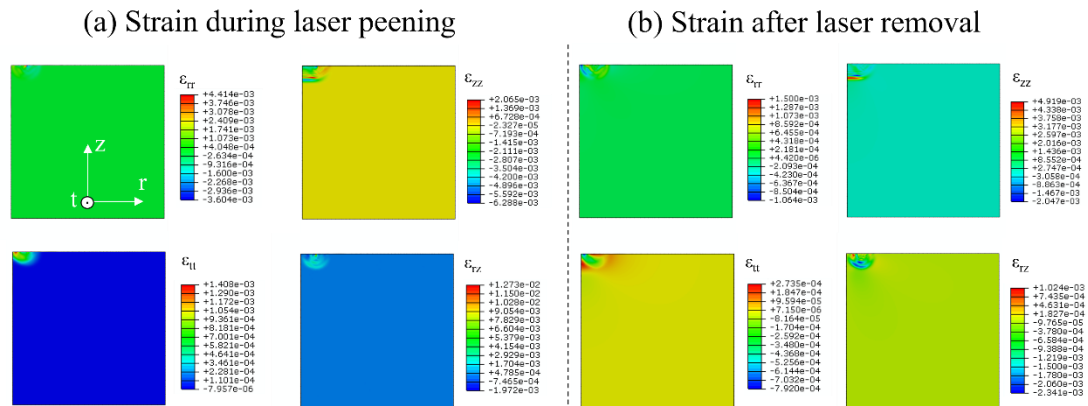


Figure 4.13. FE simulated results of 2D logarithmic strain components (a) during laser peening and (b) after laser removal using coordinate system defined in (a).

4.4. Conclusions

In this work, the effects of fs-LSP with ultralow pulse energy on the mechanical, corrosion, and tribocorrosion behavior of WE43 Mg alloys were investigated in a corrosive environment relevant to biomedical implant applications. It was found that

surface morphology and the degree of peening effects strongly depend on the fs-LSP condition such as direct vs. confined ablation, with and without a confining medium and an absorbent layer. The optimum peening effect was found to occur in confined ablation conditions with the combination of a black tape and a quartz layer at 28 GW/cm². Comprehensive microstructure characterization indicates that fs-LSP leads to significant dislocation generation but no phase transformation or grain refinement below the surface. Such modified surface microstructure led to the enhancement of surface hardness, corrosion, and tribocorrosion resistance. The treated surface exhibits rapid-repassivation ability and high charge-transfer resistance, allowing the surface to quickly self-repair in a physiological environment once mechanically scratched. The coupling of advanced material characterization and FE simulation indicates that the generation of dislocations rather than residual stress contributes primarily to the remarkable enhancement of the surface performance of fs-LSP-treated WE43 Mg alloys.

References:

1. Niinomi, M. Recent metallic materials for biomedical applications. *Metall. Mater. Trans. A* 2002, 33, 477–486.
2. Hermawan, H.; Ramdan, D.; Djuansjah, J. R. Metals for Biomedical Applications. In *Biomedical Engineering - From Theory to Applications*; InTech, 2011; pp 411–430.
3. Gepreel, M. A.-H.; Niinomi, M. Biocompatibility of Ti-alloys for long-term implantation. *J. Mech. Behav. Biomed. Mater.* 2013, 20, 407–415.

4. Pietrzak, W. S.; Sarver, D.; Verstynen, M. Bioresorbable implants - Practical considerations. *Bone* 1996, 19, S109–S119.
5. Nagels, J.; Stokdijk, M.; Rozing, P. M. Stress shielding and bone resorption in shoulder arthroplasty. *J. Shoulder Elb. Surg.* 2003, 12, 35–39.
6. Milosev, I. Metallic materials for biomedical applications: Laboratory and clinical studies. *Pure Appl. Chem.* 2010, 83, 309–324.
7. Zhen, Z.; Xi, T.-f.; Zheng, Y.-f. A review on in vitro corrosion performance test of biodegradable metallic materials. *Trans. Non-ferrous Met. Soc. China* 2013, 23, 2283–2293.
8. Prakasam, M.; Locs, J.; Salma-Ancane, K.; Loca, D.; Largeteau, A.; Berzina-Cimdina, L. Biodegradable materials and metallic implants-a review. *J. Funct. Biomater.* 2017, 8, No. 44.
9. Staiger, M. P.; Pietak, A. M.; Huadmai, J.; Dias, G. Magnesium and its alloys as orthopedic biomaterials: a review. *Biomaterials* 2006, 27, 1728–1734.
10. Marukawa, E.; Tamai, M.; Takahashi, Y.; Hatakeyama, I.; Sato, M.; Higuchi, Y.; Kakidachi, H.; Taniguchi, H.; Sakamoto, T.; Honda, J.; et al. Comparison of magnesium alloys and poly-L-lactide screws as degradable implants in a canine fracture model. *J. Biomed. Mater. Res., Part B* 2016, 104, 1282–1289.
11. Rude, R. K.; Gruber, H. E. Magnesium deficiency and osteoporosis: animal and human observations. *J. Nutr. Biochem.* 2004, 15, 710–716.
12. Virtanen, S. Biodegradable Mg and Mg alloys: Corrosion and biocompatibility. *Mater. Sci. Eng.: B* 2011, 176, 1600–1608.

13. Atrens, A.; Liu, M.; Abidin, N. I. Z. Corrosion mechanism applicable to biodegradable magnesium implants. *Mater. Sci. Eng.: B* 2011, 176, 1609–1636.
14. Gu, X. N.; Zhou, W. R.; Zheng, Y. F.; Cheng, Y.; Wei, S. C.; Zhong, S. P.; Xi, T. F.; Chen, L. J. Corrosion fatigue behaviors of two biomedical Mg alloys-AZ91D and WE43-In simulated body fluid. *Acta Biomater.* 2010, 6, 4605–4613.
15. Jamesh, M.; Wu, G. S.; Zhao, Y.; Chu, P. K. Effects of silicon plasma ion implantation on electrochemical corrosion behavior of biodegradable Mg-Y-RE Alloy. *Corros. Sci.* 2013, 69, 158–163.
16. Witte, F.; Kaese, V.; Haferkamp, H.; Switzer, E.; Meyer-Lindenberg, A.; Wirth, C. J.; Windhagen, H. In vivo corrosion of four magnesium alloys and the associated bone response. *Biomaterials* 2005, 26, 3557–3563.
17. Frankel, G. S.; Samaniego, A.; Birbilis, N. Evolution of hydrogen at dissolving magnesium surfaces. *Corros. Sci.* 2013, 70, 104–111.
18. Thomas, S.; Medhekar, N. V.; Frankel, G. S.; Birbilis, N. Corrosion mechanism and hydrogen evolution on Mg. *Curr. Opin. Solid State Mater. Sci.* 2015, 19, 85–94.
19. Vignesh, R. V.; Padmanaban, R.; Govindaraju, M. Study on the corrosion and wear characteristics of magnesium alloy AZ91D in simulated body fluids. *Bull. Mater. Sci.* 2020, 43, No. 8.
20. Jacobs, J. J.; Hallab, N. J.; Skipor, A. K.; Urban, R. M. Metal degradation products: a cause for concern in metal-metal bearings? *Clin. Orthop. Relat. Res.* 2003, 417, 139–147.
21. Montross, C. S.; Wei, T.; Ye, L.; Clark, G.; Mai, Y.-W. Laser shock processing and

- its effects on microstructure and properties of metal alloys: a review. *Int. J. Fatigue* 2002, 24, 1021–1036.
22. Fabbro, R.; Peyre, P.; Berthe, L.; Scherpereel, X. Physics and applications of laser-shock processing. *J. Laser Appl.* 1998, 10, 265– 279.
 23. Lu, J.; Luo, K.; Zhang, Y.; Zhou, J.; Cui, X.; Zhang, L.; Zhong, J. Effects of laser shock processing and strain rate on tensile property of LY2 aluminum alloy. *Mater. Sci. Eng.: A* 2010, 528, 730–735.
 24. Lu, J.; Wu, L.; Sun, G.; Luo, K.; Zhang, Y.; Cai, J.; Cui, C.; Luo, X. Microstructural response and grain refinement mechanism of commercially pure titanium subjected to multiple laser shock peening impacts. *Acta Mater.* 2017, 127, 252–266.
 25. Zhang, R.; Zhou, X.; Gao, H.; Mankoci, S.; Liu, Y.; Sang, X.; Qin, H.; Hou, X.; Ren, Z.; Doll, G. L.; et al. The effects of laser shock peening on the mechanical properties and biomedical behavior of AZ31B magnesium alloy. *Surf. Coat. Technol.* 2018, 339, 48–56.
 26. Park, C.; Jung, D.; Chun, E.-J.; Ahn, S.; Jang, H.; Kim, Y.-J. Effect of laser shock peening without coating on fretting corrosion of copper contacts. *Appl. Surf. Sci.* 2020, 514, No. 145917.
 27. Lu, J.; Qi, H.; Luo, K.; Luo, M.; Cheng, X. Corrosion behaviour of AISI 304 stainless steel subjected to massive laser shock peening impacts with different pulse energies. *Corros. Sci.* 2014, 80, 53–59.
 28. Sundar, R.; Ganesh, P.; Gupta, R. K.; Ragvendra, G.; Pant, B.; Kain, V.; Ranganathan, K.; Kaul, R.; Bindra, K. *Laser Shock Peening and its Applications: A*

- Review. *Lasers Manuf. Mater. Process.* 2019, 6, 424–463.
29. Gujba, A. K.; Medraj, M. Laser peening process and its impact on materials properties in comparison with shot peening and ultrasonic impact peening. *Materials* 2014, 7, 7925–7974.
30. Mao, B.; Liao, Y.; Li, B. Gradient twinning microstructure generated by laser shock peening in an AZ31B magnesium alloy. *Appl. Surf. Sci.* 2018, 457, 342–351. (31)
- Ge, M.-Z.; Xiang, J.-Y.; Yang, L.; Wang, J. Effect of laser shock peening on the stress corrosion cracking of AZ31B magnesium alloy in a simulated body fluid. *Surf. Coat. Technol.* 2017, 310, 157–165.
32. Ge, M.-Z.; Xiang, J.-Y. Effect of laser shock peening on microstructure and fatigue crack growth rate of AZ31B magnesium alloy. *J. Alloys Compd.* 2016, 680, 544–552.
33. Chin, K. S.; Idapalapati, S.; Ardi, D. T. Thermal stress relaxation in shot peened and laser peened nickel-based superalloy. *J. Mater. Sci. Technol.* 2020, 59, 100–106. (34)
- Tong, J.; Dalby, S.; Byrne, J.; Henderson, M. B.; Hardy, M. C. Creep, fatigue and oxidation in crack growth in advanced nickel base superalloys. *Int. J. Fatigue* 2001, 23, 897–902.
35. Li, Y. X.; Ren, Z. C.; Jia, X.; Yang, W. J.; Nassreddin, N.; Dong, Y. L.; Ye, C.; Fortunato, A.; Zhao, X. The effects of the confining medium and protective layer during femtosecond laser shock peening. *Manuf. Lett.* 2021, 27, 26–30.
36. Lee, D.; Kannatey-Asibu, E., Jr. Experimental investigation of laser shock peening using femtosecond laser pulses. *J. Laser Appl.* 2011, 23, No. 022004.
37. Lu, C.; Ge, L.; Zhu, B.; Li, Y.; Chen, X.; Zeng, X.; Chen, Y. Effective femtosecond

- laser shock peening on a Mg–3Gd alloy at low pulse energy 430 μ J of 1 kHz. *J. Magnesium Alloys* 2019, 7, 529–535.
38. Wang, H.; Jürgensen, J.; Decker, P.; Hu, Z.; Yan, K.; Gurevich, E. L.; Ostendorf, A. Corrosion behavior of NiTi alloy subjected to femtosecond laser shock peening without protective coating in air environment. *Appl. Surf. Sci.* 2020, 501, No. 144338.
 39. Zhang, R. X.; Hou, X. N.; Zhou, X. F.; Gao, H. Y.; Mankoci, S.; Qin, H. F.; Ren, Z. C.; Doll, G. L.; Martini, A.; Dong, Y. L.; Sahai, N.; Ye, C. In Effects of Laser Shock Peening on the Wear and Degradation Behaviors of Magnesium Alloys, Proceedings of the ASME 11th International Manufacturing Science and Engineering Conference, 2016; Vol. 2.
 40. Li, Y.; Ren, Z.; Jia, X.; Yang, W.; Nassreddin, N.; Dong, Y.; Ye, C.; Fortunato, A.; Zhao, X. The effects of the confining medium and protective layer during femtosecond laser shock peening. *Manuf. Lett.* 2021, 27, 26–30.
 41. Fabbro, R.; Fournier, J.; Ballard, P.; Devaux, D.; Virmont, J., Physical study of laser-produced plasma in confined geometry. *Journal of applied physics* 1990, 68 (2), 775-784.
 42. Ye, Y.; Feng, Y.; Lian, Z.; Hua, Y., Plastic deformation mechanism of polycrystalline copper foil shocked with femtosecond laser. *Applied surface science* 2014, 309, 240-249.
 43. Stein, P.; García, O.; Morales, M.; Huber, H.; Molpeceres, C., Numerical simulation of laser ablation for photovoltaic materials. *Applied surface science* 2012, 258 (23),

9288-9291.

44. Kim, J. H.; Kim, Y. J.; Kim, J. S., Effects of simulation parameters on residual stresses for laser shock peening finite element analysis. *Journal of Mechanical Science Technology* 2013, 27 (7), 2025-2034.
45. Platts, A. T., Understanding and Simulating High Strain Rate Deformation of Magnesium WE43 Plate Products. The University of Manchester (United Kingdom): 2019.
46. Mraied, H.; Wang, W. B.; Cai, W. J. Influence of chemical heterogeneity and microstructure on the corrosion resistance of biodegradable WE43 magnesium alloys. *J. Mater. Chem. B* 2019, 7, 6399–6411.
47. Elango, K.; Hoppius, J. S.; Kukreja, L. M.; Ostendorf, A.; Gurevich, E. L. Studies on ultra-short pulsed laser shock peening of stainless-steel in different confinement media. *Surf. Coat. Technol.* 2020, 397, No. 125988.
48. Tull, B. R.; Carey, J. E.; Mazur, E.; McDonald, J. P.; Yalisove, S. M. Silicon surface morphologies after femtosecond laser irradiation. *MRS Bull.* 2006, 31, 626–633.
49. Zhao, X.; Shin, Y. C. A two-dimensional comprehensive hydrodynamic model for femtosecond laser pulse interaction with metals. *J. Phys. D: Appl. Phys.* 2012, 45, No. 105201.
50. Toyserkani, E.; Rasti, N. Ultrashort Pulsed Laser Surface Texturing. In *Laser Surface Engineering: Processes and Applications*; Elsevier, 2015; pp 441–453.
51. Raillard, B.; Mücklich, F. Ablation Effects of Femtosecond Laser Functionalization on Surfaces. In *Laser Surface Engineering*; Elsevier, 2015; pp 565–581.

52. Han, Y.; Qu, S. The ripples and nanoparticles on silicon irradiated by femtosecond laser. *Chem. Phys. Lett.* 2010, 495, 241–244.
53. Zhang, S.; Xie, H.; Zeng, X.; Hing, P. Residual stress characterization of diamond-like carbon coatings by an X-ray diffraction method. *Surf. Coat. Technol.* 1999, 122, 219–224.
54. Williamson, G.; Hall, W. X-ray line broadening from filed aluminium and wolfram. *Acta Metall.* 1953, 1, 22–31.
55. Chen, X.; Li, Y.; Zhu, Y.; Yang, B. Enhanced irradiation and corrosion resistance of 316LN stainless steel with high densities of dislocations and twins. *J. Nucl. Mater.* 2019, 517, 234–240.
56. Yu, H. B.; Liu, J. L.; Karamched, P.; Wilkinson, A. J.; Hofmann, F. Mapping the full lattice strain tensor of a single dislocation by high angular resolution transmission Kikuchi diffraction (HR-TKD). *Scr. Mater.* 2019, 164, 36–41.
57. Cai, W.; Bellon, P.; Beaudoin, A. J. Probing the subsurface lattice rotation dynamics in bronze after sliding wear. *Scr. Mater.* 2019, 172, 6–11.
58. Bland, L.; King, A.; Birbilis, N.; Scully, J. Assessing the corrosion of commercially pure magnesium and commercial AZ31B by electrochemical impedance, mass-loss, hydrogen collection, and inductively coupled plasma optical emission spectrometry solution analysis. *Corrosion* 2015, 71, 128–145.
59. Feliu, S. Electrochemical impedance spectroscopy for the measurement of the corrosion rate of magnesium alloys: Brief review and challenges. *Metals* 2020, 10, No. 775.

60. Chen, J.; Xiao, J. W.; Poplawsky, J.; Michel, F. M.; Deng, C.; Cai, W. J. The origin of passivity in aluminum-manganese solid solutions. *Corros. Sci.* 2020, 173, No. 108749.
61. Mraied, H.; Wang, W.; Cai, W. Influence of chemical heterogeneity and microstructure on the corrosion resistance of biodegradable WE43 magnesium alloys. *J. Mater. Chem. B* 2019, 7, 6399–6411.
62. Ren, X.; Huang, J.; Zhou, W.; Xu, S.; Liu, F. Surface nano-crystallization of AZ91D magnesium alloy induced by laser shock processing. *Mater. Des.* 2015, 86, 421–426.
63. Gabersček, M.; Pejovnik, S. Impedance spectroscopy as a technique for studying the spontaneous passivation of metals in electrolytes. *Electrochim. Acta* 1996, 41, 1137–1142.

Chapter 5. Summary and Future Work

5.1. Summary of the thesis

In this dissertation, microstructure design has been introduced in several metallic systems (i.e., Zr-based, Al-based and Mg-based) via the introduction of chemical and/or structural heterogeneity with controlled length-scale. The effects of such heterogeneity on the corrosion and tribocorrosion resistance of metals have been successfully investigated, providing a potential microstructural design strategy to obtain high performance metallic materials.

In the first study, the effects of nanoscale chemical heterogeneity on wear, corrosion and tribocorrosion behaviors in ZrCuNiAl TFMG have been studied. ZrCuNiAl TFMG with homogeneous or heterogeneous local composition were obtained by controlling Ar pressure during magnetron sputtering and subsequently affecting kinetics energy of sputtered atoms. The heterogeneous ZrCuNiAl TFMG performed higher ductility but lower hardness than the homogeneous counterpart since the deformation mode has been transformed to strain percolation of multiple shear bands from local soft areas, rather than traditional stress-nucleation driven shear bands. Pitting corrosion and tribocorrosion resistance of heterogeneous ZrCuNiAl TFMG also exhibited better than that of homogeneous ZrCuNiAl TFMG in 0.6M NaCl solution at room temperature. It is attributed to generating passive film with low defect density and rapid repassivated capability during tribocorrosion.

In the second study, the effects of nanoscale chemical and structural heterogeneity were investigated in Al-based nanostructured metallic multilayers. The abundant interfaces and chemical modulation at nanoscale significantly optimized mechanical properties and reduced pitting susceptibility in 0.6 M NaCl solution at room temperature due to interaction between Al and different underlying constituents. Based on the results of X-ray photoelectron spectroscopy, the passive films in Al/Mg and Al/Cu NMMs were mainly composed of Al, which is consistent with mixed potential theory predication in micro-galvanic corrosion. Similar results were observed in Al/Ti (i.e., Al was the only element to participate in passive film generation), although Ti had a broader passivity window. Transmission electron microscopy images of post-tribocorrosion surfaces suggested that the material loss in Al/Mg and AlCu NMMs was mostly dependent on corrosion, instead of severe plastic deformation in Al/Ti.

Lastly, the structural heterogeneity was successfully introduced into the bulk biodegradable WE43 Mg alloys via femtosecond laser shock peening technique with ultra-low laser pulse energy. The adsorption layer (i.e., black tape) and confining medium (i.e., quartz) were applied to assist in the energy adsorption and shock wave confinement in this work, resulting in the peening effect. At 28 GW/cm² laser power density, the optimized peening effect contributed to surface strengthening, corrosion and tribocorrosion resistance enhancement, compared with untreated WE43 Mg alloys. Transmission electron microscopy images of the treated surface revealed the presence of dislocation density gradient near the surface and lattice rotation, which are responsible for high surface performance. Unlike other previous LSP work, the

compressive residual stress was not significant in the current work through finite element analysis investigation.

5.2. Proposed future work

Based on the current results in this dissertation, three future research works are proposed in order to optimize the corrosion and tribocorrosion resistance of metals such as Zr, Al and Mg, and to fundamentally understand the processing-microstructure-performance relationships of these metals.

Firstly, metallic glasses (MGs) without crystalline features exhibit excellent physical and chemical properties, such as high wear and corrosion resistance, due to the amorphous microstructure, as studied in Chapter 2. Although Pd-based BMGs with a maximum diameter of 85 mm had been successfully synthesized [1], the specimen size of BMGs is far from adequate for practical applications. As a result of the development of metal additive manufacturing [2], it promises to disrupt size limitations and fabricate more complex geometries. Unlike the conventional fabrication techniques (e.g., rapid solidification methods), metal additive manufacturing methods are more diverse and specific in terms of composition and microstructure design. However, most metal fabrication methods are based on layer deposition, and it is essential to understand and design the manufacturing parameters to avoid crystallization in the cyclic thermal process and simultaneously optimize the tribocorrosion performance. In addition, it would be of significance to control defects and residual stresses in the manufacturing process and to understand how they affect corrosion and tribocorrosion in amorphous microstructures fabricated by metal additive manufacturing. Thus, one of the interesting

future research directions is to fabricate MGs using additive manufacturing methods, to achieve enhanced tribocorrosion resistance by tailoring processing parameters and residual stress.

Secondly, in Chapter 3, nanostructured metallic multilayer/nanocomposites exhibit improved hardness, corrosion and tribocorrosion due to the high density of interfaces and chemical modulation. However, it is also because of the high-density interface that micro-galvanic coupling still significantly affects the corrosion and tribocorrosion performance, especially in Al/Mg and Al/Cu multilayer. The effects of the interface on corrosion at the atomic scale are not yet clear and it is of relevance to study it through experiments and molecular dynamics simulations. In addition, the current interface, known as the two-dimensional interface, suffers from sudden discontinuities in microstructure and material properties due to sharp boundaries on the atoms, resulting in ductility reduction. Recently, the design and fabrication of three-dimensional interfaces at the atomic level have revealed noticeable improvements in yield and flow strength [3]. By tuning the sputter power, gradients in composition at the interface can be obtained and it would be interesting to study its effects on the corrosion and tribocorrosion behaviors.

Lastly, the LSP processing is not determined by a single parameter, as described in Chapter 4. Multiple processing parameters (e.g., power density, overlapping ratio, numbers of scanning, processing temperature, etc.) [4] are involved and affect the eventual peening effect, leading to different electrochemical and tribocorrosion behaviors of WE43 Mg alloys. In addition, the compressive residual stress introduced

after the LSP is a crucial and attractive factor that cannot be neglected. The effects of the order of magnitude and depth of compressive residual stress on the corrosion resistance and tribocorrosion of Mg alloys is rarely studied. Therefore, it's worthwhile to establish the connection between these factors in femtosecond LSP with ultra-low pulse energy and the properties of Mg alloys through synergistic experimental and finite element analysis studies, which can be valuable for the future surface modification design of metals with high surface reactivity, low strength and poor ductility like Mg alloys.

References:

1. Nishiyama, N., Takenaka, K., Miura, H., Saidoh, N., Zeng, Y., Inoue, A. The world's biggest glassy alloy ever made. *Intermetallics*, 2012, 30, 19-24.
2. Li, X. Additive manufacturing of advanced multi-component alloys: bulk metallic glasses and high entropy alloys. *Advanced Engineering Materials*, 2018, 20(5), 1700874.
3. Chen, Y., Li, N., Hoagland, R. G., Liu, X. Y., Baldwin, J. K., Beyerlein, I. J., Mara, N. A. Effects of three-dimensional Cu/Nb interfaces on strengthening and shear banding in nanoscale metallic multilayers. *Acta Materialia*, 2020, 199, 593-601.
4. Gujba, A. K., Medraj, M. Laser peening process and its impact on materials properties in comparison with shot peening and ultrasonic impact peening. *Materials*, 2014, 7(12), 7925-7974.